

FCH551: Polymer Techniques Lab

Expt. F: X-ray Diffraction

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Overview:

This experiment introduces the student to the use of x-ray diffraction methods in the study of polymer crystal structure and morphology. Both 'film' and diffractometry methods will be used.

Objectives:

Upon completion of this experiment the student will be familiar with fundamentals of x-ray diffraction by polymers and methods of data collection and analysis using both 'film' and diffractometry methods. The student will be able to calculate interplanar spacings, d_{hkl} ; to understand the relation of lattice constants to interplanar spacings, measurement of the degree of orientation, f ; crystallite size using the Scherrer equation and a crystallinity fraction.

Introduction and Background^{1,2}

a) Production of X-rays

X-rays are a form of electromagnetic radiation with a wavelength between 0.01 and 1 nm, where $1 \text{ nm} = 10^{-9} \text{ m}$. (Another widely used unit is the Ångstrom where $1 \text{ Å} = 0.1 \text{ nm} = 10^{-8} \text{ cm}$.) X rays can be produced in many ways. In the laboratory, X-rays are usually produced by bombarding a metal surface with high-energy electrons traveling along an evacuated pathway. On impact these electrons exchange momentum with electrons in the metal including inner shell

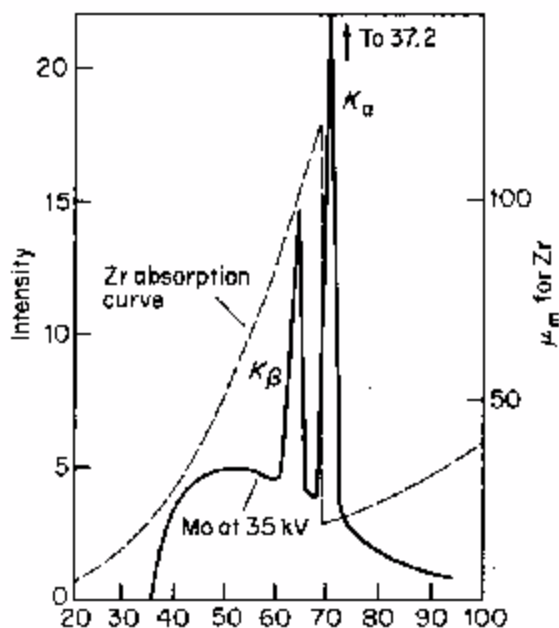


Figure 1. Emission spectrum for a Molybdenum target and absorption spectrum for a Zirconium absorption edge filter.

electrons. When an inner shell electron is removed, it is replaced by an electron from a higher-level shell, *i.e.* radiation is released with a specific energy corresponding to the difference in energy levels between the initial and final states of the electron dropping into the lower energy shell. Thus, $\text{CuK}\alpha$ radiation arises when an electron in the L shell ($n=2$) drops into the K shell ($n=1$). In this convention, Cu designates the target metal, K designates the ground state of the transition and α designates $\Delta n = 1$. Figure 1 shows typical x-ray emission and absorption spectra of metals.

Note the discontinuity in the absorption spectrum. This shows that zirconium could be used as a filter to remove high energy, continuous emissions and the $\text{K}\beta$ emission line of molybdenum leaving mainly $\text{K}\alpha$ radiation. Such filters are called *absorption edge filters*. Molybdenum and copper,

which we shall use, are the major x-ray sources used in diffraction studies of organic and biological materials. For copper, CuK_α radiation has a wavelength of 1.5418 \AA while CuK_β is about 1.39 \AA . Nickel is the appropriate absorption edge filter for copper.

b) *Constructive Interference and Bragg's Law*

For light of this wavelength, a diffraction grating would need to have a spacing of about 1 \AA to, perhaps, several hundred \AA . A crystal, which is a periodic array of atoms or molecules in three dimensions, can act as such a grating. In the crystal identical parts of molecules are related by translations along the principle axes of a 3-dimensional lattice. This lattice is defined by 3 vectors, a , b , and c , and the interfacial angles, α , β , γ , between them. The volume element defined by these 6 parameters is the unit cell. Every unit cell in a crystal has the same atomic composition and placement as every other unit cell and is related to every other unit cell by translation of the unit cell an integral number of times along one or more of the principle axes. If you could define the positions of the atoms within any unit cell, you would know the structure of the molecule and the precise way in which different molecules interact and pack with one another. This can be accomplished by an analysis of the intensity distribution in the diffraction pattern.

