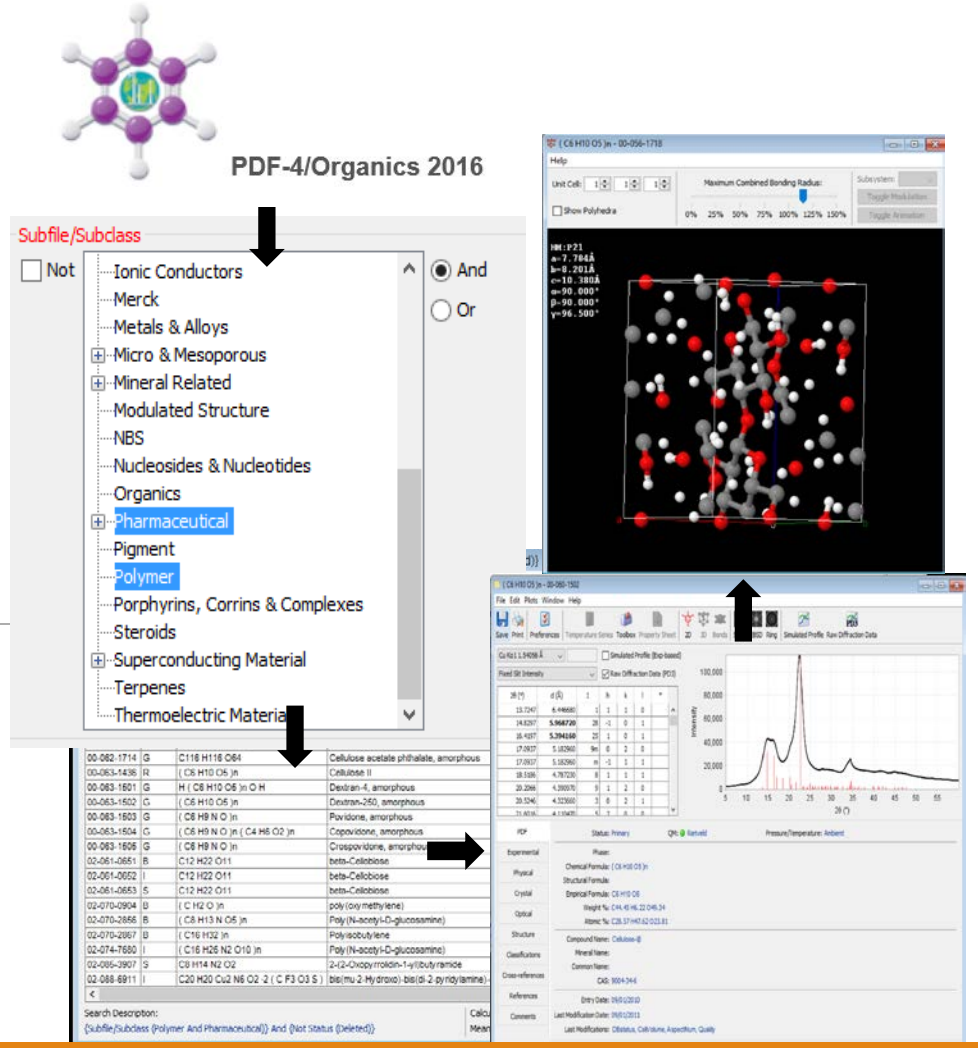
ICDD Powder Diffraction File® Coverage of Polymers Used in Pharmaceutical and Biomedical Applications



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S. MISTURE, ALFRED UNIVERSITY

This document was presented at PPXRD - Pharmaceutical Powder X-ray Diffraction Symposium

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PPXRD Website – www.icdd.com/ppxrd

ICDD Website - www.icdd.com

What is a polymer?

The word polymer is derived from the Greek words *polus*, meaning many, and *meros*, meaning parts.

A long-chained molecule that is composed of individual units, called monomers.

A compound typically of high molecular weight derived either by the **addition** of many smaller molecules, such as polyethylene, or by the **condensation** of many smaller molecules with the elimination of water, alcohol, or the like, such as nylon.

Polymers can be natural or synthetic

There are inorganic polymer and coordination polymer materials, we will focus on carbon or silicone based polymers

Polymer analysis using XRD

Many techniques are used for polymer characterization

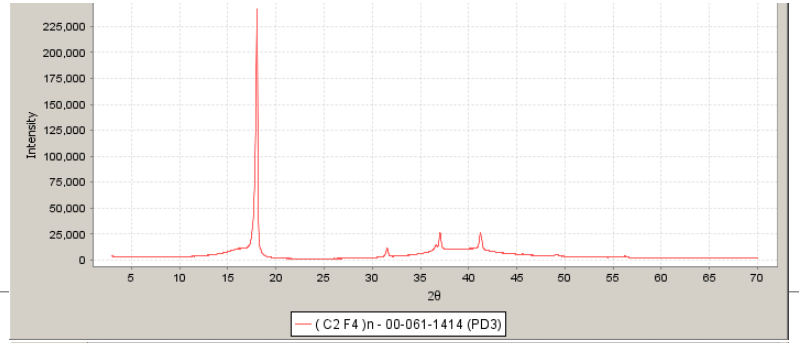
- IR, NMR, GC/MS, etc.

Why use XRD?

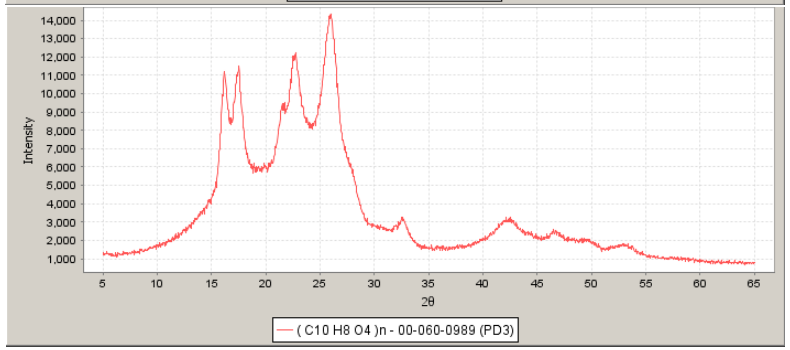
- Polymers can have amorphous and crystalline regions
- Crystallite size is small and measurable by XRD
- Polymers are often used as the base component in pharmaceutical and biomedical composite materials

Polymer order:

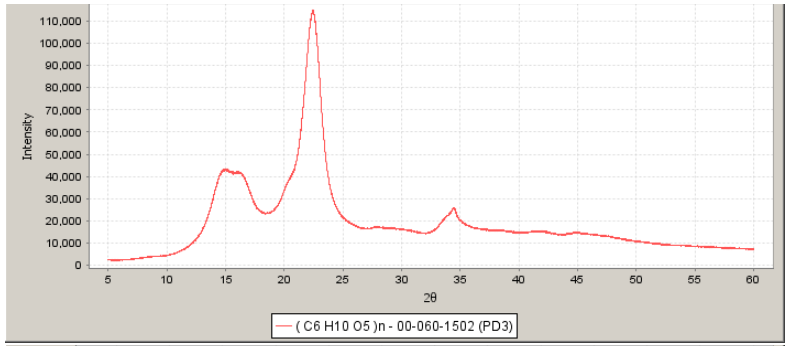
Highly crystalline - Teflon



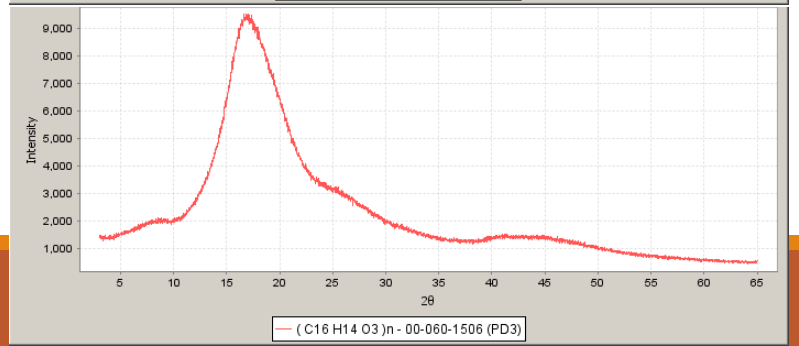
Semi crystalline – polyethylene terephthalate



