How to Analyze Polymers Using X-ray Diffraction

Polymers – An Introduction

This tutorial will cover the following topics

- How to recognize different types of polymers
  - Crystalline, semi-crystalline and amorphous
- Identification of Polymers
- Measuring Crystallinity

Polymers

- Polymers come in many forms. They can be crystalline, microcrystalline or amorphous. In a single polymer, you often find all three forms depending on how the polymer was made and processed, frequently, forms are mixed in a single sample.

- Polymers, like other crystalline solids, can also have polymorphs, polytypes,

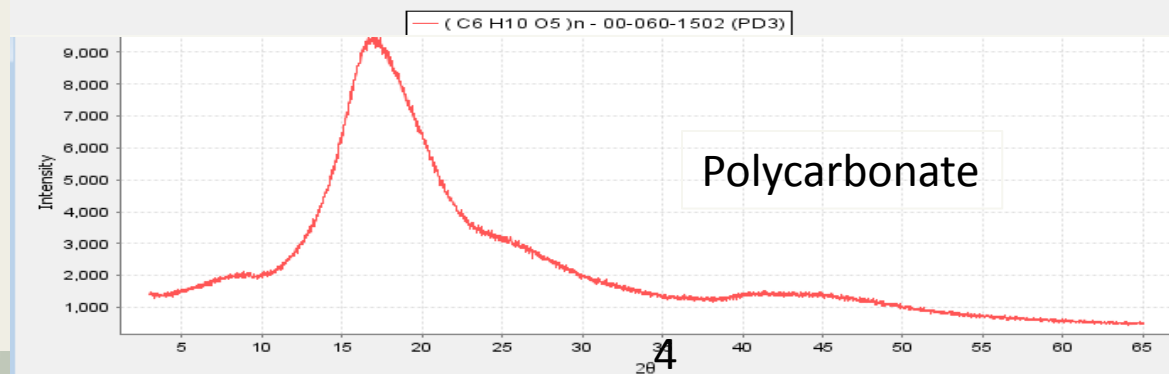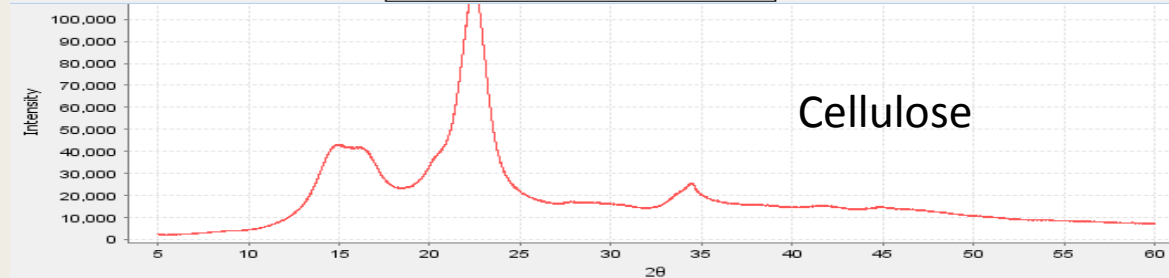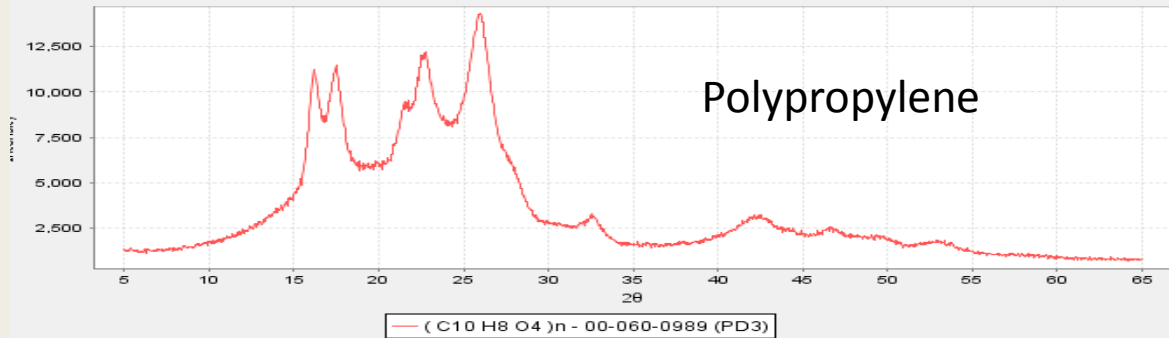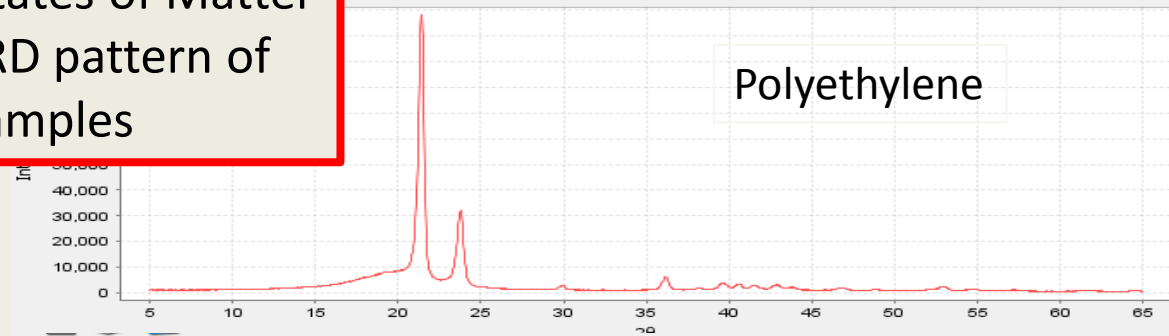 and all types of solid state molecular arrangements.

Highly Crystalline

(very small amorphous)

Semi-crystalline

(partially crystalline partially amorphous)

Microcrystalline

Amorphous

Polymer States of Matter and the XRD pattern of known examples

Polyethylene

Polypropylene

(C10 H8 O4)n - 00-060-0989 (PD3)

Cellulose

(C6 H10 O5)n - 00-060-1502 (PD3)

Polycarbonate

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Polymer Diffraction

- To understand polymer diffraction, you need to know a few basics of polymer chemistry and diffraction physics. The references on the next page usually cover one of these two topics, but not both at the same time.

- The tutorial also contains several common terms used in polymer chemistry. If you are not familiar with them you will need to look them up. Examples are given on polymer chemistry and crystallization, these are given as examples and are not intended to be comprehensive. There are many types of polymerization chemistry and mechanisms of crystalline formation.

- Polymers solidify in several states of matter. Most common commercial polymers are a mixture of these states. In fact, a common application of polymer diffraction is to determine crystallinity or to try to differentiate between amorphous, semicrystalline and nanocrystalline states.

  Even the polymers shown in this tutorial as "highly crystalline" would have a quantifiable small amount of amorphous content, when analyzed by an expert.

References

<u>A basic primer on polymers and their properties</u>

- http://www.pslc.ws/mactest/maindir.htm

- University of Southern Mississippi, School of Polymers "Macrogalleria"

**<u>150 Full Patterns of Polymers and their blends, available for sale from the ICDD</u>**

- "X-ray Diffraction Patterns of Polymers", June Turley, ICDD, 1965

Note: Many illustrations in this tutorial are from this book.

<u>Fundamental Texts on Diffraction Theory of Polymers</u>

- "X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials", Harold P. Klug and L. R. Alexander, Wiley-Interscience, 1974, available from Wiley-Interscience
- "X-ray Diffraction Methods in Polymer Science", L. R. Alexander, Wiley-Interscience, 1969 (<u>Note: Hard to find, not currently available</u>), Kreiger Publishing, 1979