If you now draw a larger box containing several unit cells in each direction, you can join together the corners or lattice points forming planes. The geometry of diffraction from a set of parallel planes separated by a distance, d , from one another is shown in Figure 2.

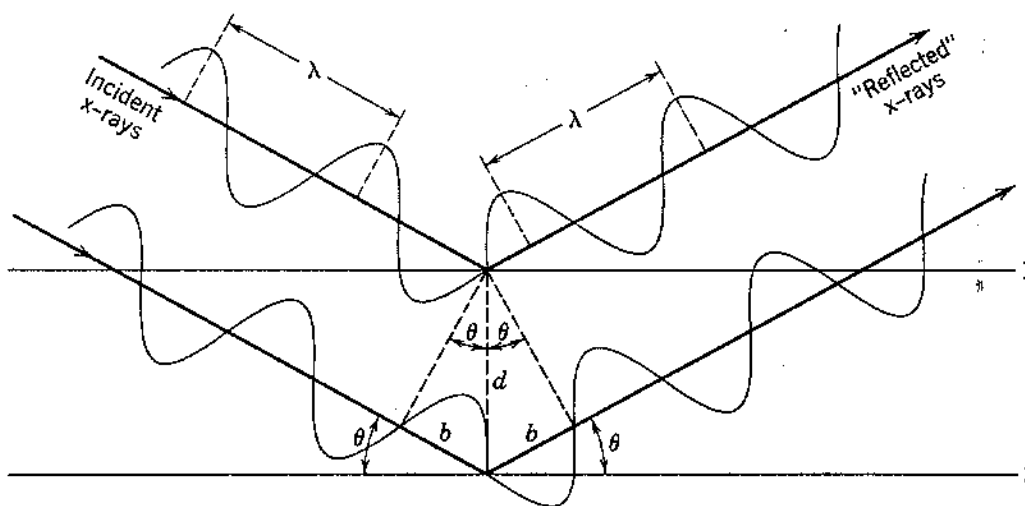


Fig 2. Geometric Construction for Bragg's Law - Constructive Interference by Reflection from a Set of Parallel Planes separated by a Distance 'd'

The difference in path lengths of the upper and lower rays is $b + b$ and for constructive interference, this distance must be an integral number of wavelengths, $n\lambda$. Since $b = d \sin(\theta)$ it follows that

$$n\lambda = 2d \sin(\theta)$$

and for first order effects $\mathbf{I} = d \sin(\theta)$.

c) Miller Indices and Unit Cell Determination

The possible lattice planes are named using the method of Miller indices, h , k , and l . Starting from any lattice point, select 3 points at distances a/h , b/k , and c/l from the origin, where h, k , and l are positive or negative integers or zero. Joining these three points together defines the Miller plane with indices, hkl . Note that a Miller index of 0 implies that the plane runs parallel to that axis. You can see this by drawing planes such as 100 , 110 , 200 etc. Selecting adjacent lattice points as the origin point for the process can generate a set of parallel planes, having this

$$(d_{hkl})^{-2} = (h/a)^2 + (k/b)^2 + (l/c)^2$$

same index. The distance, d_{hkl} , between these planes is directly related to the dimensions and shape of the lattice. For a rectangular, *i.e.* orthorhombic, lattice the relationship is

Inspection of this equation shows that reflections with the smallest indices have the largest interplanar spacings and that the spacings for the 100 , 010 , and 100 correspond, respectively, to the lengths of the a , b , and c axes. At the other extreme, the maximum values of h , k , and l are restricted by the fact that the Bragg equation indicates that the smallest possible observable spacing is $\lambda/2$. Each set of Miller planes gives rise to a constructive interference (also referred to as a spot or a reflection) in the diffraction pattern. By assigning trial indices to observed reflections it is possible to generate a trial model of the unit cell parameters. Subsequent adjustment of those parameters by, for example, a least-squares analysis leads to a unit-cell model which predicts all of the observed spacings with minimal difference between the observed and calculated values of the d -spacings.