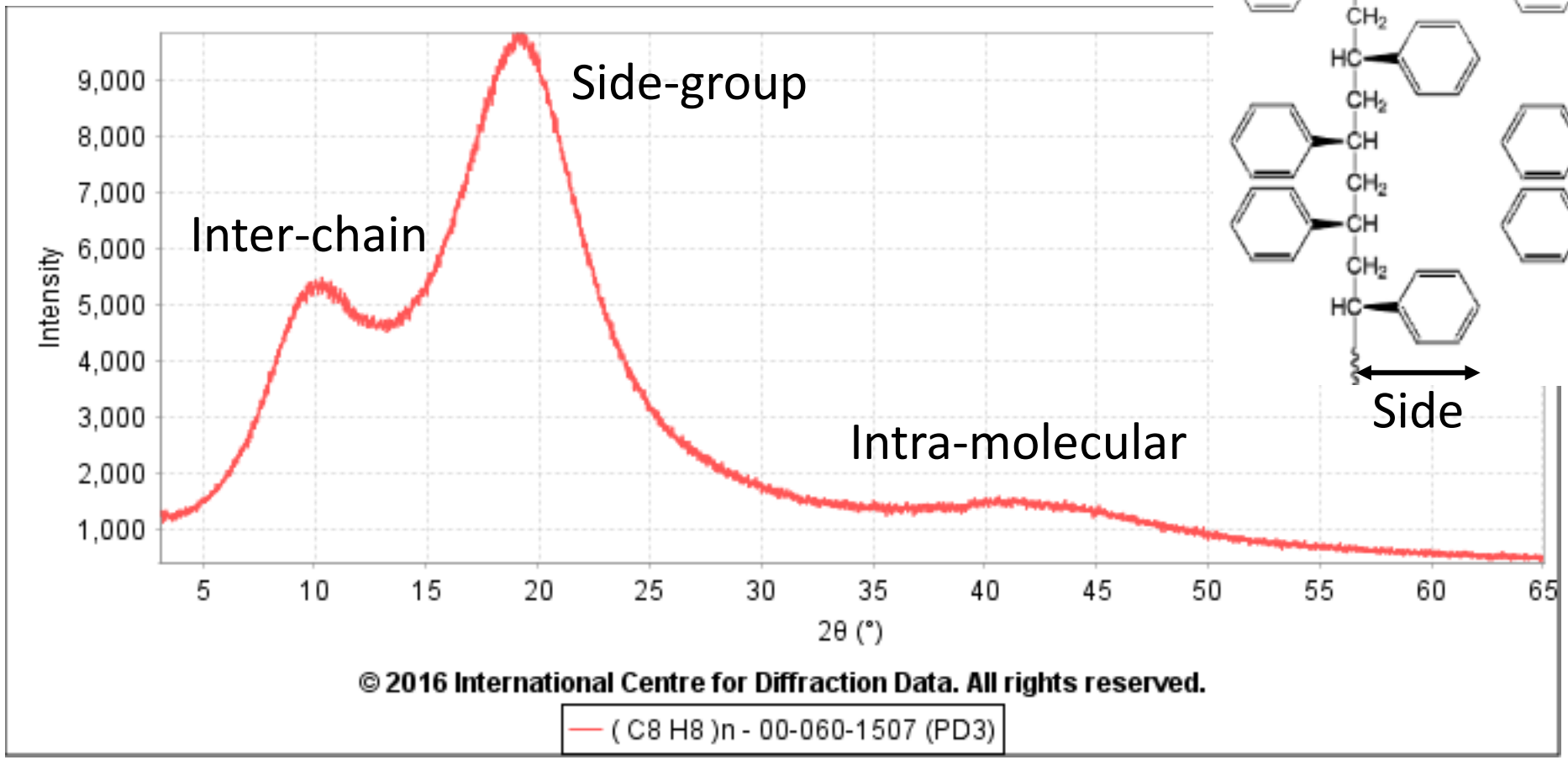
Micro crystalline – cellulose 1β

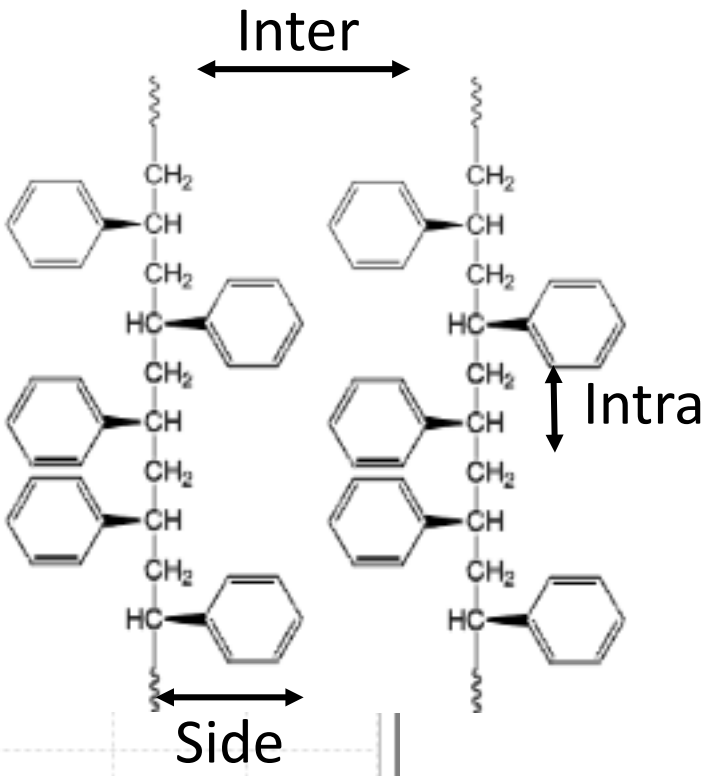


Amorphous - polycarbonate



XRD pattern for atactic polystyrene – effect of the polymer chain structure

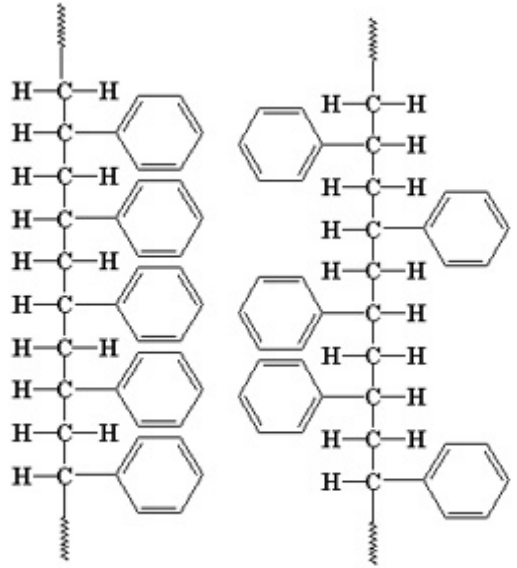


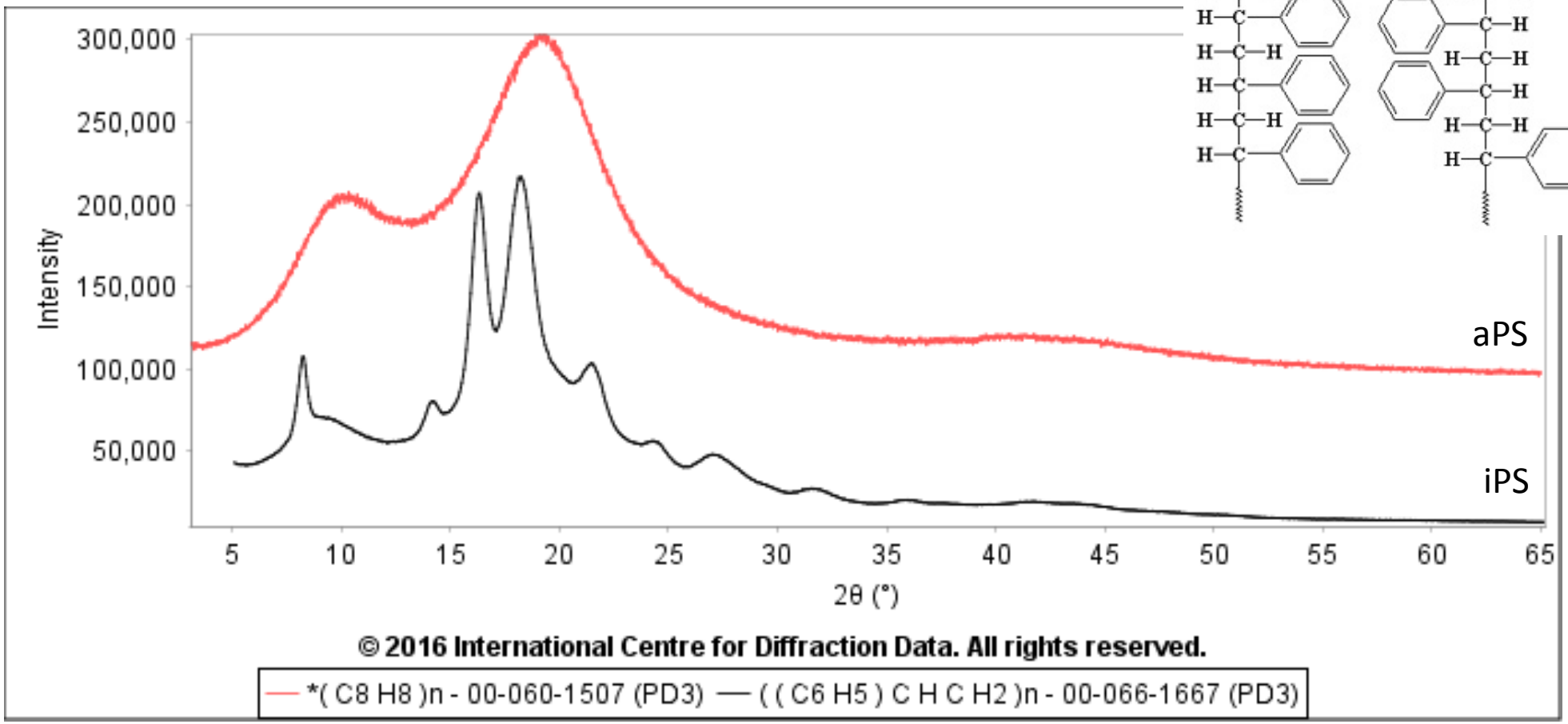


Effect of tacticity on polymer order

Isotactic PS

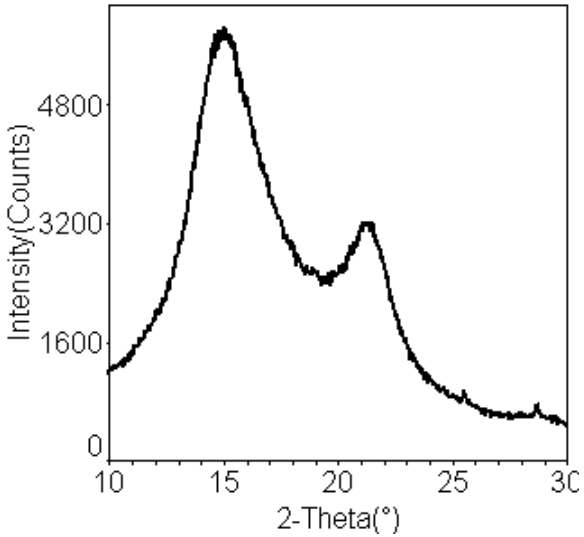
Atactic PS

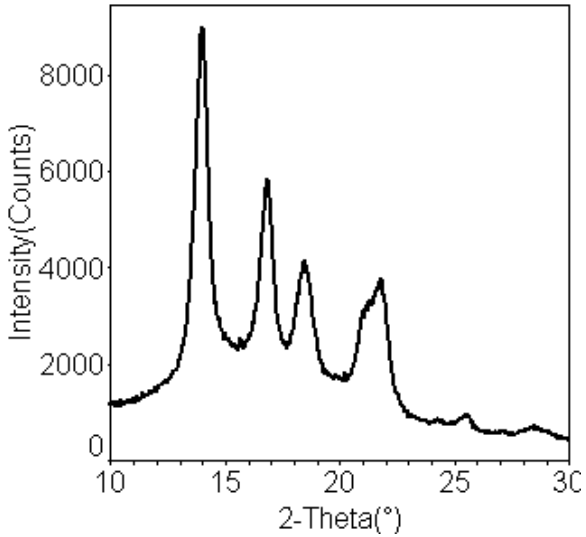


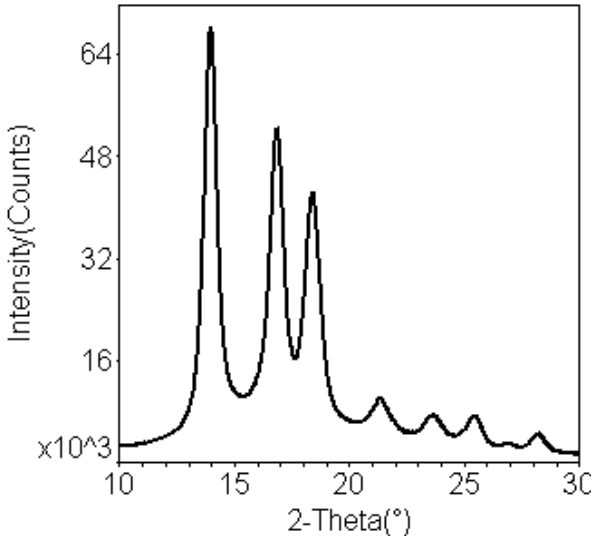


Rhombohedral R-3c
a=22.049Å
C=6.723Å

Bragg Brentano Reflection Mode XRD Patterns - Effect of Processing on Polypropylene





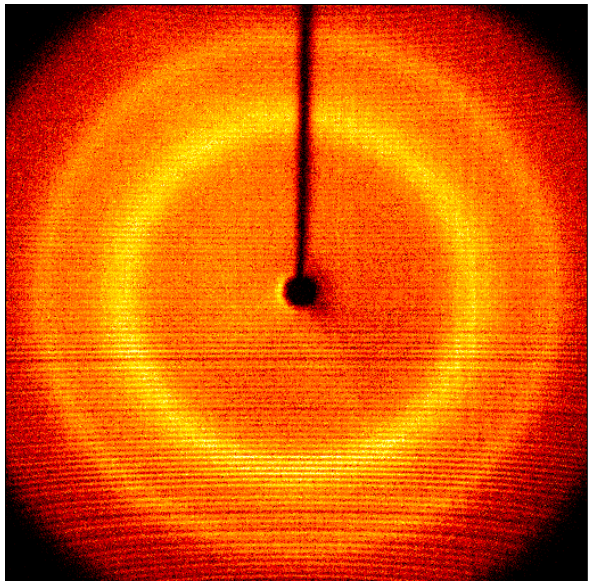


Cast
No heatset
No stretch

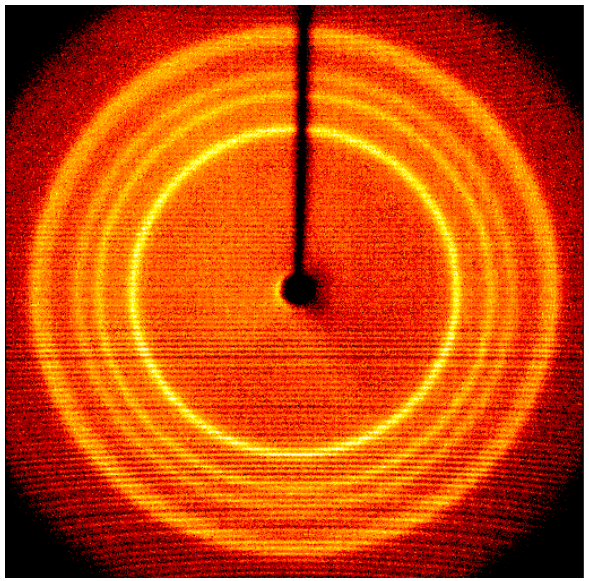
Heatset
120 °C, 10s
No stretch

Heatset
6X
Uniax stretch

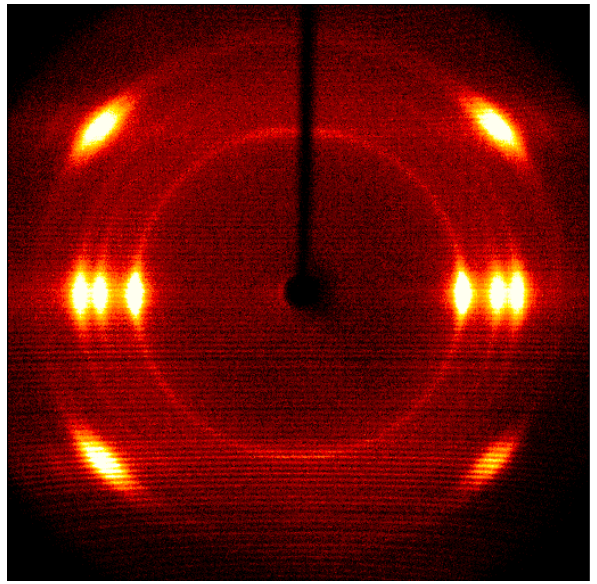
2-D transmission XRD patterns - Effect of processing and sample orientation on polypropylene XRD patterns