Polystyrene
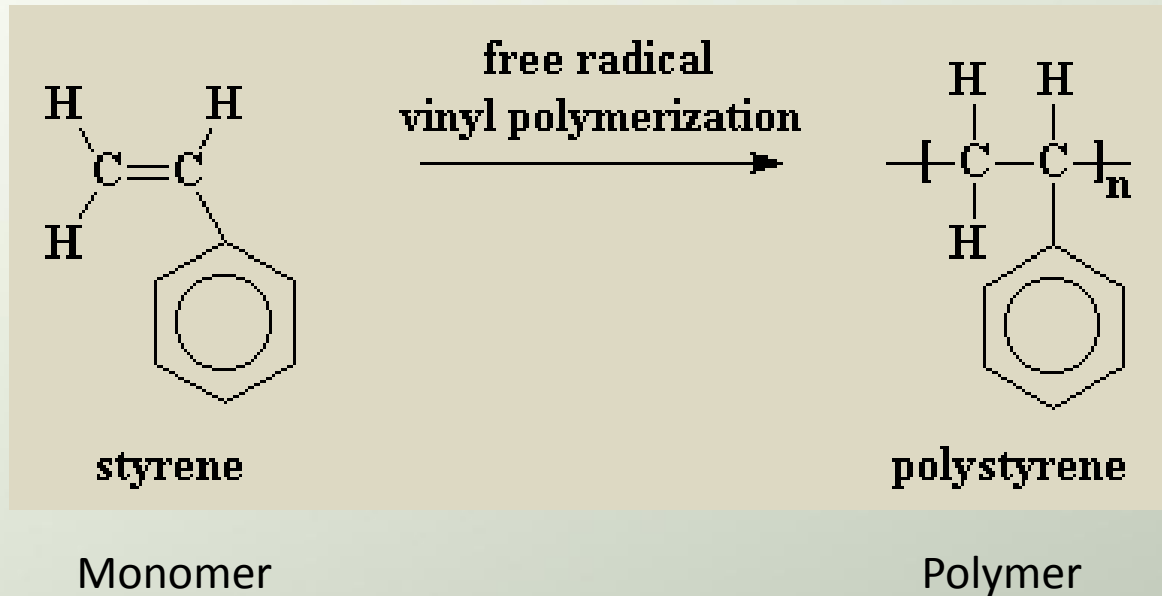
Monomer   Polymer

Polymers are created from monomers as shown above for Polystyrene. There are many ways for monomers to link together to form polymers, creating a wide diversity of polymers. The example shown is one mechanism, a free radical polymerization.
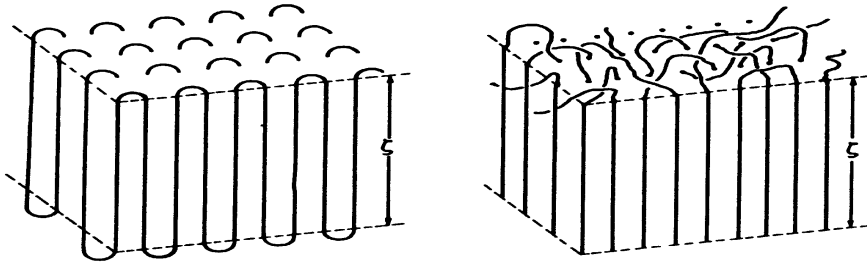
Once the monomers link together they form long chains sort of like strands of spaghetti.

The chains can move and fold – chain folding is one means by which crystalline regions can form, hydrogen bonds (and other types of intermolecular forces) often help in linking chains together.
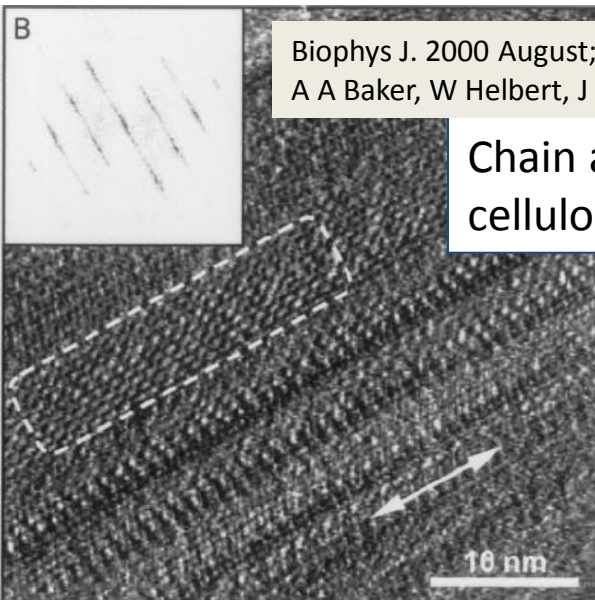
Crystalline region
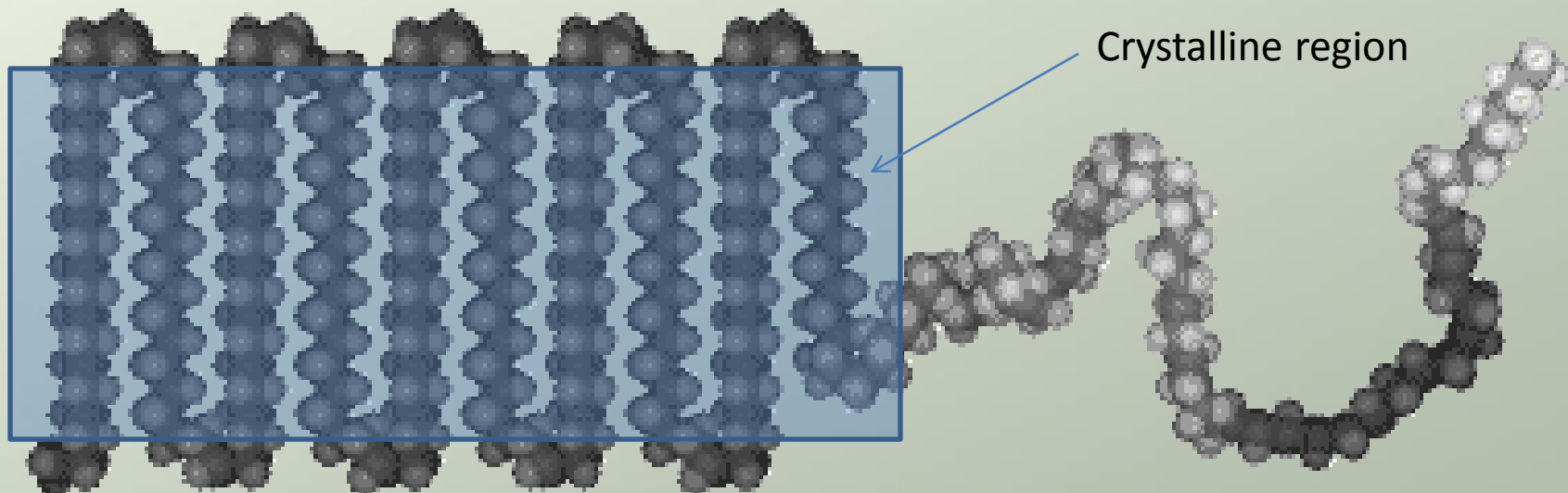
FOLDED POLYMER MOLECULES

Flory, P. J., J. Am. Chem. Soc. 84, 2857 (1962)

Chain folding was proposed by Flory in the 1960's and has subsequently been confirmed in many polymers by atomic resolution microscopy. Adjacent chain alignment is seen in cellulose.
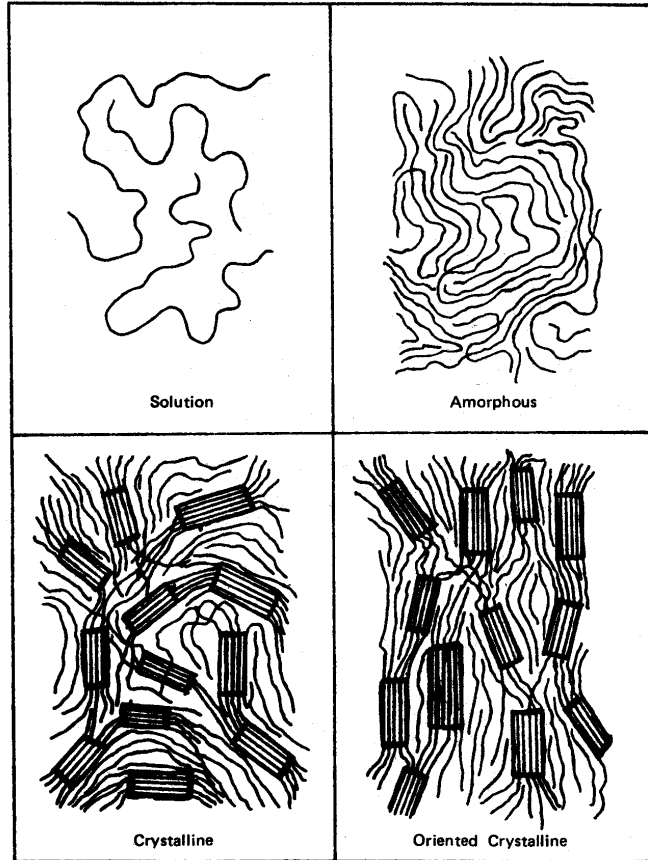
Chain alignment in cellulose microfibrils

10 nm

amorphous region   crystal nucleus   tie molecules

lamellar fibrils
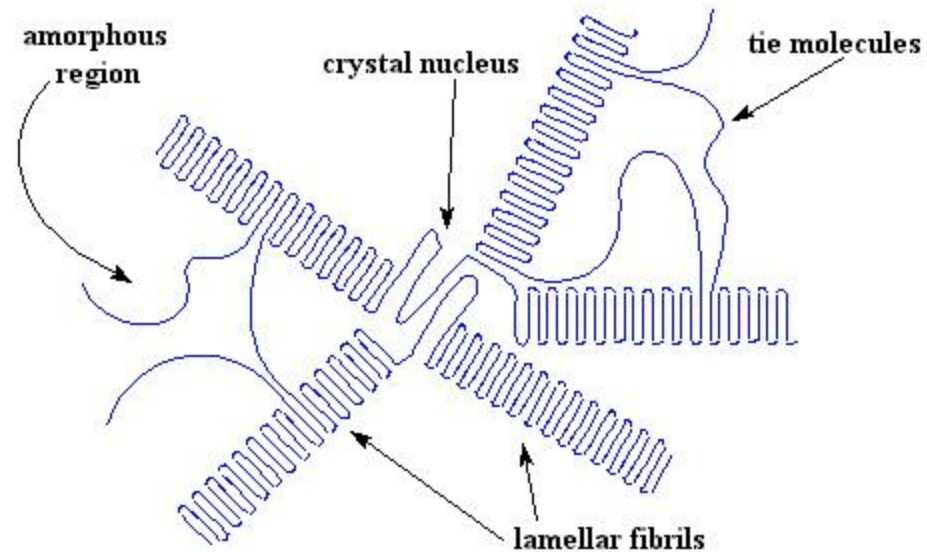
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a polymer crystalline spherulite