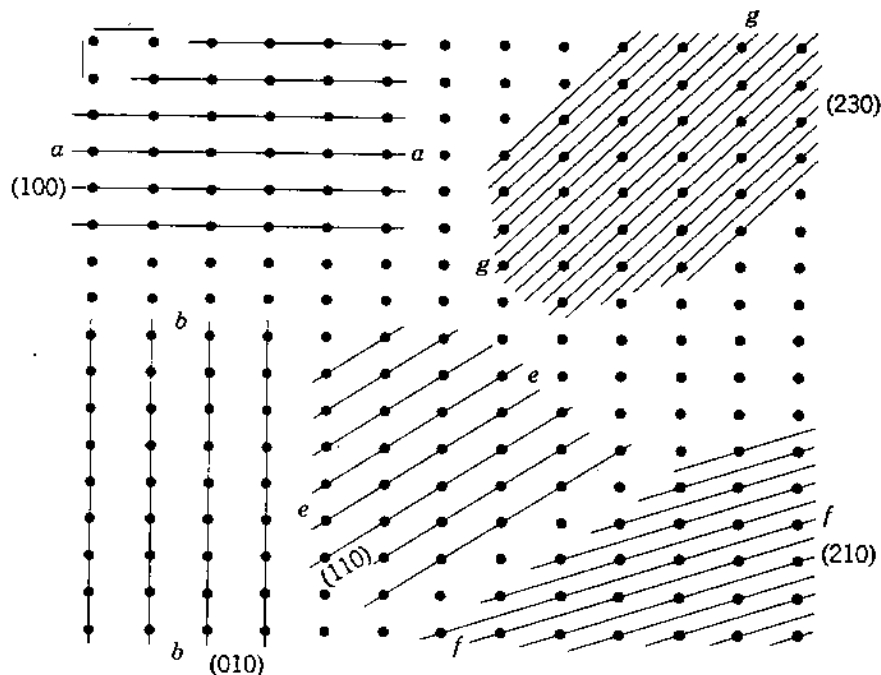


Fig 3. Illustration of Planes and Their Miller Indices on a Rectangular 2-Dimensional Lattice

d) *Crystallite Size*

In general, the larger a crystalline domain is, the sharper the resulting Bragg reflection. This means that angular width of the spot in the 2θ direction is inversely related to crystallite size. Scherrer proposed, in 1918, that the mean dimension of a crystallite in the direction normal to the planes (hkl) was given by

$$L_{hkl} = A / (ds)_s$$

where A is a geometry dependent proportionality constant, that we shall take to be 1.0 and ds is the peak width at half height expressed in units of s , the scattering vector which is given by $s = 2 \sin \mathbf{q}/\lambda$. A more practical form of this equation is given in the procedure below. Polymer crystallite sizes tend to be very small, often less than 10 nm. For this reason, the sample one looks at in an x-ray diffraction experiment normally contains a large ($> 10^4$) number of crystallites.

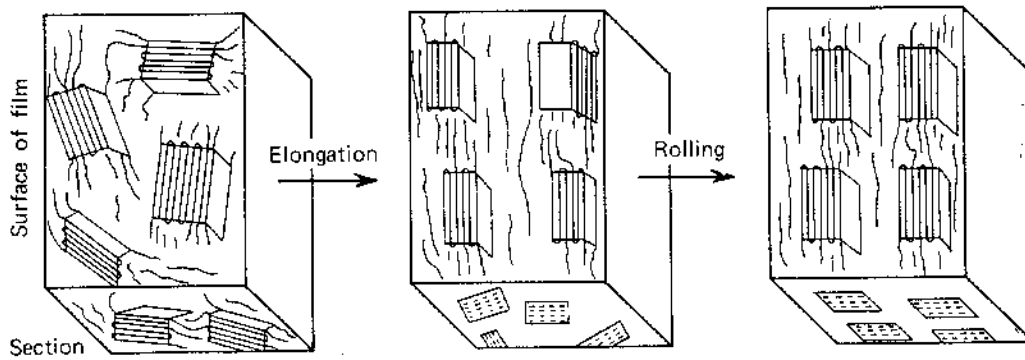


Fig. 4. Crystallites Undergoing Alignment in Response to External Stresses in a Film

