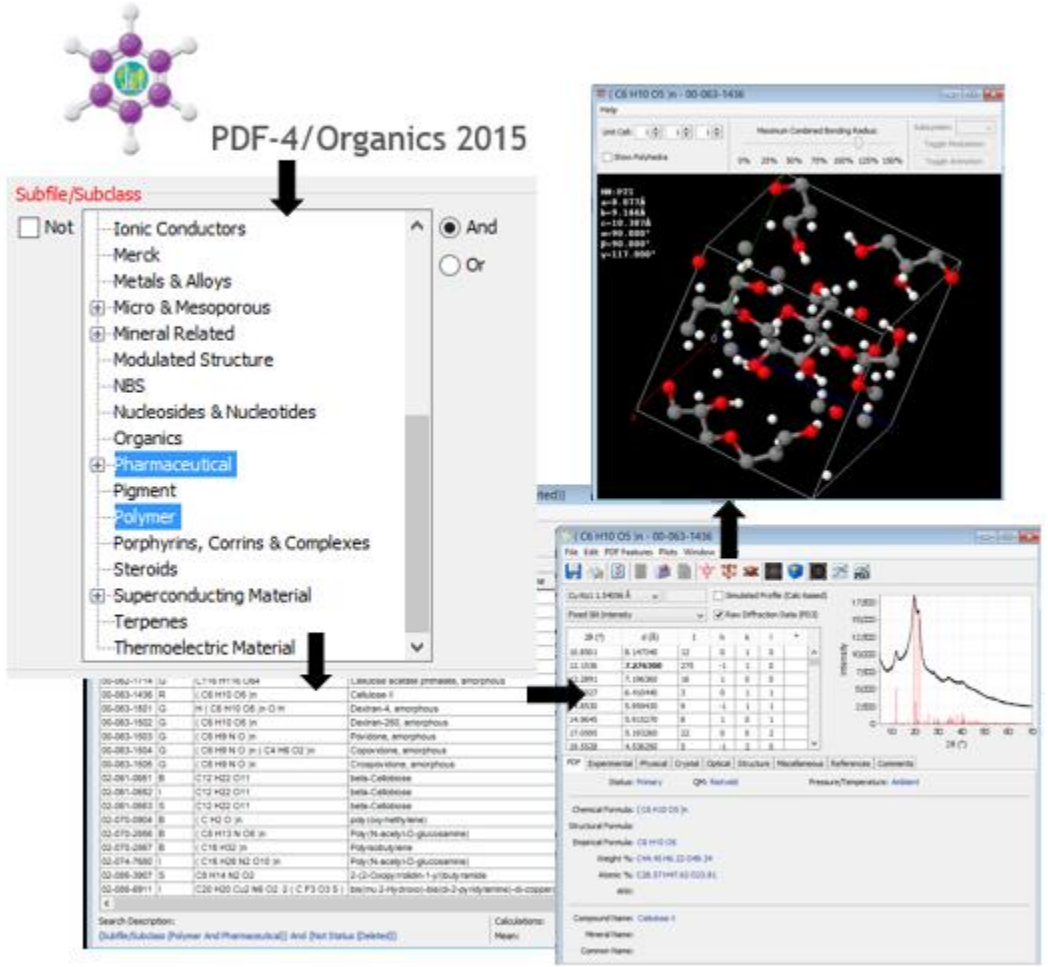
ICDD Powder Diffraction File® Coverage of Polymers Used in Pharmaceutical and Biomedical Applications

TOM BLANTON AND STACY GATES, ICDD



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

Sponsored by The International Centre for Diffraction Data

PPXRD Website – www.icdd.com/ppxrd

ICDD Website - www.icdd.com

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Kai Zhong

Rose Vithayathil

Mike Carr

Janet Grande

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/organic based polymers

Polymer analysis using XRD

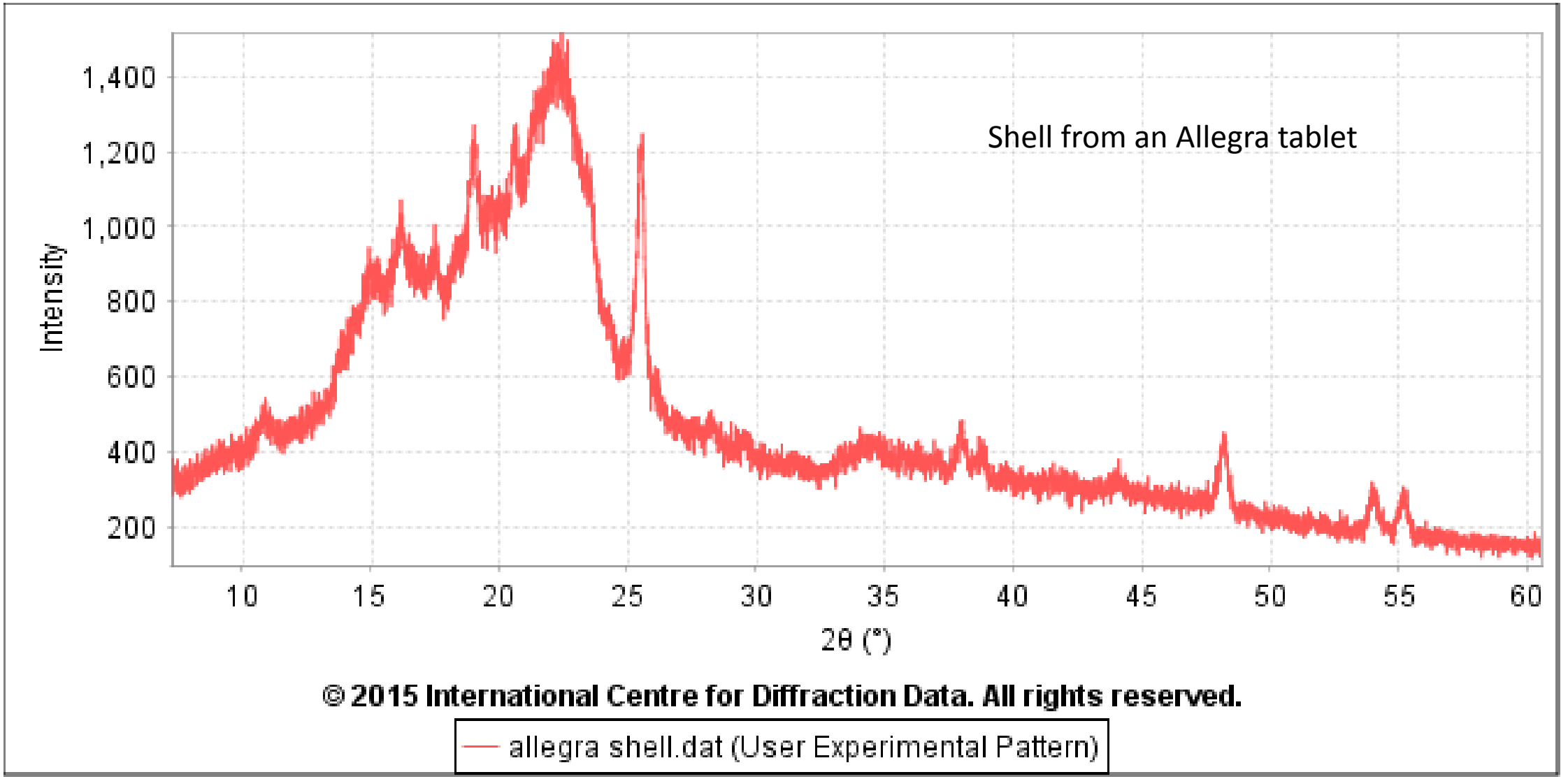
Many techniques are used for polymer characterization

- IR, NMR, GC/MS, etc.

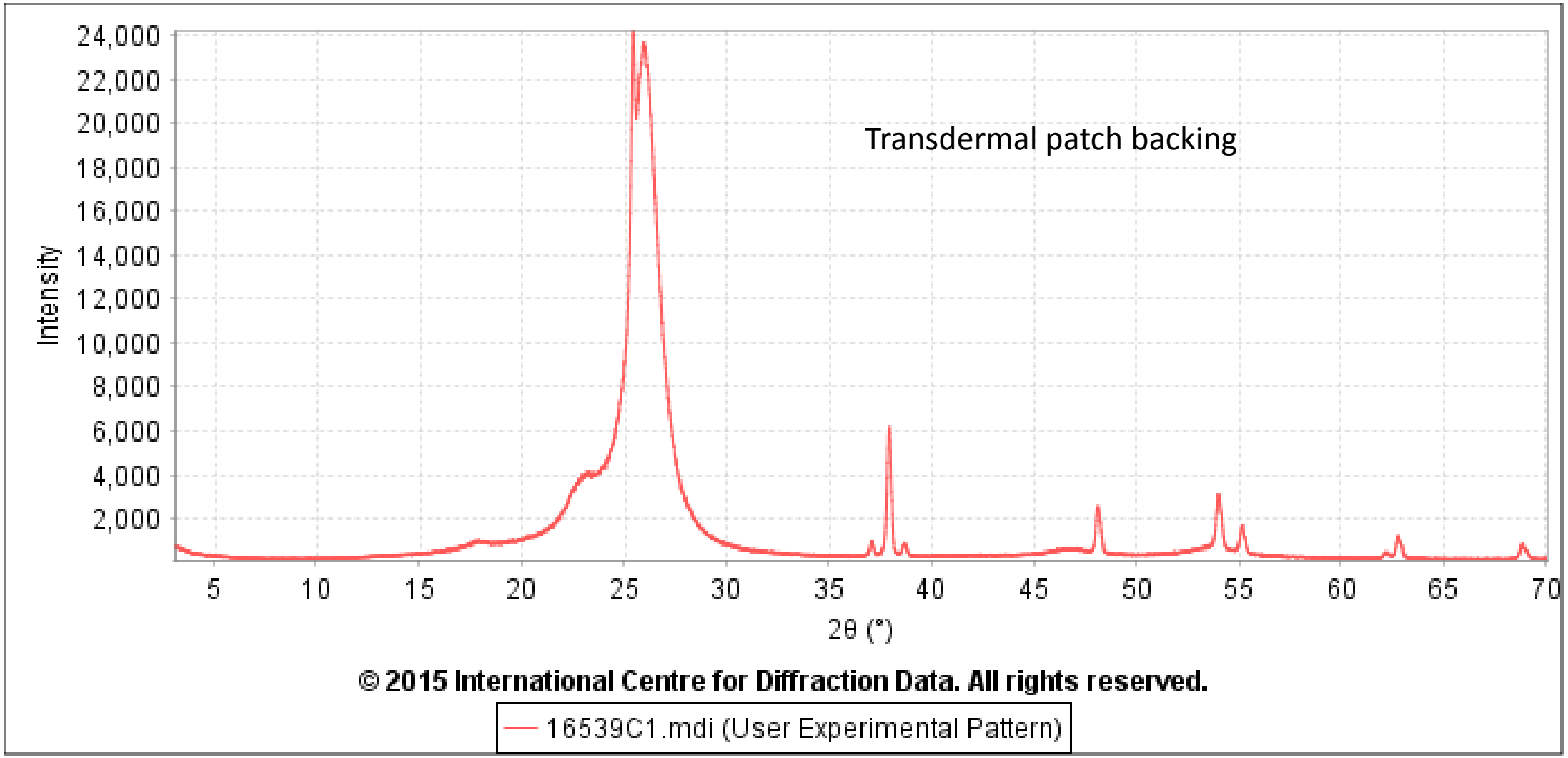
Why use XRD?

- 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

Pharmaceuticals

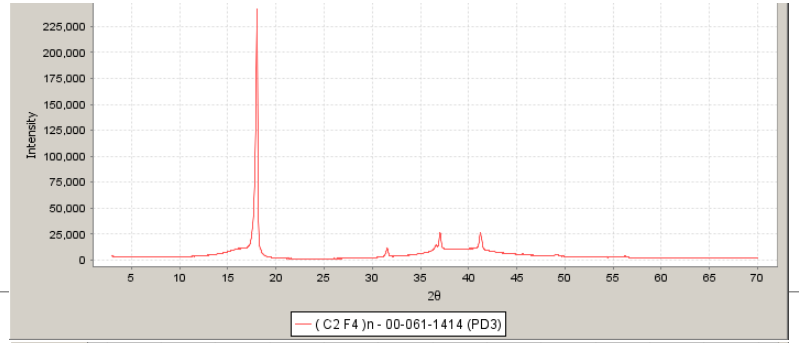


Biomedical devices

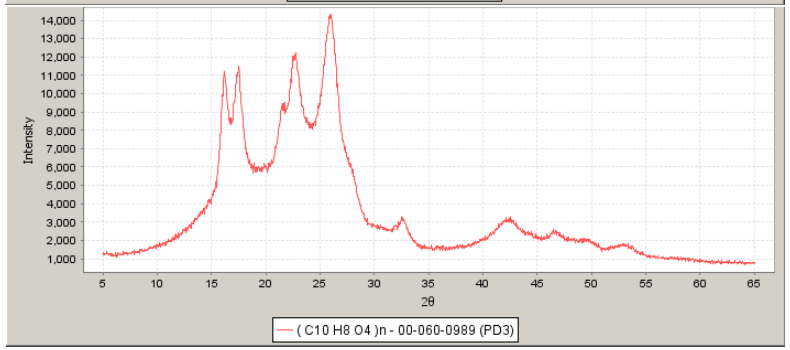


Polymer order: chemistry matters

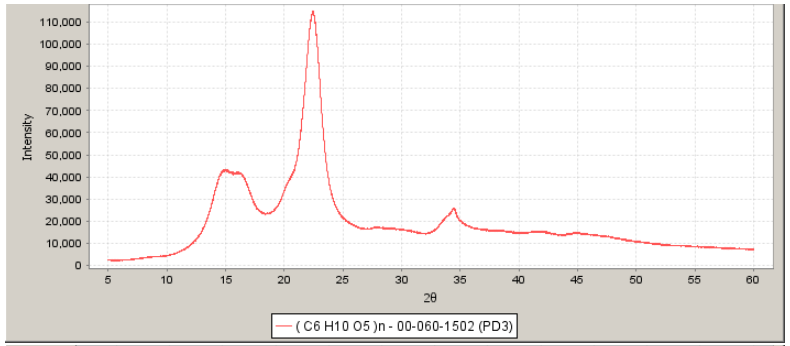
Highly crystalline - Teflon



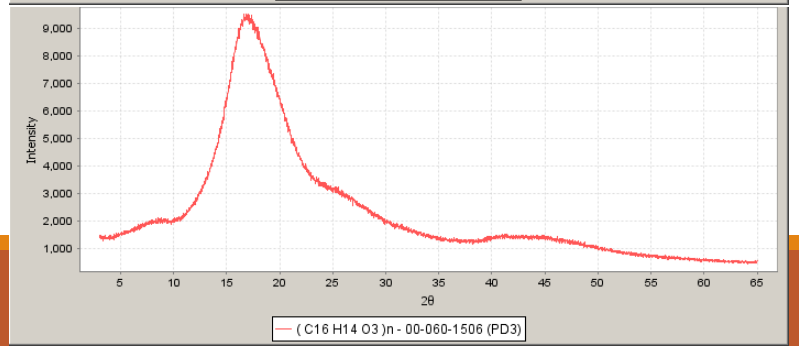
Semi crystalline – polyethylene terephthalate