Polymer states shown schematically and representative XRD patterns

Sharp well-defined peaks

Highly crystalline

Semi-crystalline
(partially crystalline partially amorphous
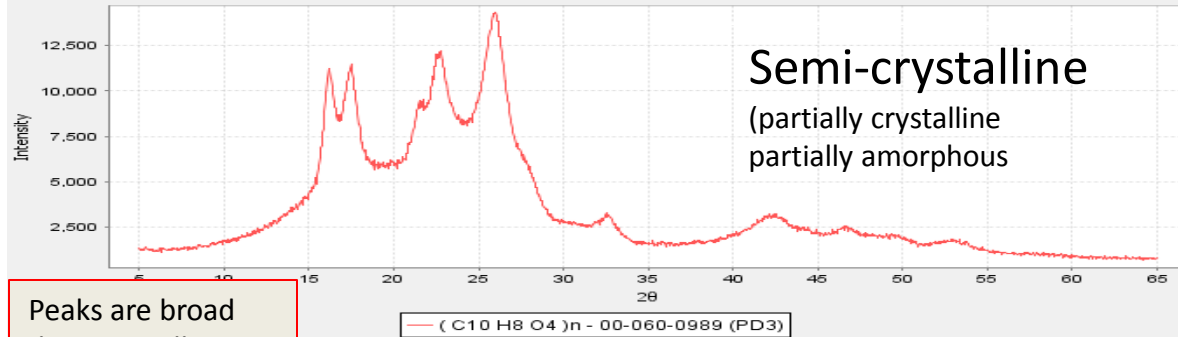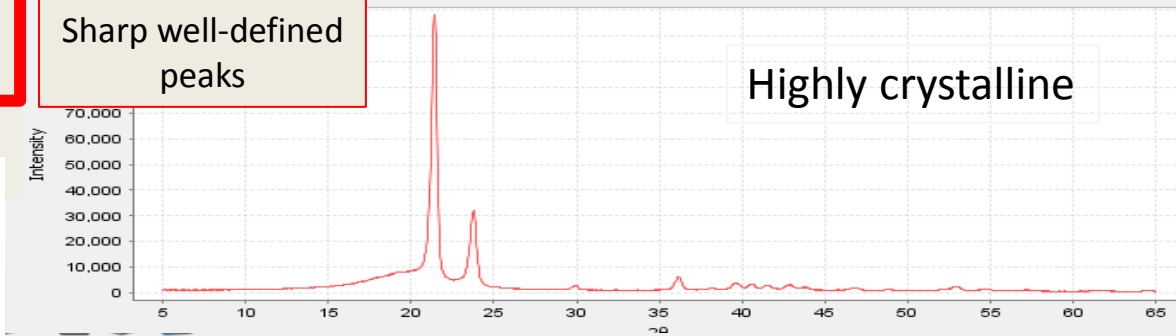
Peaks are broad due to small crystallites, can be assigned with a crystal structure
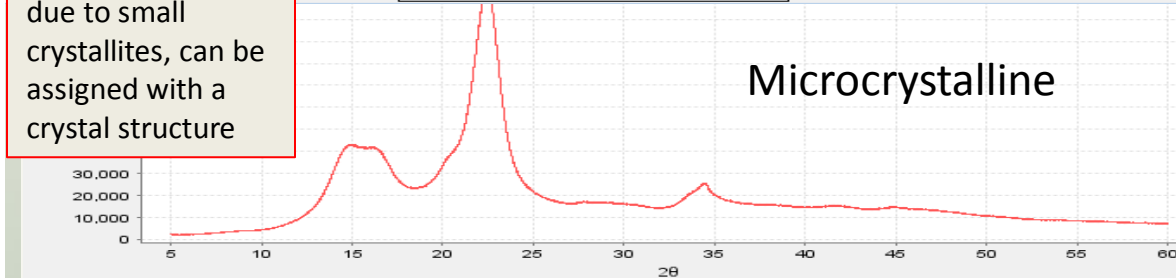
Microcrystalline

Very broad features, not defined by a crystalline model
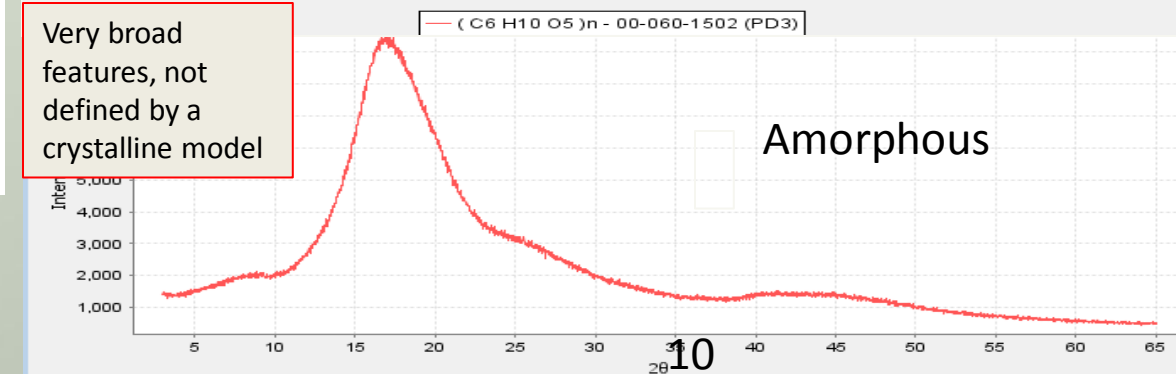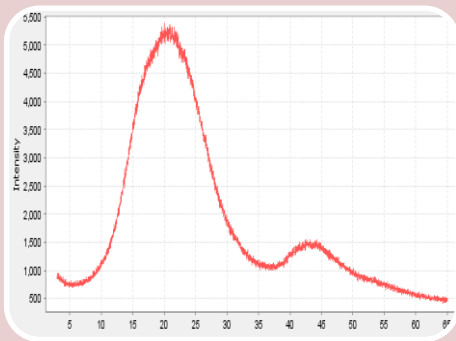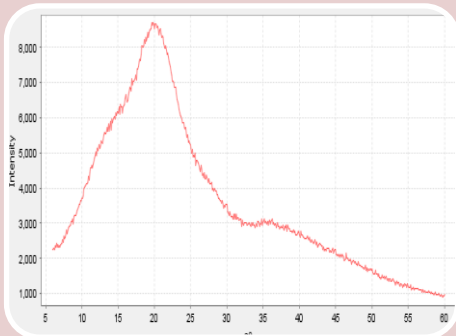
Amorphous

Solution

Amorphous

Crystalline

Oriented Crystalline

From "Selected Papers
Of Turner Alfrey", Marcel
Dekker Inc, 1986

(C10 H8 O4)n - 00-060-0989 (PD3)

(C6 H10 O5)n - 00-060-1502 (PD3)

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Amorphous
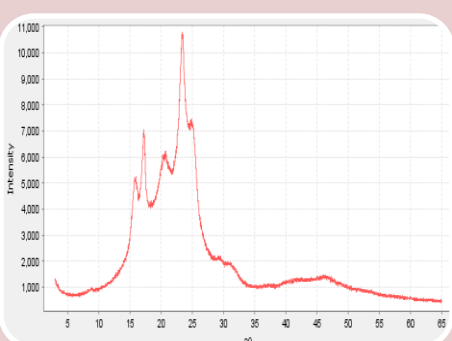
Semicrystalline

Highly Crystalline
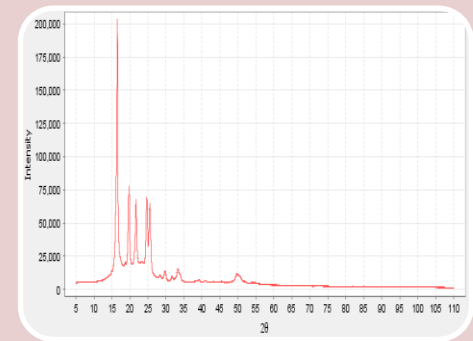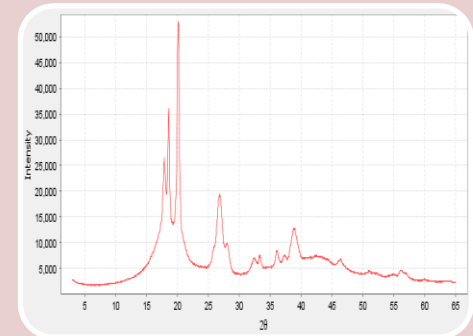
In many cases, we do not have a crystal structure available, the state of matter can be inferred from the pattern appearance. On the far right, the polymer patterns consist of multiple sharp peaks consistent with "*diffraction*" from a crystalline lattice. On the far Left, the patterns have very broad features consistent with "*incoherent scatter*" from an amorphous solid. The patterns in the middle are more complex, exhibiting a mix.