e) *Data Collection*

Diffraction Data is collected in two very different ways. The first uses photographic films, imaging plates or CCD devices too directly record an image in two dimensions. The geometry of this first experiment is shown in Figure 5. The collimated, $K\beta$ filtered radiation passes through the sample but is blocked from the film or imaging plate by a lead beamstop. The diffracted beams expose the entire film or plate and all data are collected simultaneously over a suitable time period – ranging from several minutes to several hours. In this experiment it is important to know the exact distance from the specimen to the film/imaging plate. Typically, the sample is dusted with a calibrant such as sodium fluoride ($d = 2.319 \text{ \AA}$) or calcite ($d = 3.029 \text{ \AA}$). The measured radius, x , of the calibration ring can be used to determine the film to specimen distance from the relation

$$x/r = \tan (2\mathbf{q}_{calib})$$

where r is the film to specimen distance, and q_{calib} is calculated from the d spacing of the calibrant material using the Bragg relation for first order diffraction. Once r is determined the same value applies to the specimen under test, since the calibrant powder was dusted on its surfaces.

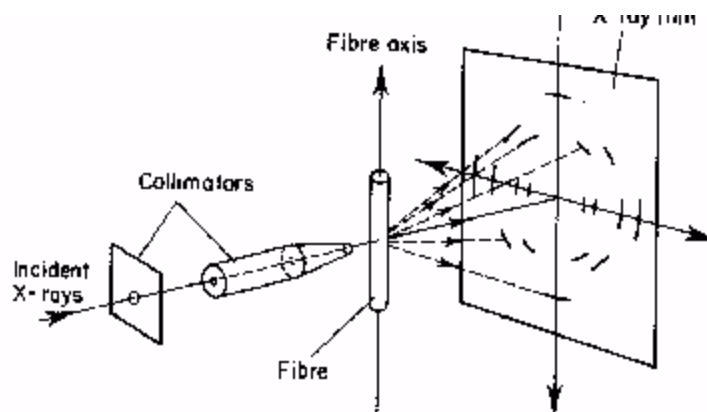


Fig. 5. Geometry of a fiber diffraction experiment using a photographic film/imaging plate.

Alternatively one can use a suitable photon counter such as a proportional counter, scintillation counter etc. moving on an arc of a circle in a horizontal plane and centered on the intersection of the incident x-ray beam with the specimen. This geometry is shown in Figure 6.

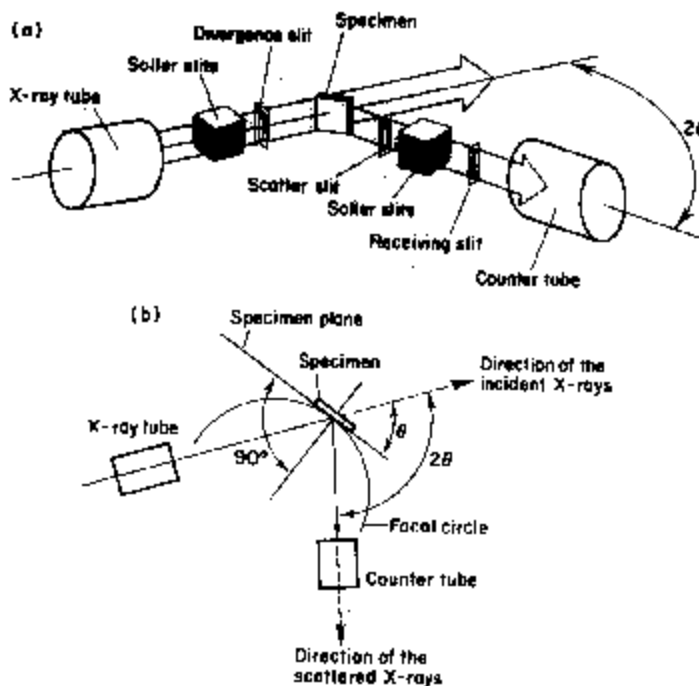


Fig. 6. Geometry of the X-ray diffractometry experiment

In small molecule, powder diffractometry, the sample rotates through an angle, θ , while the counter moves through an angle, 2θ and the data is collected in reflection. This synchronized

motion preserves the geometry shown in Figure 2 throughout the data collection process. In polymer studies it is more common to work in transmission and the sample stays in a fixed position while the counter records the diffracted intensity as a function of 2θ or the detector stays at fixed 2θ

f. Degree of Crystallinity

Real diffraction patterns, such as those shown for polyethylene, in Figure 7, show relatively sharp rings or spots for diffraction from crystalline regions and thick, diffuse rings for x-ray scattering from non-crystalline or amorphous domains.

