

X-Ray Diffraction Experiments (A survey of
polymer crystallization by X-ray diffraction .
chapter 3)

メタデータ	言語: en 出版者: SKP 公開日: 2008-01-31 キーワード (Ja): キーワード (En): 作成者: Asano, Tsutomu, Mina, Md. Forhad メールアドレス: 所属:
URL	http://hdl.handle.net/10297/550

Chapter 3. X-Ray Diffraction Experiments

3.1 Properties of X-rays

We have already discussed that X-rays are electromagnetic radiation like visible light. X-ray wavelengths are generally considered to lie between 0.1 and 10 Å (1 Å = 10⁻¹⁰ m). To produce such radiation, it requires loss of kinetic energy of electrons. The production of one X-ray quantum requires much greater energy (~ keV) than that needed for the production of a visible light (~ eV).

The photon energy is given by:

$$E = h\nu, \dots\dots\dots (3.1)$$

where h is Planck's constant and ν is the frequency of the electromagnetic wave.

The electromagnetic wave has a relation of the form:

$$\lambda\nu = c, \dots\dots\dots (3.2)$$

where, λ and c are the wavelength and the velocity of light, respectively.

Then, Eq.(3.1) can be written as:

$$E = \frac{hc}{\lambda} \dots\dots\dots (3.3)$$

As a result of the acceleration by a voltage V , the kinetic energy of the electron becomes eV .

Then,

$$\lambda = \frac{hc}{eV} \dots\dots\dots (3.4)$$

By substituting the values of h , e and c , and the wavelength in Å, Eq. (3.4) becomes:

$$\lambda = \frac{12.4}{V} \dots\dots\dots (3.5)$$

From Eq. (3.5), one can easily determine the minimum wavelength (Å) from the known accelerating voltage (V) of the order of kV (10³V).

3.2 Generation of X-rays by Tubes

When a metal filament is heated under vacuum at high temperature, thermal electrons are emitted. If these electrons are accelerated by a voltage between the filament and a target, then X-rays are generated. The radiation emitted by the target metal, for instance Cu, is schematically shown in Fig.3.1. It is seen that the spectrum consists of continuous X-rays as well as characteristic X-rays showing discrete and high intensity peaks (K_α and K_β). The conventional X-ray tube is demonstrated in Fig.3.2.

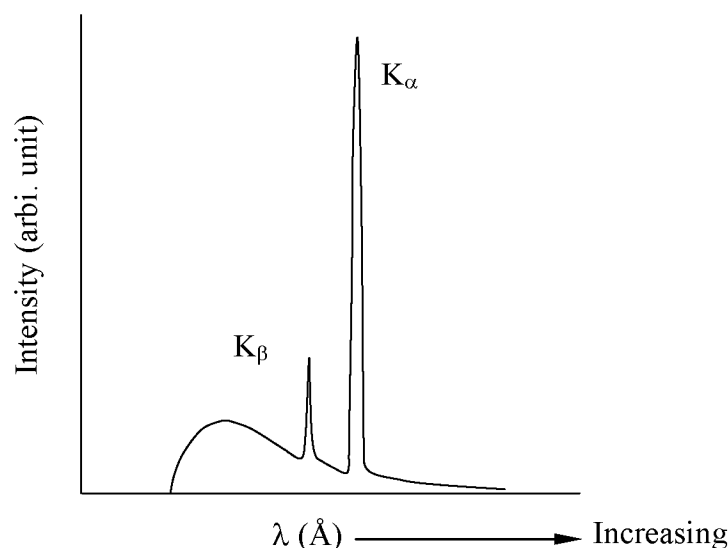


Fig.3.1. Schematic drawing of the spectrum generated by an X-ray tube.

3.2.1 Continuous X-rays

The most important process of the generation of the continuous X-ray is the deceleration of the emitted electron by interaction with the metal target. According to the C.E theory, a decelerated electron emits electromagnetic radiation. The minimum wavelength, determined by Eq.(3.4), is reversely related to the voltage between the filament and the target. Due to accidental conditions of the electrons when they are approaching to the target, the conversion from the kinetic to the electromagnetic energy is lower than eV for each electron. Corresponding to the lower converted energies, the wavelengths of the continuous X-rays spread to the longer values.

3.2.2 Characteristic X-rays

The sharp peaks in Fig.3.1 can be explained by the direct interaction between the emitted electron and the target metal. When an electron is ejected from the K shell of the metal atom, the vacancy is produced in this shell. The K shell is then filled by an electron from higher energy shell (L, M, etc.). Then X-ray photon, having the energy difference between the two shells, will be emitted by the latter electron.