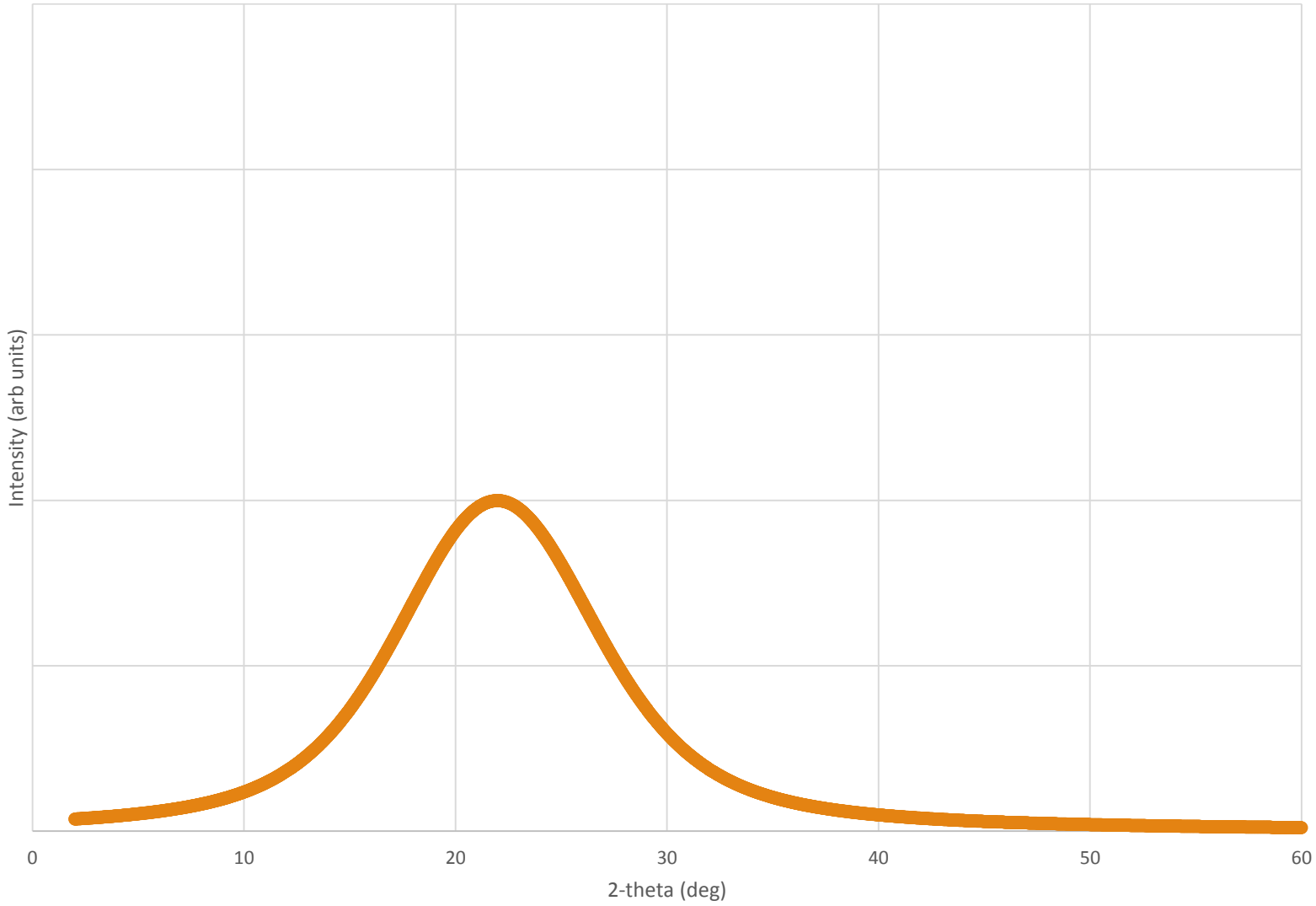
Micro crystalline – cellulose 1β



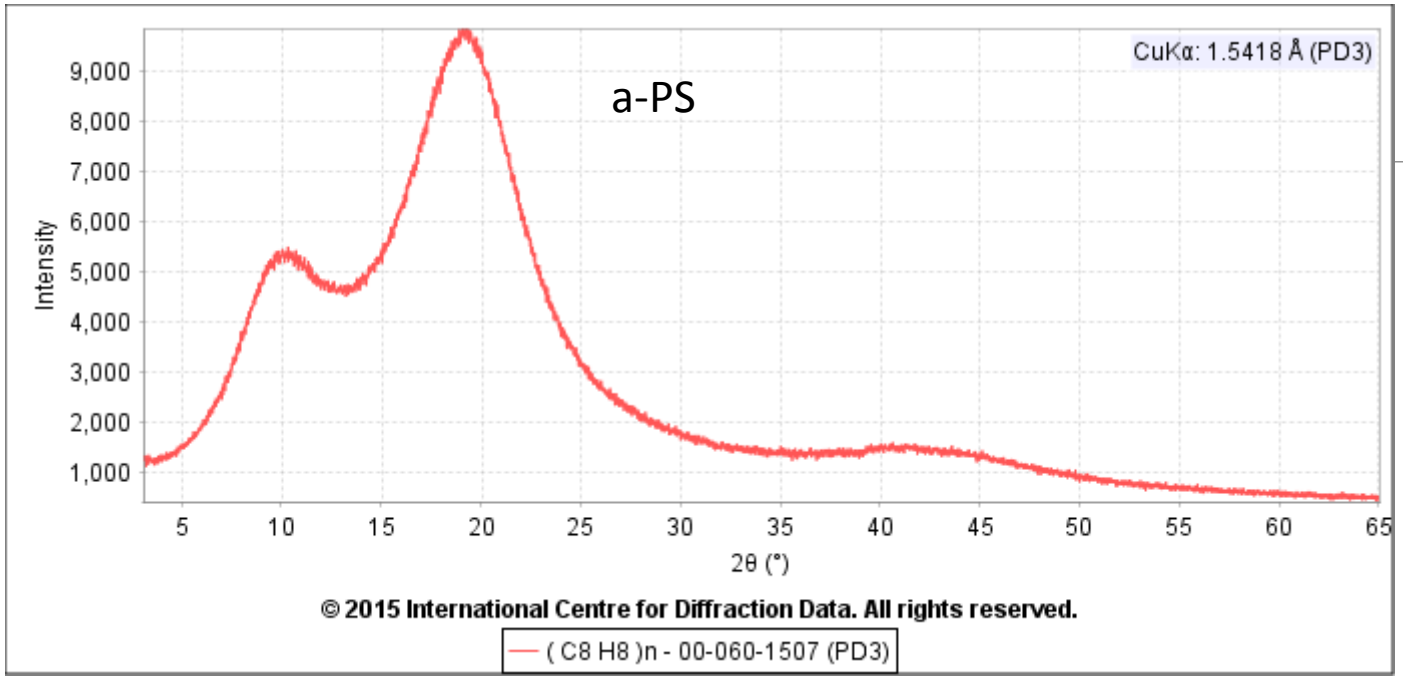
Amorphous - polycarbonate



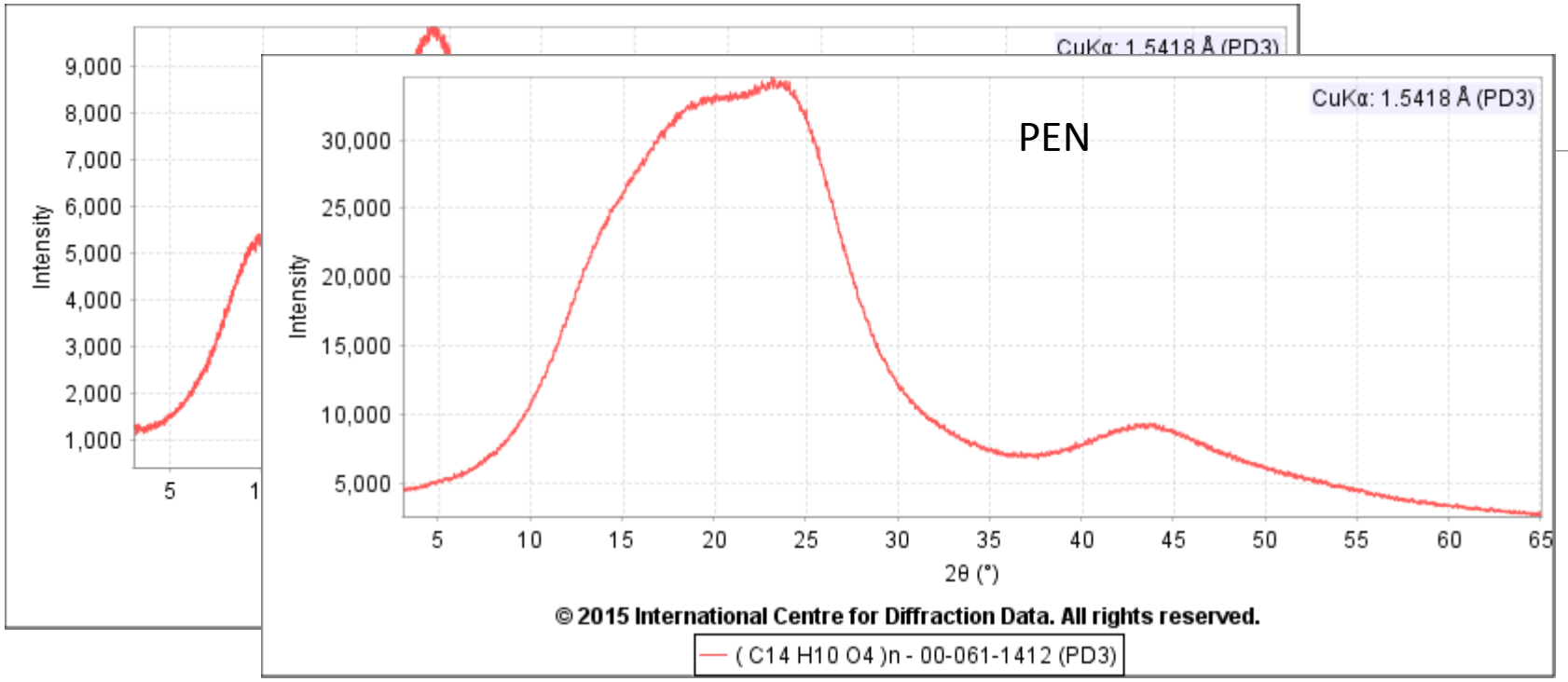
Can I just model the polymer amorphous component as a single peak?



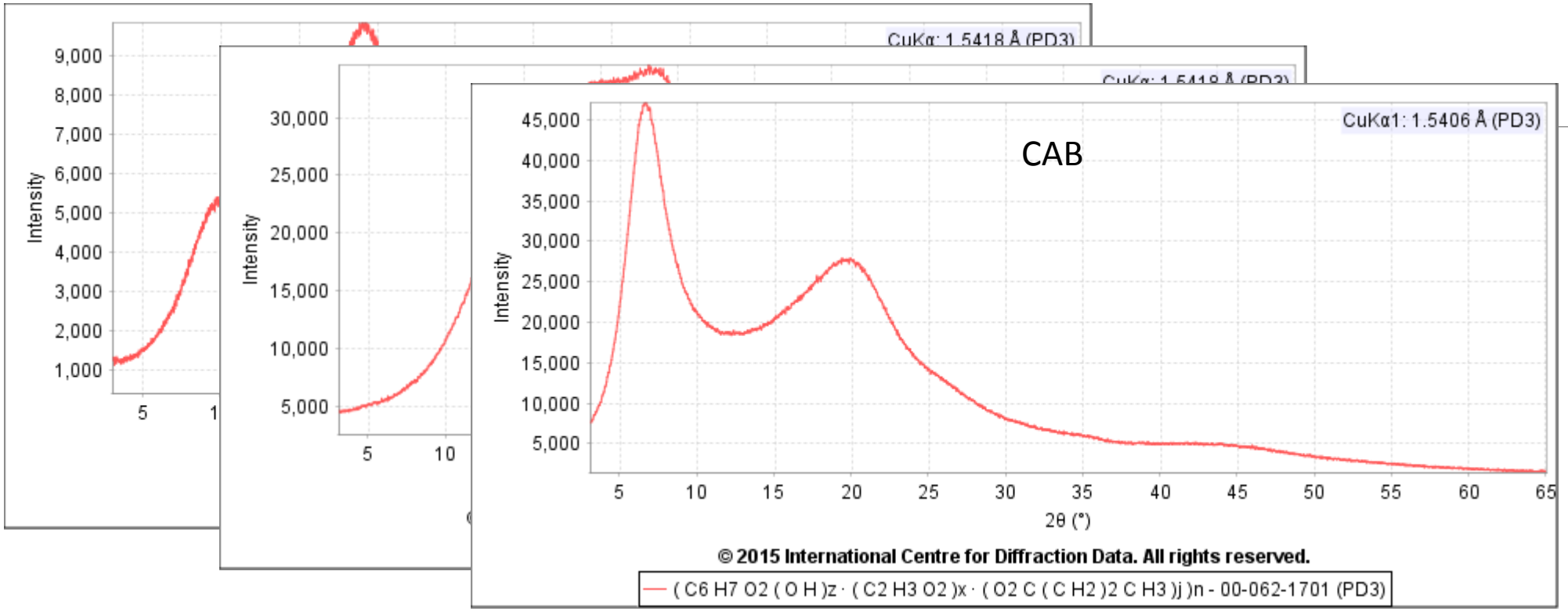
Amorphous patterns – usually not a single peak



Amorphous patterns – usually not a single peak



Amorphous patterns – usually not a single peak



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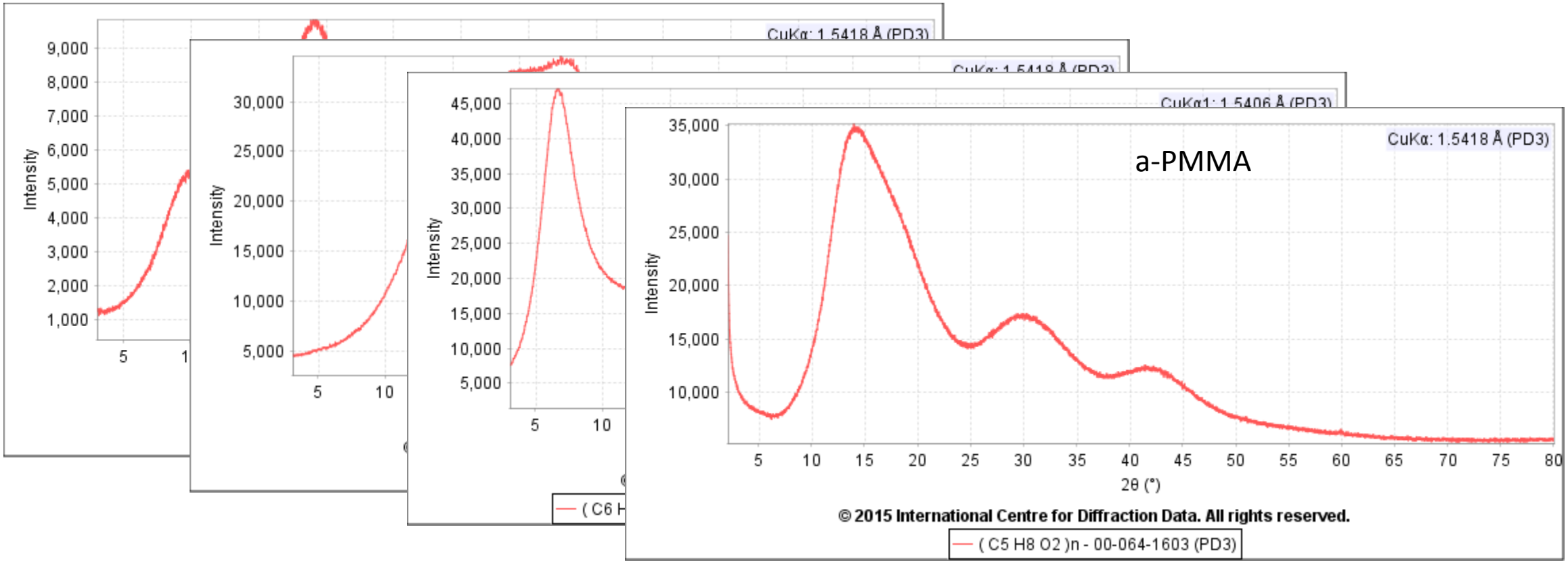
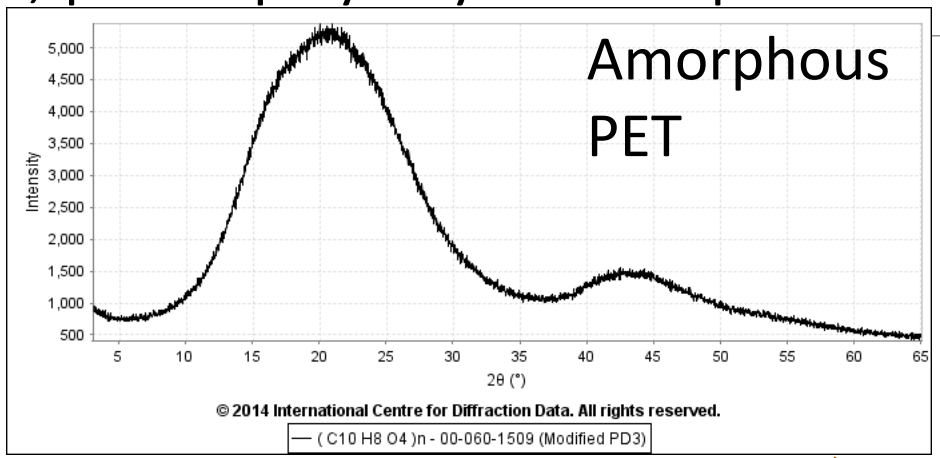
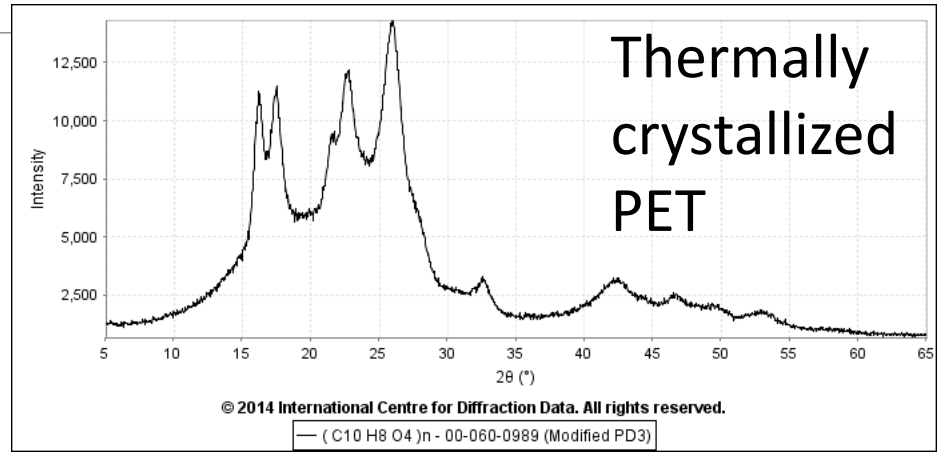


Polymer microstructure: processing matters

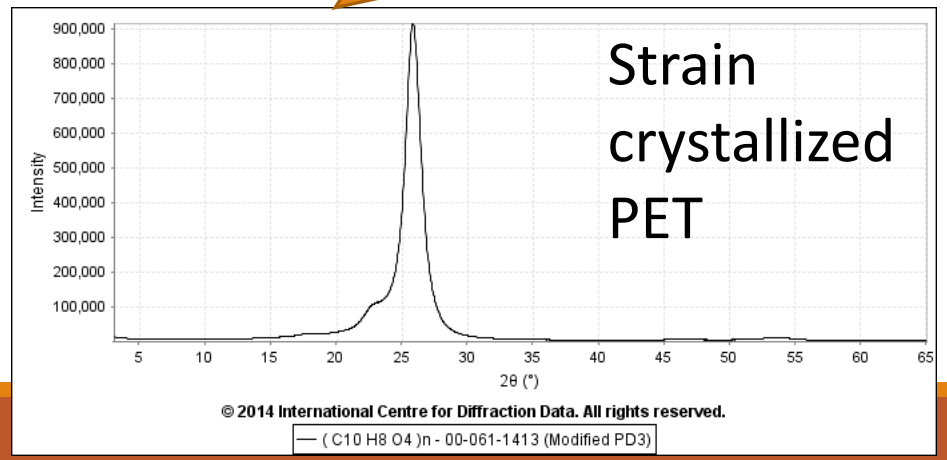
Melt,quench polyethylene terephthalate (PET)