Bragg's Law

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

Crystalline diffraction, coherent scattering, can be described by Bragg's Law

Scattering Function

$$s = \frac{2\sin\theta}{\lambda}$$

Amorphous diffraction, incoherent scattering, can be described using a Debye function. Debye related scattering functions to radial distribution functions. Klug described this as "Each atom possesses permanent neighbors at definite distances and in definite directions."

Crystalline Polymers

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

- *n is an integer*
- *λ is the wavelength*
- *d is the inter-planar spacing*
- *θ is the diffraction angle*

(a)

Planes of High Atomic Density

(b)

microcrystalline cellulose
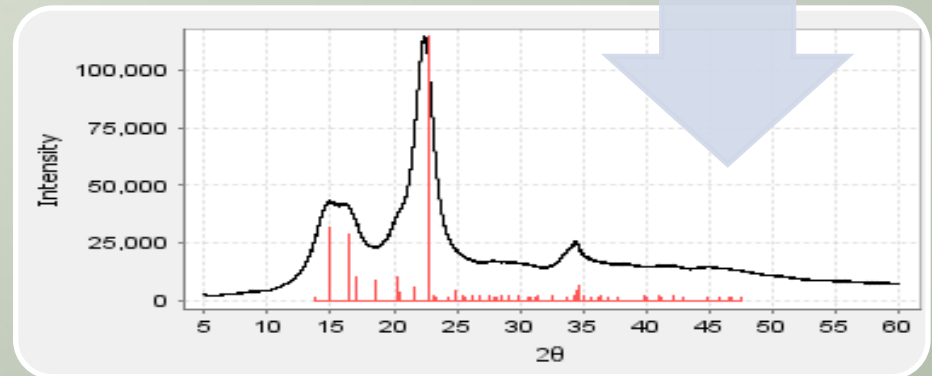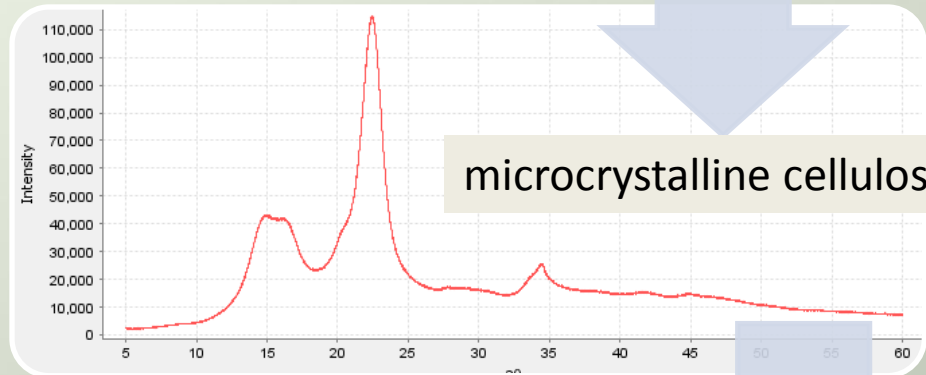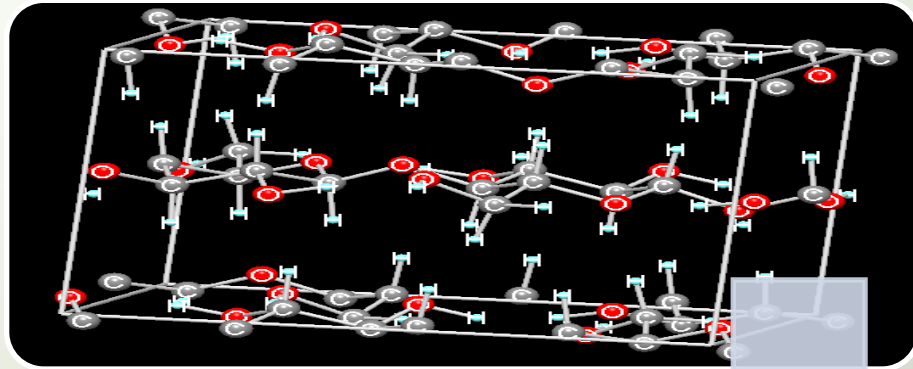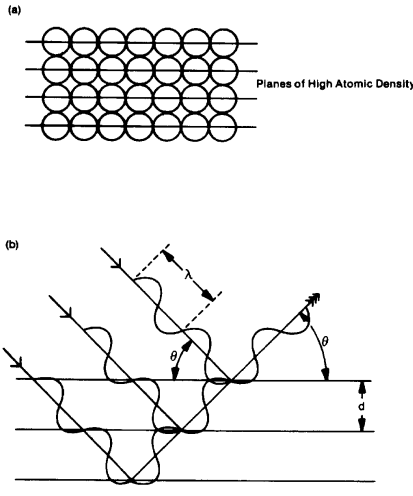
If the polymer is crystalline, then the diffraction pattern (middle right) is a result of a crystal structure (top right) as related by Bragg's law (left) and the pattern can be indexed (bottom right) and represented by a stick pattern of positions and intensities.
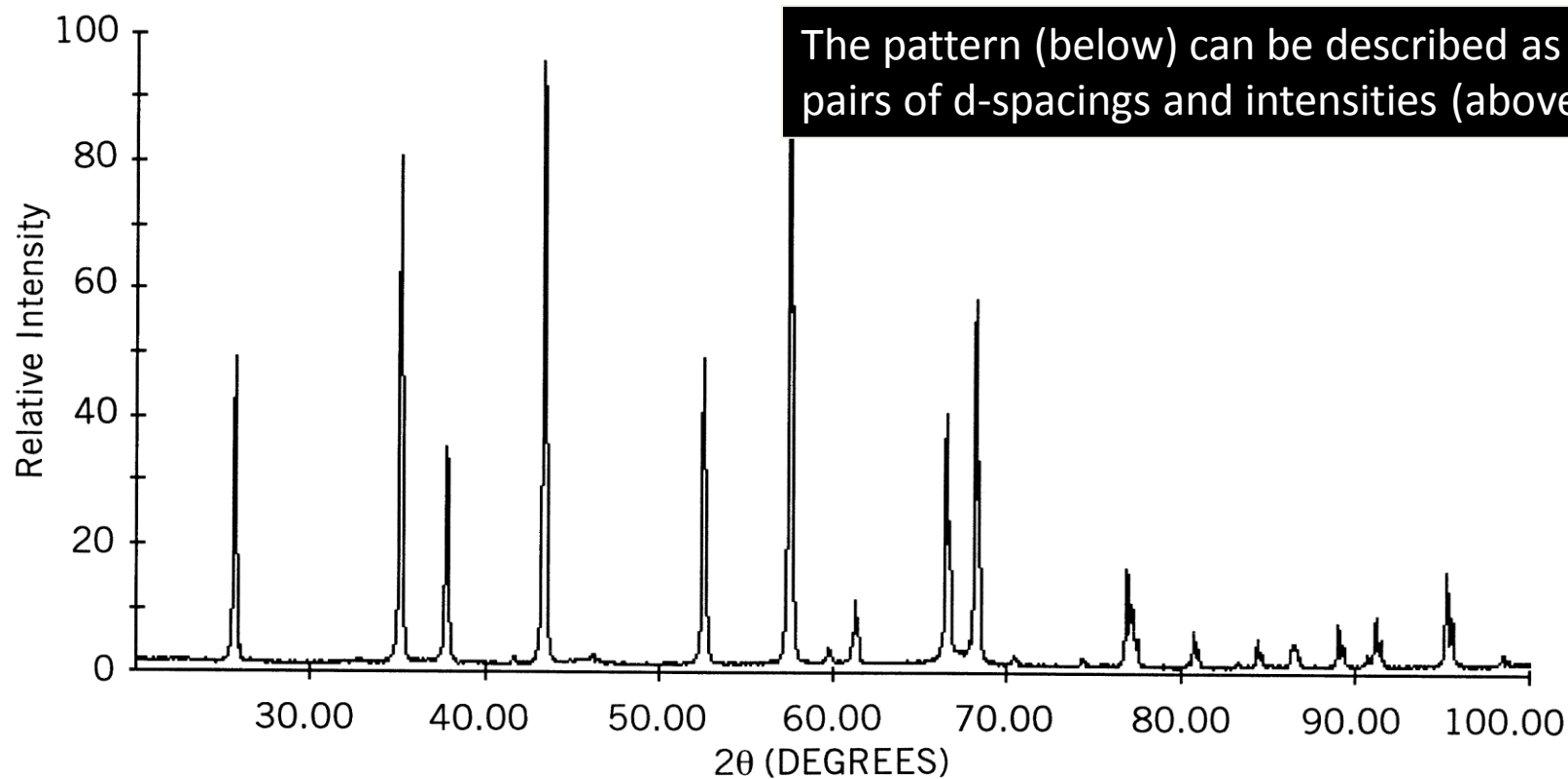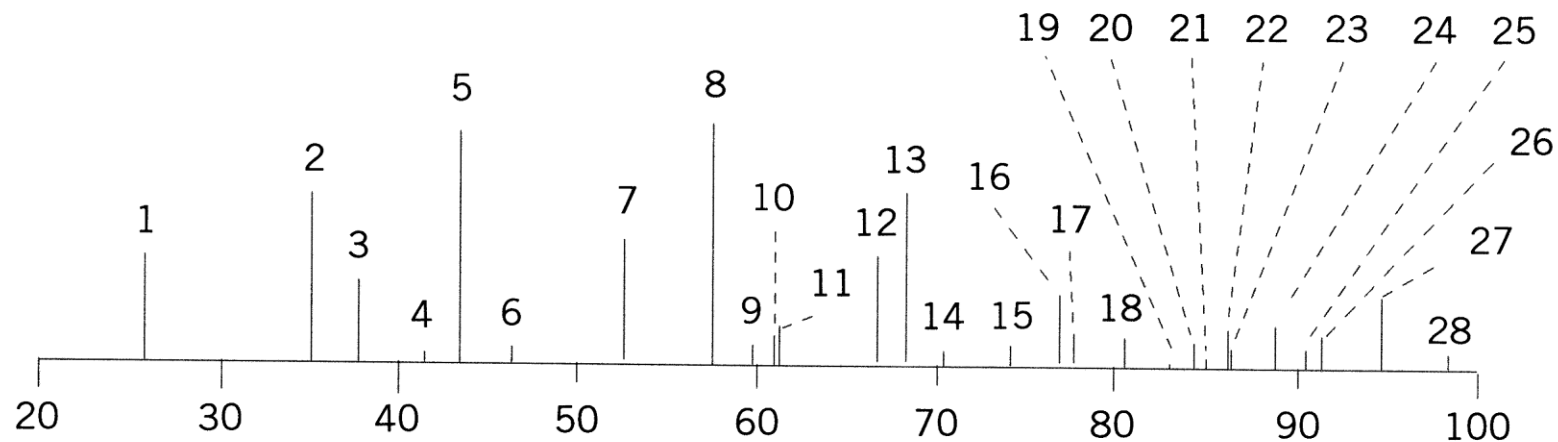
The pattern (below) can be described as pairs of d-spacings and intensities (above).