The X-rays coming out due to the fall of electrons from L, M shell into the K shell are known as K_{α} , K_{β} radiations, respectively. These radiations are called characteristic X-rays because the wavelength (or the energy) is fixed by the target metal. In the case of Cu, the wavelengths of K_{α} , K_{β} , are 1.54 Å and 1.39 Å, respectively. For the case of Mo, they are 0.71 Å and 0.63 Å, respectively.

3.2.3 X-ray tube

The basic design and wiring diagram of an X-ray tube is illustrated in Fig. 3.2. A filament of tungsten (cathode) is enclosed in a vacuum envelop, and heated by a low voltage to emit thermal electrons. These electrons are then accelerated to strike the target material

(anode) by a high voltage (typically 40 kV for the Cu target). As a temperature of the metal anode increases due to collision of the electron beam, it is necessary to cool down by circulation of water. The X-rays are emitted in all directions from the surface of the target. A small portion of the generated X-rays is passed out through the windows of the tube to be used for experiments. For the practical use, the target metals are Cu, Mo, Fe, Co, etc., and the tube and window metals are Fe and Be, respectively.

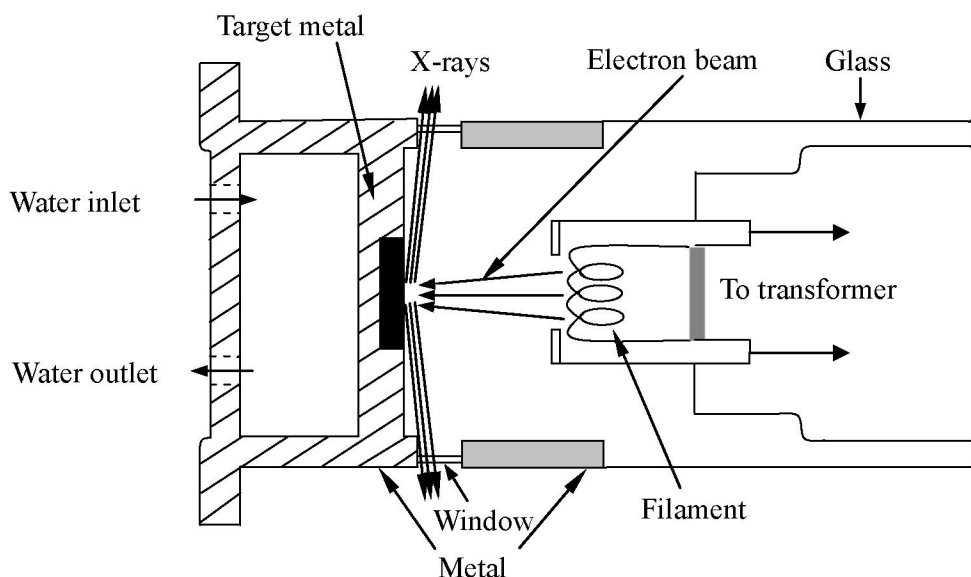


Fig. 3.2 Schematic illustration of an X-ray tube

3.2.4 Rotating anode tube

The beam intensity of X-rays, irradiated by the above tube, is limited by the electron current from the filament to the target. Due to concentration of the electrons on the small area (10mm x 1mm) of the metal surface, the target is damaged over the limited current. Using a cylindrical anode rotating in vacuum, the current is possible to increase more than 10 times up to several hundreds mA. Then the rotating anode tube produces a stronger X-ray beam.

3.3 Synchrotron Radiation

Synchrotron radiation is extremely high intensity electromagnetic radiation with continuous spectral distribution emitted by a high energy electron storage ring. In the synchrotron facility, electrons (or positrons) are accelerated to nearly the velocity of light in a high vacuum closed orbit. Using a series of magnets, the beam of the charged particles runs along the storage ring having a diameter ranging several hundreds meters. The flux of the generated X-rays is many orders of magnitude greater than that obtained by the conventional X-ray tubes.