Δ

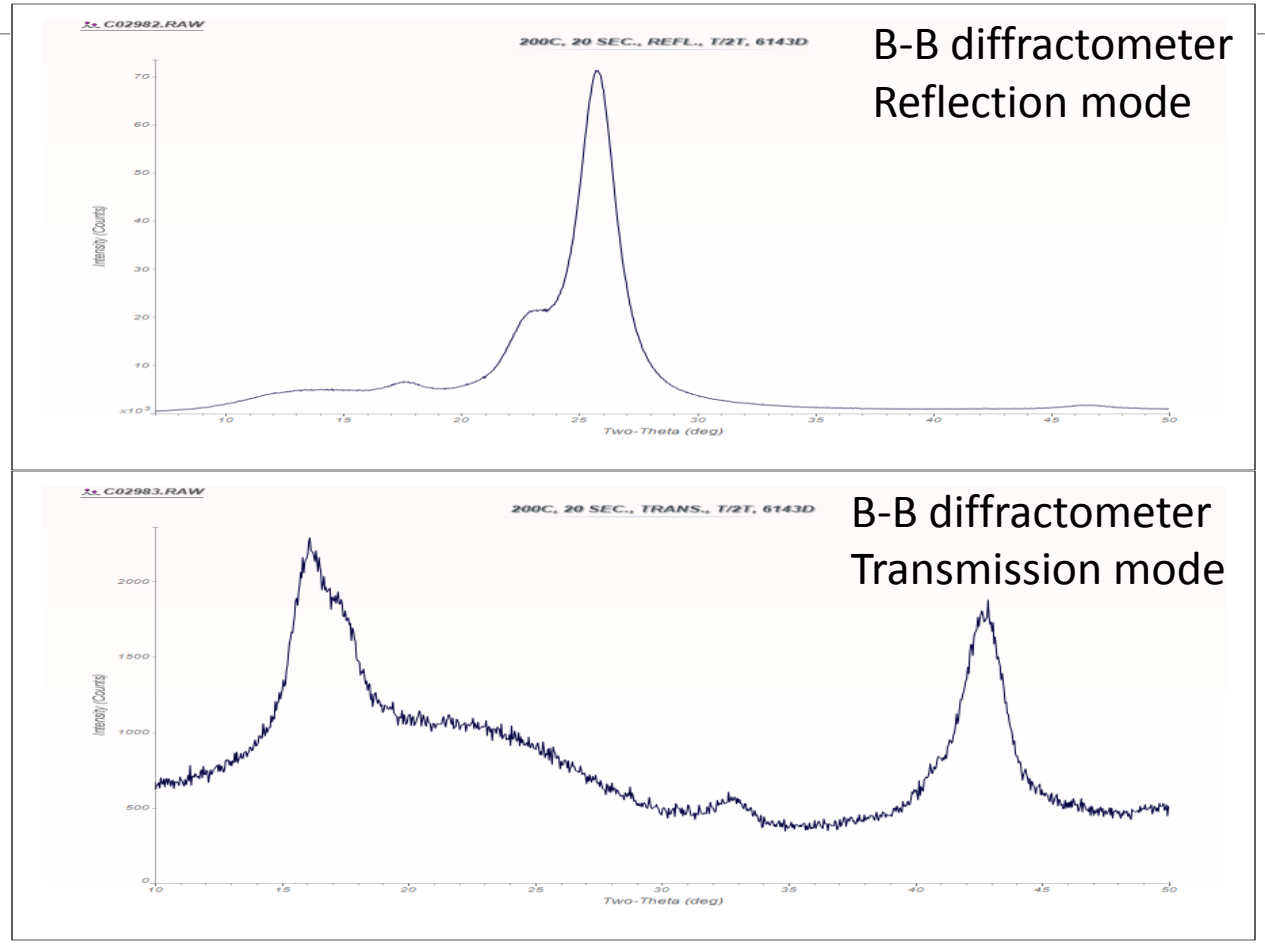


ε

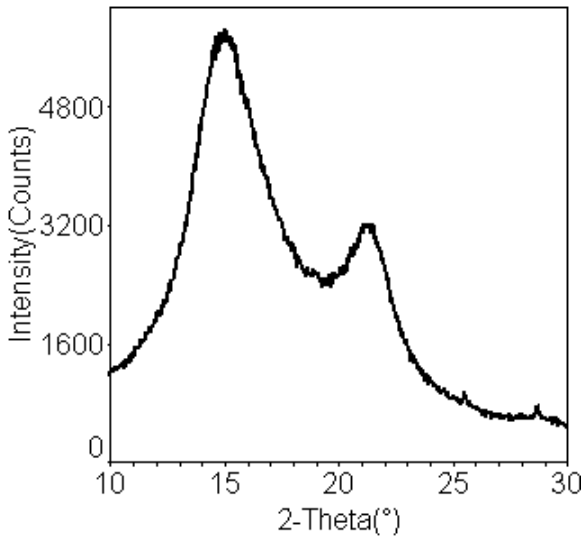


Polymer diffraction pattern: sample orientation matters

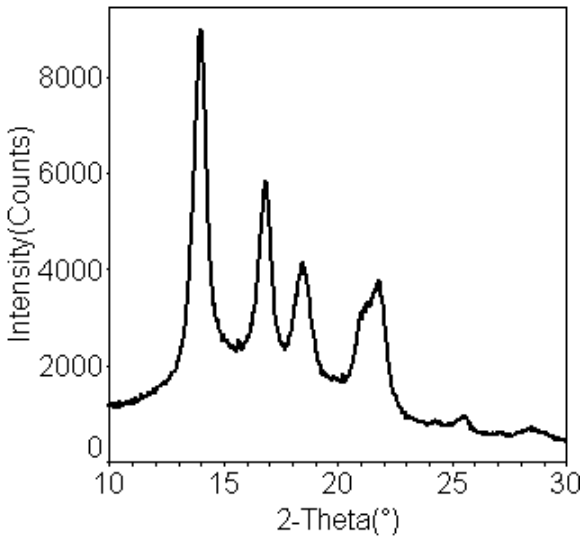
Strain crystallized PET



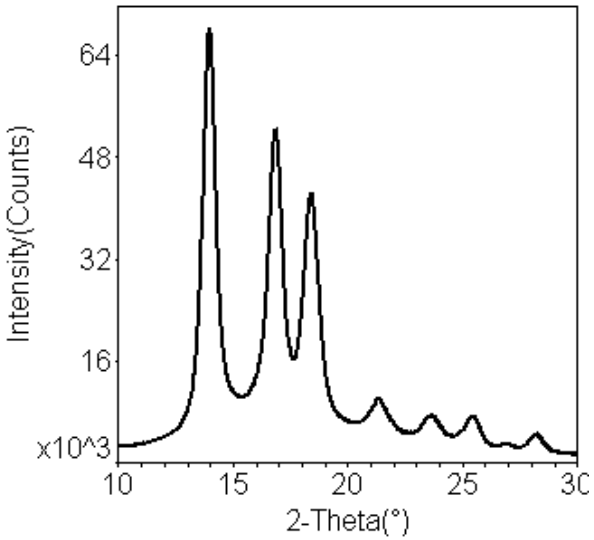
Bragg Brentano reflection mode XRD patterns - Effect of processing and sample orientation on polypropylene XRD patterns



Cast
No heatset
No stretch

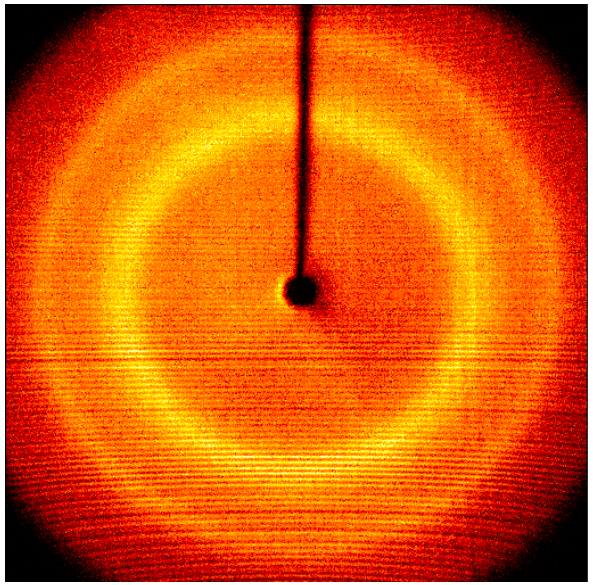


Heatset
120 °C, 10s
No stretch

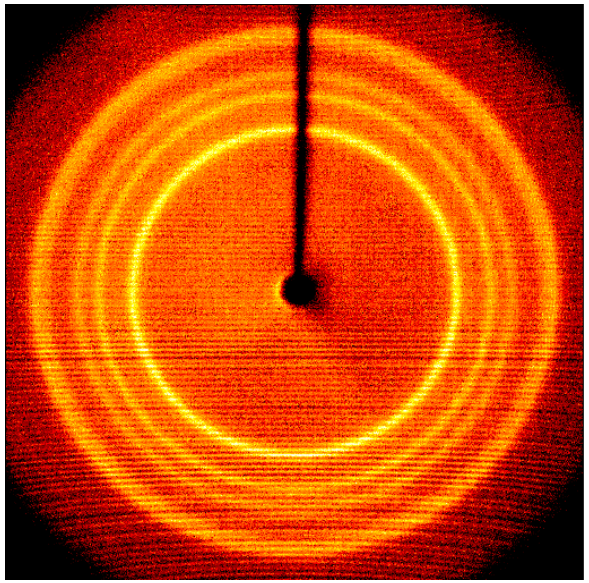


Heatset
6X
Uniax stretch

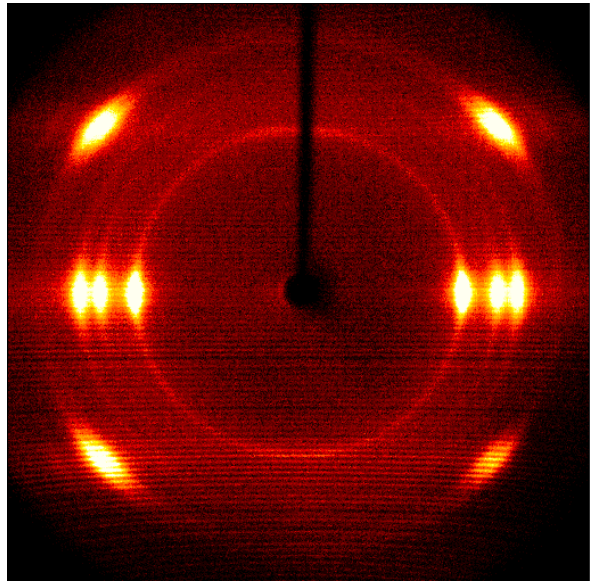
2-D transmission XRD patterns - Effect of processing and sample orientation on polypropylene XRD patterns



Cast
No heatset
No stretch

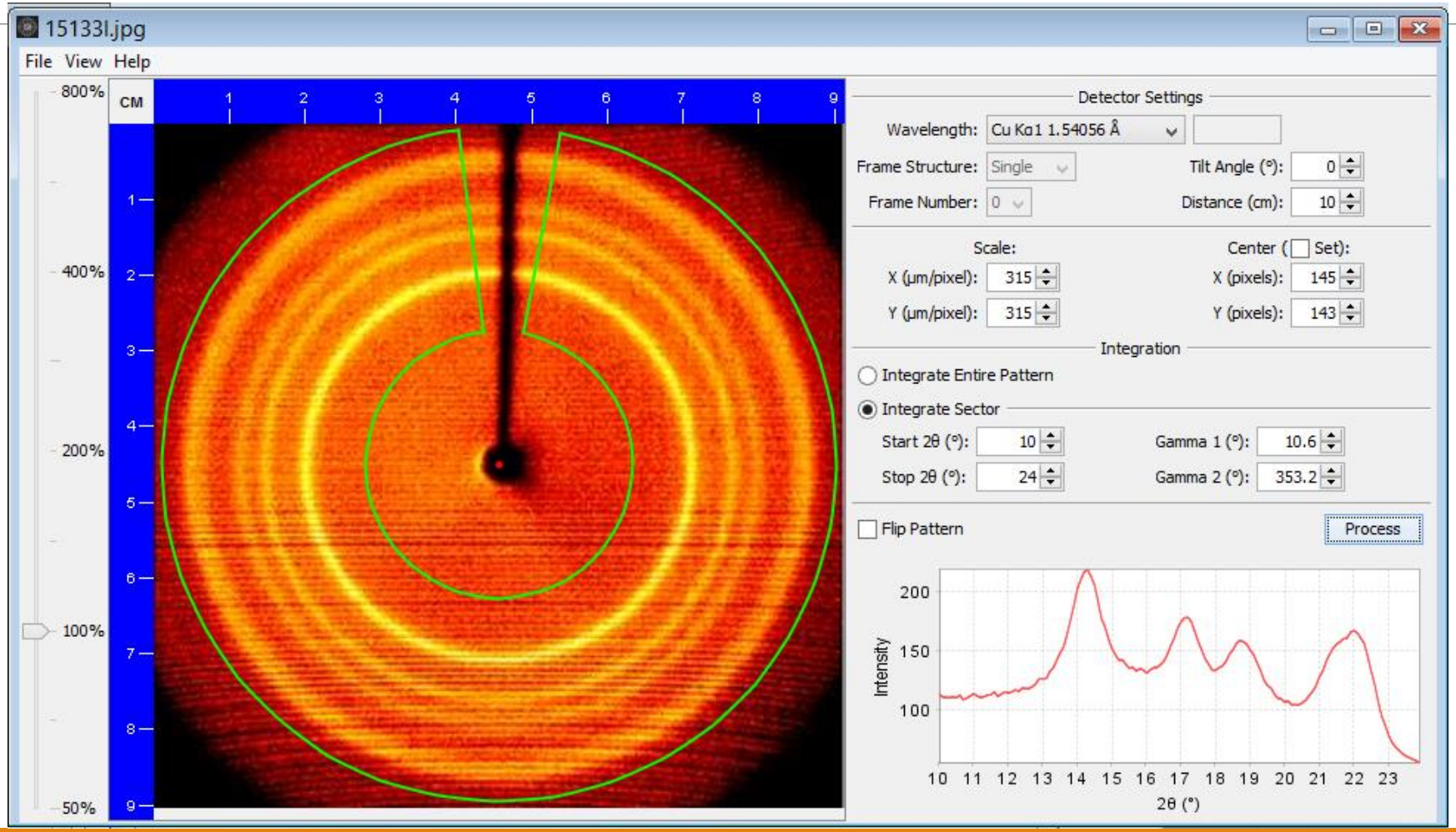


Heatset
120 °C, 10s
No stretch

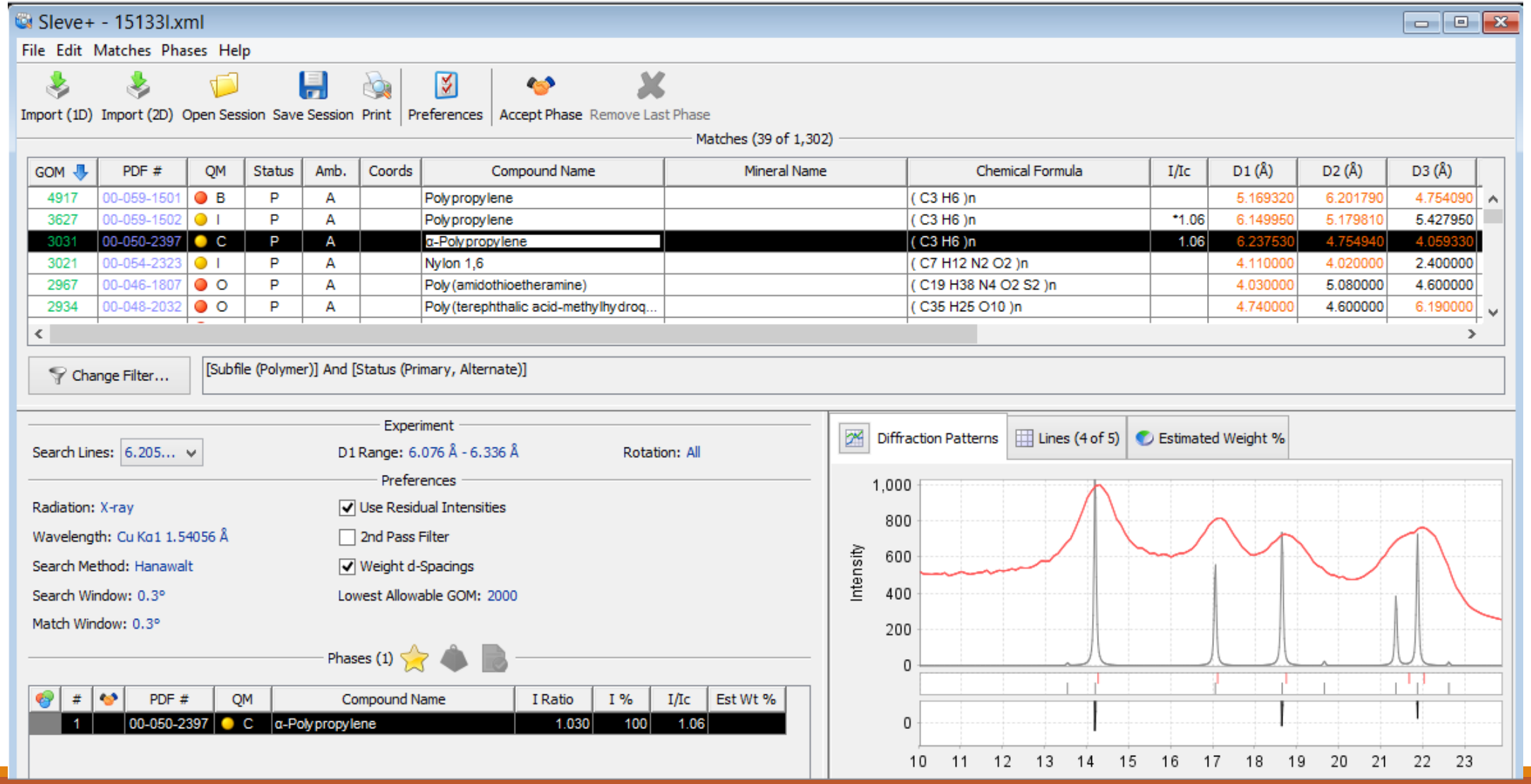


Heatset
6X
Uniax stretch

Import 2D diffraction image files for phase ID using ICDD Sieve – New feature for PDF 2015 databases