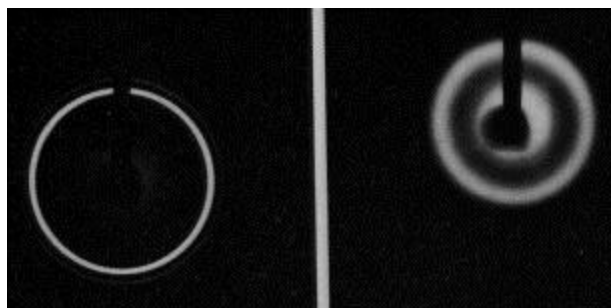


Fig. 7. X-ray diffraction patterns of unoriented Polyethylene, left) crystalline and right) non-crystalline.

Theory predicts that the total intensity of x-rays scattered by a given material is independent of the state of order. This suggests that if one could partition the scattering into scattering arising from the crystalline component and scattering arising from the amorphous component, it would be possible to measure the mass fraction of crystalline material *i.e.* the degree of crystallinity. In practice this is a very complex process due to a number of factors such as disorder within the crystalline phase, thermal vibrations of atoms, and our inability to measure the complete scattering profile from $0 - 180^\circ$ in θ . Ruland, in 1961, proposed a method for achieving this partitioning.³ More commonly, approximate, calibrated methods of measuring crystallinity, w_c , are employed where

$$w^c = I_c / (I_c + KI_a)$$

g. Crystallite size determination

The theory of x-ray scattering can be used to show that the constructive interference or reflection associated with each Miller index should be a point if the crystal is large.

Safety Statement:

X-rays are a form of high-energy ionizing radiation and are capable of causing severe tissue damage. The X-ray source that you are using has a protective shutter system, which

protects the user from accidental exposure to the beam. The instructor will assist you with all sample manipulations and mounting. No student should attempt to open the doors on the experiment chamber, except under the explicit instruction of the instructor. Failure to obey this regulation may result in damage to the equipment and/or injury to the student. No experiments are to be conducted without an approved operator present.

Equipment:

The experiment is written for use with a rotating anode X-ray generator such as the Rigaku RU200, however any X-ray generator may be used if exposure times are adjusted. A Molecular Dynamics imaging phosphor is used to collect 2-dimensional data, although X-ray film could be substituted. Sodium fluoride powder, $d = 2.319 \text{ \AA}$, is used as the calibrant and should be dusted lightly on each specimen using a fine artist's paintbrush.

Experimental:

The sample we use is the strap from a 6-pack. This is made of polyethylene. Cut two pieces each about 4 x 15 mm from the strap. One piece should be tightly clamped in the film mount for the diffractometer. The gap should be about 5mm, note its value. The second piece should be dusted with NaF and fastened in front of the collimator in the flatfilm camera.