According to the CE theory, if a charged particle oscillates with a frequency ν , a wave of frequency ν is emitted. At low energy, the radiation is emitted in a non-directional pattern. At a high energy, when the velocity of the charged particle is close to the velocity of light, and the energy is extremely larger than its rest mass energy, relativistic effects provoke a sharp forward peaking of the radiation and simultaneously a large increase in the total radiated energy takes place. This radiation is highly polarized with the electric vector in the plane of the acceleration. Properties of the synchrotron radiation for the scattering experiments can be summarized as follows:

- (i). It has continuous spectrum from the infrared to the hard X-rays region
- (ii). It has very high intensity and brightness as compared to the conventional X-rays.
- (iii). The beam of synchrotron radiation has high collimation.
- (iv). It is highly polarized with the electric field vector in the orbital plane

Therefore, the synchrotron facility has become widely used for the structural measurement of a variety of materials including polymers. Using the high intensity radiations, time resolved measurements, such as dynamics of crystallization, phase transition, etc., are extensively performed. For detailed treatments of the synchrotron radiation in the polymer field, the reader can refer to a review [1]. For the detailed description of the recent experimental method for polymers, the reader can refer the text books [2-4]

3.4 Monochromatization

3.4.1 Single crystal monochromator

In the majority of practical experiments, X-ray diffraction requires a source which is as nearly monochromatic as possible. However, X-rays generated from the tube are a mixture of radiations having various wavelengths (Fig. 3.1). A single crystal method is generally used for subsequent isolation of the desired wavelength. When a beam of the continuous radiation is incident upon a single crystal by an angle θ , the reflection beam has a single wavelength selected by the Bragg's relation shown in Eq.(1.3). It is possible to select a desired wavelength to adjust the incident and reflection angle θ . A special attention is necessary for the crystal monochromator. For the setting angle of the wavelength λ , the radiations of $\lambda/2$, $\lambda/3$, etc are simultaneously included because the higher order radiation is satisfied by the Bragg's condition.

3.4.2 Filtration

In order to obtain substantially monochromatic X-rays, it is necessary to remove unwanted wavelengths. As the K_α radiation has comparatively high intensity, a filter method can be employed to distinguish the K_α radiation from other radiations. When the beam of continuous X-rays is passed through a filter that especially absorbs unwanted K_β radiation, the relative intensity of the K_α radiation is emphasized. Although the resulting radiation is still a mixture, this method is commonly used in the filtration of X-ray. Nickel-filtered CuK_α radiation is generally used for polymer studies.

3.5 X-ray Detection

3.5.1 Photographic film

The conventional method for detection of an X-ray diffraction pattern is attained by exposing photographic film, which contains silver bromide emulsion (AgBr). X-ray initiates a photochemical reaction in the film. Then, the silver bromide can be reduced to free silver grains through suitable development. Therefore, the detection of X-rays is directly proportional to the amount of AgBr. The practical double-coated film will absorb about 50% of the incident X-ray radiation.

3.5.2 Imaging Plate

An Imaging Plate (IP) is a highly advanced photosensitive plate. The IP is composed of BaFBr:Eu²⁺; barium fluorobromide containing a trace amount of divalent europium as a luminescence center. As a photosensitive material is sandwiched between a flexible plastic support and a thin protective layer, the appearance of the IP resembles to a conventional X-ray film. For practical use in the diffraction experiments, the IP is placed within a protective cassette to prevent exposure from the visible light. During the exposure, the photosensitive chemicals of the IP are excited by the diffracted X-rays. After ending the exposure time, the IP is removed and placed on the scanner for developing. It utilizes a Helium-Neon laser to scan into producing the luminescence from the excited chemicals. The detected luminescence is then counted by a photomultiplier and converted into a digital picture by a computer.

3.5.3 Counters

Counters are also the main detecting methods in the X-ray diffraction studies. The function of these detectors is to convert the individual X-ray photon into voltage pulses. These pulses are subsequently either counted or integrated by counting equipment, yielding various forms of visual indication of X-ray intensity. Counters are available in the detection of conventional X-ray diffraction measurements. We use several types such as gas counters, scintillation counters and solid state detectors. Each detector has its own characteristics but is based on the principle that the X-rays ionize the matter. In the following, we shall limit our discussion to the gas counter.

When an X-ray photon interacts with an atom of inert gas, the atom ionizes into an ion pair i.e. an electron and a positive ion. Then the electron is accelerated by the anode potential and further ionizes the inert gas molecules into producing the pairs. The anode will have a signal by these electrons proportional to the original X-ray photon. This is the main function of the proportional counter. In the usual measurements by a proportional counter, the X-ray intensity is measured point-by-point. Then, it is necessary to scan the counter along the diffraction angle.

3.5.4 Position Sensitive Proportional Counter (PSPC)

In the PSPC, a detecting window is opened along the scattering angle. Using a retardation circuit, the position of the X-ray photon can be detected along the window. Then, peak detection along the scattering angle is performed without scanning the counter, which

saves the measuring time as compared to the usual proportional counter.