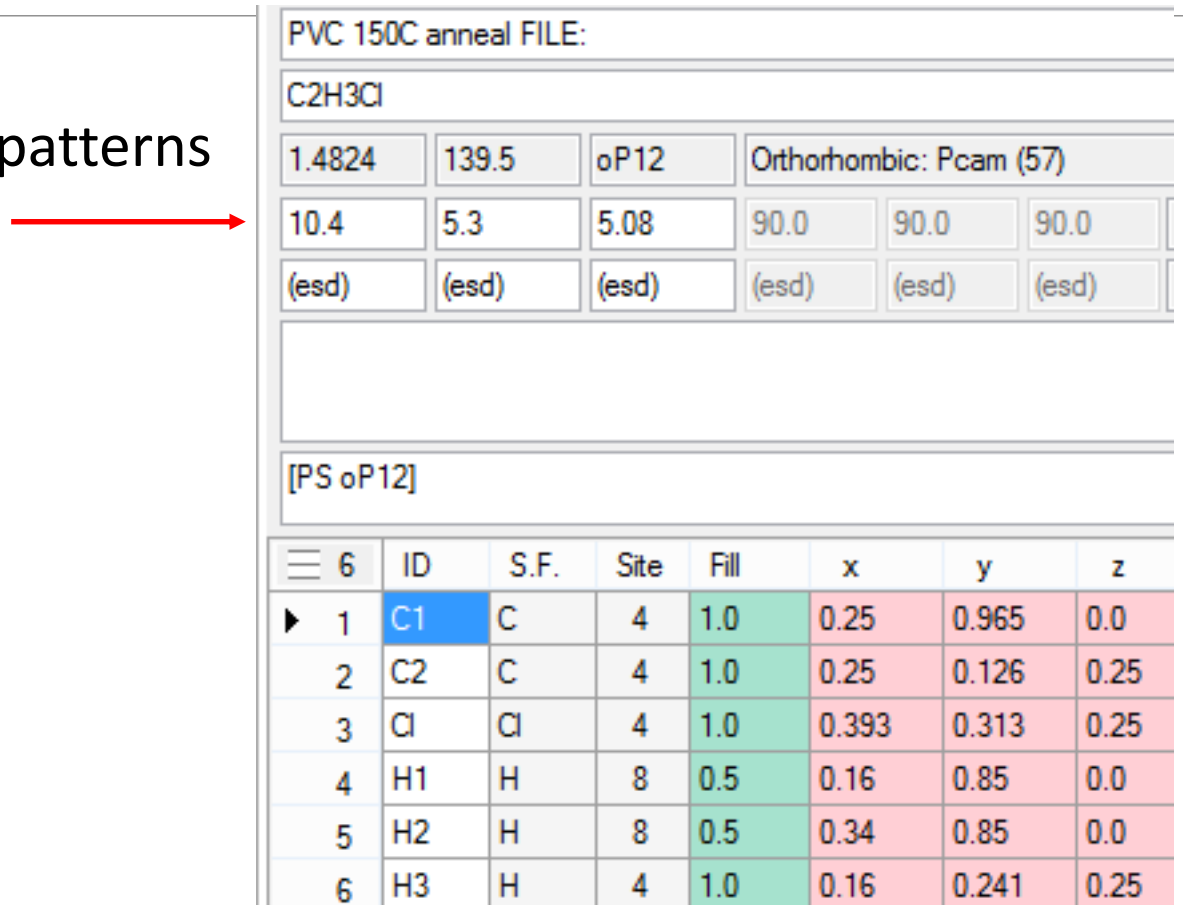


Import 2D diffraction image files for phase ID using ICDD Sieve – New feature for PDF 2015 databases



XRD analysis of polyvinyl chloride (PVC) polymer

Unit cell from fiber patterns



PVC 150C anneal FILE:

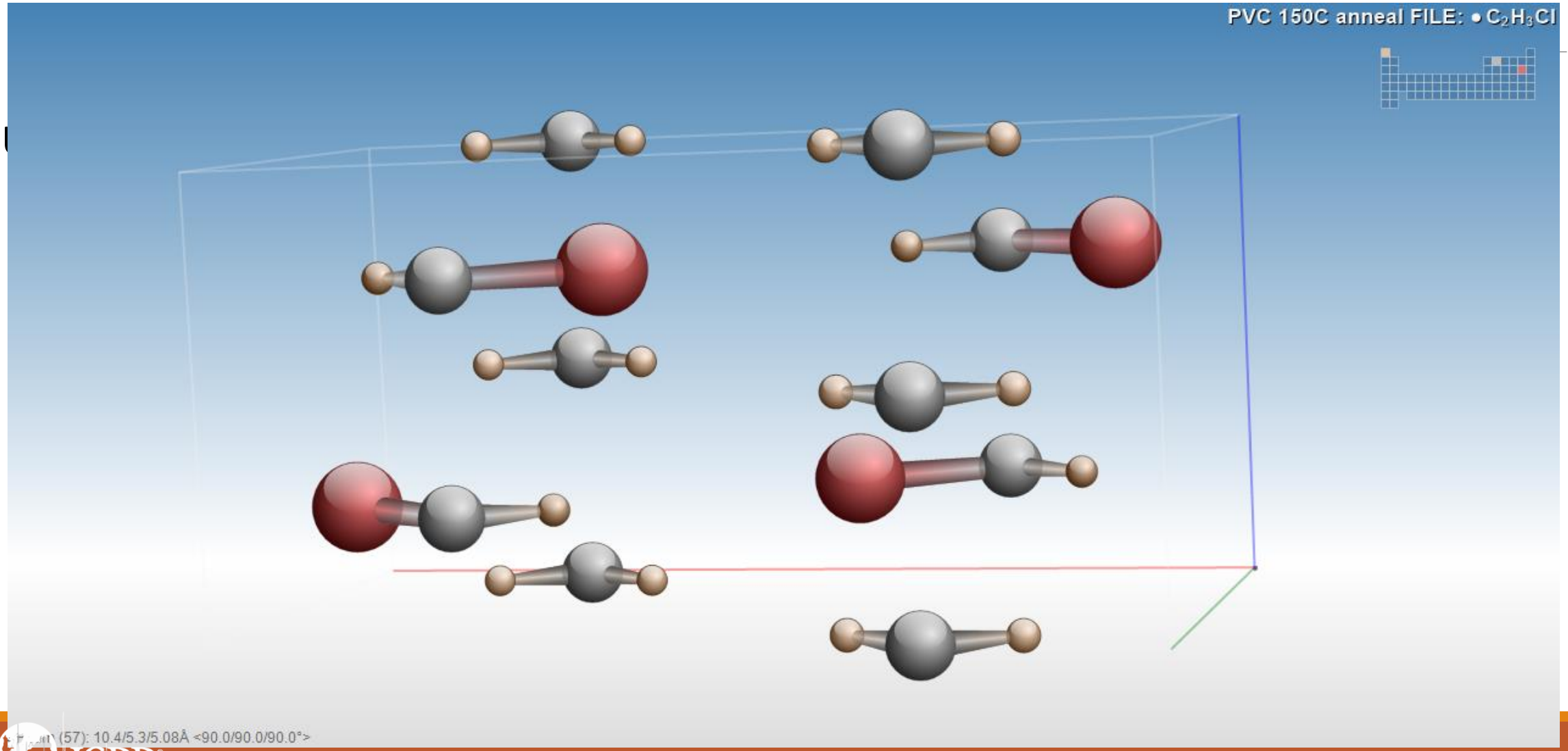
C2H3Cl

1.4824	139.5	oP12	Orthorhombic: Pcam (57)		
10.4	5.3	5.08	90.0	90.0	90.0
(esd)	(esd)	(esd)	(esd)	(esd)	(esd)

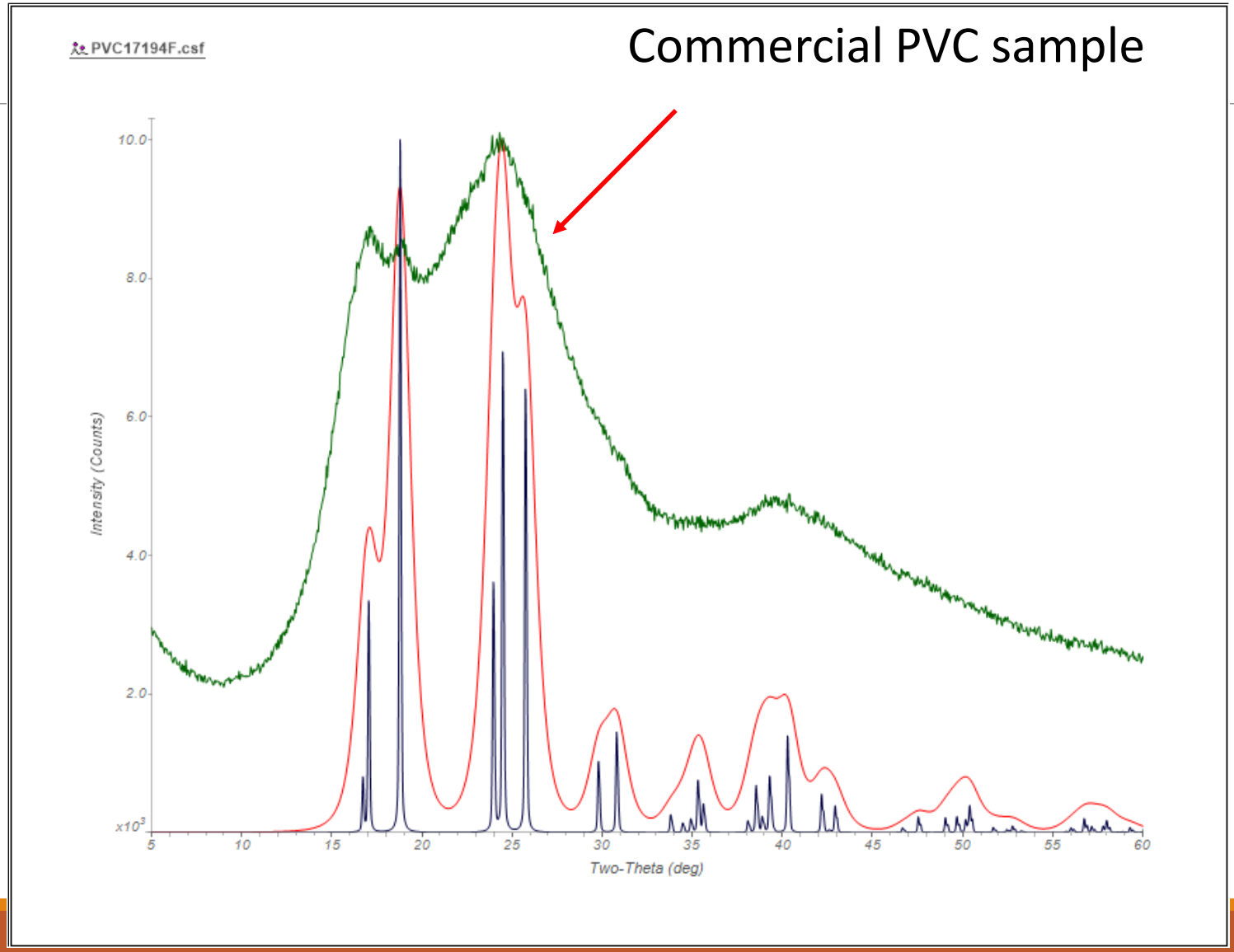
[PS oP12]

6	ID	S.F.	Site	Fill	x	y	z
1	C1	C	4	1.0	0.25	0.965	0.0
2	C2	C	4	1.0	0.25	0.126	0.25
3	Cl	Cl	4	1.0	0.393	0.313	0.25
4	H1	H	8	0.5	0.16	0.85	0.0
5	H2	H	8	0.5	0.34	0.85	0.0
6	H3	H	4	1.0	0.16	0.241	0.25

XRD analysis of polyvinyl chloride (PVC) polymer

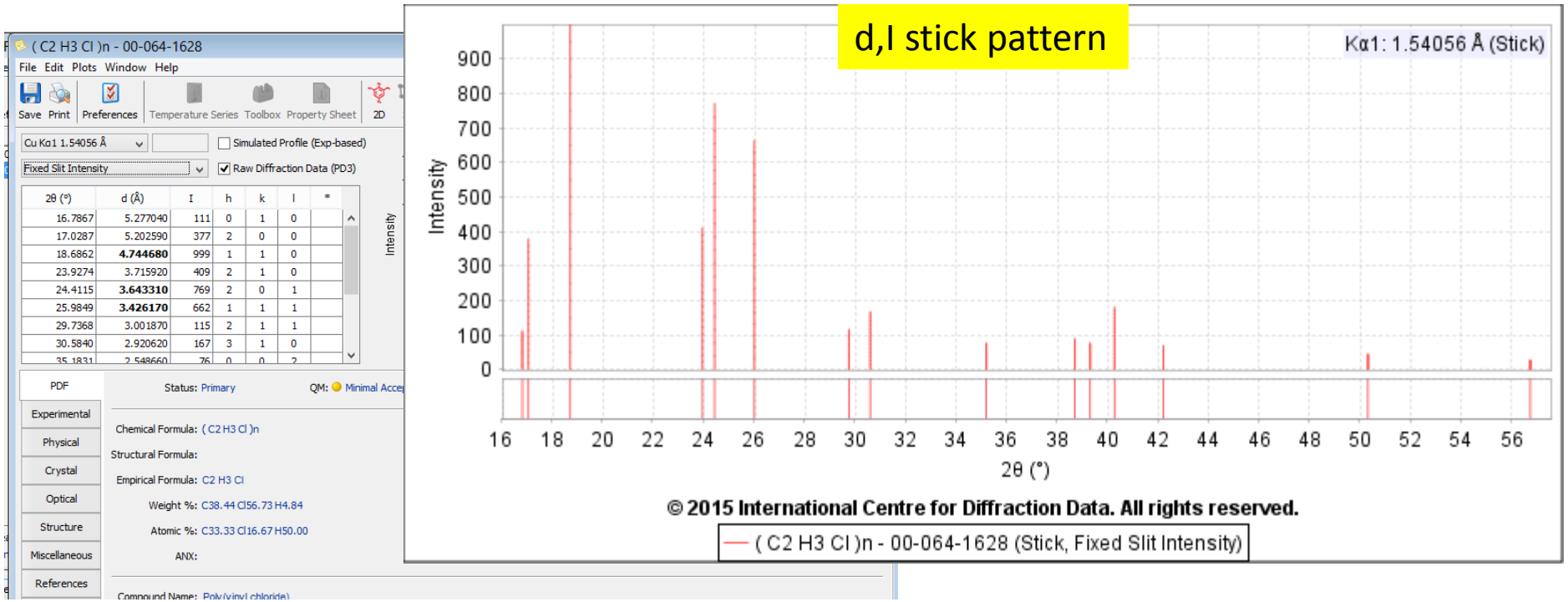


PVC – XRD powder patterns calculated vs. observed



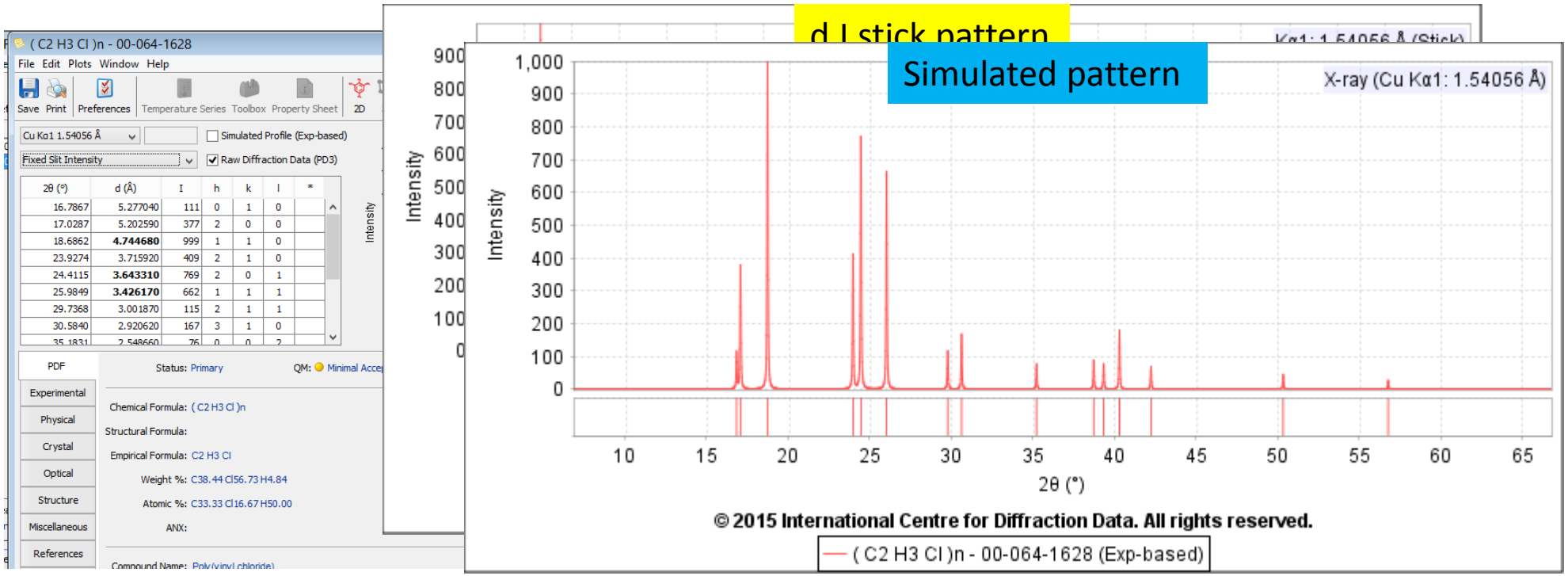
Diffraction polymer entries in ICDD PDF databases

Polyvinyl chloride



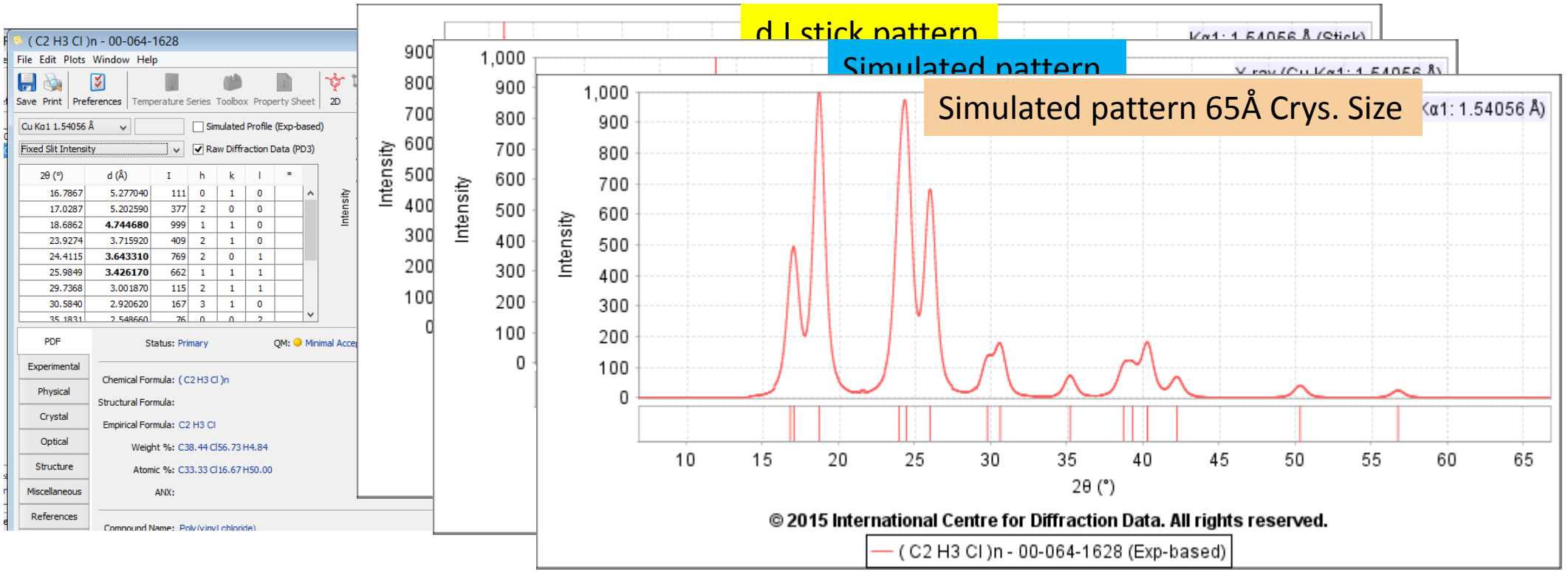
Diffraction polymer entries in ICDD PDF databases