Cast
No heatset
No stretch

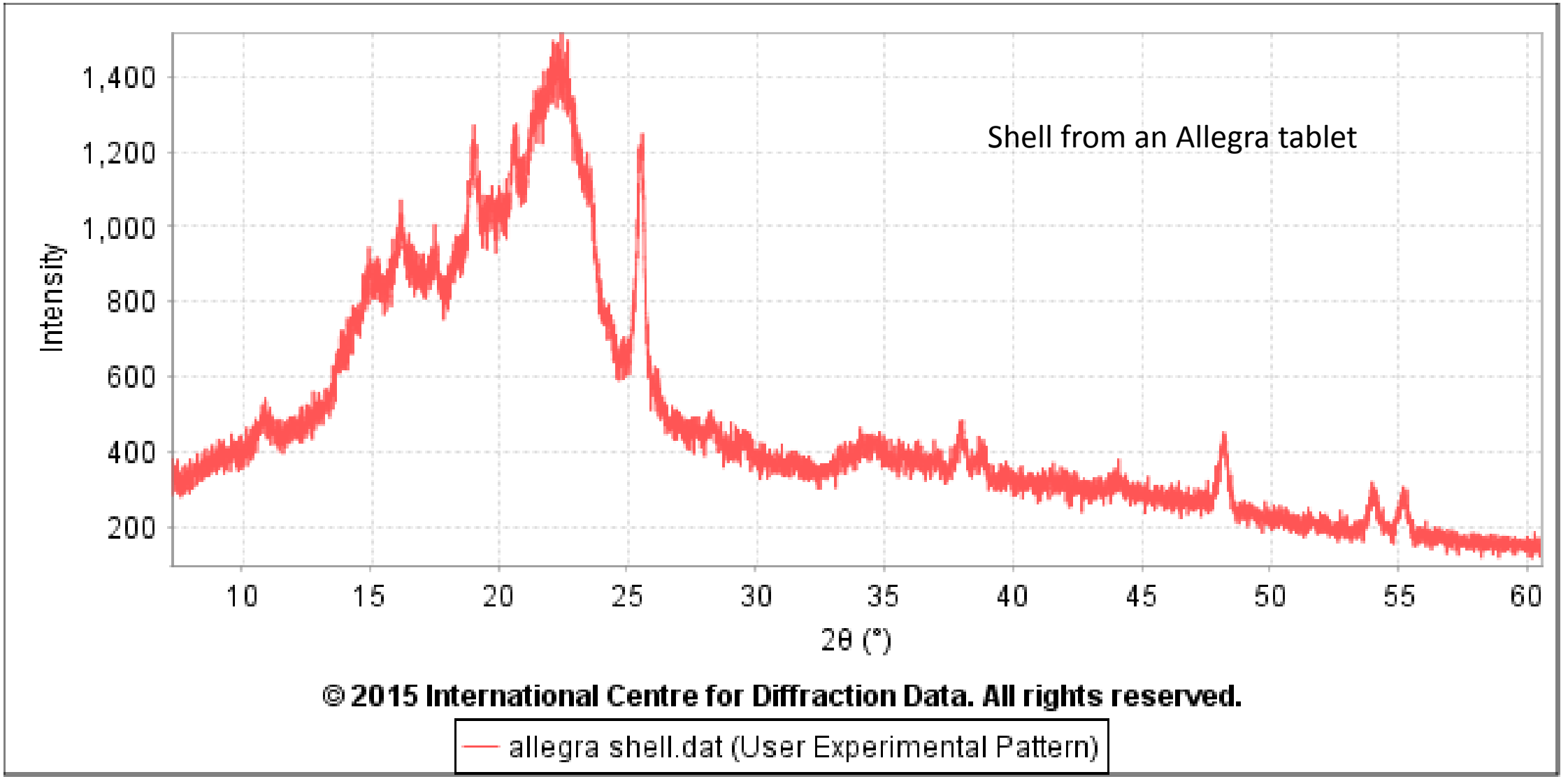


Heatset
120 °C, 10s
No stretch

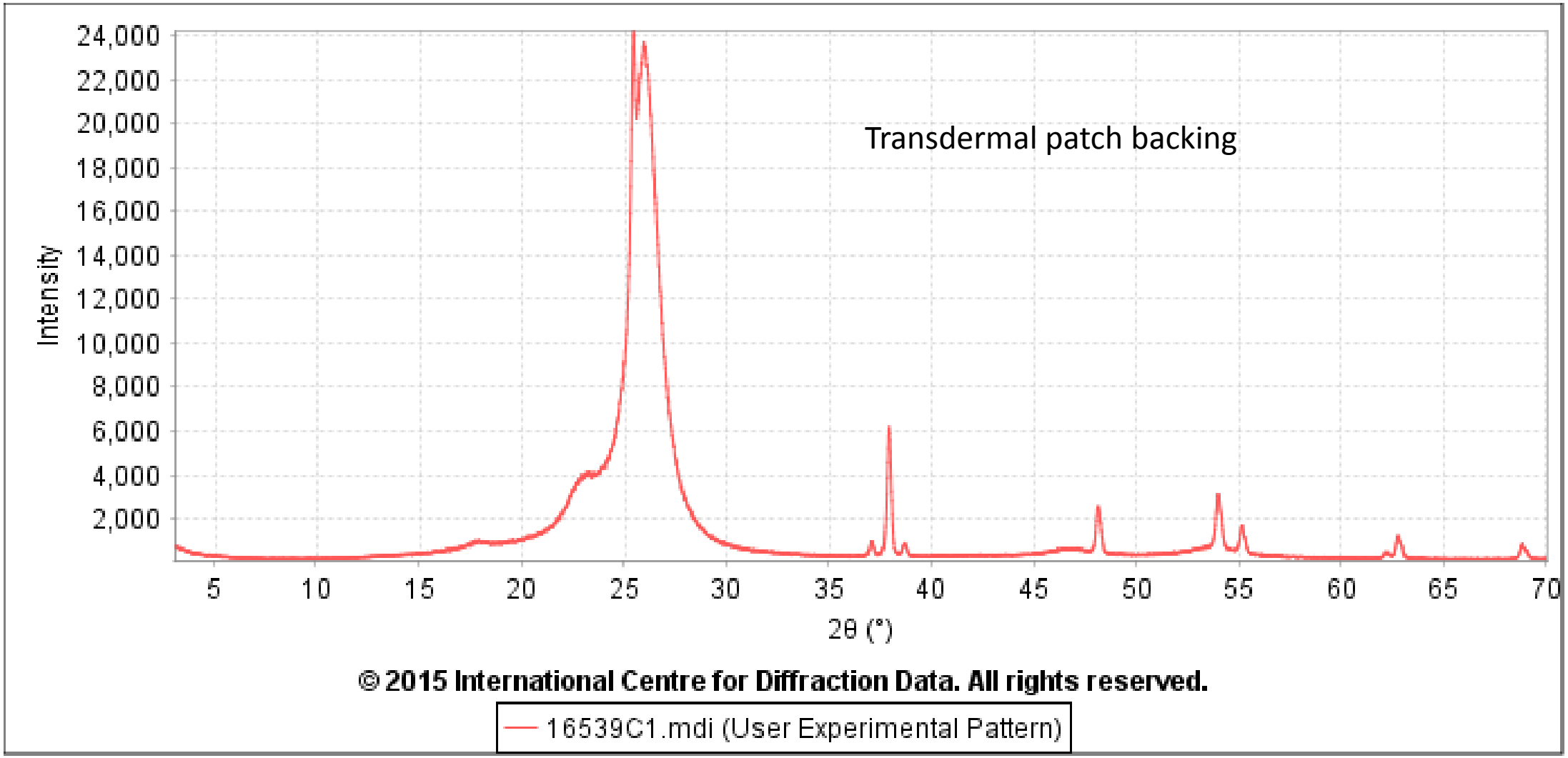


Heatset
6X
Uniax stretch

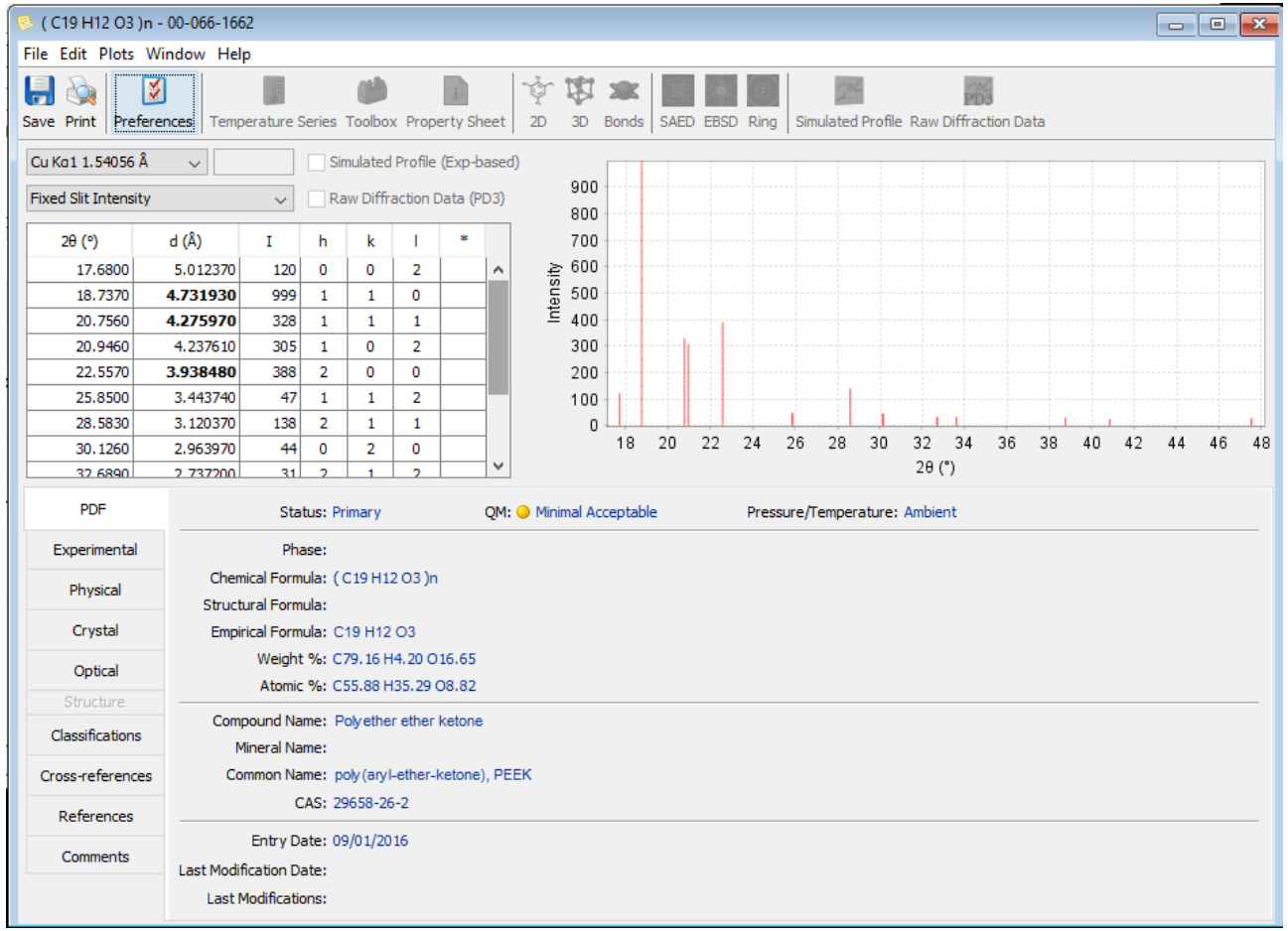
Pharmaceuticals



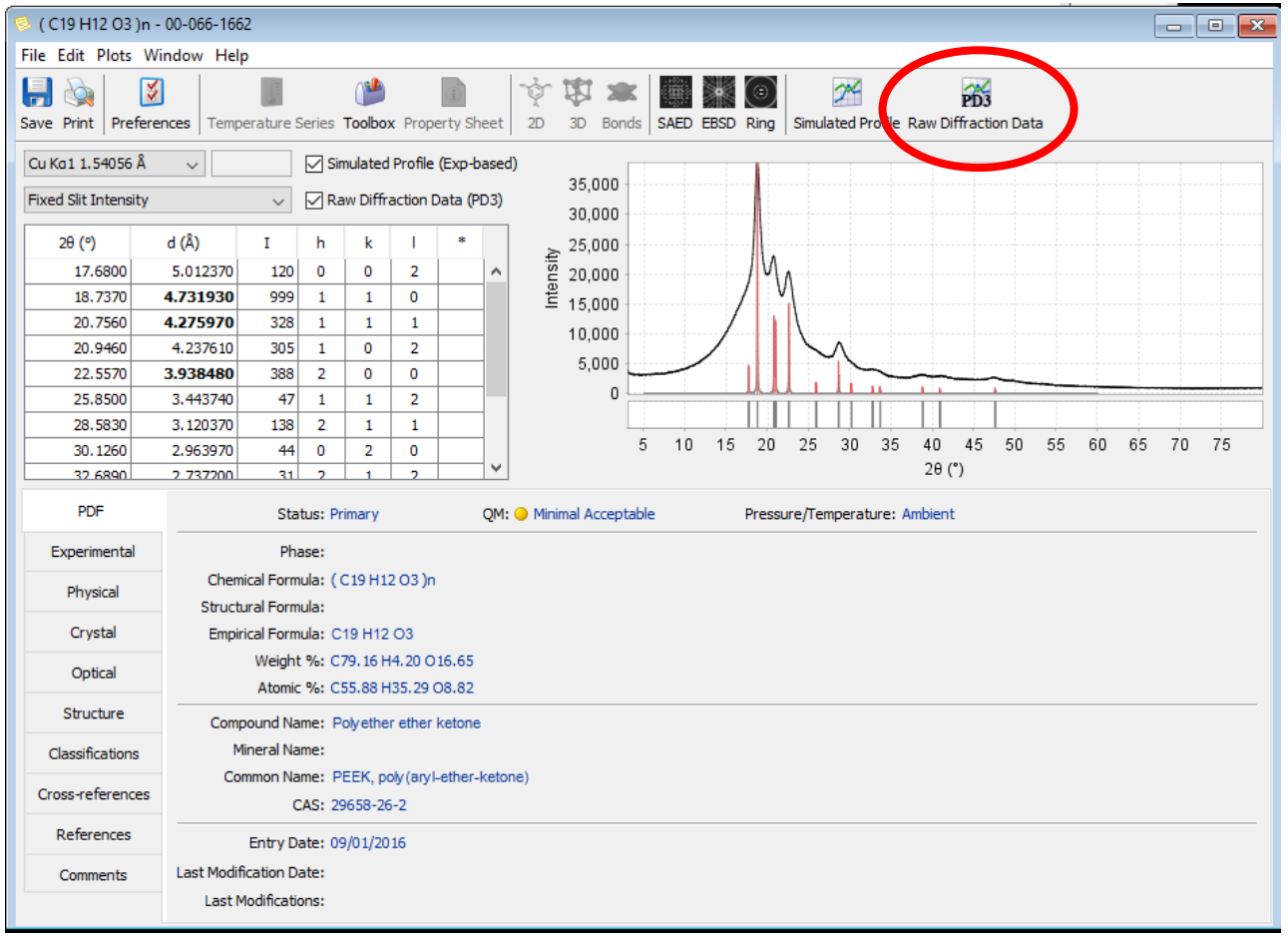
Biomedical devices



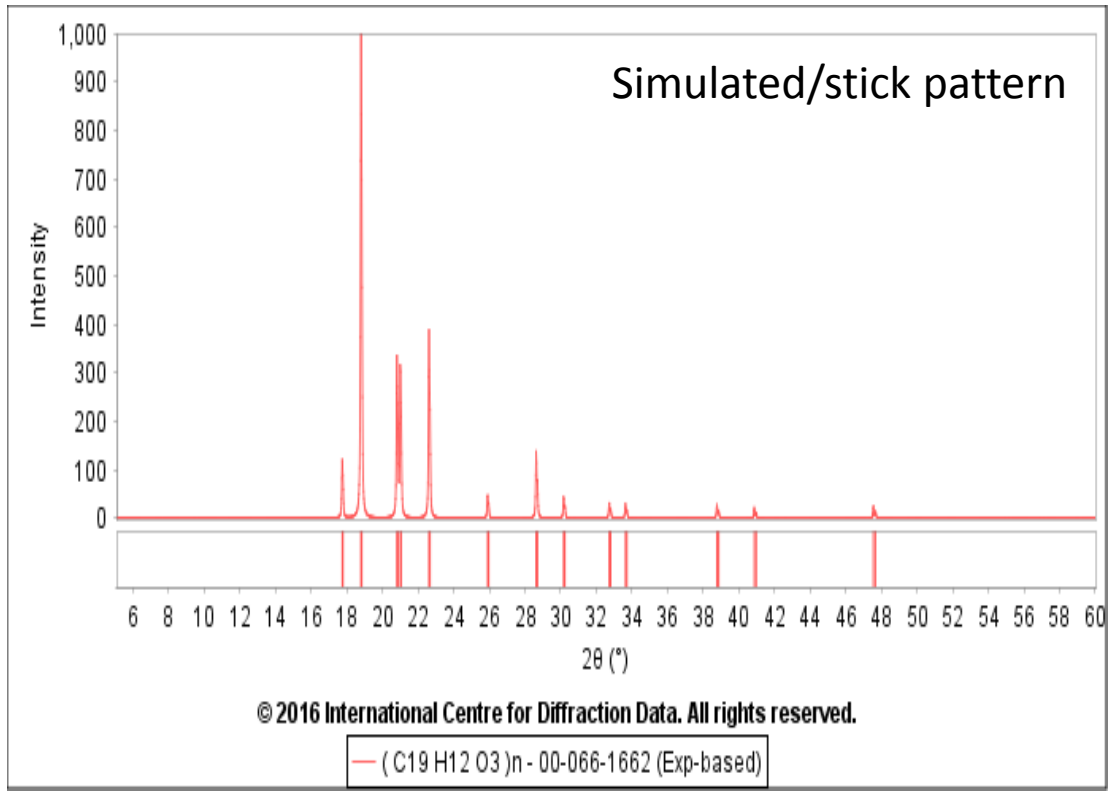
Powder Diffraction File PDF Polymer Entry – PEEK Polymer

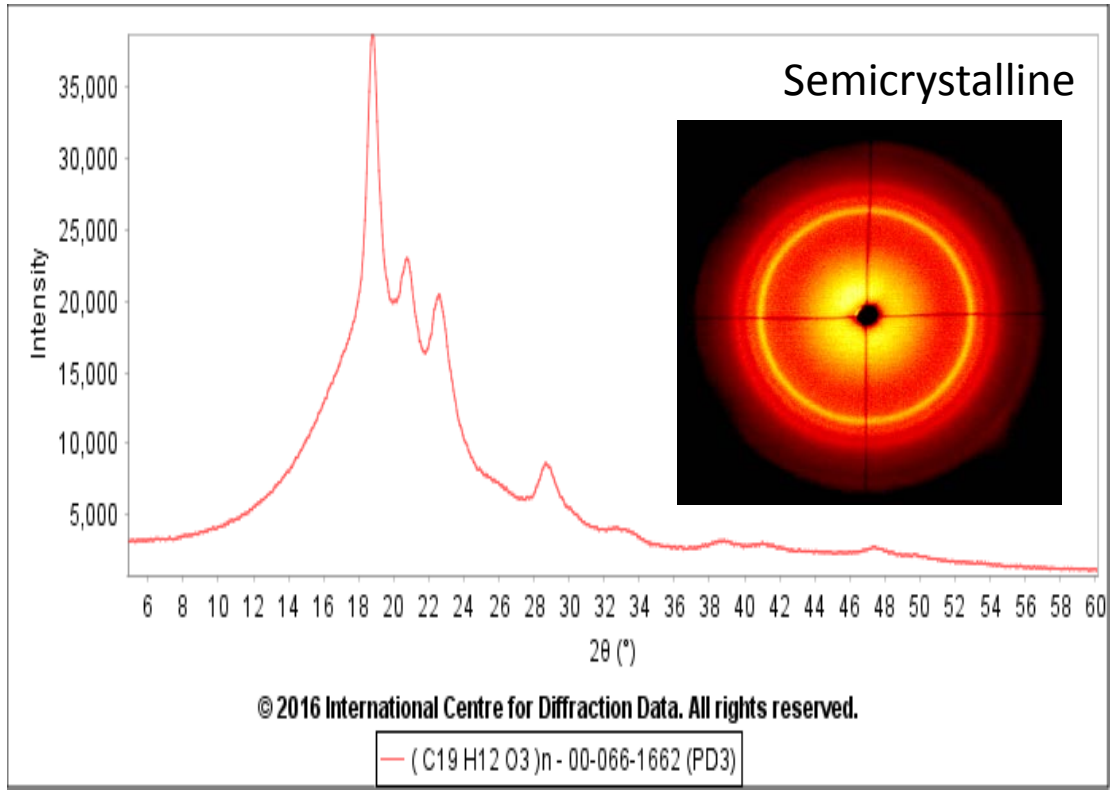


Powder Diffraction File PDF Polymer Entry – PEEK Polymer



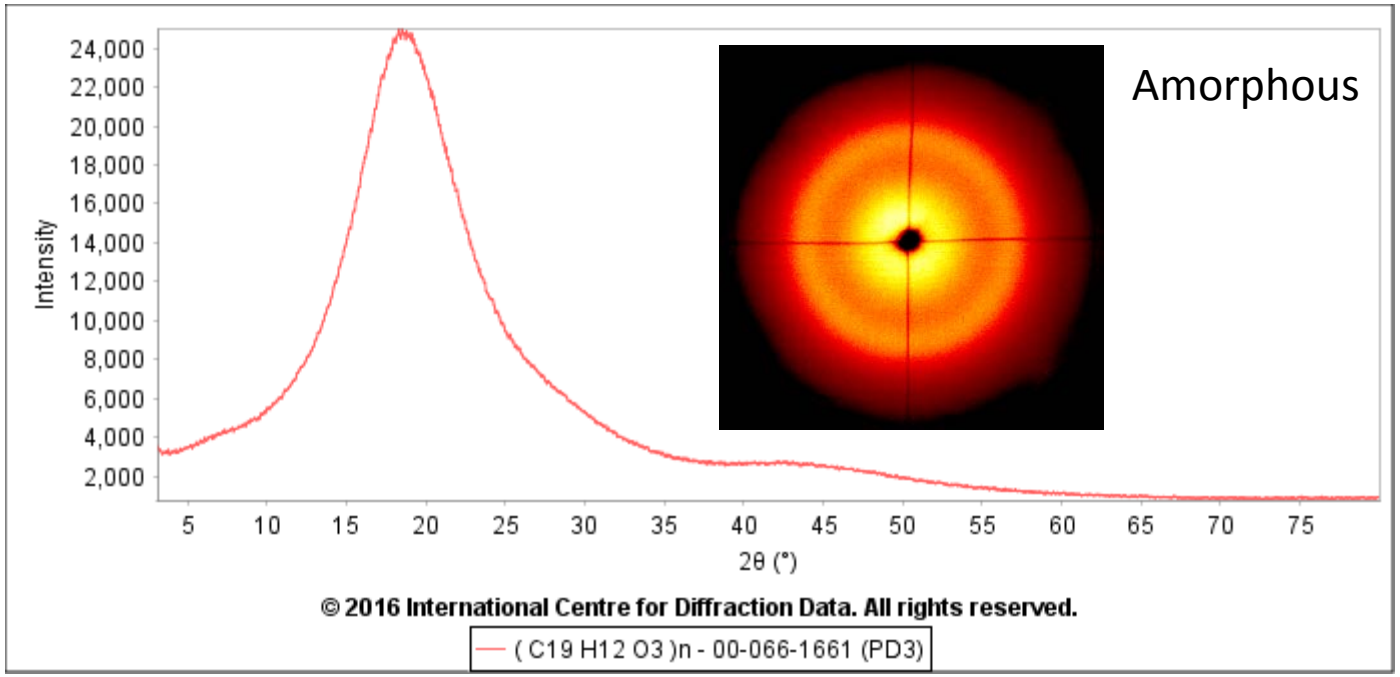
PD3 Raw Data Patterns in the Powder Diffraction File – PEEK Polymer



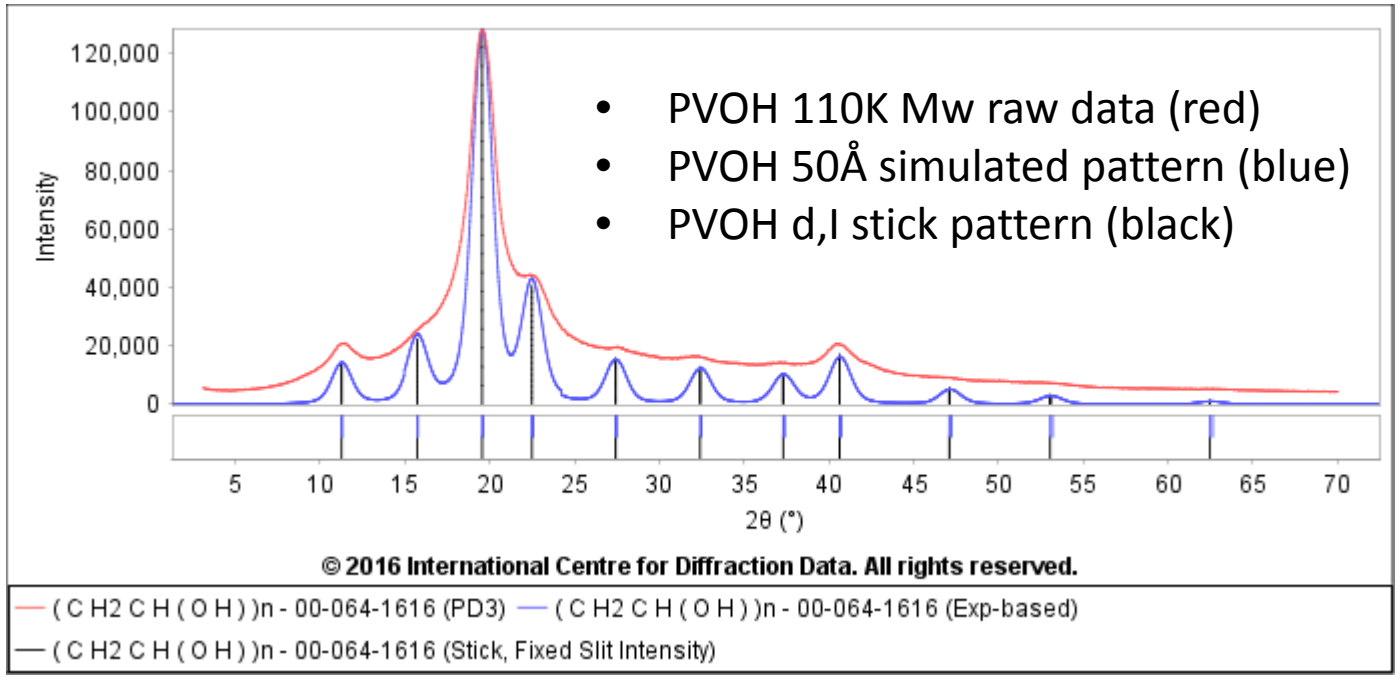


Orthorhombic Pbcn
a=7.831Å b=5.891Å c=9.958Å

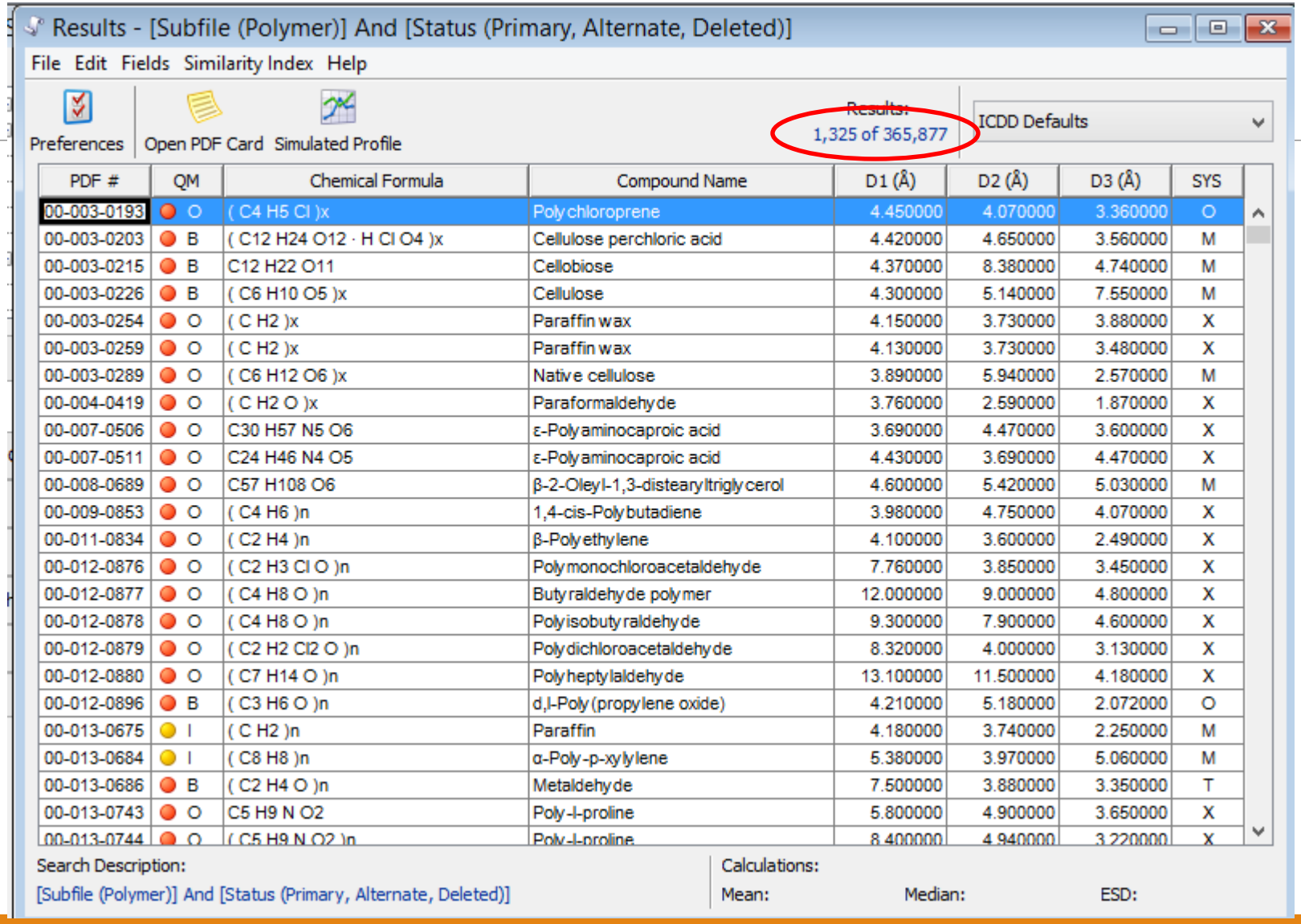
PD3 Raw Data Patterns in the Powder Diffraction File – PEEK Polymer