In the case of the oriented polymers, equatorial reflections are simultaneously measured when the window of the PSPC is perpendicular to the draw direction. The diffraction angle is usually marked using a standard sample.

3.5.5 CCD

The rapid two-dimensional measurement is available using a charge-coupled device (CCD). The accuracy and sensitivity of this system are very much improved in these years. Using a high intensity synchrotron radiation, the dynamic phenomena during the phase transition are possible to measure like a movie. The results are memorized by a video, CD or DVD.

3.6 Wide-Angle X-ray Scattering (WAXS)

3.6.1 Experimental set-up

According to the Bragg's relation presented in Eq. (1.3) for a fixed wavelength (λ), the value of the θ will be larger when d_{hkl} becomes smaller. If the X-ray diffraction measurement is performed by a region $\theta > 5^\circ$, then the measurement technique is called wide angle X-ray scattering (WAXS). WAXS measurements are carried out to detect the lattice parameters of the order of a few angstrom. The detectors, such as IP or PSPC, are placed near the sample. There are various techniques for WAXS measurements but we shall limit specific techniques used in our experiments.

3.6.2 Flat film technique (Photographic film or IP)

For X-ray studies of polymers, flat film cameras are widely used, because they are simple and convenient to record characteristic features of unoriented or oriented materials. With a quick inspection on the pattern, it is easy to distinguish whether the material is amorphous or crystalline. Figure 3.3 shows a schematic diagram for WAXS set up using a flat film. A collimated parallel beam is incident on the sample. The diffracted beam is recorded on the film, which is put in the cassette consisting of a metal back and paper front. A beam-stopper (~0.5 mm thick lead disk) is placed on the paper, preventing the film center from an excessive blackening by the direct beam.

The Bragg angle, θ , corresponding to any diffraction spot or ring can be derived from:

$$\tan 2\theta = \frac{x}{R}, \dots\dots\dots (3.6)$$

where x is the distance from the center of the direct beam (center of the beam-stopper) to the diffraction spot, and R is the distance from the sample to the film. Then, the lattice parameter or plane distance, d_{hkl} , is calculated by Eq.(1.3).

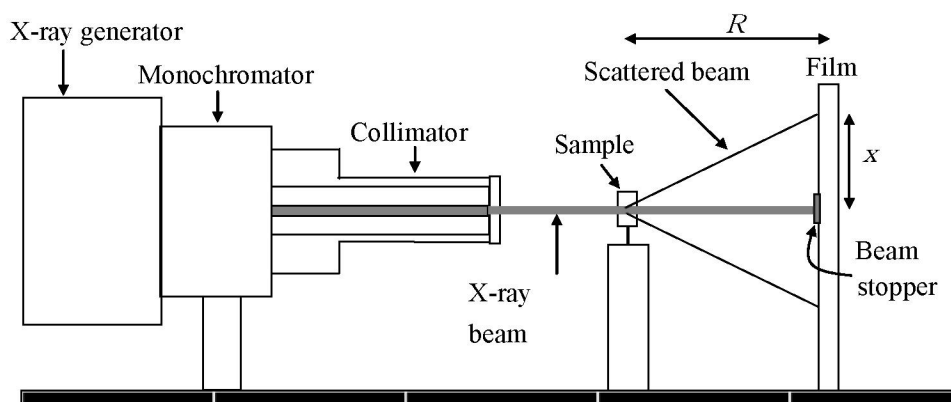


Fig.3.3 Schematic design of WAXS using a flat film camera.

3.6.3 Cylindrical camera

Oriented polymers give rise to a characteristic pattern, so-called a fiber pattern, resembling to those obtained by a rotation crystal method. It is convenient to use cylindrical film to detect a fiber diffraction pattern. In Fig.3.4, the sample is mounted at the center of the camera, setting on the top of a goniometer for fine positioning. The sample is adjusted so as to make the orientation direction parallel to the camera axis. The film is placed in the inner surface of a cylindrical cassette which is mounted concentrically with its axis coinciding with the camera axis.

If the sample polymer is oriented along the draw-direction, the diffraction pattern shows layer lines perpendicular to the draw-direction. Using a cylindrical camera, the layer lines are aligned on a straight line parallel to the equator..