1. Typical operating settings are $Kv = 120$, $mA = 50$. All operation of the generator and the diffractometer should be through the computer interface.
2. Make sure all shutters are closed; turn the safety interlock key first clockwise and then counterclockwise. A red light should come on in the interlock box along with an unpleasant high-pitched beep. You can now open the sliding doors to the sample chamber.
3. Mount the flat film camera on its track, then add the beam stop unit and then clamp the imaging plate so that it stands vertically directly behind the beam stop. The plate should be inside a light tight bag. Expose for about 1 h.
4. Mount the film clamp in the fiber specimen unit on the right hand side (diffractometer).
5. Check the slits, horizontal opening should be small 0.5 or 1.0 mm vertical opening should be large, 2.0+ mm.
6. Close the sliding doors, first the left and then the right. The alarm should go off.
7. Open the left shutter by pushing its toggle switch up. Note the time.
8. Run a 2θ scan from 3 to 50 degrees at 10 degrees / minute.
9. Examine the scan using the chart program and determine the position of maximum intensity.
10. Run a β scan at 100 deg/minute with 2θ set at the maximum value observed in step 9.
11. Close the left shutter and open the sliding doors as above.
12. Use the threaded rods to stretch the clamped sample by 2 mm, then 5mm, 5mm and finally to full extension.
13. For each stretch in step 12 repeat the β scan described in step 10.
14. After a total exposure of at least 1 h remove the imaging plate, read it and print the diffraction pattern. Erase the plate and repeat the experiment using the fully stretched polyethylene.
15. Also, repeat the 2θ scan for the fully stretched sample.

16. Plot each 2θ scan on a separate sheet. You will probably have to plot it at 2 different y-axis scales to see all of the data.
17. Plot all of the beta scans on a single sheet.
18. Remove the second image plate, shut down the generator and process the image plate.

Analysis:

The first step in measuring the diffraction pattern is to determine its exact center. Remember that the spots are symmetrically arranged about the true center. You might also recall from geometry that the radius of a circle passes through the center as does the perpendicular bisector of a chord of a circle.. Locate and mark the center of the diffraction pattern.

1. *d*-Spacings

where

$$d = \lambda / 2 \sin (\theta_{hkl})$$

$$\lambda = 1.5418 \text{ \AA} \text{ for CuK}\alpha \text{ radiation}$$

For the film data, samples were dusted with a calibrant whose innermost d-spacing is shown in the table below. Calculate θ_{calib} and use this to determine the film to specimen distance, r , given that

where x is the radius of the calibration ring. Since the calibrant was dusted on your

$$x/r = \tan (2 \theta_{\text{calib}})$$

sample, this is the distance from the specimen to the film or plate on which the data was collected.

Material	Calib spacing (\AA)
NaF	2.319
Calcite	3.029

Use the calculated value of r to and the individually measured spot radii, x_{hkl} , determine $\tan (2 \theta_{hkl}) / r = \tan (2 \theta_{hkl})$ for each of the spots (reflections) in the pattern and present your results in a table. Perhaps a spreadsheet might be a good way to do this calculation.

Compare the values obtained by analysis of the film data with those obtained from the peak positions in the diffractometer traces. The diffractometer traces, which extend from 0.5° to $40\text{--}60^\circ$, are plots of intensity vs 2θ in degrees.

2. Lattice constants

$$1/d_{hkl}^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2)$$

The equation shown above is for the special case of an orthorhombic unit-cell, i.e. a rectangular solid where all faces are perpendicular to one another. Similar equations exist for other crystal shapes (classes) and may be found in most standard textbooks on x-ray diffraction.

Use this equation to assign indices to the measured maxima in your polyethylene patterns assuming that you have the orthorhombic crystal form of polyethylene.. Keep in mind that in diffraction patterns of oriented materials, reflections which fall on the equator have Miller indices of the type $hk0$, those on the layers above (or below) the equator are $hk1$ then $hk2$ etc.

Given the polyethylene lattice constants of $a = 7.46$, $b = 4.94$ and $c = 2.54 \text{ \AA}$, calculate the d -spacings for all equatorial reflections out to $hk0 = 220$ and assign indices to the peaks you measured in your patterns.

3. Preferred orientation , f .

$$f = (3 \langle \cos^2 \phi \rangle - 1) / 2$$

Method 1:

For our purposes, use a protractor to measure the spread around the circumference for one of the equatorial reflections in the diffraction pattern of the oriented (stretched) sample. We shall assume that

$$\langle \cos^2 \phi \rangle = \cos^2 \phi$$

Comment on the changes in orientation observed as the sample was stretched.

Method 2:

Use the beta scan diffractometer traces. These were collected at a constant 2θ value. Mark in the positions where the intensity is 50% of the maximum value and measure the difference in angle across the peak. This is the “full-width at half-maximum intensity” or FWHM peak width. Use this value as the value of ϕ and compute f , the degree of orientation. Compare it with the value you obtain from the film plates.