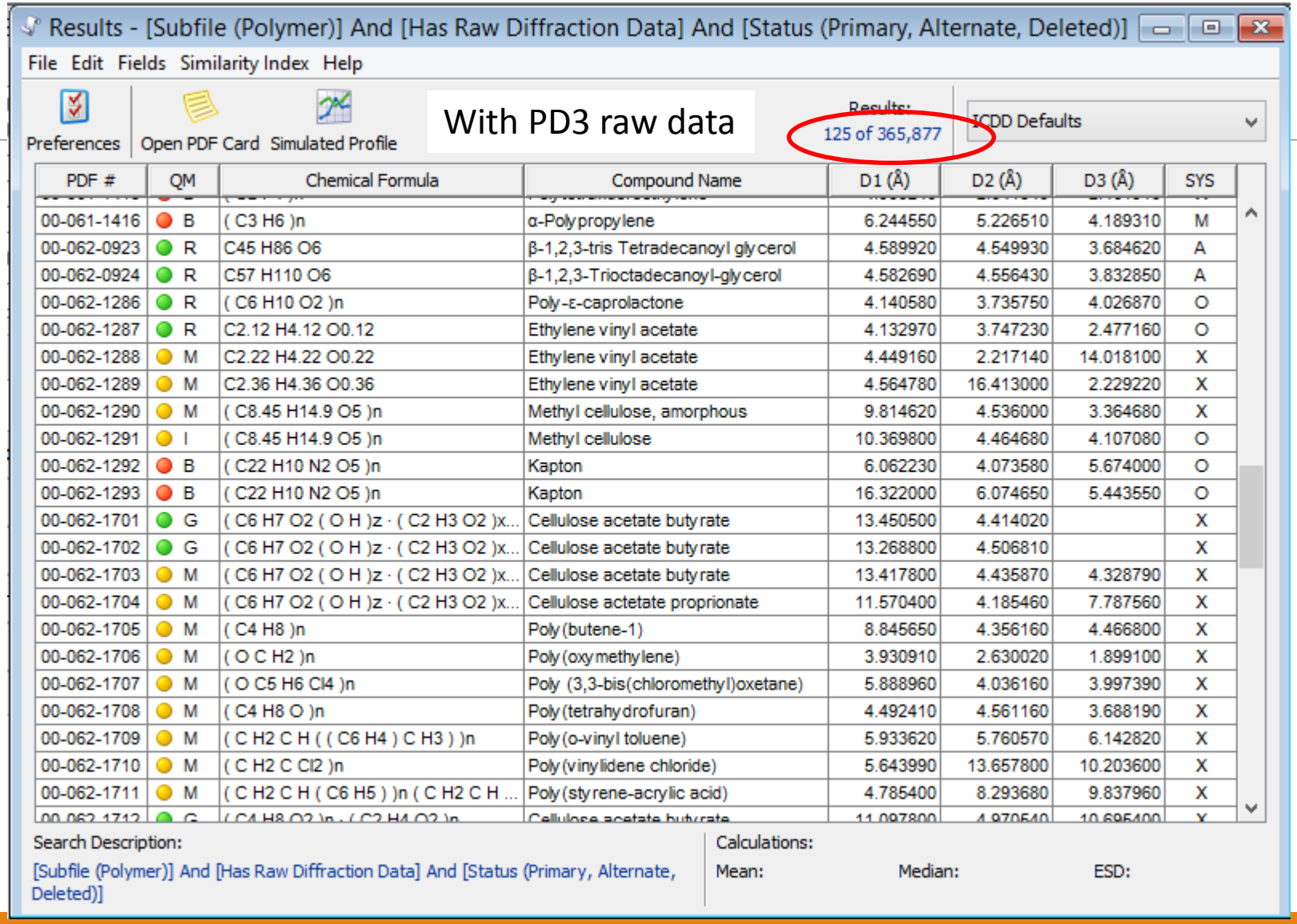
Stick vs. Simulated vs. PD3 (PVOH – tablet packaging)



Polymer entries in PDF 2015



PD3 polymer entries in PDF 2015



ICDD pharmaceutical polymers project

Polymer	Mol. Formula	PDF Entry	PD3
poly(acrylic acid), PAA	(C3H4O2)n	N	N
poly(ethylene oxide), PEO	(C2H4O)n	Y	N
poly(ethylene glycol), PEG	(C2H4O)n	Y	N
poly(vinyl pyrrolidone), PVP	(C6H9NO)n	N	N
poly(vinyl alcohol), PVOH, PVA	(C2H4O)n	Y	Y
polyacrylamide, PAM	(C3H5NO)n	N	N
poly(N-isopropylacrylamide)	(C6H11NO)n	N	N
cellulose	(C6H10O5)n	Y	Y
methyl cellulose	(C6H7O5R1, 2, 3)n R=CH3	Y	Y
ethyl cellulose	((C6H8O5(C2H5)2)n	N	N
carboxymethyl cellulose	(C6H7O5R1, 2, or 3)n R=H or CH2CO2H	N	N
hydroxyethyl cellulose	(C6H7O5R1, 2, or 3)n R=H or CH2CH2OH	N	N
hydroxypropyl cellulose	(C6H7O5R1,2, or 3)n R=H or CH2CH(OH)CH3	N	N
hydroxypropyl methyl cellulose, HPMC	(C6H7O5R1,2, or 3)n R=H or CH3 or CH2CH(OH)CH3	N	N
cellulose acetate phthalate	(C6H7O5R1,2, or 3)n R=H or CH3CO or C6H4COCOOH	Y	Y
alginic acid	(C6H8O6)n	N	N
chitosan	(C6H11O4N)n	Y	N
hyaluronic acid	(C14H21NO11)n	N	N
pectinic acid	(C13H14O13)n	N	N
poly(lactide-co-glycolic acid, PLGA)	(C3H4O2)m(C2H2O2)n	N	N
starch	(C6H10O5)n	Y	N
sodium starch glycolate	(C2H4O3Na)n	N	N
dextran	H(C6H10O5)nOH	Y	Y
xanthum Gum	C35H49O29 (monomer)	N	N
gelatin	(C35H55N12O12)n	Y	Y

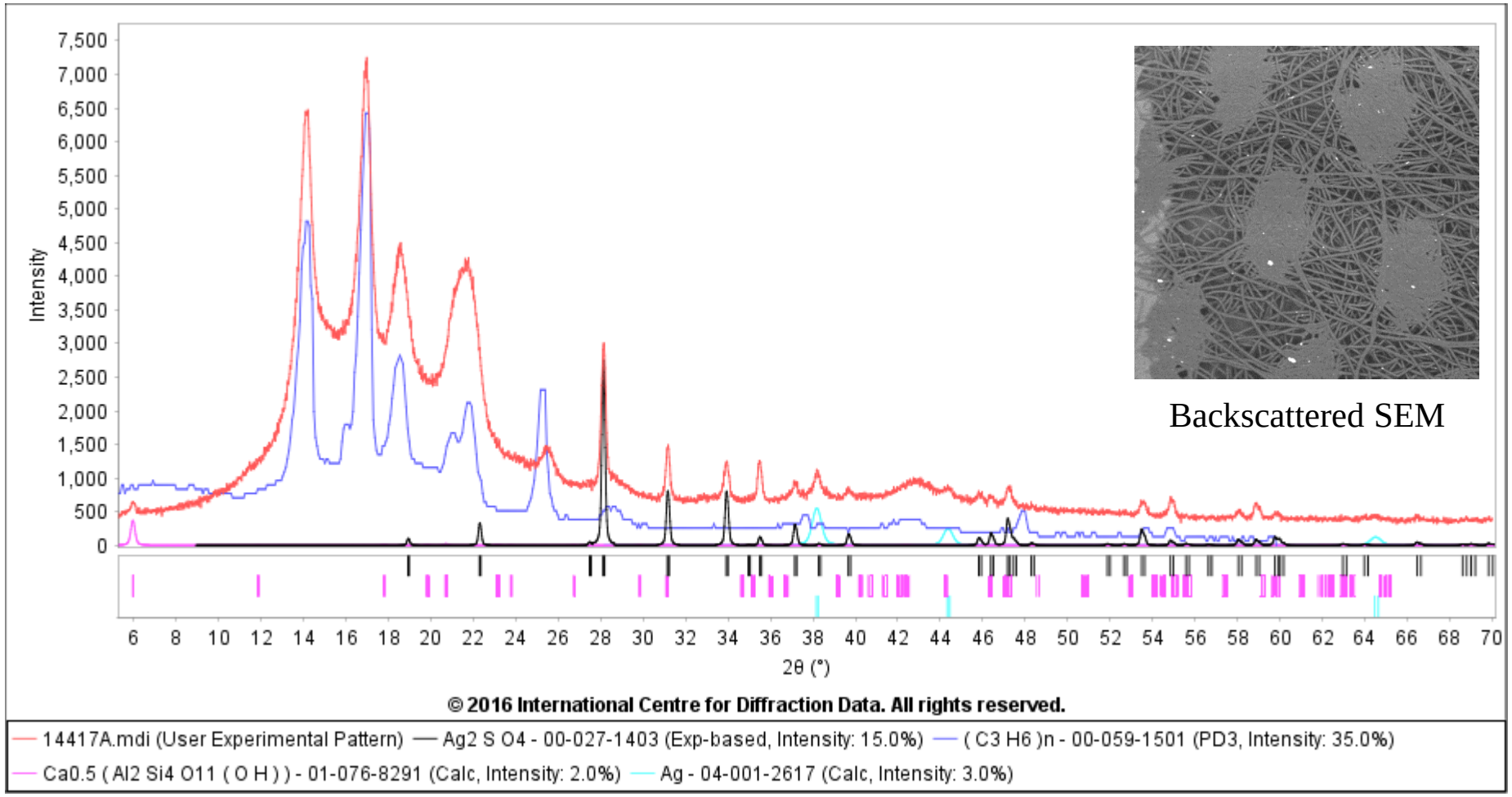
ICDD biomedical polymers

Polymer	Mol. Formula	PDF Entry	PD3
polyurethane, PU	(R-NHCO2)n	Y	N
silicone	(OSiR2)n	Y	N
polycarbonate, PC	(ROCO2)n	Y	Y
polychloroprene	(C4H5Cl)n	Y	N
polyisobutylene, PIB	(CH2C(CH3)2)n	Y	N
polycyanoacrylate	(C5H5O2N)n	N	N
poly(vinyl acetate), PVAc	(C4H6O2)n	N	N
polystyrene, PS atactic	(C8H8)n	Y	Y
polystyrene, PS isotactic	(C8H8)n	Y	N
polypropylene, PP	(C3H6)n	Y	Y
poly(vinyl chloride), PVC	(C2H3Cl)n	Y	Y
polyethylene	(C2H4)n	Y	Y
poly (methyl methacrylate)	(C5H8O2)n	Y	N
poly(hydroxyethyl methacrylate)	(C6H10O3)n	N	N
Ethylene vinyl acetate, EVA	(C2H4)m(CC4H6O2)n	Y	Y
poly(ethylene terephthalate, PET	(C10H8O4)n	Y	Y
polyether ether ketone	(OC6H4OC6H4COC6H4)n	N	N

2016 PDF-4 new polymer entries (PHR, BIO subfiles)

PDFID	Name	Chemical Formula	Common Name
00-66-1656	Ethylene vinyl alcohol	(C H2 C H2)n (C H2 C H O H)n	Clarene
00-66-1657	Nylon 11	(N H (C H2)10 C O)n	Rilsan
00-66-1658	Polysulfone	(C6 H4 C (C H3)2 C6 H4 O C6 H4 S O2 C6 H4 O)n	Udel
00-66-1659	Ethyl cellulose	(C6 H8 O5 (C2 H5)2)n	Ethocel 45
00-66-1660	Ethyl cellulose	(C6 H8 O5 (C2 H5)2)n	Ethocel 100
00-66-1661	Polyether ether ketone	(C19 H12 O3)n	PEEK - Amor
00-66-1662	Polyether ether ketone	(C19 H12 O3)n	PEEK - Crys
00-66-1663	Hydroxypropyl cellulose	(C36 H70 O19)n	Methocal K15M
00-66-1666	Acetal	(C H2 O)n	Delrin
00-66-1667	Polystyrene, isotactic	((C6 H5) C H C H2)n	i-PS
00-66-1668	Polyethoxazoline	(N (C O C H2 C H3) C H2 C H2)n	PEOx
00-66-1669	Polyarylate	(C O (C6 H4) C O2 (C6 H4) C (C H3)2 (C6 H4) O)n	Ardel

Phase ID – Ag based antimicrobial hospital gown

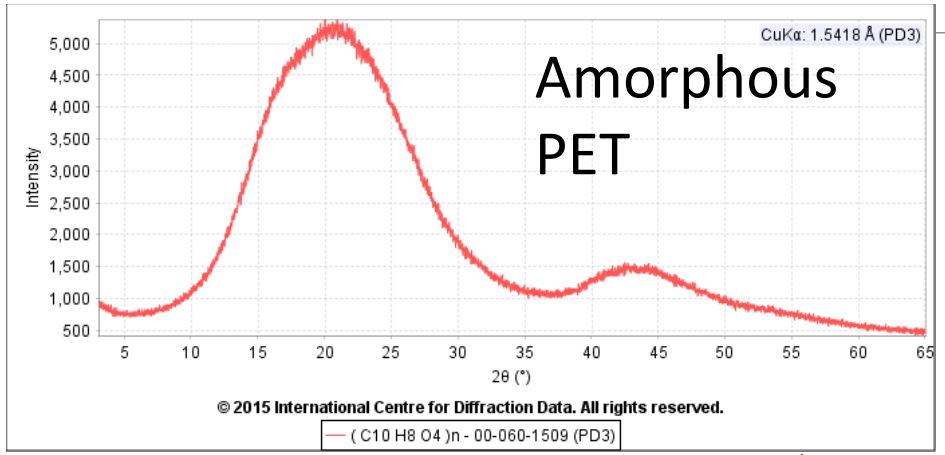


Ag_2SO_4 compounded in polypropylene was analyzed for phase composition. Using PDF-4 tools, phases were identified. Phases present: α-polypropylene (base polymer), Ag_2SO_4 (antimicrobial agent), Ag^0 (Ag_2SO_4 reduced during compounding), and montmorillonite (clay for improving polymer physical properties)

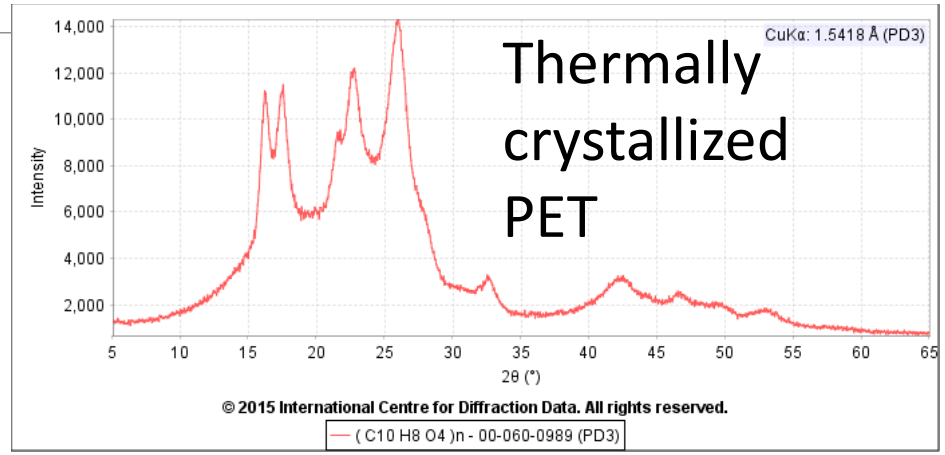
Do you need multiple Entries in the PDF Database for a polymer?