CRYSTALLINE POLYETHYLENE

Orthorhombic

hkl	d	2θ
110	4.091A	21.73
200	3.681	24.18
210	2.947	30.33
020	2.461	36.53
120	2.334	38.59
011	2.253	40.02
310	2.196	41.11
111	2.154	41.94
201	2.088	43.35
220	2.046	44.29
211	1.922	47.31
400	1.841	49.54
301	1.763	51.87
320	1.737	52.69
410	1.724	53.14
121	1.717	53.38
311	1.660	55.37
130	1.602	57.58
221	1.592	57.95

Walter & Reding
J. Polymer Sci. 21, 561 (1956)

Triclinic

hkl	d	2θ
010	4.553	19.50
100	3.803	23.39
1̄10	3.549	25.10
110	2.537	35.38
1̄01	2.444	36.77
001	2.370	37.96
1̄20	2.317	38.86
020	2.276	39.60
1̄11	2.239	40.29

Turner–Jones
J. Polymer Sci. 62, S53 (1962)

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Reference Data For Polymers

In ICDD reference databases (PDF-2, PDF-4+, PDF-4/Organics) we now have over 1200 reference patterns of polymers. Most have been collected from decades of work.

In the twentieth century most polymer data were represented by using d,I pairs such as the data shown on the bottom. This was good for identification purposes, which searches d,I pairs, but not for measuring crystallinity.

Since 2009, ICDD has been collecting polymer data as full digital patterns. In Release 2011 there are 43 digital polymer patterns (middle). The data collection process is focused on high volume commercial polymers.

Since 2010, the ICDD has been collecting well-characterized sample and reference data for amorphous materials as shown for ABS (top).
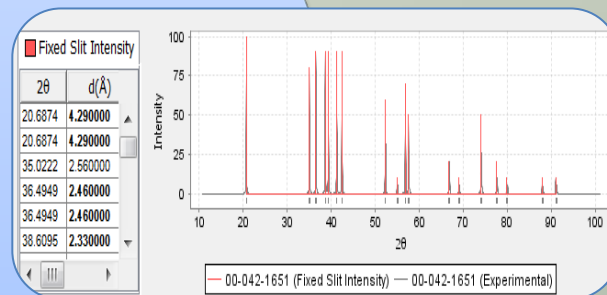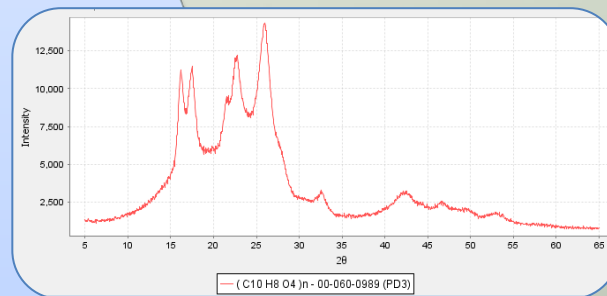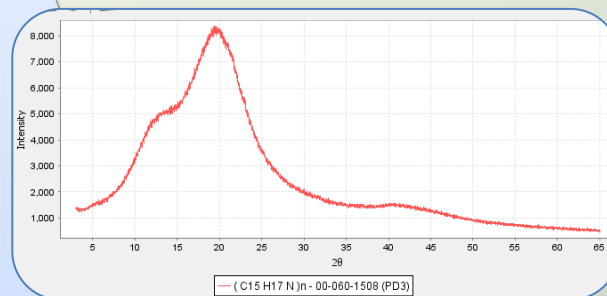
Polymer patterns are additive. In this example, we see a crystalline polymer (polyethylene) is added to a noncrystalline polymer (polyisobutene) and the resulting pattern (top) shows contributions from both polymers.

ADDITION OF A CRYSTALLINE PATTERN
AND A NONCRYSTALLINE PATTERN

68% POLYETHYLENE
32% POLY(ISOBUTENE)

POLYETHYLENE

POLY(ISOBUTENE)

INTENSITY

2θ

5°   15°   25°   35°   45°
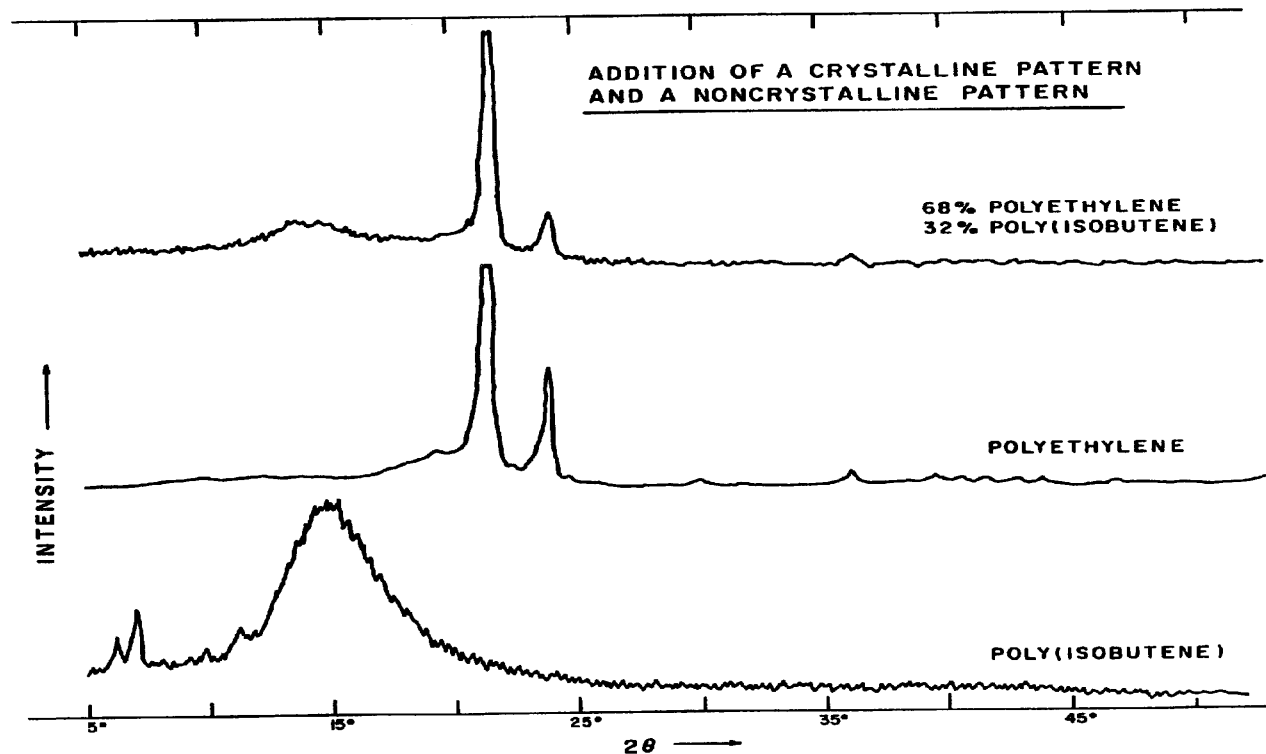
This probably indicates that these two materials were not miscible. If the polymers were atomically mixed, then a different pattern would be produced based on the new unit cell or atomic arrangement. XRD is often used to distinguish between block copolymers, alternating or randomly mixed copolymers.