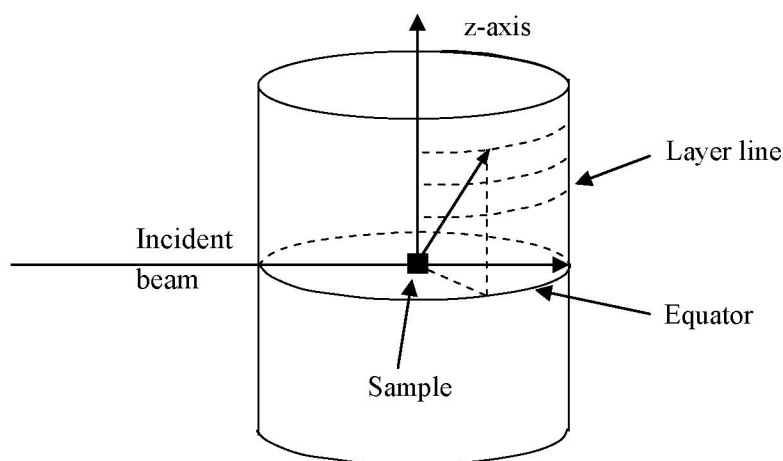


Fig. 3. 4 Schematic view of a cylindrical camera.

The example of the WAXS patterns using the cylindrical camera is shown in the chapter 4 (Figs.4.2 and 4.3, pp33-34) for the oriented poly(ethylene terephthalate) (PET), where shifting of diffraction positions from the layer line is precisely measured.

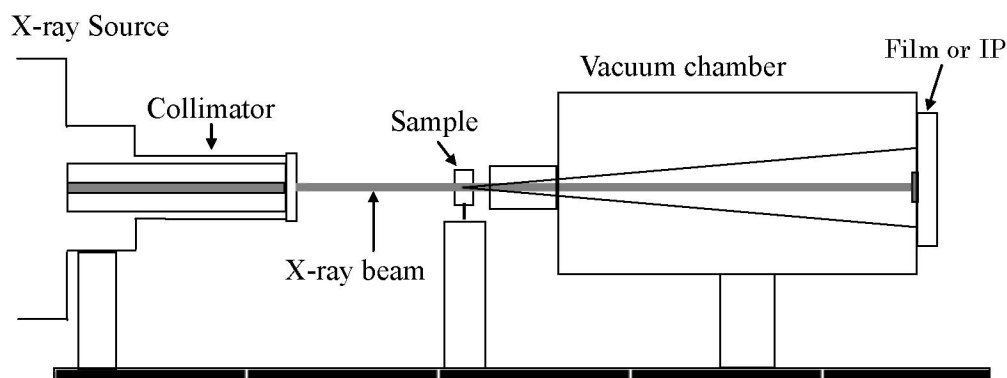


Fig.3.5 Schematic design of a SAXS set up.

3.7 Middle- and Small-Angle X-ray Scattering (MAXS & SAXS)

Likewise the WAXS, if the X-ray diffraction measurement is carried out following a technique in which Bragg angle, θ , is smaller than 5° , the technique is usually called SAXS. In the intermediate region for angles from 5° to 10° , we name sometimes MAXS. Following the Bragg's relation, MAXS and SAXS measurements are performed for larger structures than those detected by WAXS, ranging several hundreds Å. The experimental setting of the SAXS measurement is shown in Fig.3.5.

In SAXS, the film or detector is placed longer distance away from the sample. In order to reduce noise or background by the air scattering, the path between the sample and the film/detector is often evacuated in case of SAXS. The X-ray apparatus used in SAXS is almost the same as that used in WAXS.

3.8 *In-situ* X-ray Measurement

During crystallization of polymers, we measure WAXS and/or SAXS by the special apparatus on the X-ray beam line. For isothermal crystallization, the heater temperature is changed during the X-ray measurement. The TSC apparatus is set in the finely collimated X-ray beam as indicated in Figs. 5.3 (b), (c) (pp51). For *in-situ* measurement, the camera is moved with the crystallizing temperature by a motor. The example of the moving film (IP), we show in the chapter 5 (pp 65-66).

References

1. G. Elsner, C. Riekkel and H. G. Zachmann, *Adv. Polym. Sci.*, **67**, 1, 1985.
2. M. Kakudo and N. Kasai, *X-ray Diffraction by Polymers*, Elsevier Publishing Company, Ltd. Amsterdam 1972.
3. F. J. Baltá Calleja and D. G. Vonk, *X-ray Scattering of Synthetic Polymers*, Elsevier Publishing Company, Ltd. Amsterdam 1989.
4. Ryong-Joon Roe, *Methods of X-ray and Neutron Scattering in Polymer Science*, Oxford University Press, New York, Oxford, 2000