PET

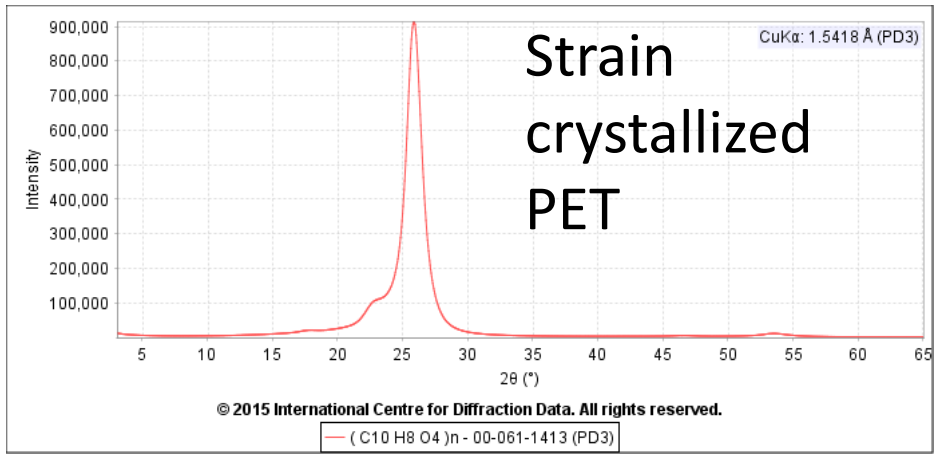
Triclinic P-1
a=5.791Å b=9.040Å c=4.561Å
α=100.64° β=112.46° γ=75.93°



Δ

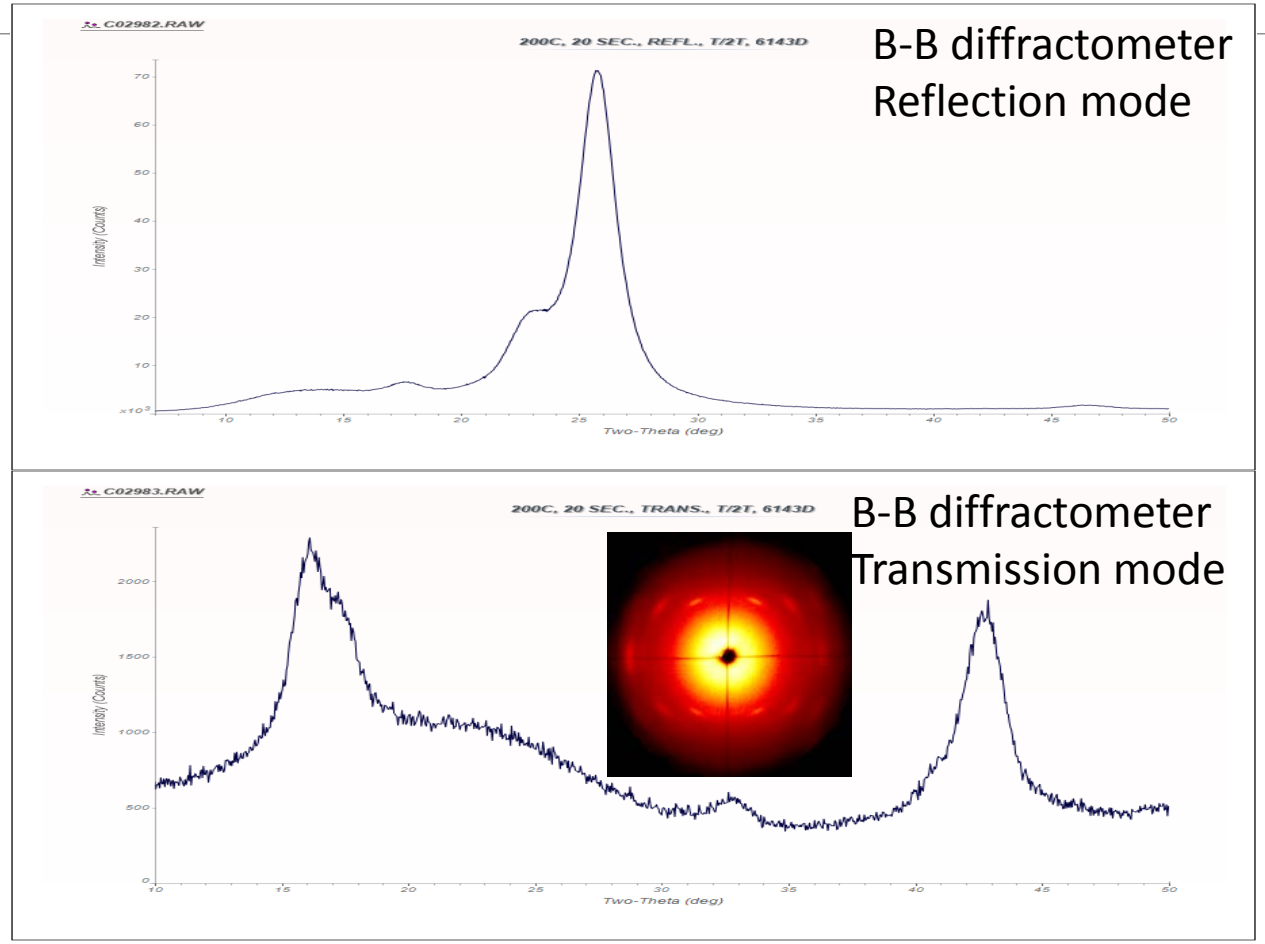


ε



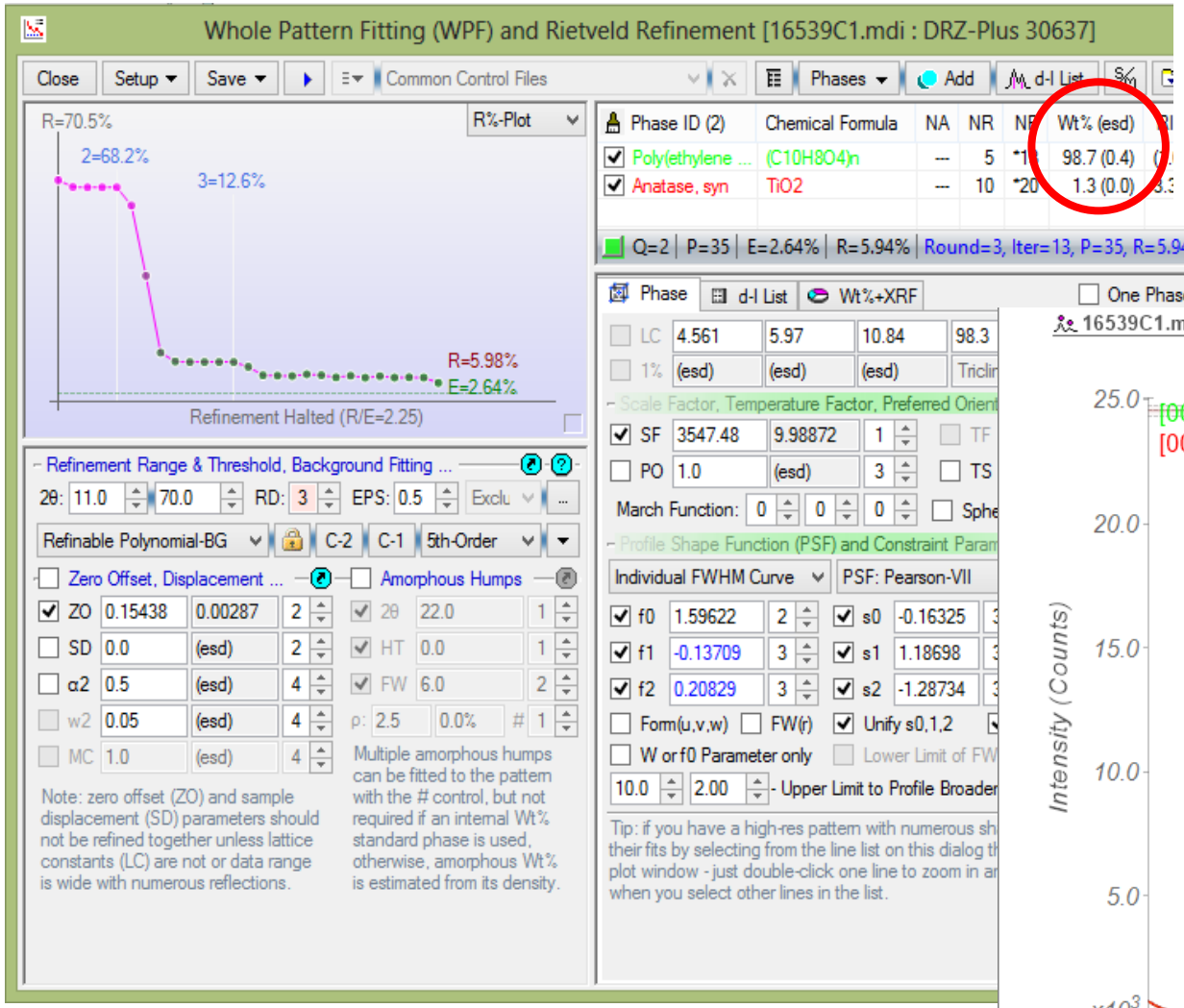
Polymer diffraction pattern: sample orientation matters

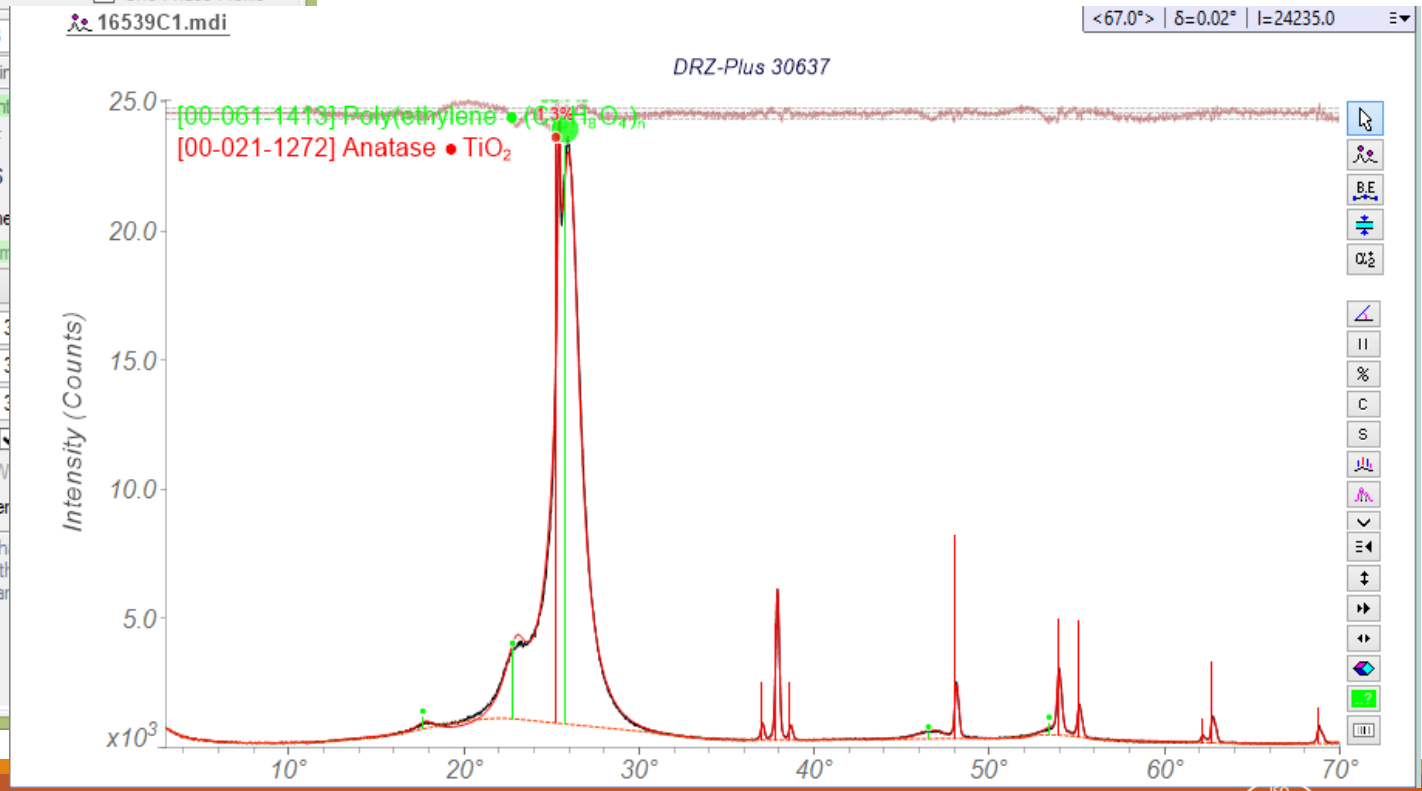
Strain crystallized PET



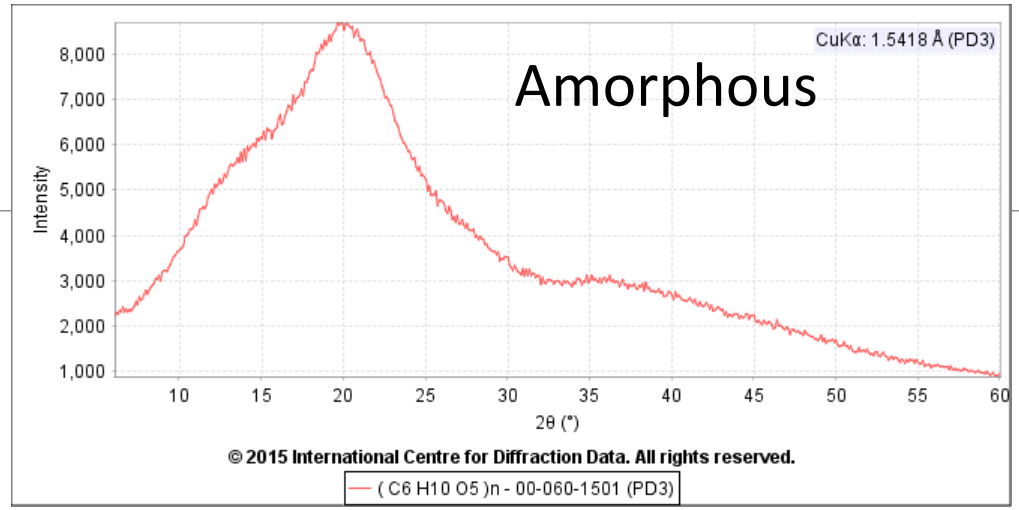
Quantitative Phase Analysis PET Composite Film

Composite used for transdermal patch backing. XRD phase analysis identified biaxially oriented poly(ethylene terephthalate) (PDF 00-061-1413) and TiO_2-anatase (00-021-1272). Since the biaxially oriented PET raw data pattern is stored in the PDF, whole pattern fitting can be used for quantitative analysis. WPF finds 1.3wt% TiO2 present, in line with the formulation calling for 1.5wt% TiO_2.