Plot the degree of orientation as a function of relative strain, D/l_0 . Comment on the changes that you observe.

4. Crystallite size determination

The Scherrer equation says that the angular width of a reflection in the 2θ direction is inversely related to the thickness of the crystal in a direction perpendicular to its Miller planes. Specifically,

$$t = \frac{0.9 \cdot \lambda}{B \cos \theta}$$

Where t is the thickness of the particle in the direction perpendicular to the hkl planes and in the same units as the wavelength, λ , B is a constant which we shall assume to be one (it generally lies in the range 0.9 to 1.0). and θ , actually θ_{hkl} , is the Bragg angle for the hkl planes.

Calculate the crystallite size for the unstretched and maximally stretched samples. Comment on the number of crystallites which might be in the beam assuming a collimator of 100 micrometers diameter and a film thickness of 4mil (0.004 in).

5. Degree of Crystallinity

Use the approximate relation

$$w^c = I_c / (I_c + KI_a)$$

Where $K = 0.884$ and the range of intensities is 10 –32 degrees in 2θ .⁴

6. Molecular Structure Determination

We will not attempt molecular structure determination in this exercise. In fact, most polymer scientists who use x-ray diffraction are not in the business of determining structures. Instead they use it for identification purposes and to study morphology as you have today.

However, if you wished to determine a structure, you would have to measure the relative intensities of all of the observable diffraction maxima in the pattern. The intensity of each reflection or maxima has contributions from every atom in the unit cell and it depends upon the position of that atom and its “atomic scattering power”. In x-ray the scattering power is related to the atomic number of the element and the angle at which the beam scatters relative to the transmitted beam direction. The two important equations here are:

$$I_{hkl} = |F_{hkl}|^2 \cdot LP \cdot A$$

Which says that the intensity, I_{hkl} , is proportional to the square of the magnitude of the scattering vector, F_{hkl} . Secondly the scattering factor, F_{hkl} is given by

$$F_{(h,k,l)} = \sum_{j=1}^{\text{atoms}} f_{(j)} \exp[2\pi \cdot i(hx_{(j)} + ky_{(j)} + lz_{(j)})]$$

where f is the atomic scattering factor for the j 'th atom, located at fractional coordinates x_j , y_j , z_j in the unit cell, hkl are the Miller indices of the reflection and i is the quantity $(-1)^{1/2}$.

Questions:

1. If these experiments were repeated using molybdenum radiation, $\lambda = 0.79 \text{ \AA}$, how would the data change, and how would the results change? Would the maximum number of potentially measurable data change?
2. Why can't we do single crystal measurements on polymers?
3. What physical properties are likely to map into orientation and crystallinity changes?

Internet Reference Sites on Polymer Diffraction:

1. <http://www.chemcomp.com/feature/diffr.htm> - deals with simulating diffraction patterns in a computer program called MOE.
2. <http://www.esf.edu/faculty/che/educate/fch796-xry.html> - notes from a 1 credit course in x-ray diffraction at SUNY-ESF (only available from on campus computers - esf.edu or syr.edu)
3. Bragg's Law - <http://www.journey.sunysb.edu/ProjectJava/Bragg/home.html>
4. Unit Cell and Atomic Positions –
<http://www.kri.physik.uni-muenchen.de/crystal/teaching/mod2.html>
5. Scherrer Equation: <http://www.rigaku.com/amia/docs/Q03.html> and a derivation of it
<http://finanz.math.tu-graz.ac.at/~kainhofer/Physics/Scherrer/>
<http://www.geol.uni-erlangen.de/vlgm/bib/Nottingham/008.html> - discusses different results obtained from different functions describing crystallite size.
<http://www.phys.vt.edu/~graupner/5555/11-4.pdf> - line broadening related to crystallite size and to strain
6. Structure Factors - <http://www-structure.llnl.gov/Xray/comp/strufac.htm>

References:

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- ² Wunderlich, B. (1980) "Macromolecular Physics v.1." pp 387-401.
- ³ Ruland, W. (1961) *Acta Cryst.* **14**, 1180.
- ⁴ Fischer, E.W. and Lorenz, R. (1963) *Koll. Z.-Z. Polym.* **189**, 97.