Patterns are additive: in this example, 2 polymer patterns are added with 2 patterns of inorganic oxides – to identify a corrosion residue collected on a cloth.

The cloth is made of two polymers- PET and cotton.
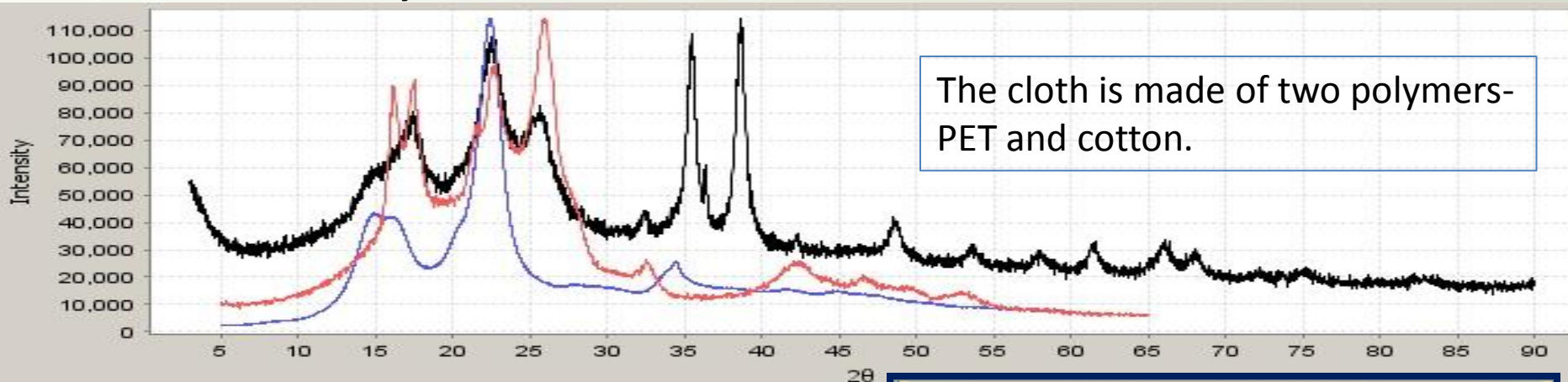
© 2010 International Centre for Diffraction

— (C10 H8 O4)n - 00-060-0989 (PD3) — (C6 H10 O5

Black Deposit inside XPS Anode on Swi
Lambda 1.5406 A, L-S cycle 100

Four pattern refined fit
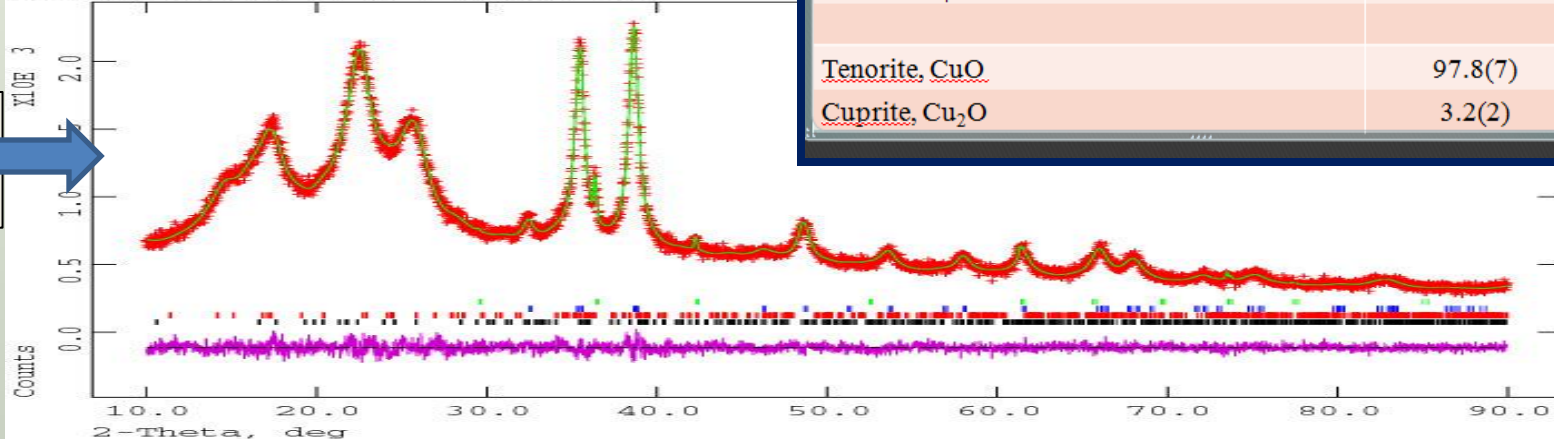
Phase	Concentration, wt%
Poly(ethylene terephthalate) = polyester	65.5(2)
Cellulose I_β = cotton	34.5(4)
Tenorite, CuO	97.8(7)
Cuprite, Cu_2O	3.2(2)

Data courtesy of J. Kaduk, Poly Crystallography Inc.

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How to Identify Polymers

Always search on the polymer subfile in an ICDD database. Polymers are weak scatterers and frequently have only a few weak peaks, you need to help the automated search process. The peaks are frequently broad so make sure your automated software is detecting them (you may need to change the program defaults).

Crystalline polymers:
Crystalline polymers can be readily identified by most search/match software on the market today. The d-spacings can be searched and d,I pairs used in the identification process. If the polymer is present in small concentrations, please keep in mind that many, if not most polymers, have only 1-3 intense peaks usually associated with interplanar spacings between polymer chains. You may need to use trace identification methods since the lack of peaks will often limit automated processes.

See the tutorial: **"Data Mining-Trace Phase Analysis"**
http://www.icdd.com/resources/tutorials/

Non-crystalline polymers:
Special methods are required that identify non-crystalline materials based on full patterns and not d,I listings. Integral indices and cluster analyses are examples of these methods. Specialized Reitveld and LeBail refinements can also be used.
They are beyond the scope of this tutorial, but examples are given in other tutorials.

See the tutorial: **"Using Similarity Indexes – Integral Index"**
http://www.icdd.com/resources/tutorials/

Examples of Analyses – Identification of Polymers

Pharmaceutical grade microcrystalline cellulose is used in a wide variety of tablets as both an excipient filler and an additive to modify drug time release. The reference pattern of microcrystalline cellulose is shown at the top.

The middle pattern is the diffraction pattern from a ground Pepcid AC tablet. The sharp crystalline peaks are due to the active ingredient famotidine and one can easily see the microcrystalline cellulose pattern. This identification would be easy by either automated or manual methods.

The bottom pattern is from a ground Benedryl tablet. This is far more typical of what ICDD has seen in pharmaceutical formulations. The microcrystalline cellulose (in box) is a much weaker pattern than the crystalline inorganic excipients (brushite reference in blue). The weak pattern and broad peaks make this a much more difficult identification.