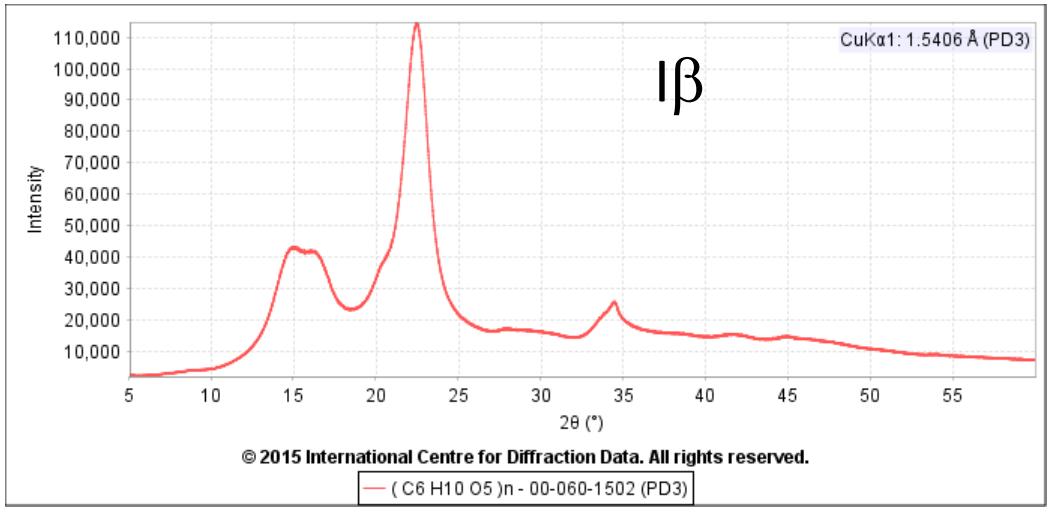




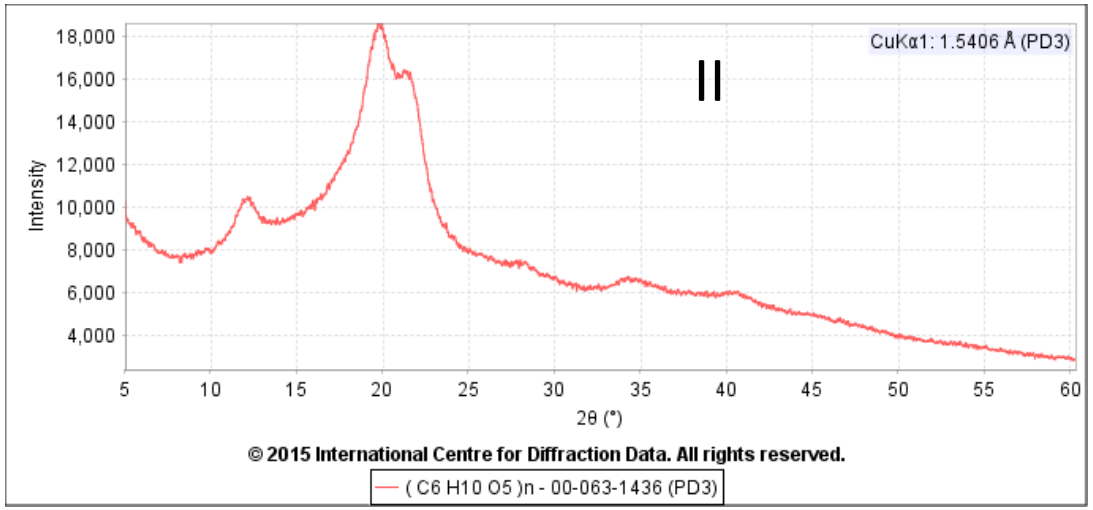
Cellulose



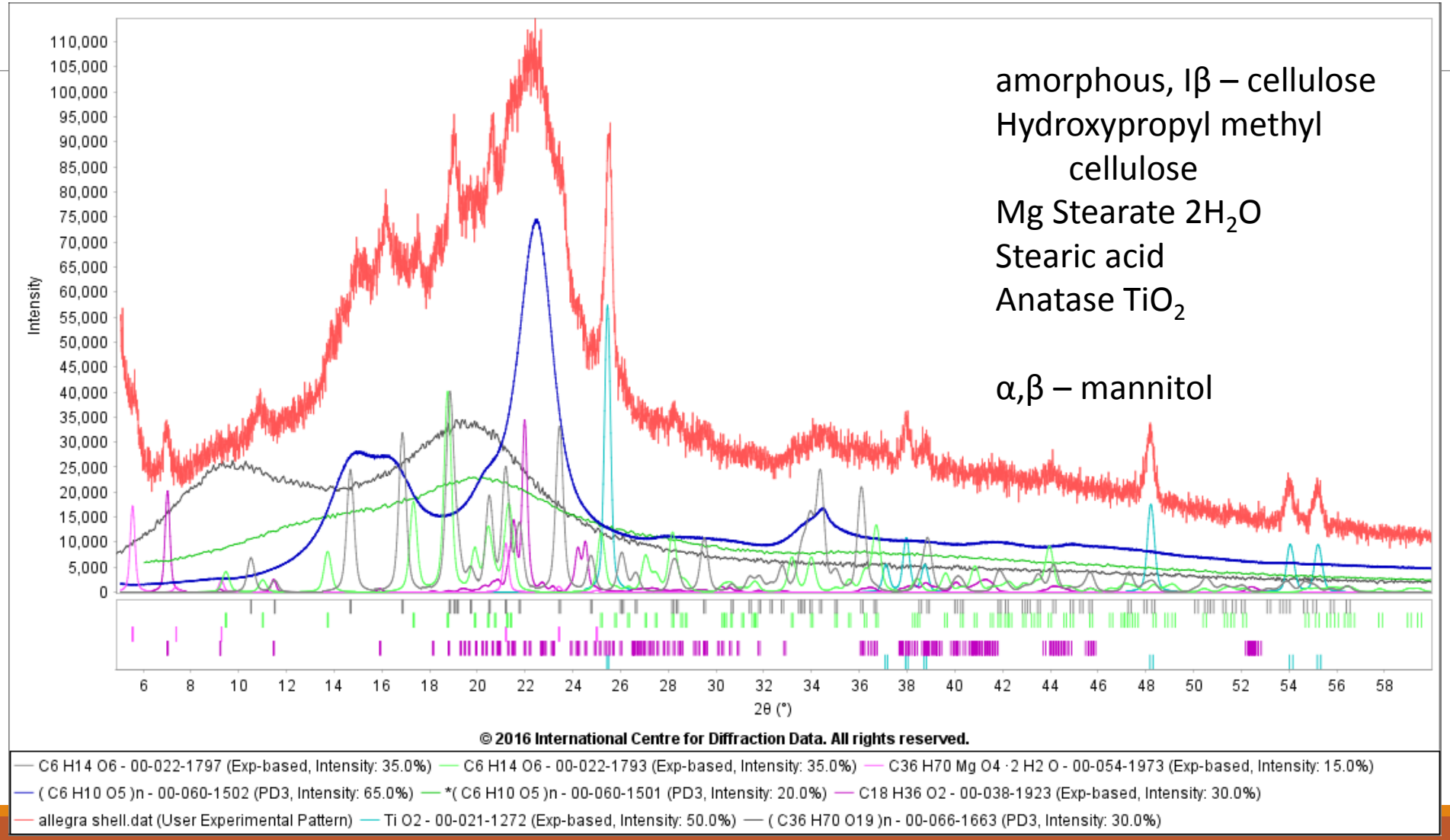
Monoclinic $P2_1$
a=8.260Å b=10.388Å c=7.740Å
β=95.80°



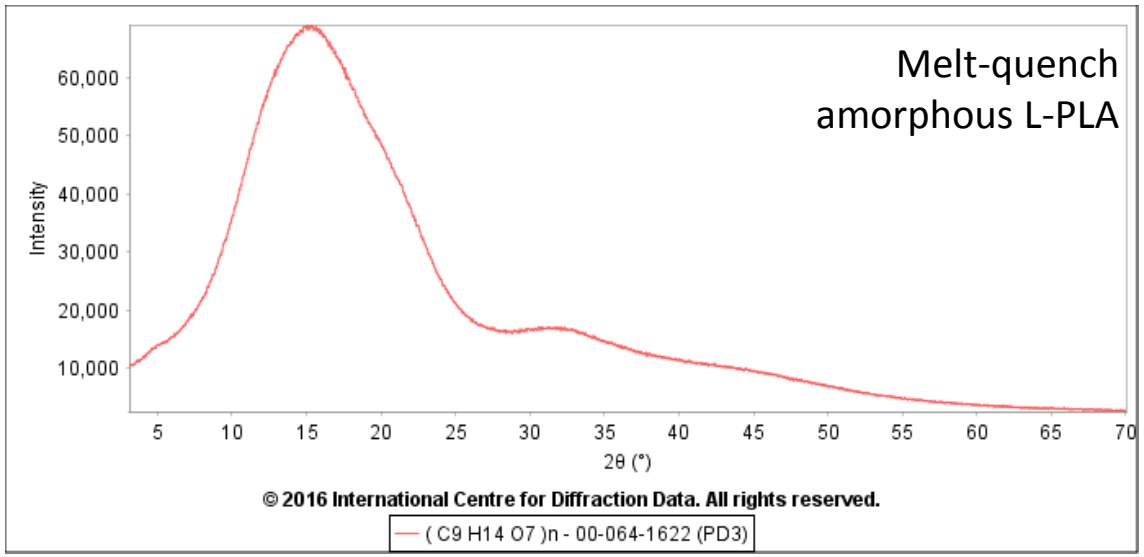
Monoclinic $P2_1$
a=9.044Å b=10.387Å c=8.077Å
β=115.73°