Polyvinyl chloride



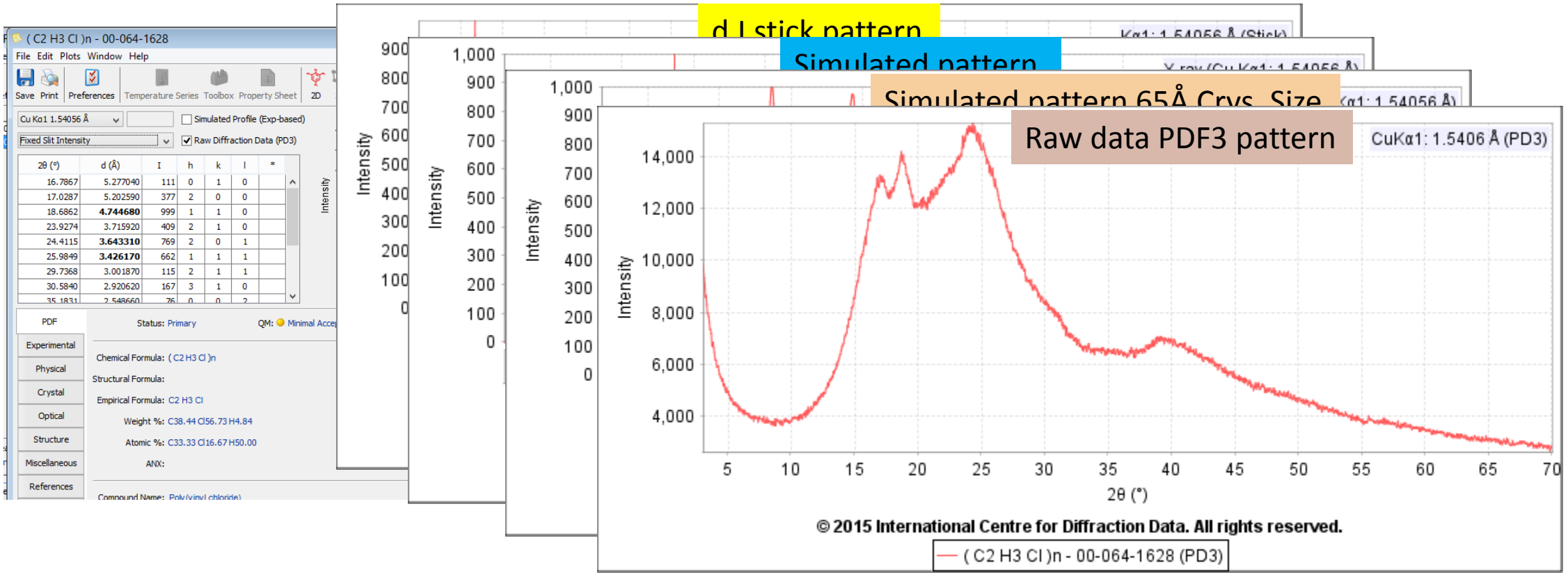
Diffraction polymer entries in ICDD PDF databases

Polyvinyl chloride



Diffraction polymer entries in ICDD PDF databases

Polyvinyl chloride

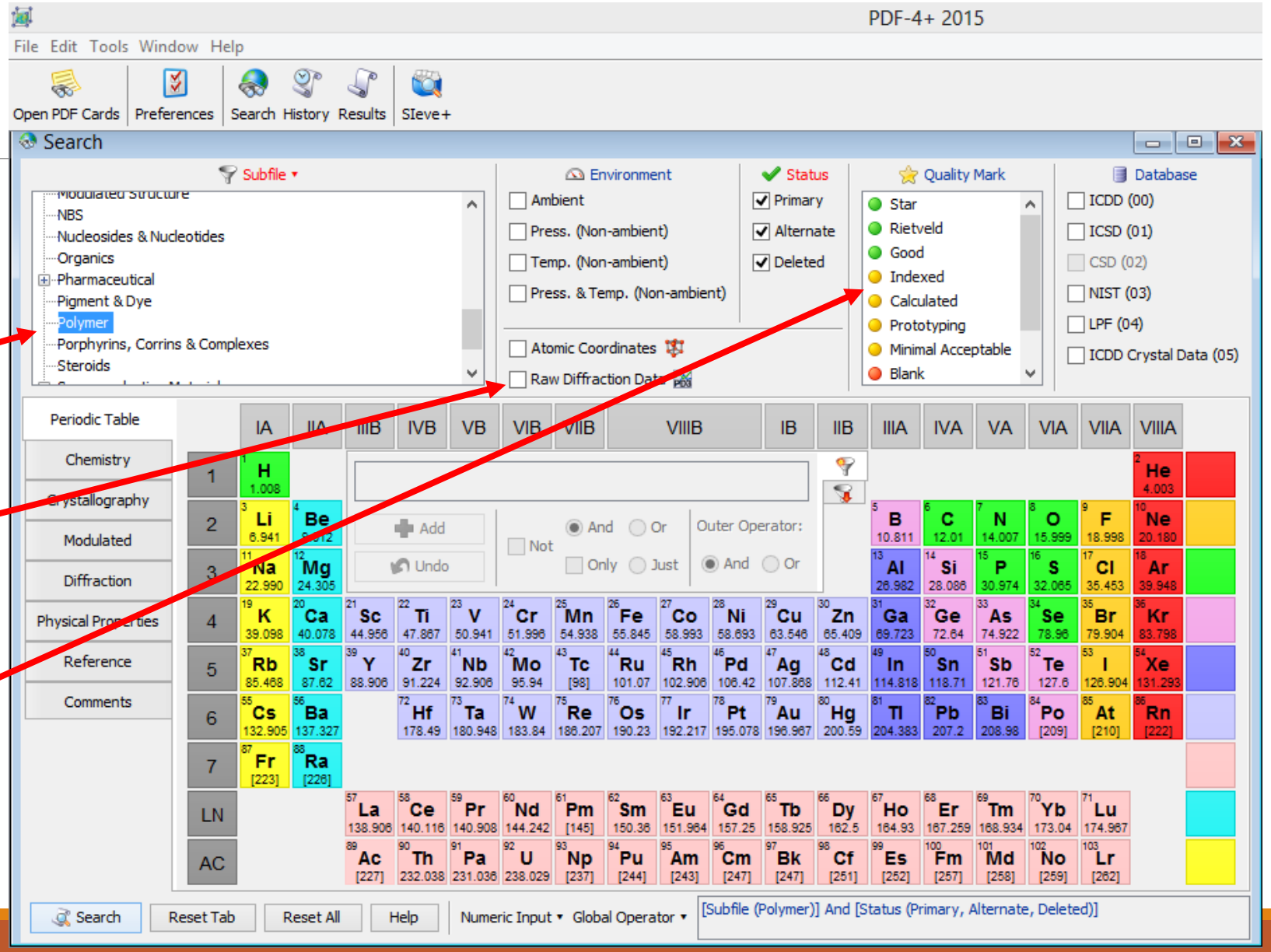


Polymer entries in PDF 2015

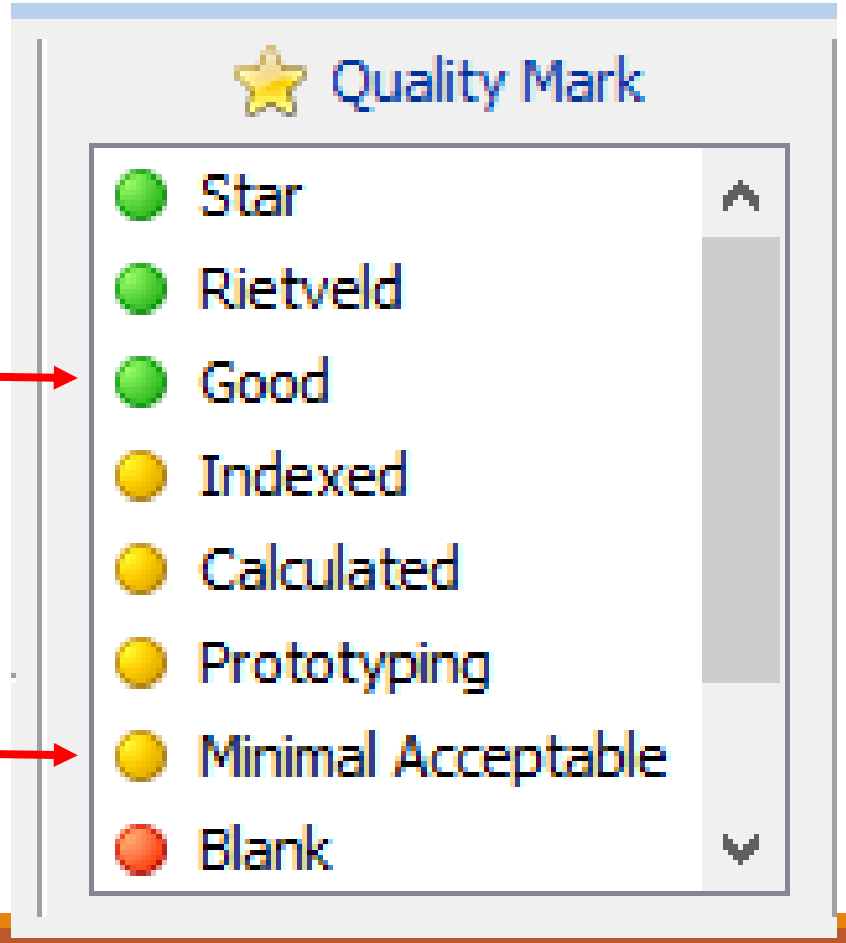
Subfile search

Entries with raw data

Quality mark



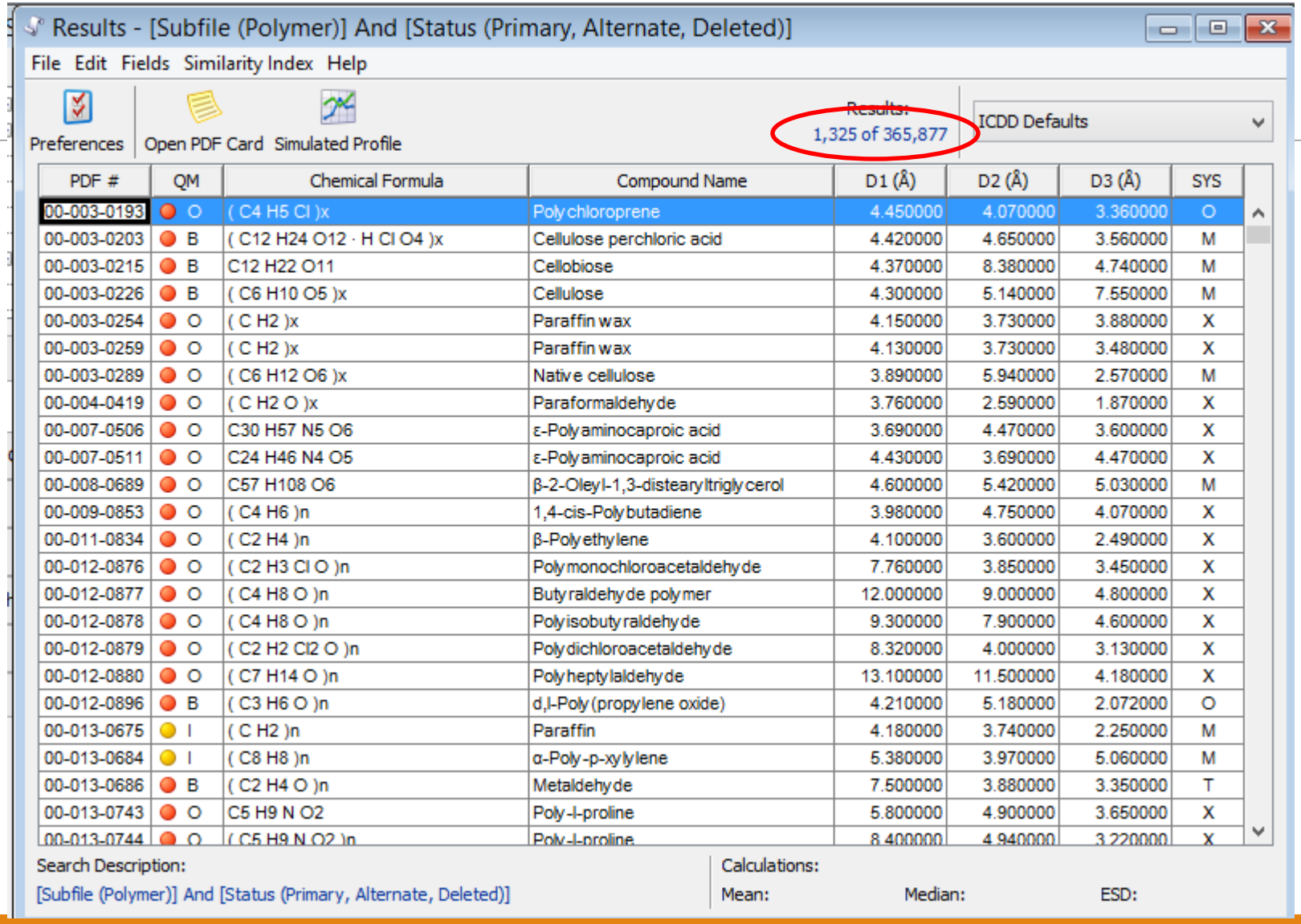
Quality Marks



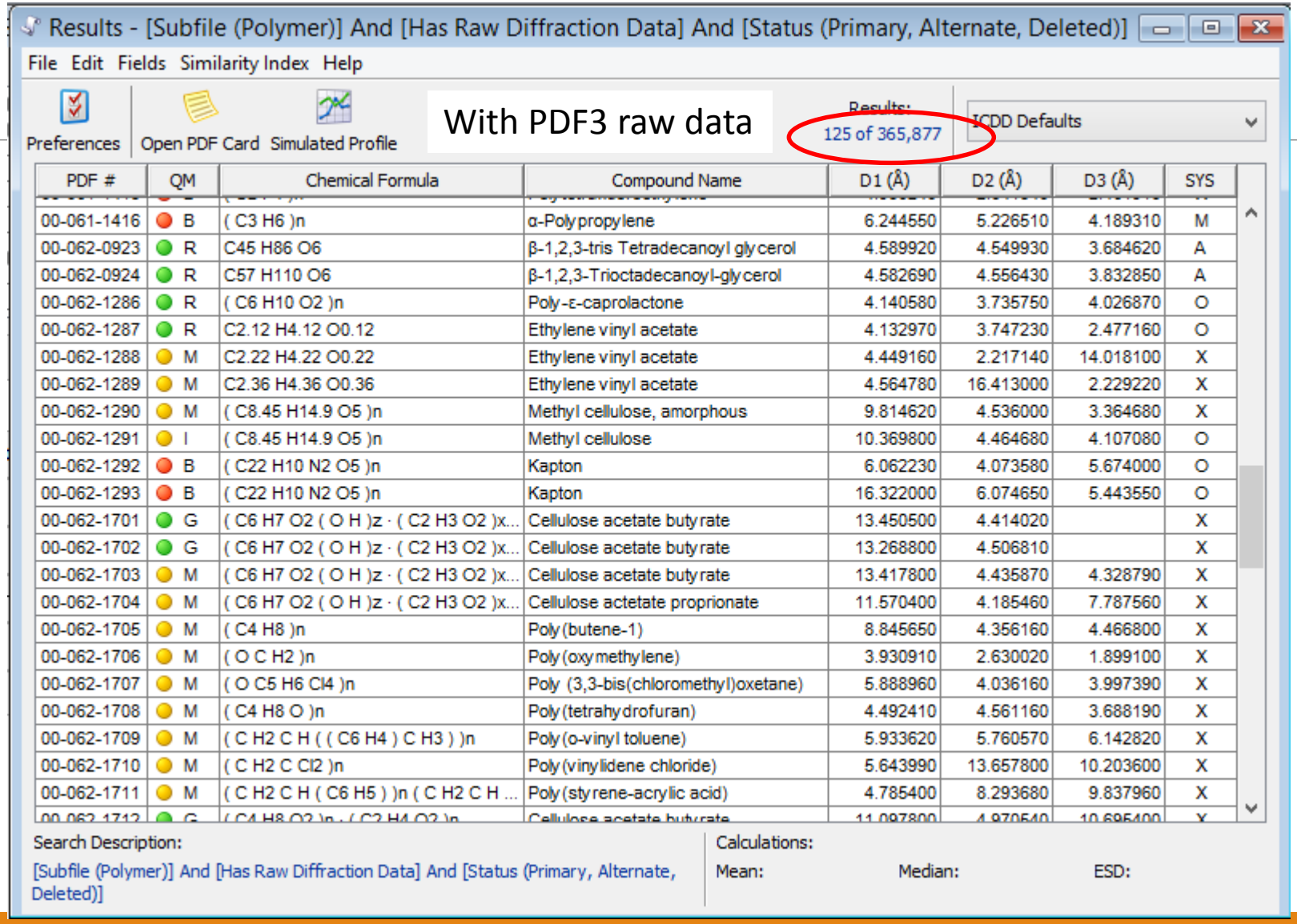
Good (G). Indicates the material has significant amorphous content, and has a digital diffraction pattern with a good signal-to-noise ratio. Additionally, some chemical analysis information has been provided to support the specified composition of the material (i.e. spectroscopy, pair distribution functions, commercial source, etc.).

Minimal Acceptable (M). Indicates the material has significant amorphous content, and has a digital diffraction pattern with a good signal-to-noise ratio. However, no chemical analysis data to support the materials composition was provided.