Microcrystalline Cellulose

Pepcid AC

Benedryl
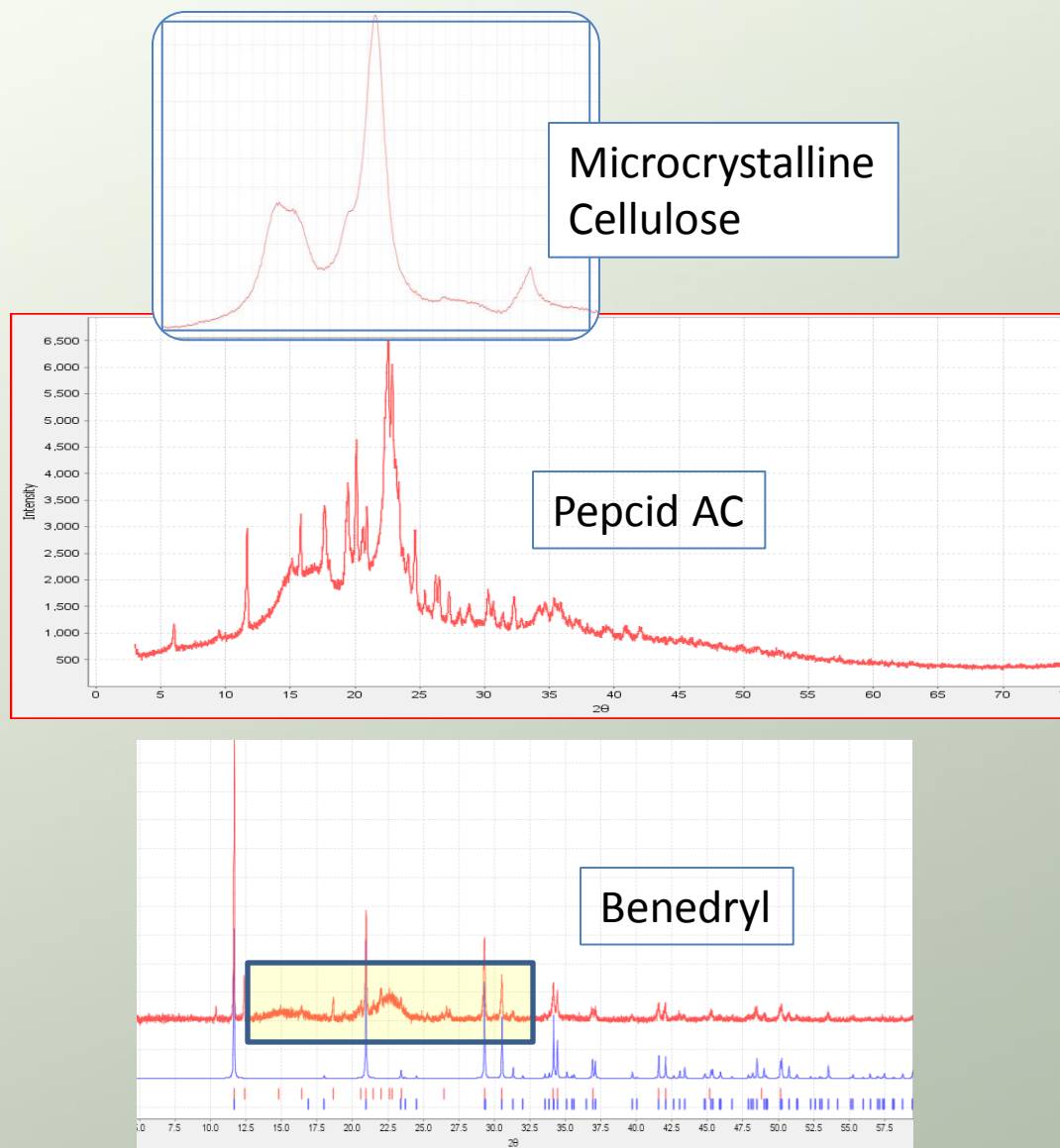
Measuring Relative Crystallinity

- The following slide shows a classical method for measuring crystallinity in polypropylene.
- It is assumed that the polymer has regions of aligned chains in small crystallites that diffract and that the remaining chains have no order and contribute to an incoherent scatter.
- The scientist trys to measure the area of both components and estimate a crystallinity.
- This method can be applicable in cases where the amorphous region is well defined within a relatively narrow angular range – as in polyethylene and polypropylene.
- Absolute standards are not necessary and this method yields a relative crystallinity. Care must be taken that the amorphous area is measured the exact same way in the exact same angular range for each specimen analyzed.
- With this relative method, all specimens need to be analyzed under identical conditions on the same instrument.

"RELATIVE" % CRYSTALLINITY IN POLYPROPYLENE
Dow research report SL87902

Crystalline area............36.6
noncrystalline area........28.1
relative % crystallinity...56.7%
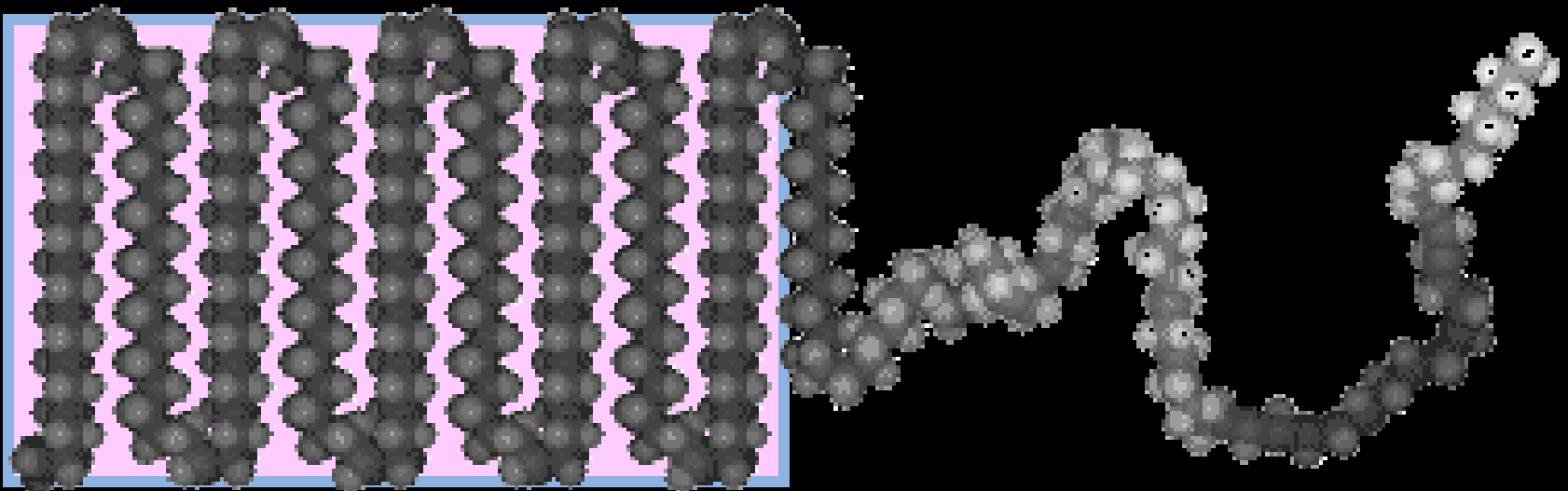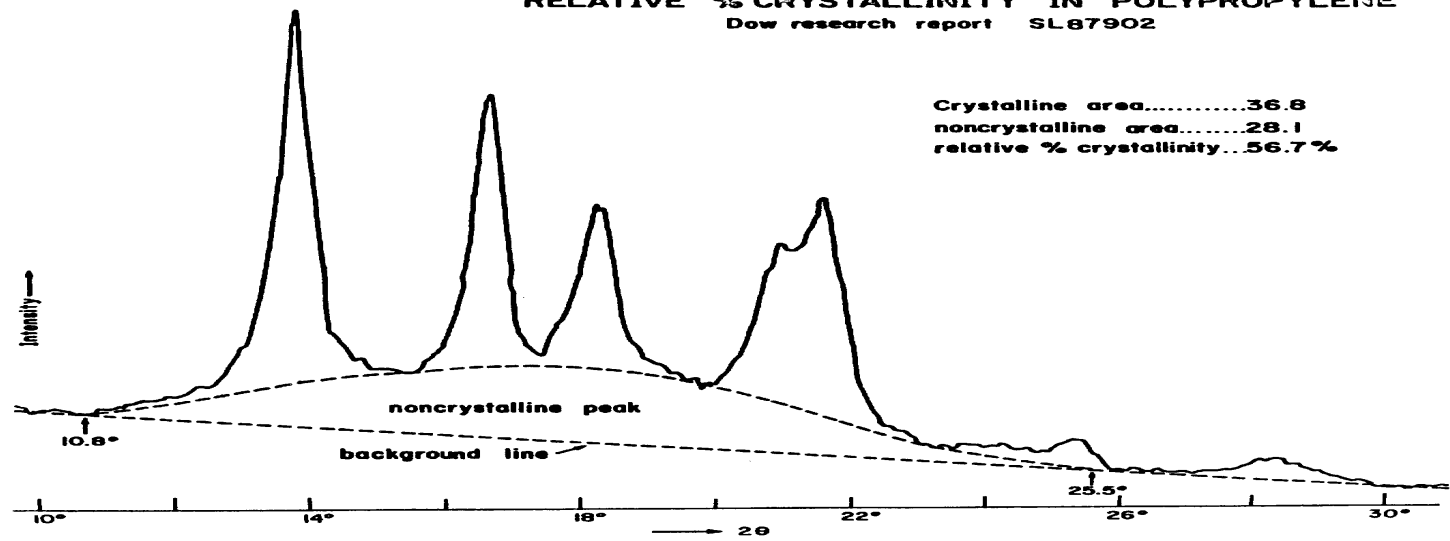
Measuring Crystallinity – Pattern Fitting Methods

- Based on the premise that patterns are additive

- Requires both a 100% crystalline reference and an amorphous reference. The ICDD database can provide many high volume commercial polymers with full digital pattern references.

- Full digital patterns are used; they need to be treated to remove background and have identical data collection ranges. Because most data scans consist of thousands of data points, it is preferred that this is a computer automated method. Graphical interfaces are advised so that the user can judge the appropriateness of the background removal and other data treatment steps.