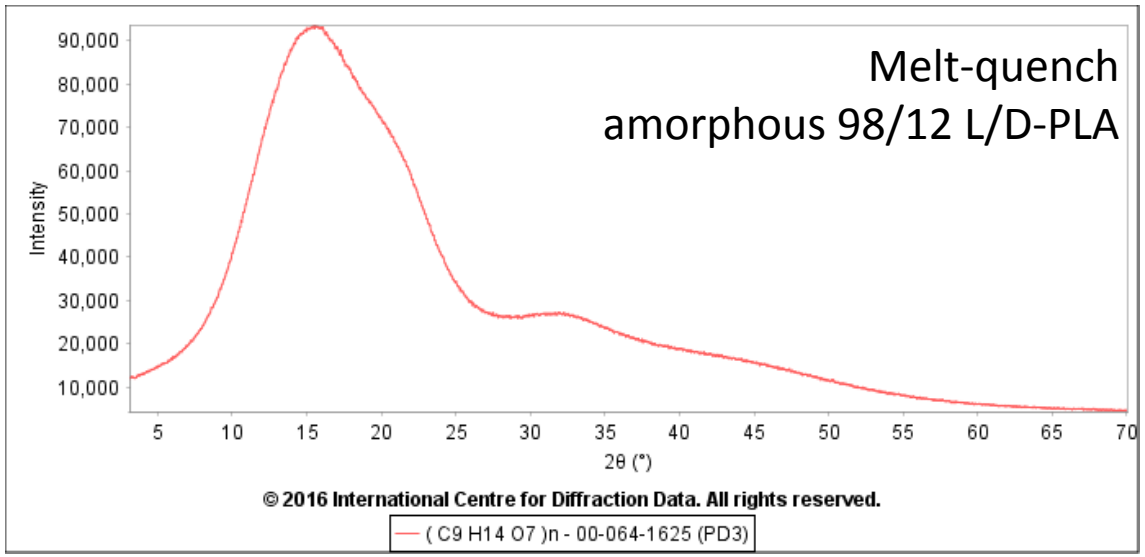


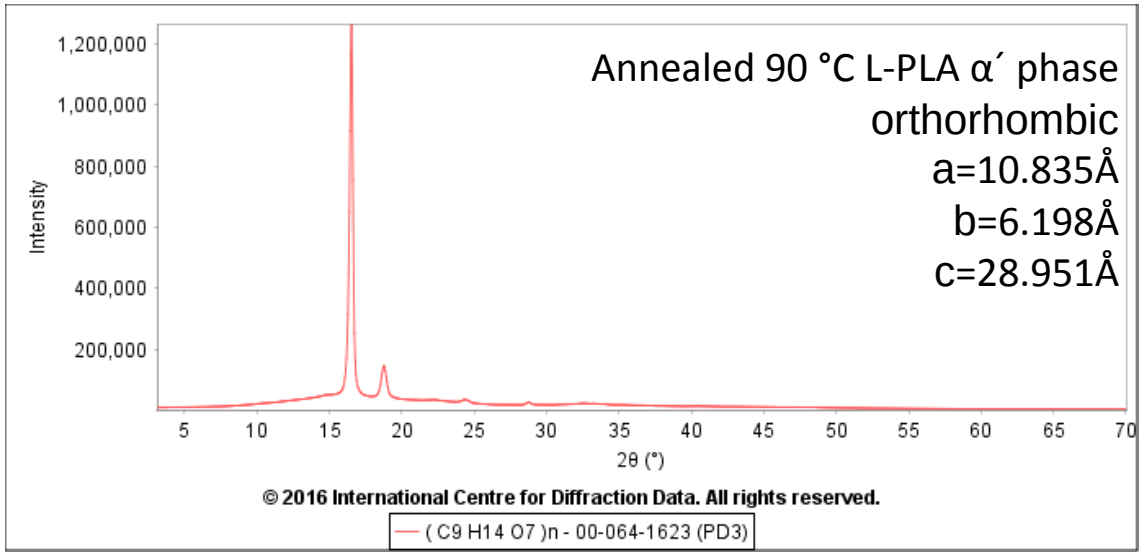
Phase identification – Allegra® shell

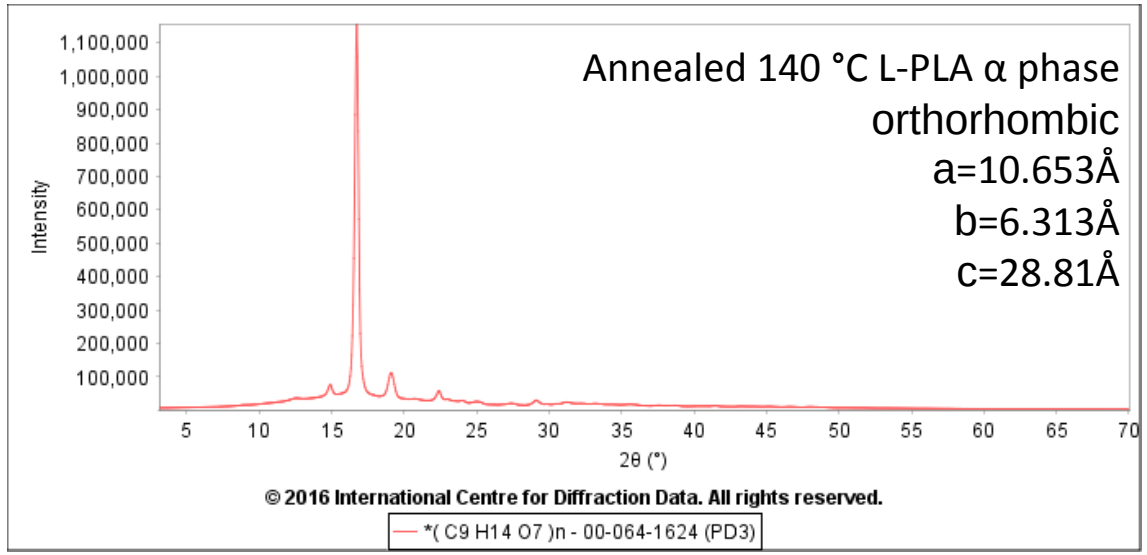


Poly Lactic Acid PLA

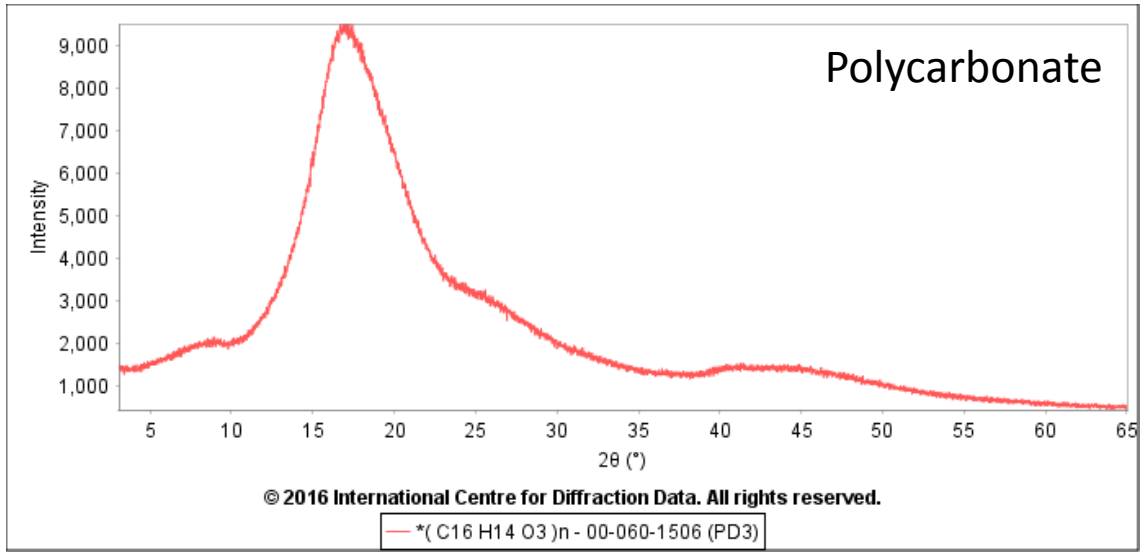


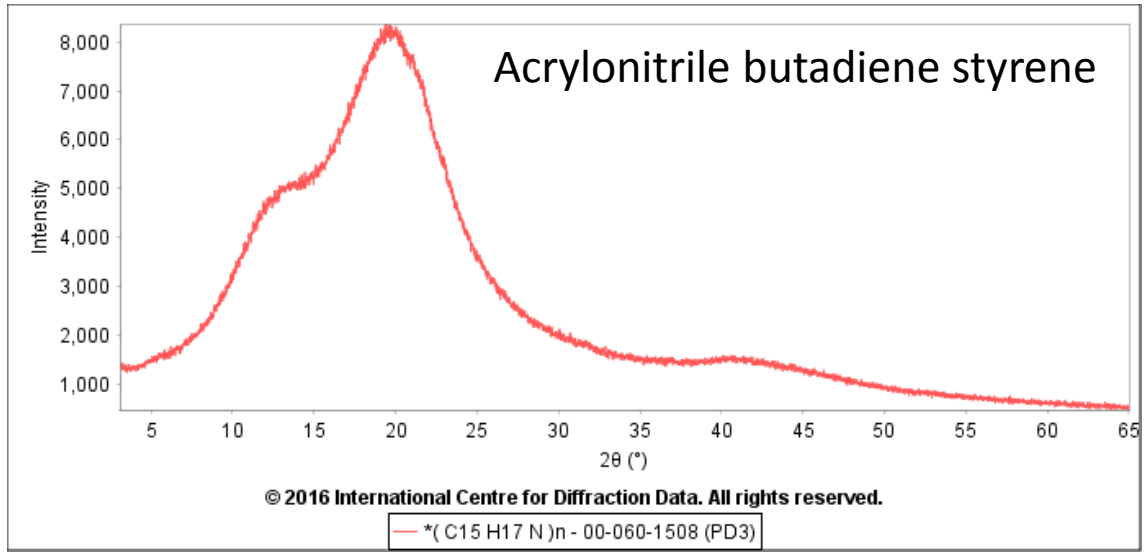




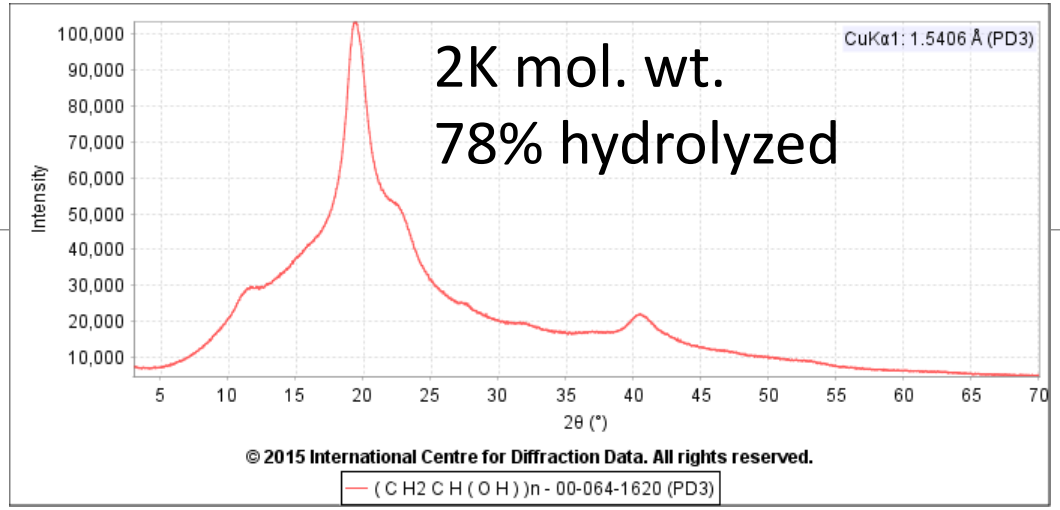


3d printing polymers, continued

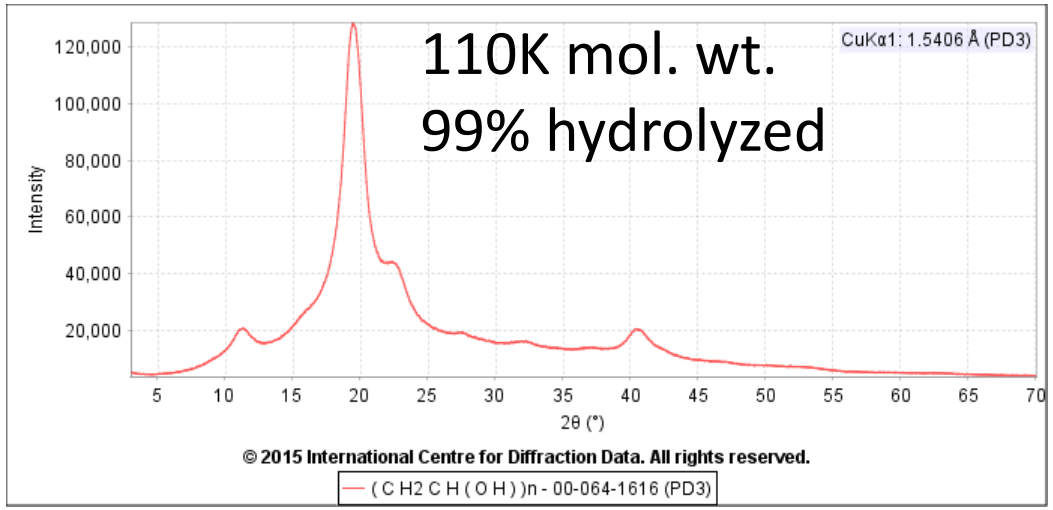


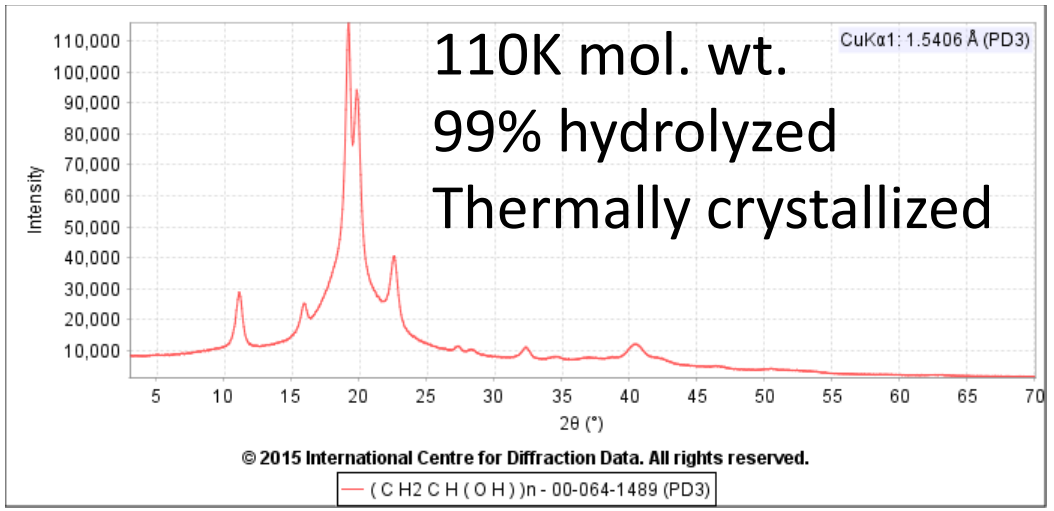


Polyvinyl alcohol

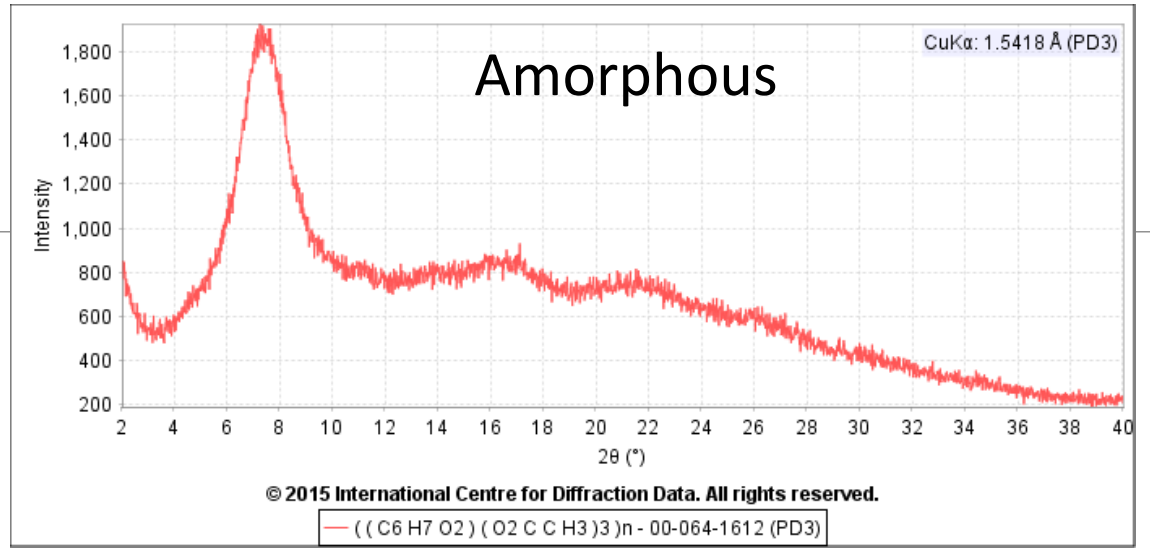


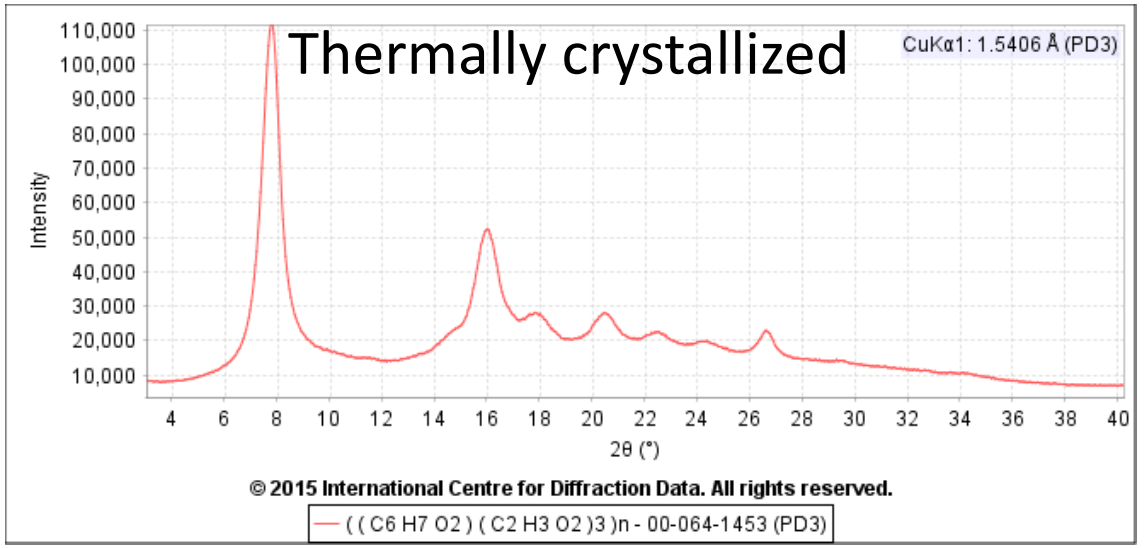
Monoclinic
a=7.773Å b=2.538Å c=5.502Å
β=92.11°