Polymer entries in PDF 2015



Polymer entries in PDF 2015



PDF #	QM	Chemical Formula	Compound Name	D1 (Å)	D2 (Å)	D3 (Å)	SYS
00-061-1416	B	(C3 H6)n	α-Polypropylene	6.244550	5.226510	4.189310	M
00-062-0923	R	C45 H86 O6	β-1,2,3-tris Tetradecanoyl glycerol	4.589920	4.549930	3.684620	A
00-062-0924	R	C57 H110 O6	β-1,2,3-Trioctadecanoyl-glycerol	4.582690	4.556430	3.832850	A
00-062-1286	R	(C6 H10 O2)n	Poly-ε-caprolactone	4.140580	3.735750	4.026870	O
00-062-1287	R	C2.12 H4.12 O0.12	Ethylene vinyl acetate	4.132970	3.747230	2.477160	O
00-062-1288	M	C2.22 H4.22 O0.22	Ethylene vinyl acetate	4.449160	2.217140	14.018100	X
00-062-1289	M	C2.36 H4.36 O0.36	Ethylene vinyl acetate	4.564780	16.413000	2.229220	X
00-062-1290	M	(C8.45 H14.9 O5)n	Methyl cellulose, amorphous	9.814620	4.536000	3.364680	X
00-062-1291	I	(C8.45 H14.9 O5)n	Methyl cellulose	10.369800	4.464680	4.107080	O
00-062-1292	B	(C22 H10 N2 O5)n	Kapton	6.062230	4.073580	5.674000	O
00-062-1293	B	(C22 H10 N2 O5)n	Kapton	16.322000	6.074650	5.443550	O
00-062-1701	G	(C6 H7 O2 (O H)z · (C2 H3 O2)x...	Cellulose acetate butyrate	13.450500	4.414020		X
00-062-1702	G	(C6 H7 O2 (O H)z · (C2 H3 O2)x...	Cellulose acetate butyrate	13.268800	4.506810		X
00-062-1703	M	(C6 H7 O2 (O H)z · (C2 H3 O2)x...	Cellulose acetate butyrate	13.417800	4.435870	4.328790	X
00-062-1704	M	(C6 H7 O2 (O H)z · (C2 H3 O2)x...	Cellulose actetate proprionate	11.570400	4.185460	7.787560	X
00-062-1705	M	(C4 H8)n	Poly(butene-1)	8.845650	4.356160	4.466800	X
00-062-1706	M	(O C H2)n	Poly(oxymethylene)	3.930910	2.630020	1.899100	X
00-062-1707	M	(O C5 H6 Cl4)n	Poly (3,3-bis(chloromethyl)oxetane)	5.888960	4.036160	3.997390	X
00-062-1708	M	(C4 H8 O)n	Poly(tetrahydrofuran)	4.492410	4.561160	3.688190	X
00-062-1709	M	(C H2 C H ((C6 H4) C H3))n	Poly(o-vinyl toluene)	5.933620	5.760570	6.142820	X
00-062-1710	M	(C H2 C Cl2)n	Poly(vinylidene chloride)	5.643990	13.657800	10.203600	X
00-062-1711	M	(C H2 C H (C6 H5))n (C H2 C H ...	Poly(styrene-acrylic acid)	4.785400	8.293680	9.837960	X
00-062-1712	G	(C4 H8 O2)n · (C2 H4 O2)n	Cellulose acetate butyrate	11.097800	4.970540	10.696400	X

2015 – ICDD pharmaceutical polymers project

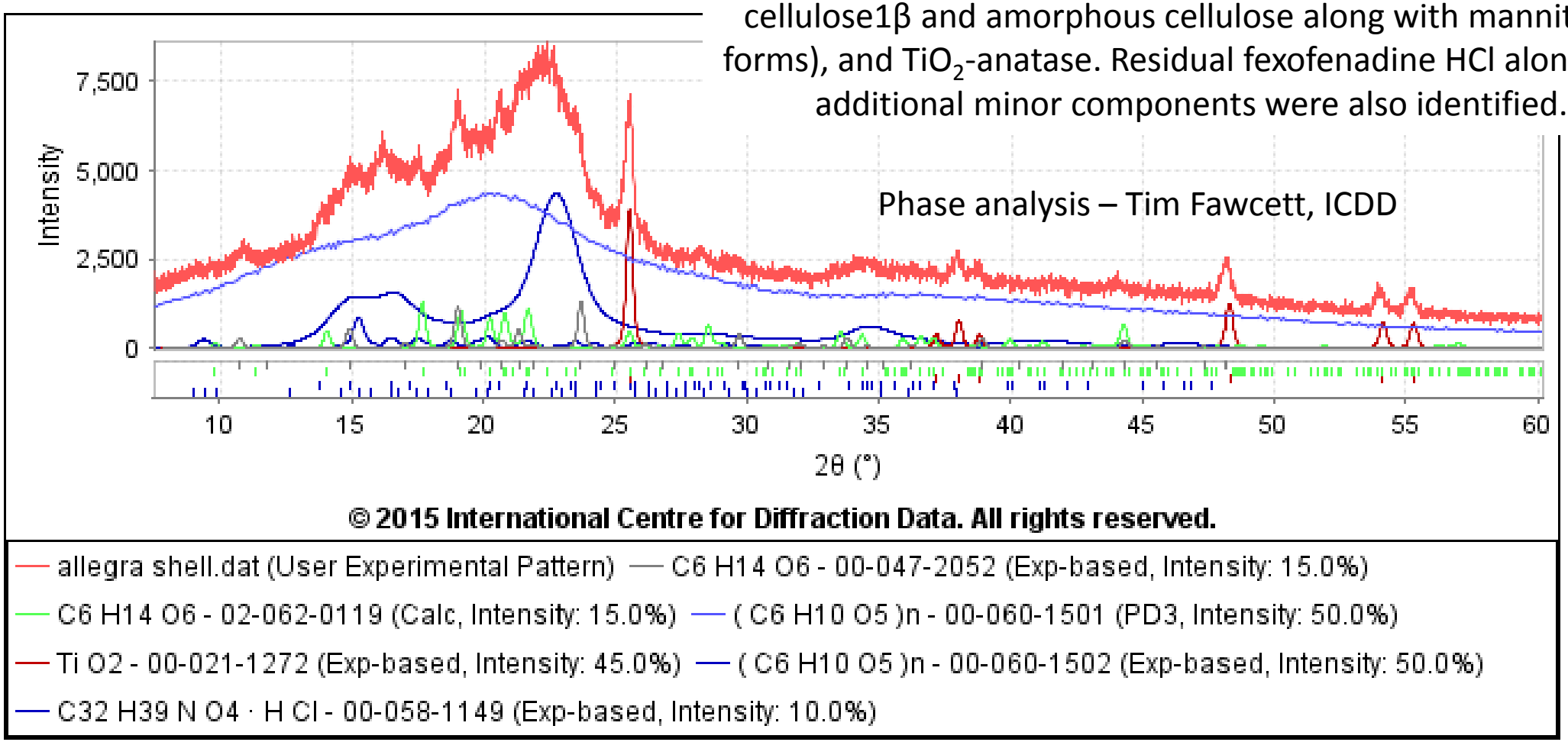
Polymer	Mol. Formula	PDF Entry	PD3
poly(acrylic acid), PAA	(C3H4O2)n	N	N
poly(ethylene oxide), PEO	(C2H4O)n	Y	N
poly(ethylene glycol), PEG	(C2H4O)n	Y	N
poly(vinyl pyrrolidone), PVP	(C6H9NO)n	N	N
poly(vinyl alcohol), PVOH, PVA	(C2H4O)n	Y	Y
polyacrylamide, PAM	(C3H5NO)n	N	N
poly(N-isopropylacrylamide)	(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

2015 – 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

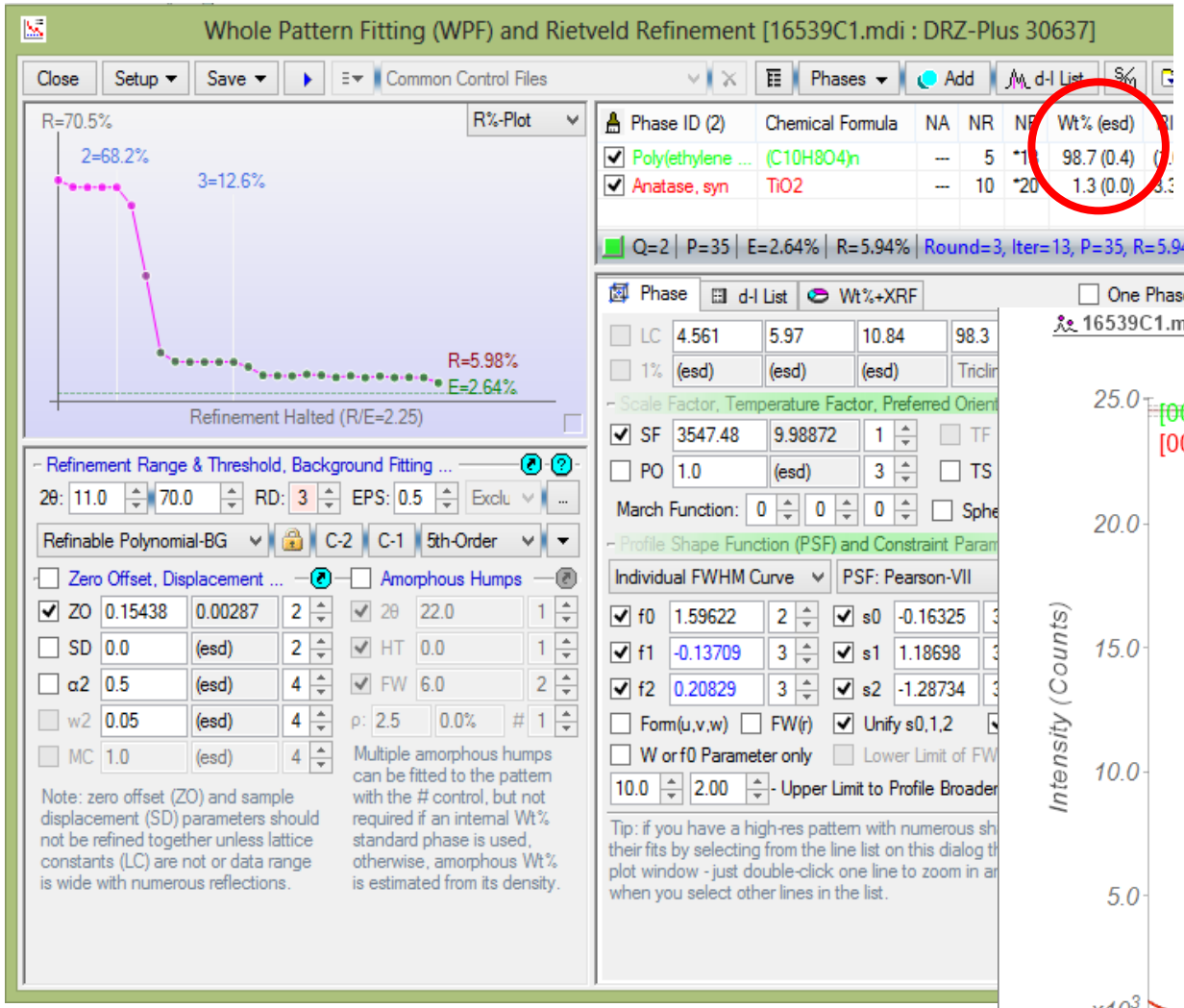
Phase ID – Allegra Shell

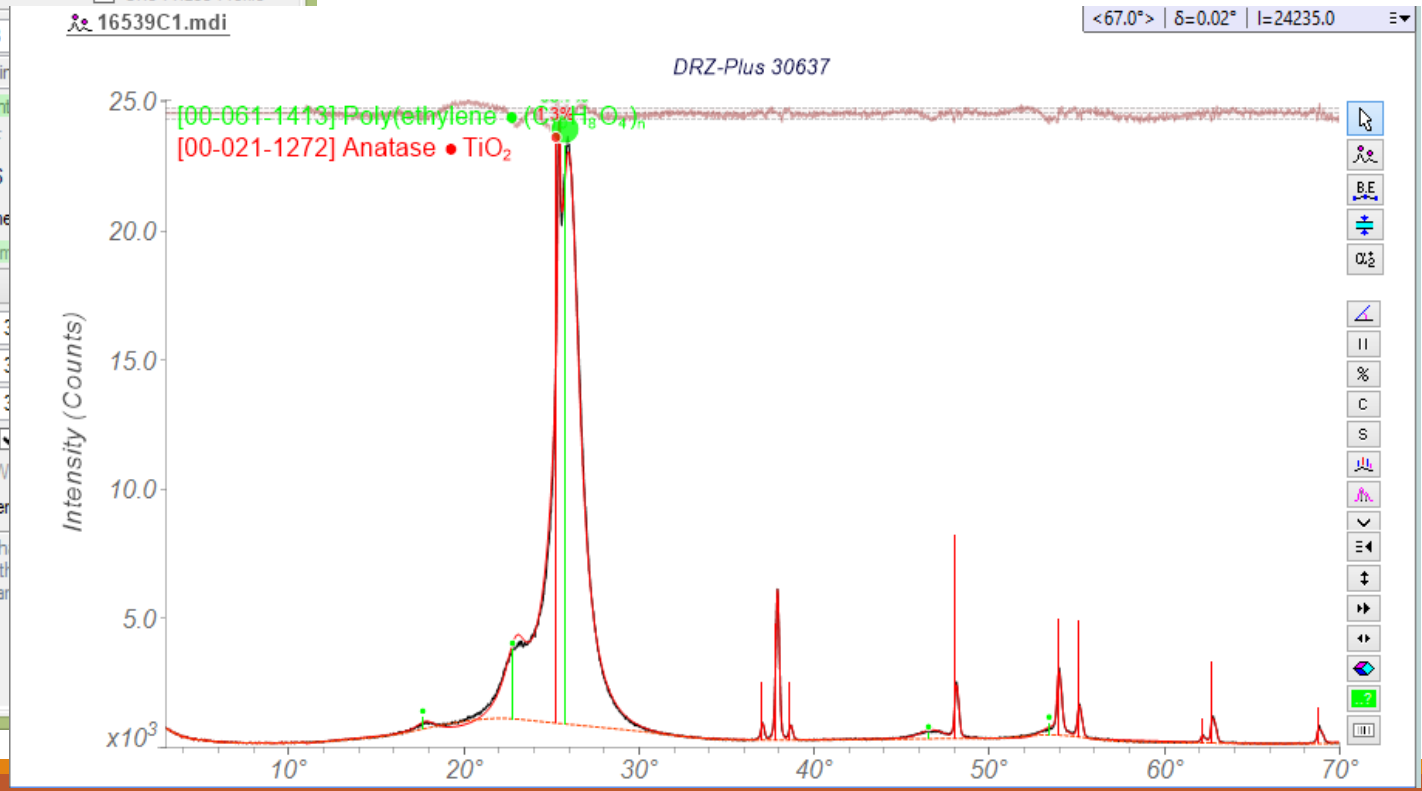
Allegra® (fexofenadine HCl) is an antihistamine used for the treatment of hay fever symptoms. XRD analysis of the shell covering reveals the major components include polymers cellulose1β and amorphous cellulose along with mannitol (2 forms), and TiO_2-anatase. Residual fexofenadine HCl along with additional minor components were also identified.



Quantitative Phase Analysis PET Composite Film

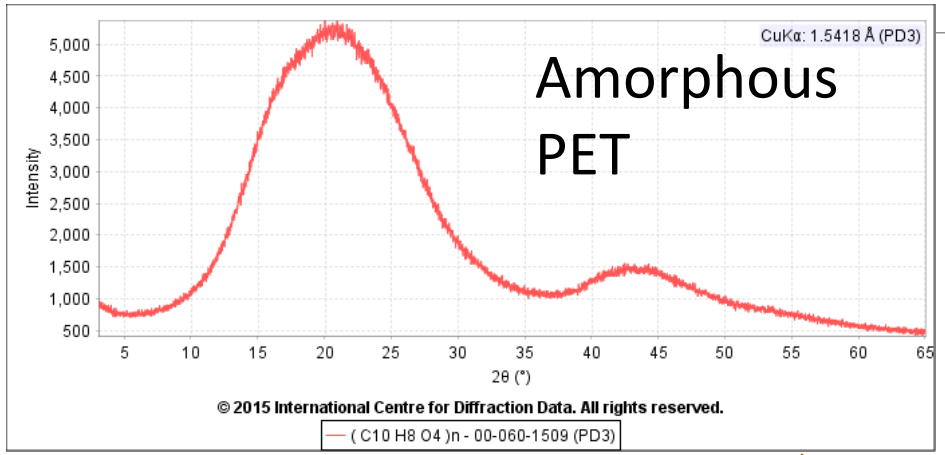
Composite used for transdermal patch backing. XRD phase analysis identified biaxially oriented poly(ethylene terephthalate) (PDF 00-061-1413) and TiO_2-anatase (00-021-1272). Since the biaxially oriented PET raw data pattern is stored in the PDF, whole pattern fitting can be used for quantitative analysis.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



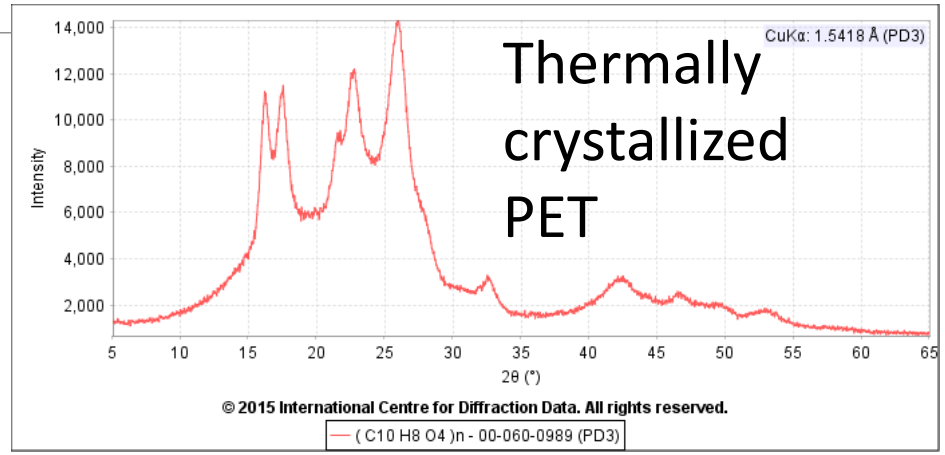


Do you need multiple Entries in the PDF Database for a polymer?