- The references can be used to calculate crystallinity using pattern fitting methods (several software packages are currently available).

- If an I/Ic value is available, or if an internal standard is used, concentrations can be calculated.

- This method is preferred in cases, like cellulose, where both the crystalline pattern and amorphous pattern heavily overlap and cover most of the measurement range.

Patterns are Additive- Measuring Crystallinity in Cellulose

Standards of native cellulose, crystalline and amorphous. The crystalline form is I beta.
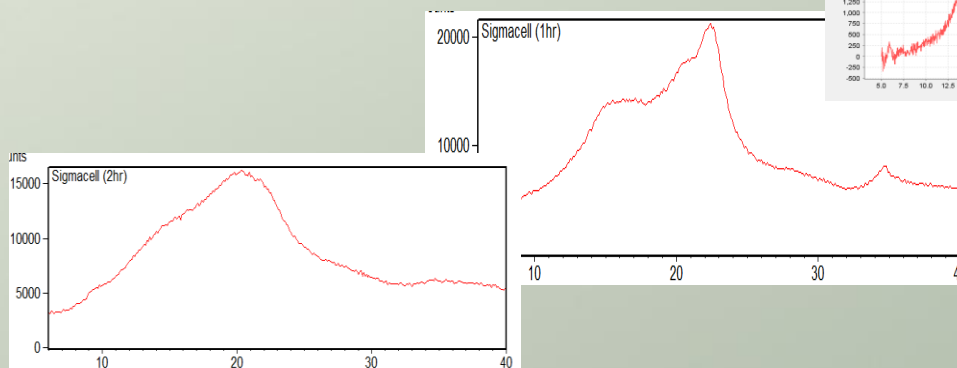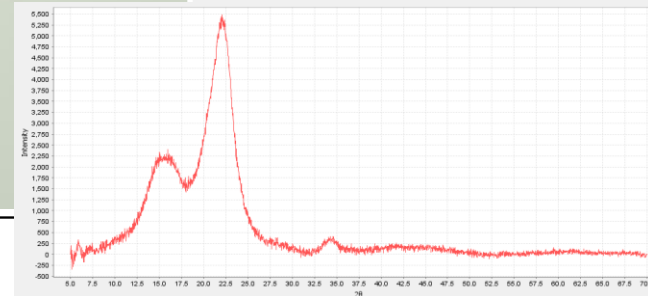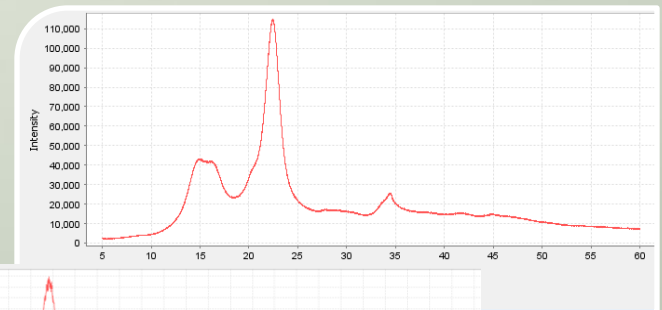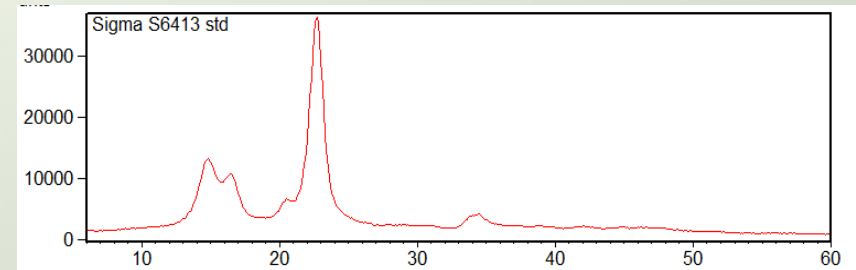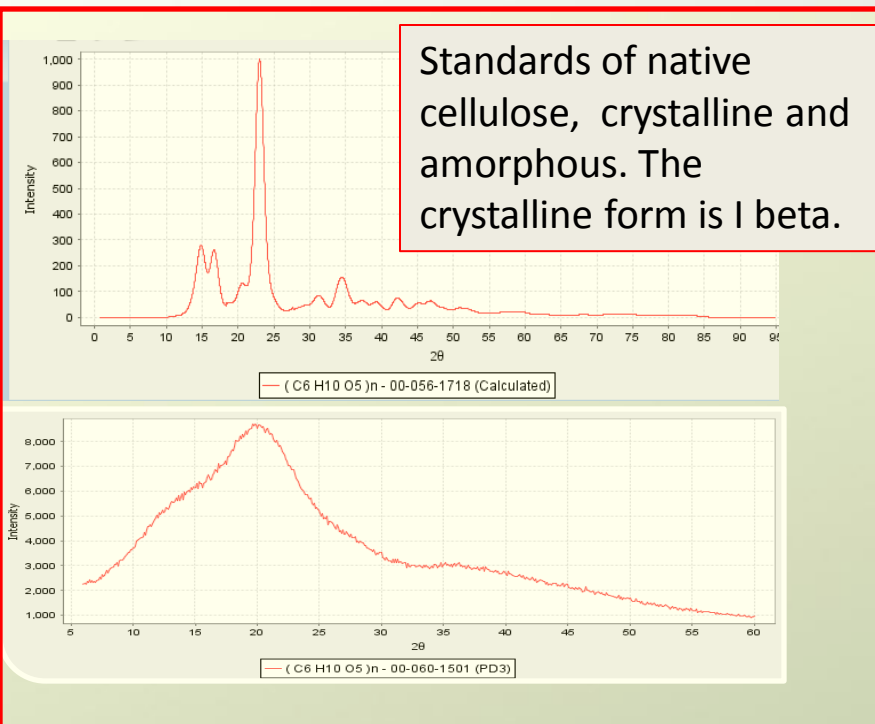
Crystallinity reduces from top to bottom. The two references can be used to calculate a % crystallinity in each sample.

A Few Words on Data Collection

$$I_{(hkl)\alpha} = \left[\frac{I_0\lambda^3}{64\pi r}\left(\frac{e^2}{m_e c^2}\right)^2\right]\left[\frac{M_{hkl}}{V_\alpha^2}|F_{(hkl)\alpha}|^2\left(\frac{1+\cos^2 2\theta \cos^2 2\theta_m}{\sin^2\theta\cos\theta}\right)\right]\left[\frac{X_\alpha}{\rho_\alpha(\mu/\rho)_s}\right].$$

A

B

This equation expresses the intensity of a diffraction peak and can be found in the fundamental texts referenced in slide 6. For polymers, terms A and B of this equation are very relevant. Term A is the scattering factor (F) which is another long equation in itself, and the factor is proportional to the atomic number Z of the atoms in the compound. *Most polymers being composed of hydrocarbons (low Z) and are weak scatters of X-rays.* The second term B, includes the mole fraction of the analyte in the material being analyzed (X) and the density of the material. *Polymers are low density.*

This means if you are collecting data on a polymer specimen, life is more difficult. A relatively high concentration of a polymer may still give you a very weak pattern (such as bottom slide 20). If your material is microcrystalline or amorphous, the pattern is spread over a wider angular range and even less intense at any given point. The powder diffraction data shown in this presentation were usually diffraction scans taken over a period of many hours so that sufficient signal was collected to do an identification or crystallinity measurements. If you use thin film or capillary specimen preparations you will need to be even more careful since you have limited specimen exposed to the X-ray beam.

Advanced Applications

An enormous amount of information can be extracted from the diffraction patterns of polymers. This tutorial only covers the fundamentals of identification and crystallinity. Polymers can be processed into fibers and films and they can be molded and extruded. Each of these processes can orient the molecules and diffraction can be used to measure the orientation – in both crystalline and non-crystalline materials. For amorphous materials, pair distribution function analysis can provide insights into the crystalline coherence length and nearest atom bonding. Low angle or small angle scattering can be used to determine the size and shapes of polymer domains within a specimen. Neutrons strongly diffract from hydrogen, so neutron diffraction can provide structural details that are difficult or impossible to see in X-ray diffraction. For additional information, use key word searches in either Google Scholar of Advances in X-ray Analysis.
http://www.icdd.com/resources/axasearch/search_based_on_vol.asp?vol_num=AXA

Key search words: polymer, Small Angle scattering (SAX), texture, pair distribution, fibers

Every three years, the Denver X-ray Conference hosts polymer scientists to give workshops and symposia on polymer diffraction. The last event was held in 2010 and the next scheduled polymer workshop/symposia is scheduled for 2013.

Thank you for viewing our tutorial.
Additional tutorials are available at the ICDD website.
www.icdd.com

International Centre for Diffraction Data

12 Campus Boulevard

Newtown Square, PA 19073

Phone: 610.325.9814

Toll Free Number in US & Canada: 866.378.0331

Fax: 610.325.9823