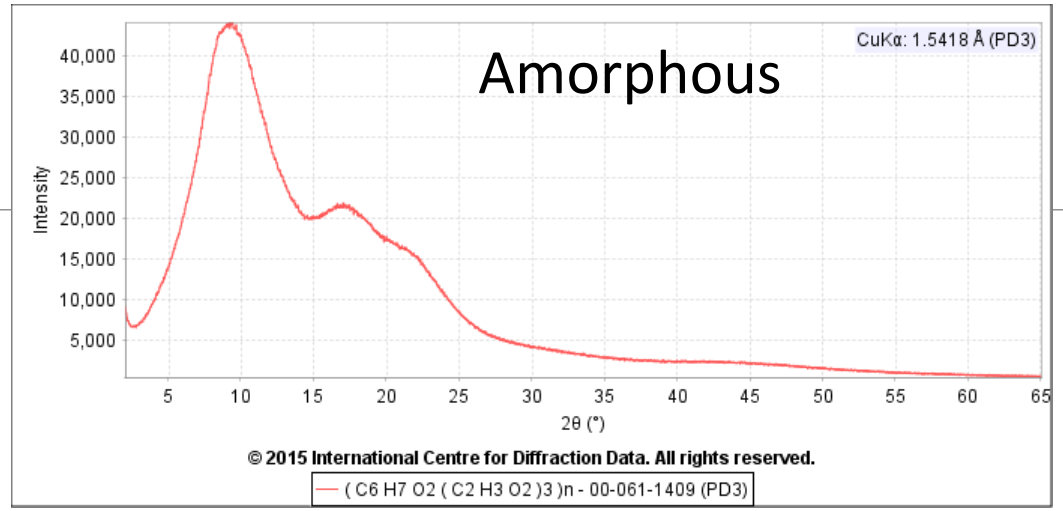
Cellulose triacetate I

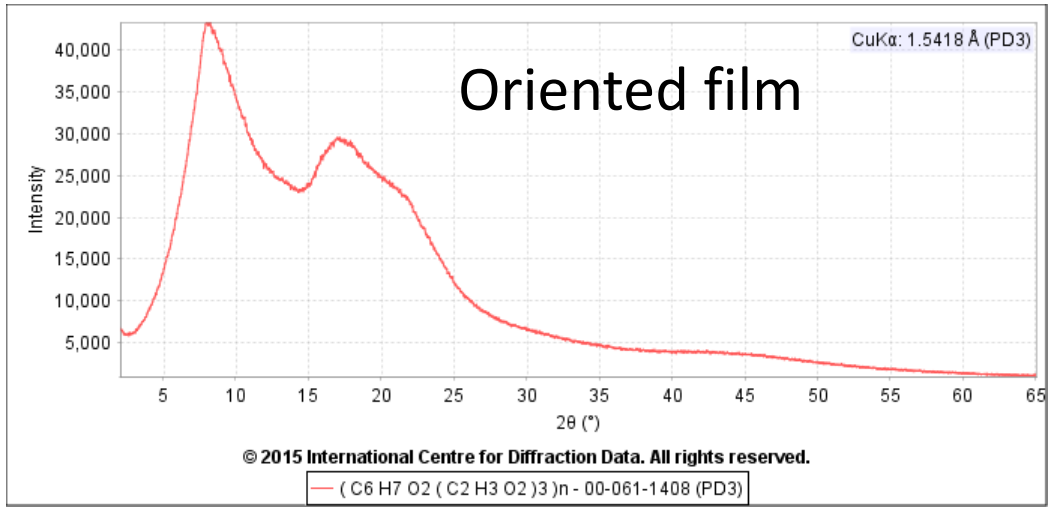


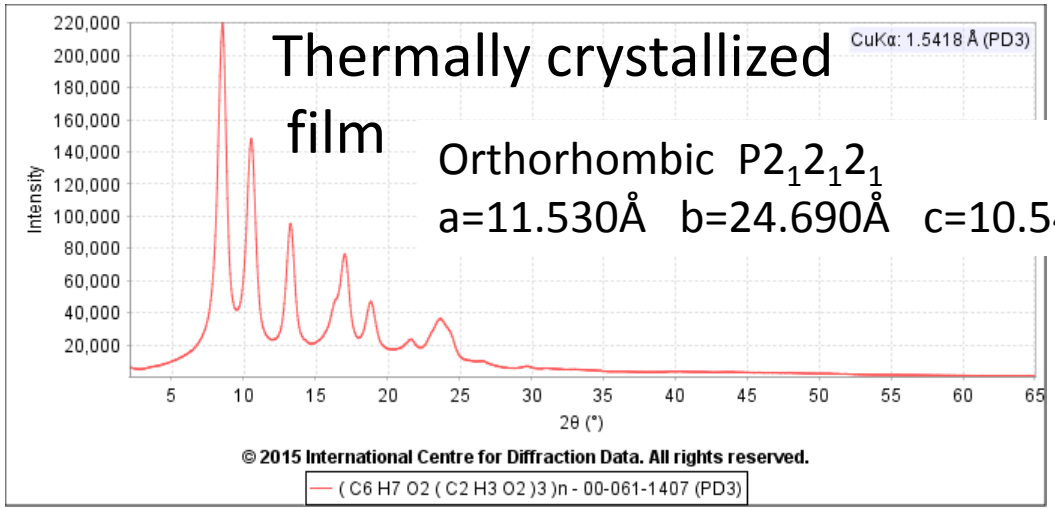


Monoclinic $P2_1$
a=11.348Å b=24.690Å c=6.060Å
β=95.60°

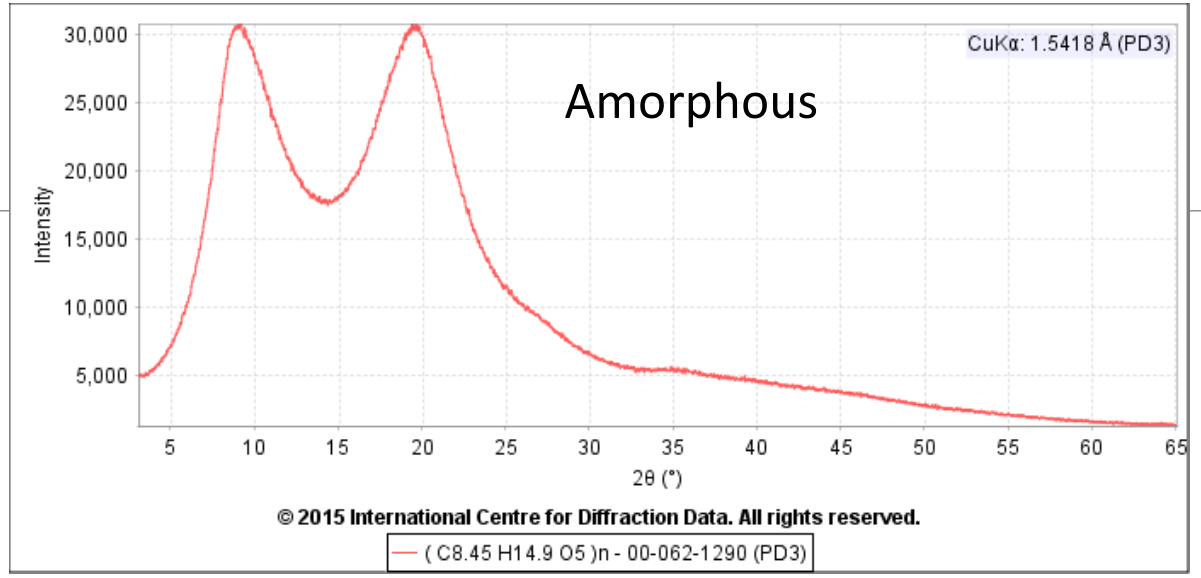
Cellulose triacetate II

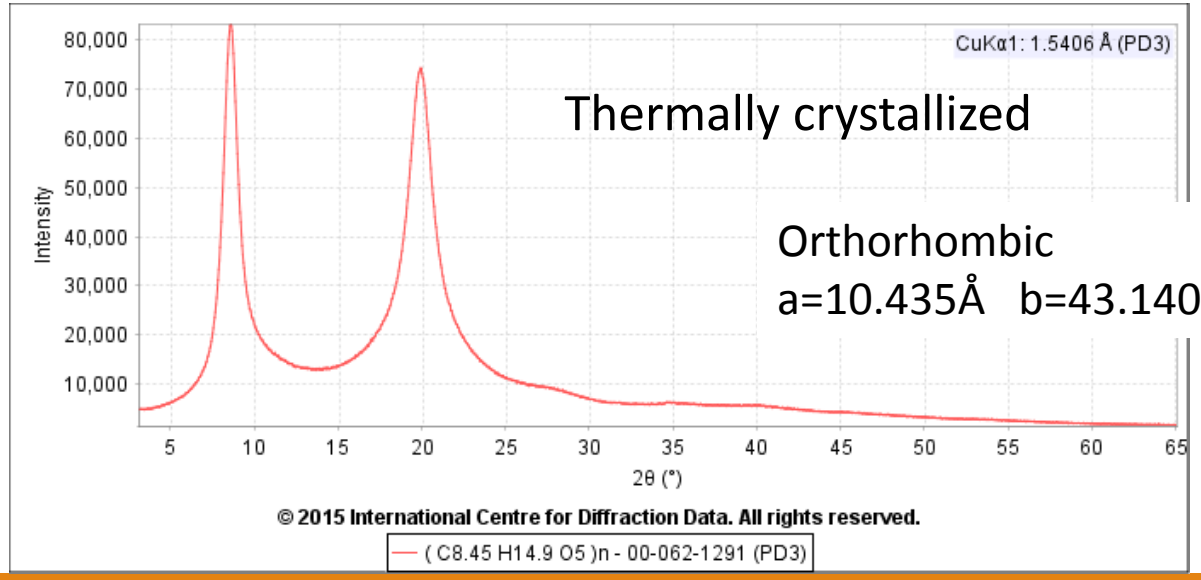






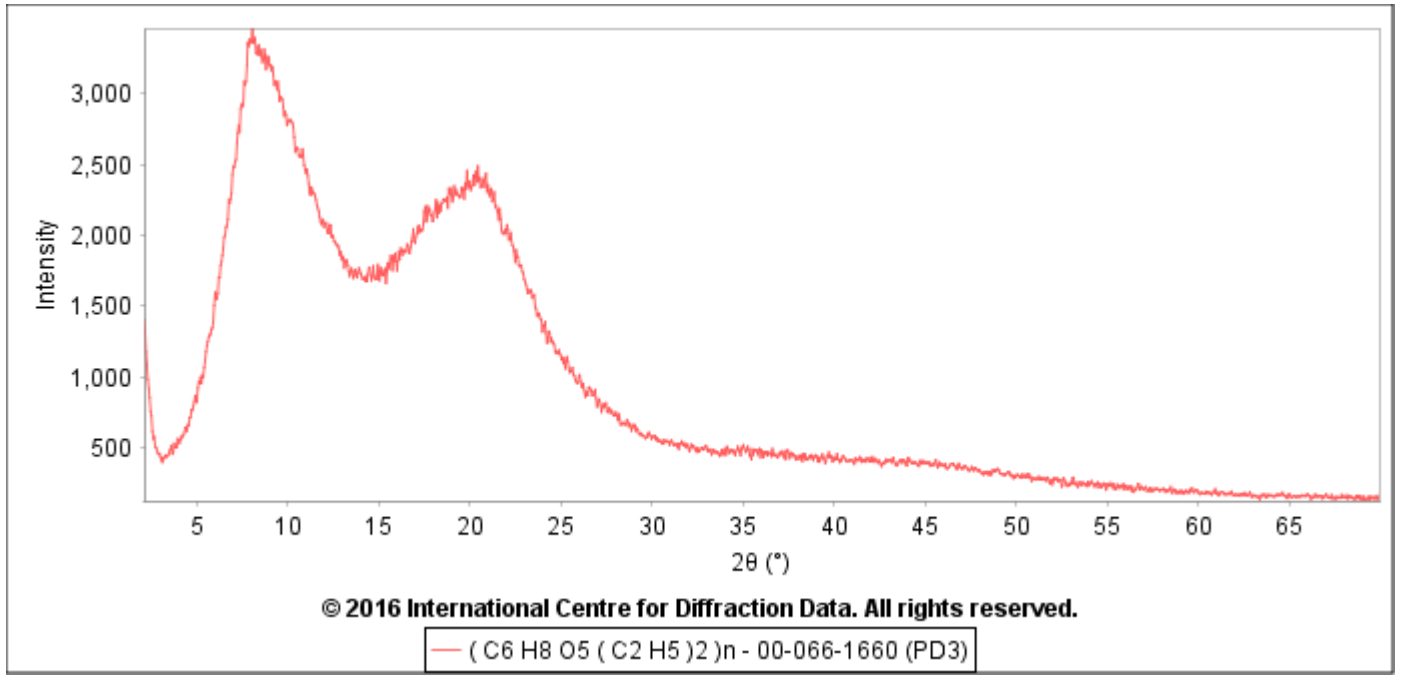
Methyl cellulose



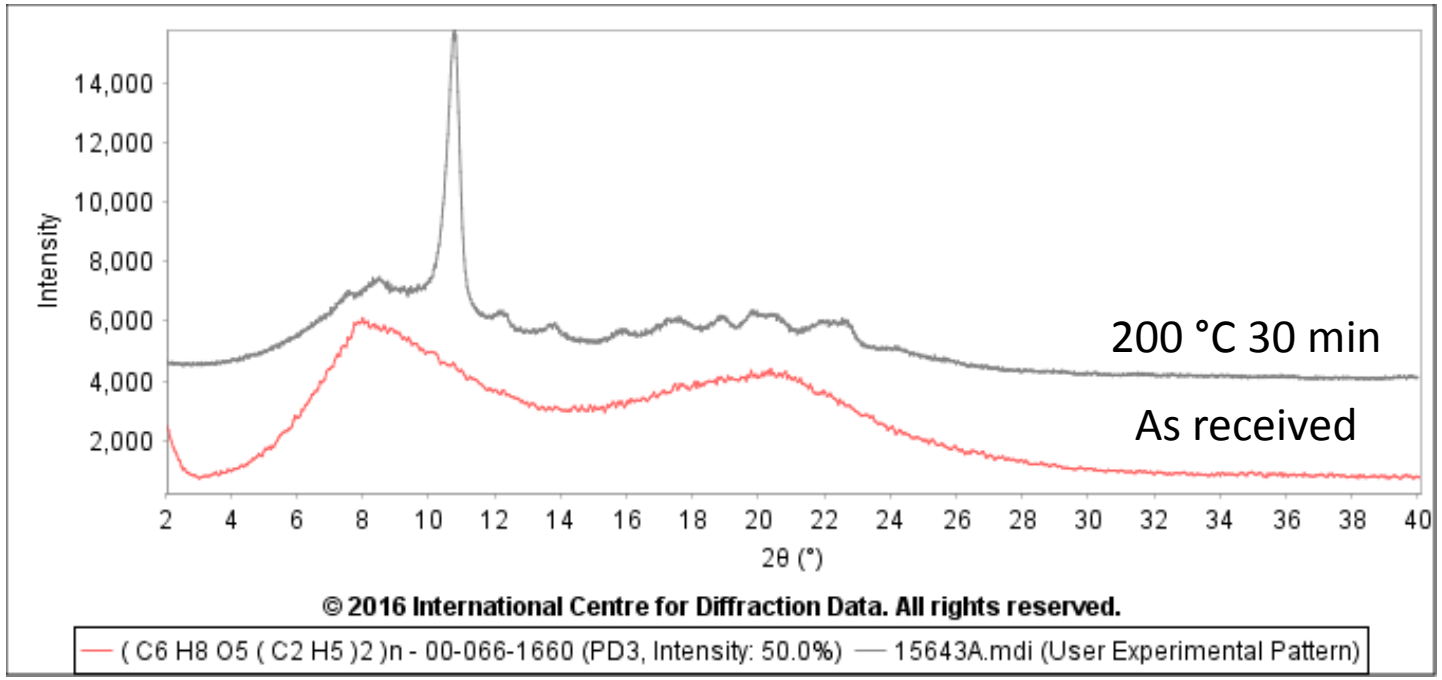


Orthorhombic
a=10.435Å b=43.140Å c=4.633Å

Ethyl cellulose – new entry for 2016



Ethyl cellulose

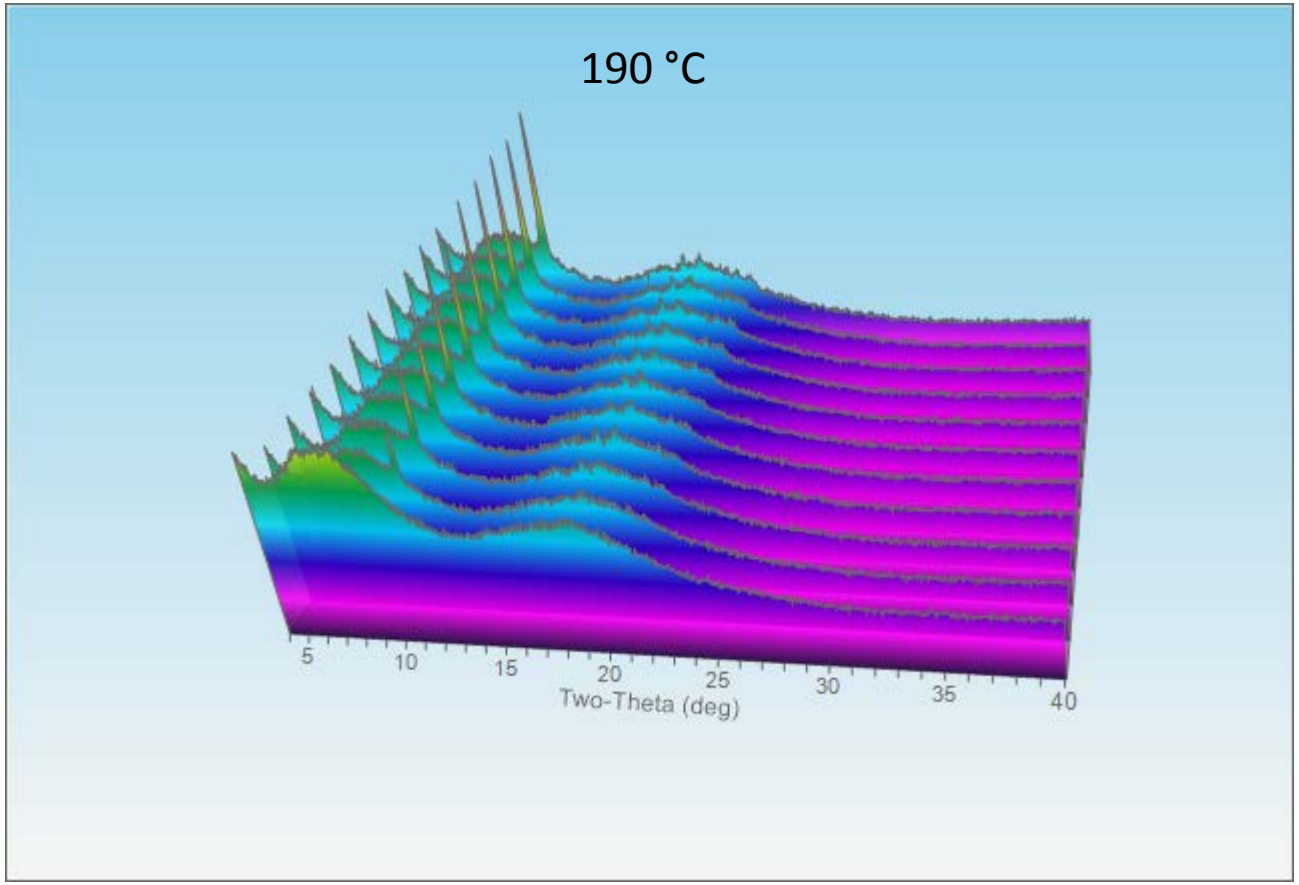


Indexing/WPF of crystalline “ethyl cellulose” phase

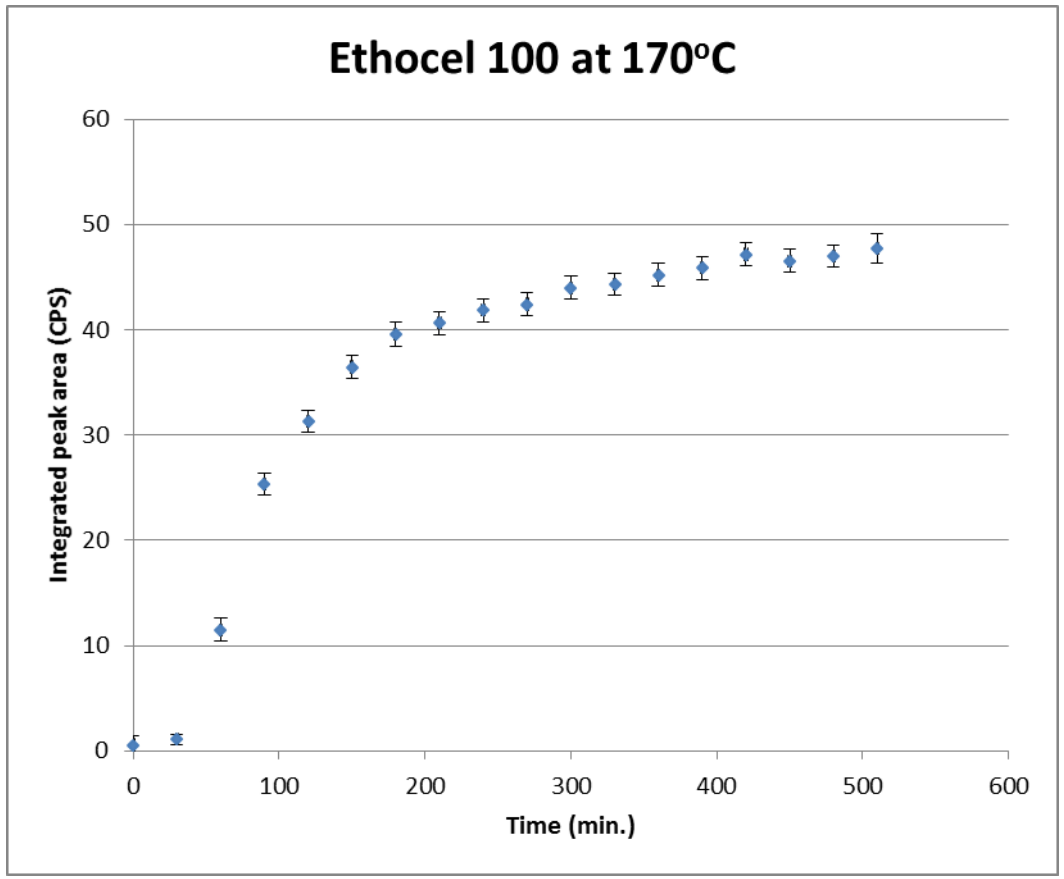
Possible cell:
Monoclinic
SG $P2_1/c$
a=11.74Å
b=23.50Å
c=7.65Å
β=95.2°

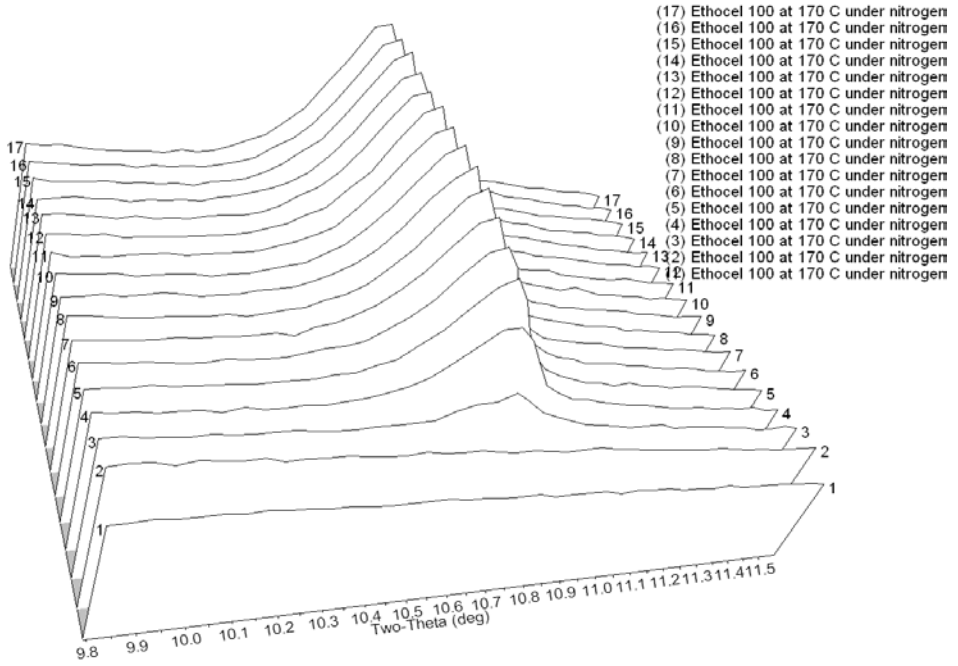
Collecting supporting data:
TGA/DSC, NMR, IR, XRF, SEM

Ethyl cellulose – isothermal anneal studies



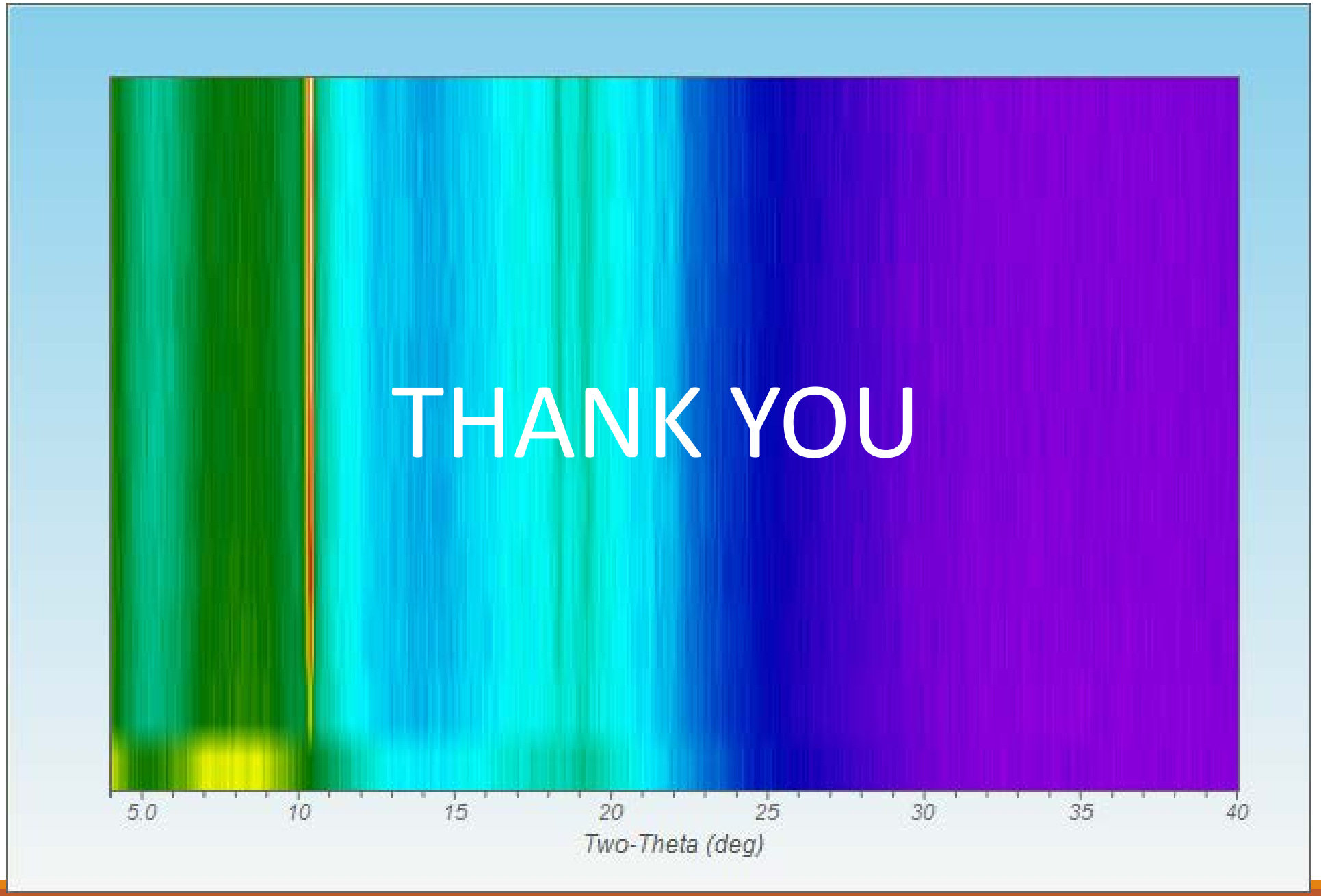
Ethyl cellulose – isothermal anneal studies





Summary

- Raw data diffraction patterns generated from analysis of polymer samples are being added to ICDD PDF-4 databases
- Important considerations:
  - Polymer chemistry
  - Polymer processing
  - Sample orientation in diffractometer - reflection vs. transmission
  - Sample type (powder, film, fiber)
- Use caution when using a single peak amorphous pattern to define the amorphous phase
- Pay attention to sample prep


THANK YOU
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Two-Theta (deg)