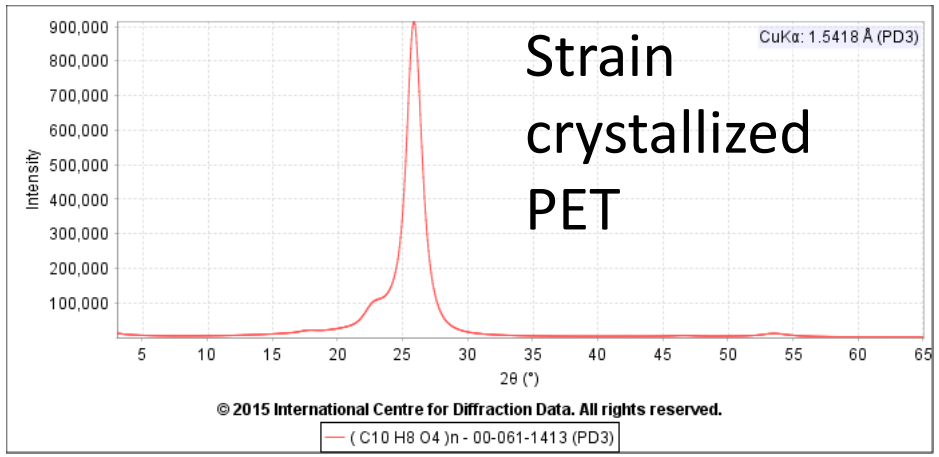
PET



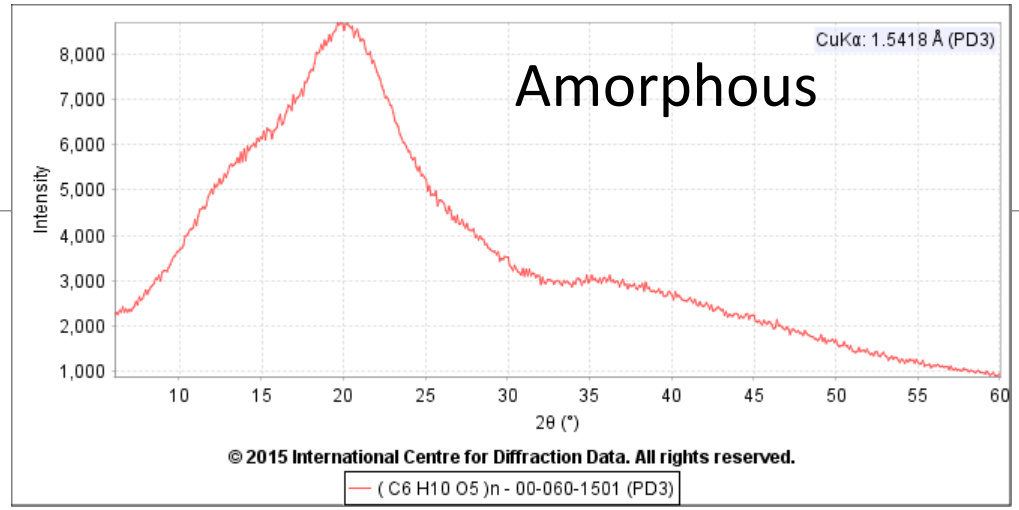
Δ

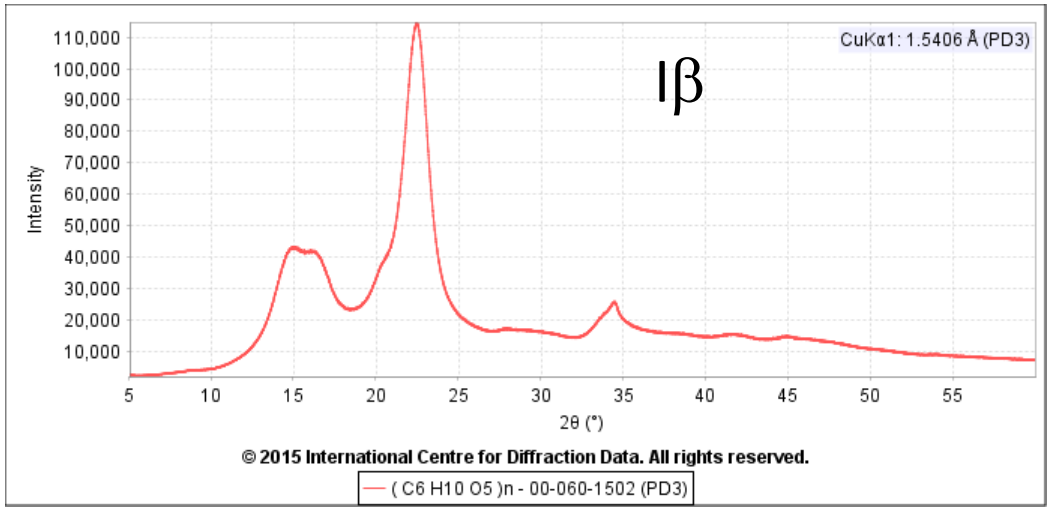


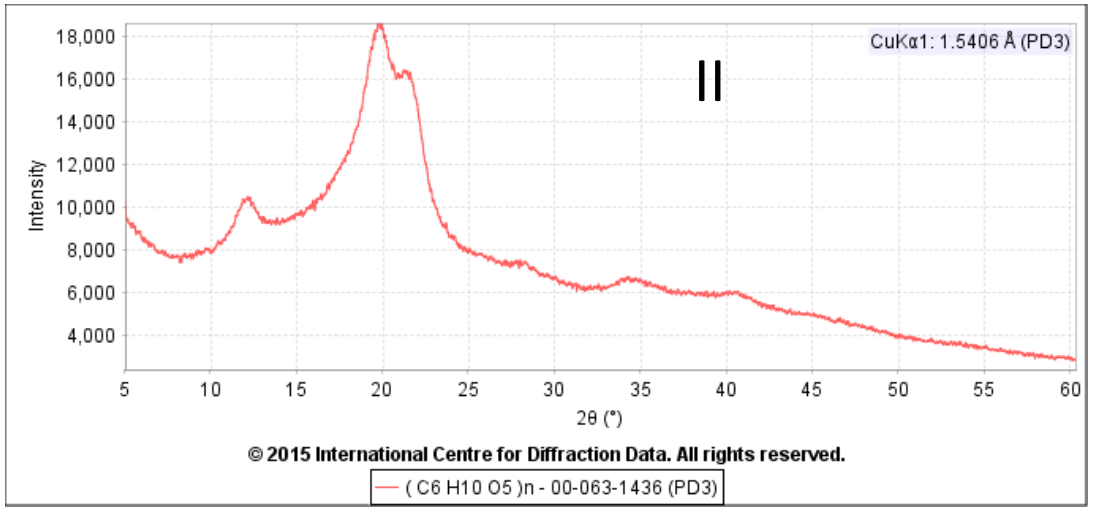
ε



Cellulose

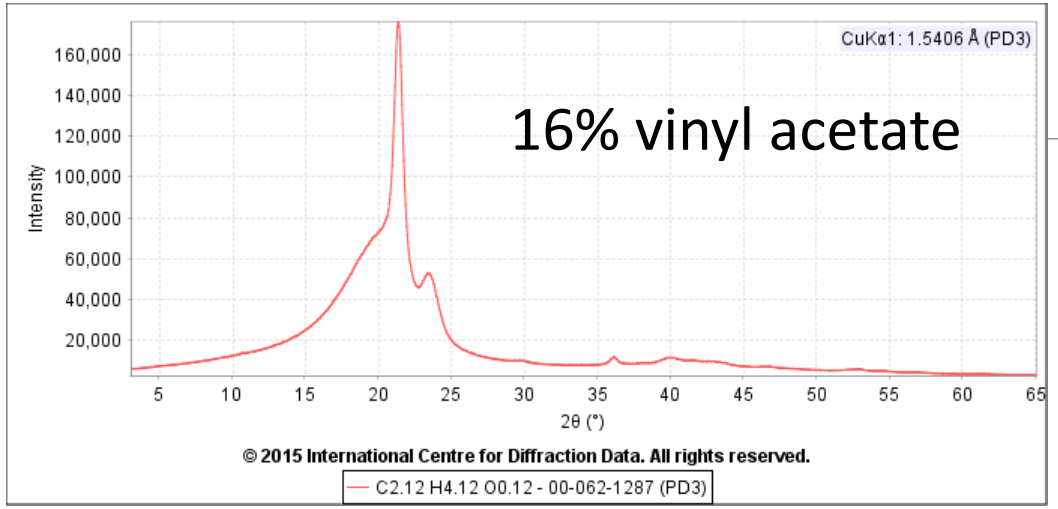


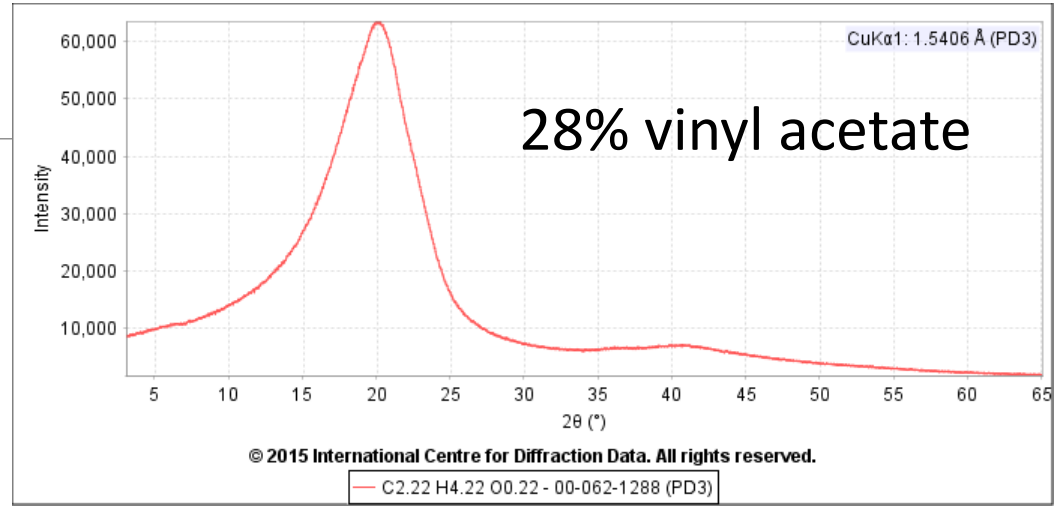


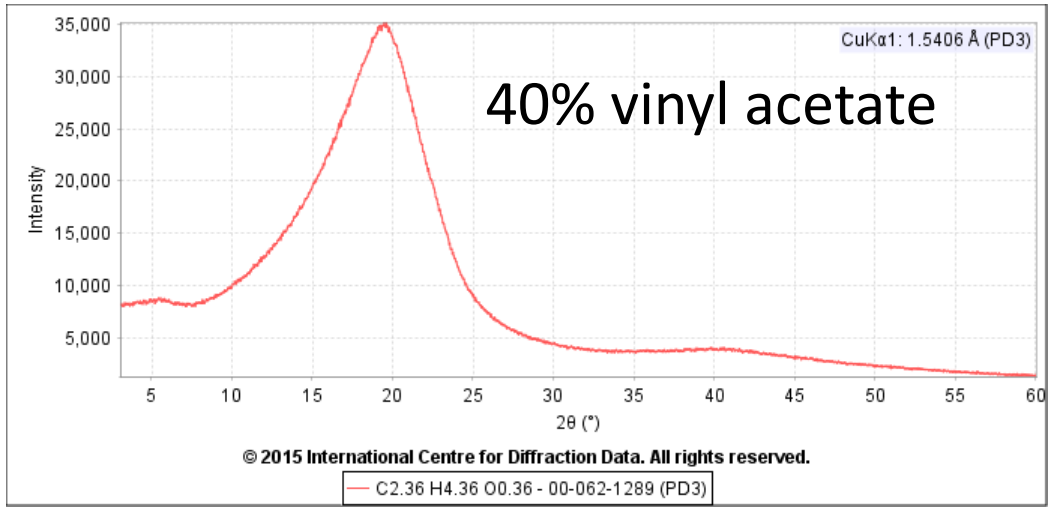


Kaduk and Blanton, Powd. Diffr., 28(3), 2013. pp194-199.

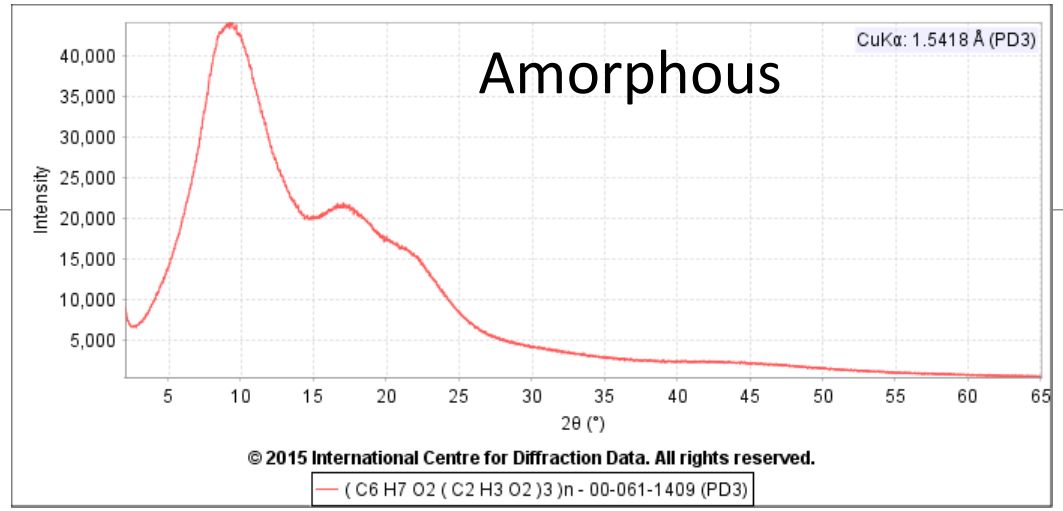
Ethylene vinyl acetate

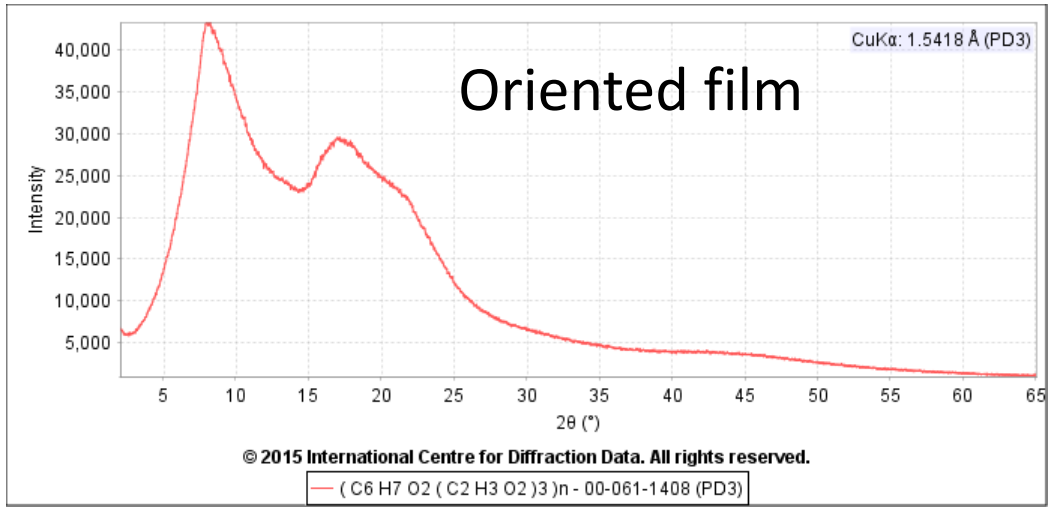


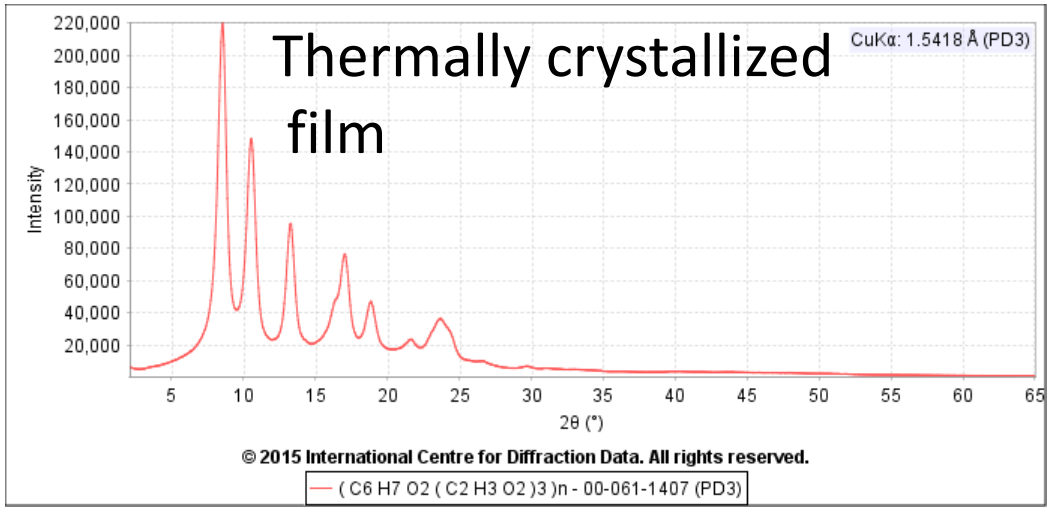




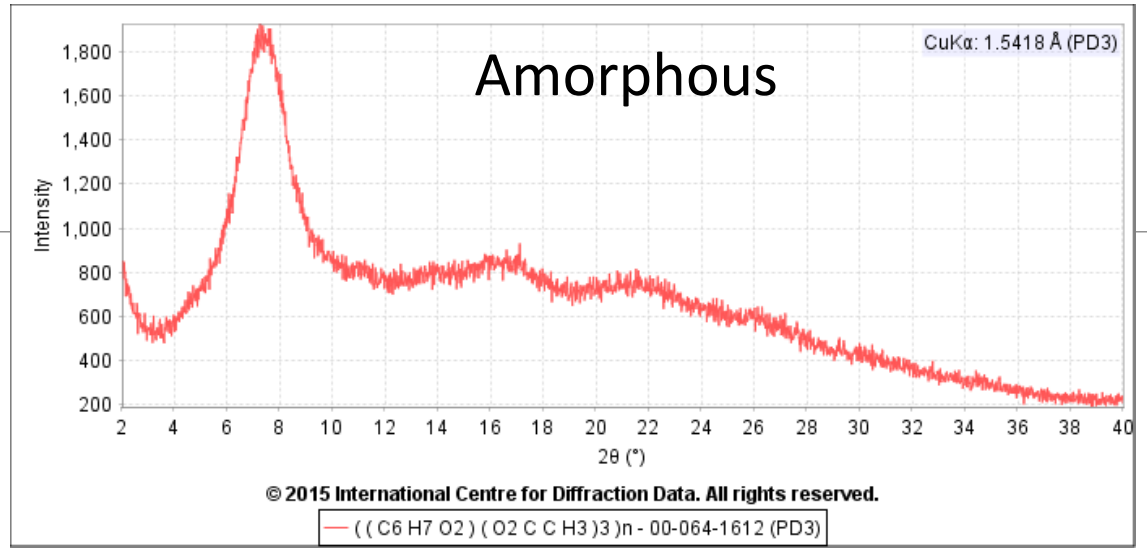
Cellulose triacetate II

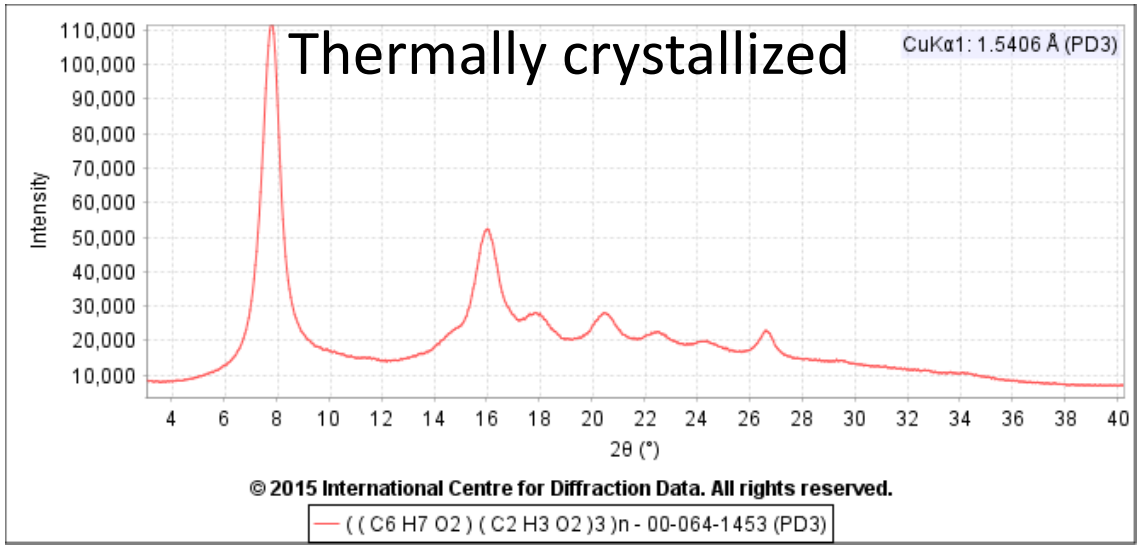






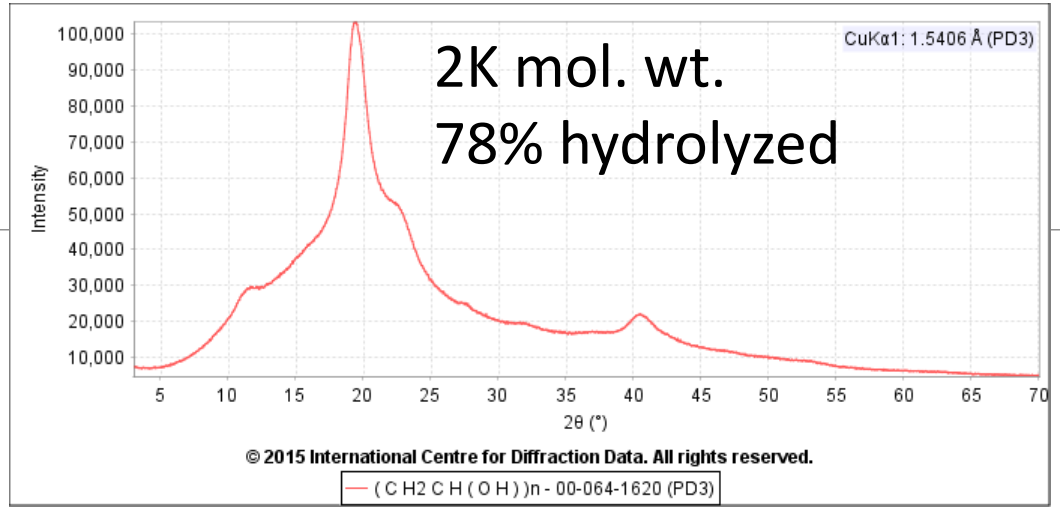
Cellulose triacetate I

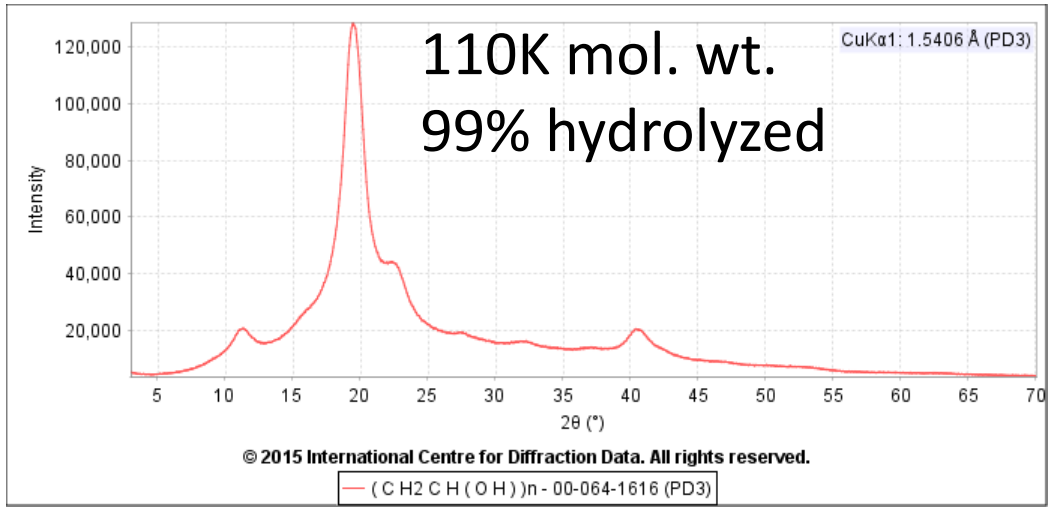


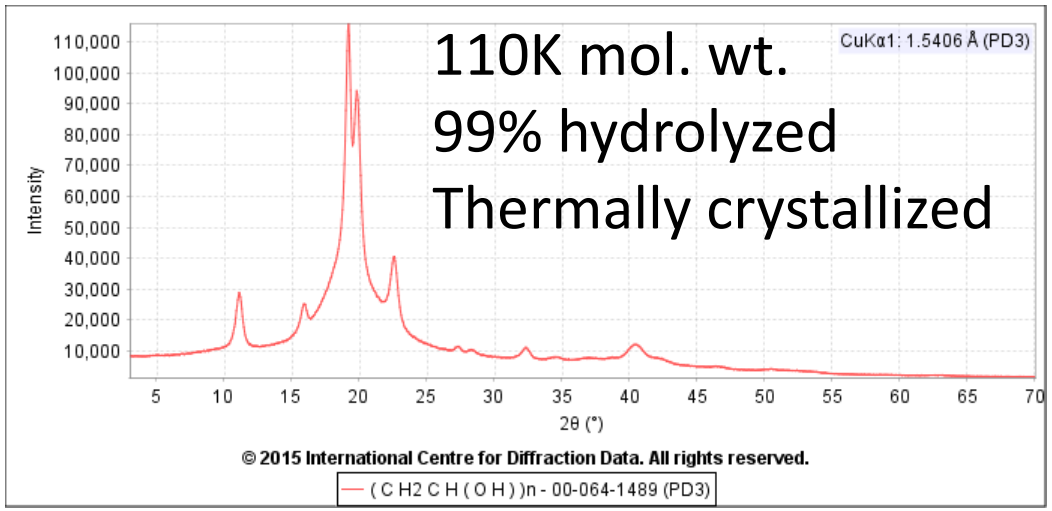


Kaduk, Gates, Blanton
PDF Entry 00-064-1453, 2014.

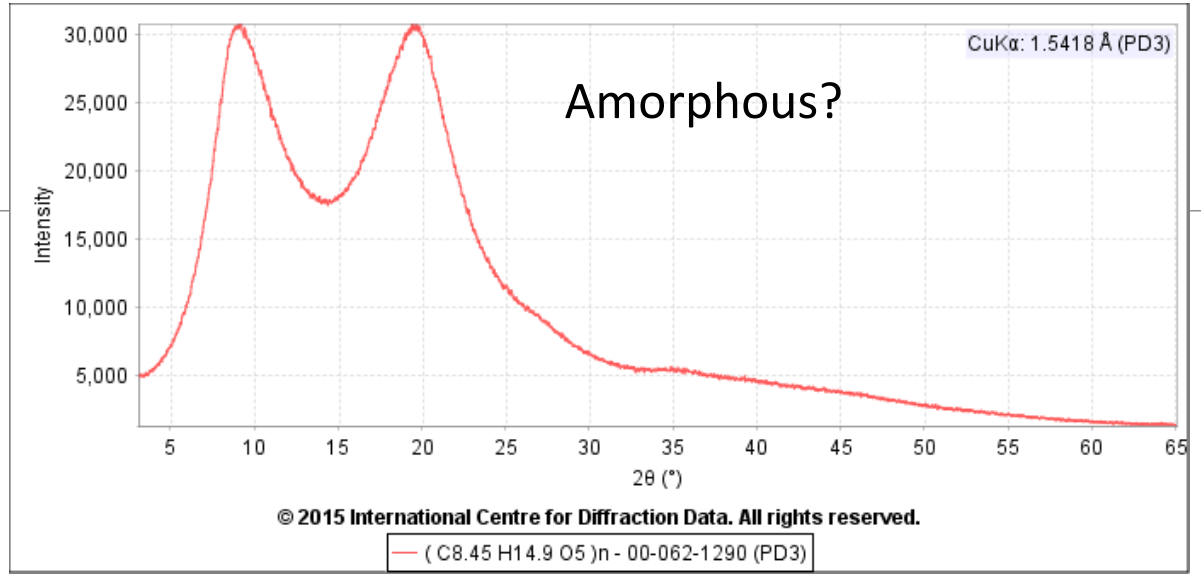
Polyvinyl alcohol

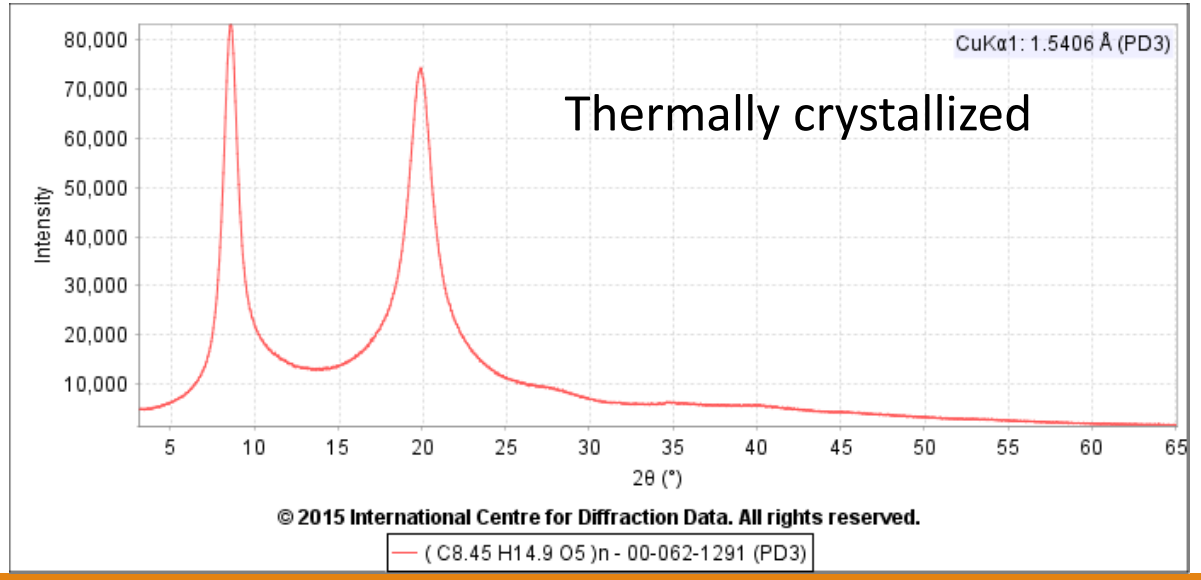






Methyl cellulose



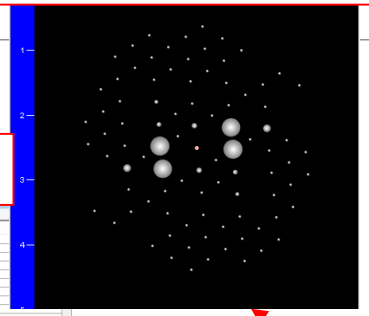


Summary

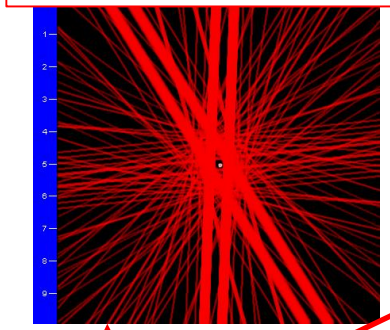
- Raw data diffraction patterns generated from analysis of polymer samples are being added to ICDD PDF-4 databases
- Important considerations:
  - Polymer chemistry
  - Polymer processing
  - Sample orientation in diffractometer - reflection vs. transmission
  - Sample type (powder, film, fiber)
- Use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

2015 PDF Data Entry

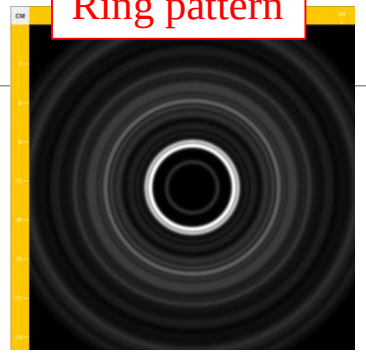
Electron diffraction pattern



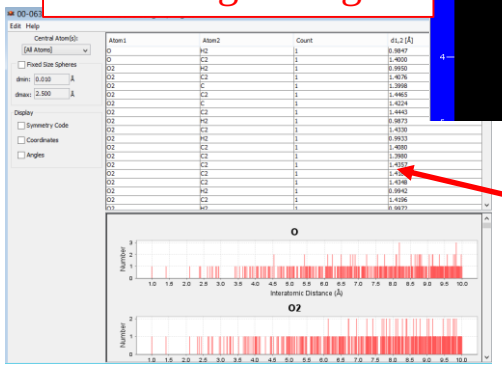
Electron backscatter pattern

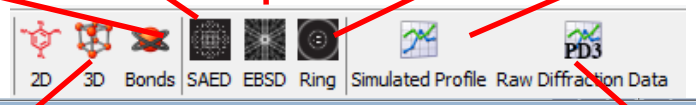


Ring pattern

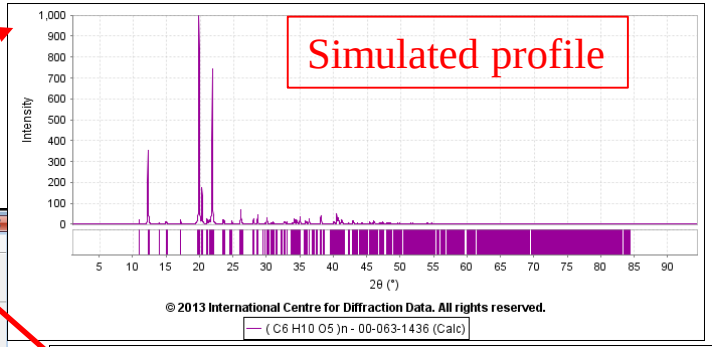


Bond lengths/angles

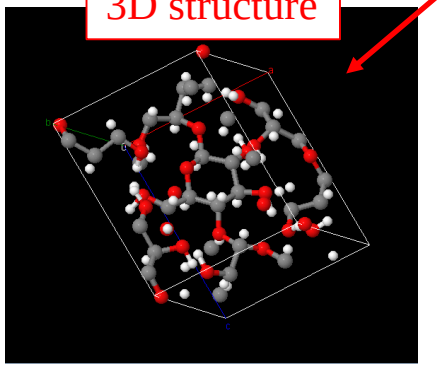


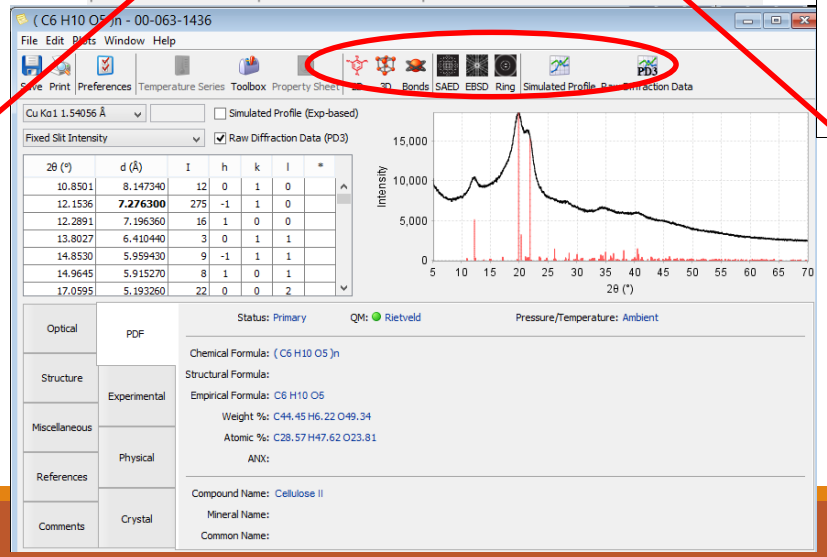


Simulated profile

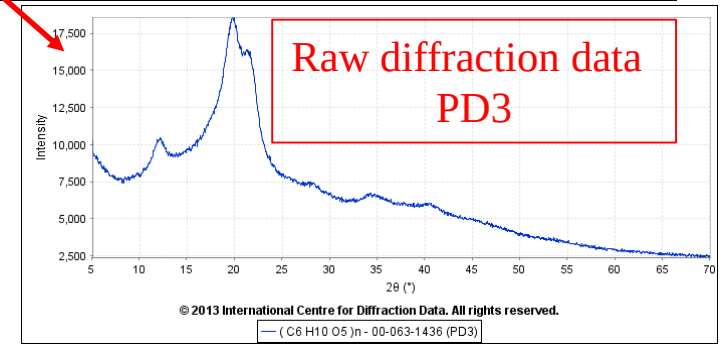


3D structure





Raw diffraction data PD3



ICDD
International Centre for Diffraction Data