X-ray diffraction in polymer science

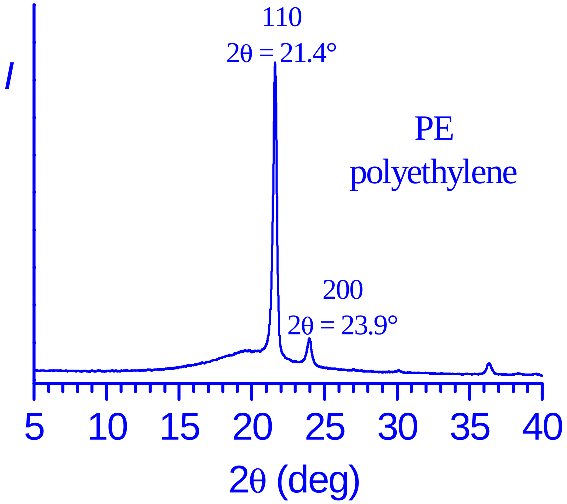
- 1) Identification of semicrystalline polymers and Recognition of crystalline phases (polymorphism) of polymers
- 2)Polymers are never 100% crystalline. XRD is a primary technique to determine the degree of crystallinity in polymers.
- 3) Microstructure: Crystallite size in polymers is usually on the nano-scale in the thickness direction. The size of crystallites can be determined using variants of the Scherrer equation.
- 4) Orientation: Polymers, due to their long chain structure, are highly susceptible to orientation. XRD is a primary tool for the determination of crystalline orientation through the Hermans orientation function.

1) Identification of semicrystalline polymers

Positions and Intensities of the peaks are used for identifying the material.

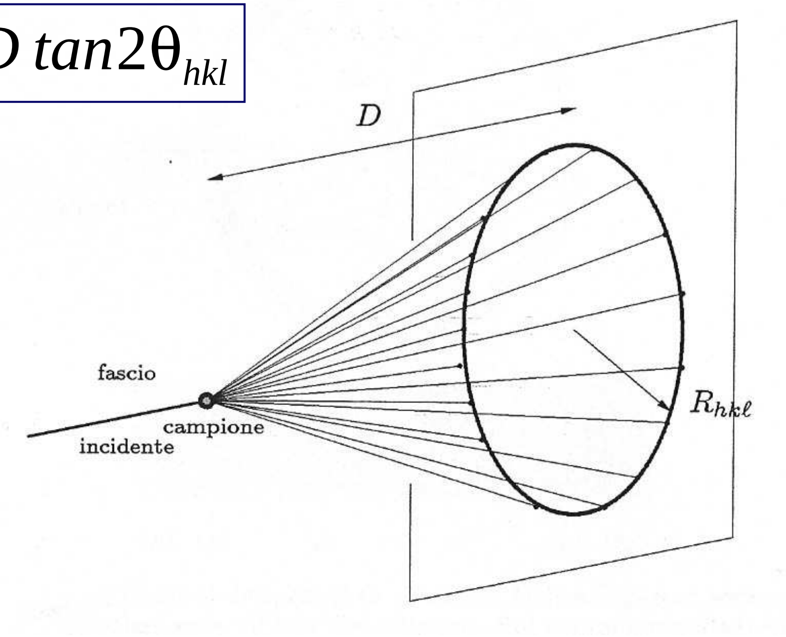
The diffraction of unoriented samples in reflection →

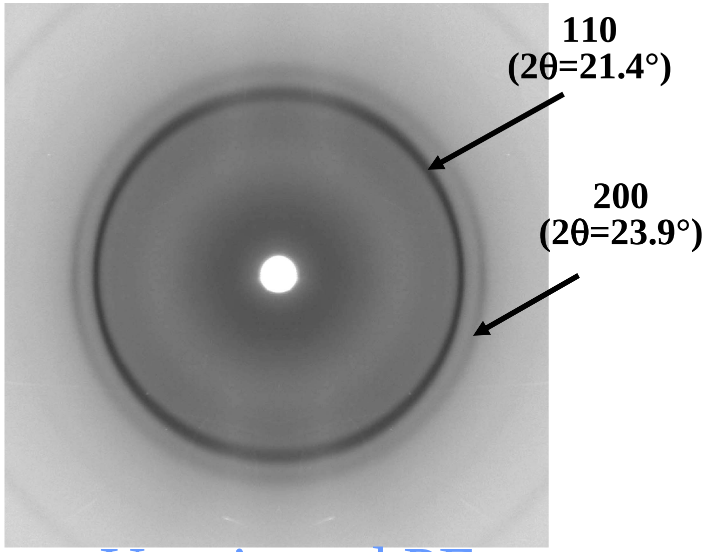
Unoriented PE



The diffraction of unoriented samples in transmission by using a flat film is characterized by concentric circles called “Debye Scherrer Rings”

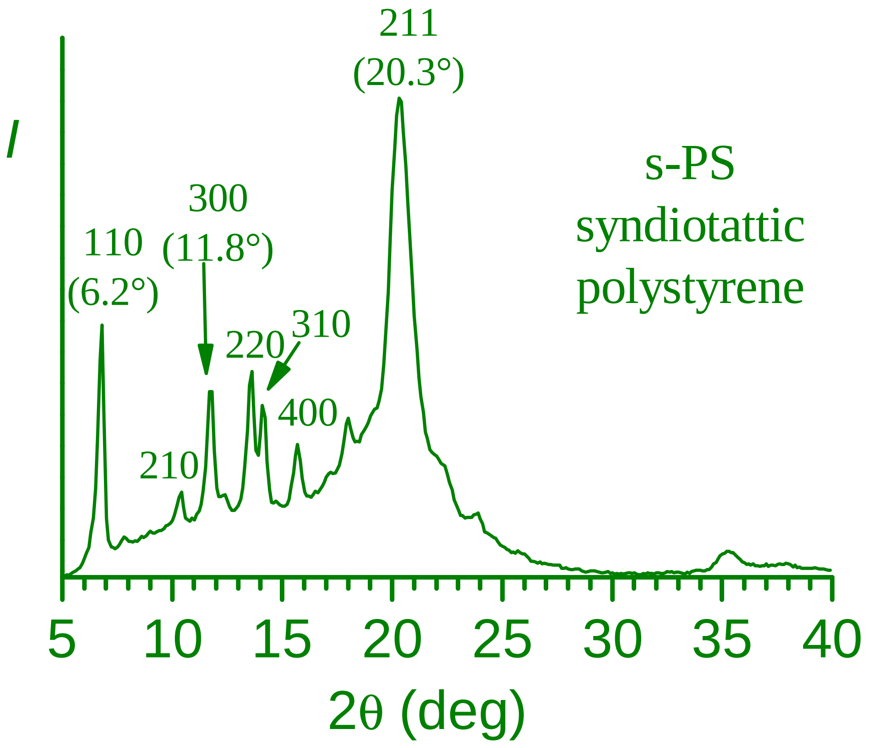
$$\boxed{R_{hkl} = D\,tan2\theta_{hkl}}$$

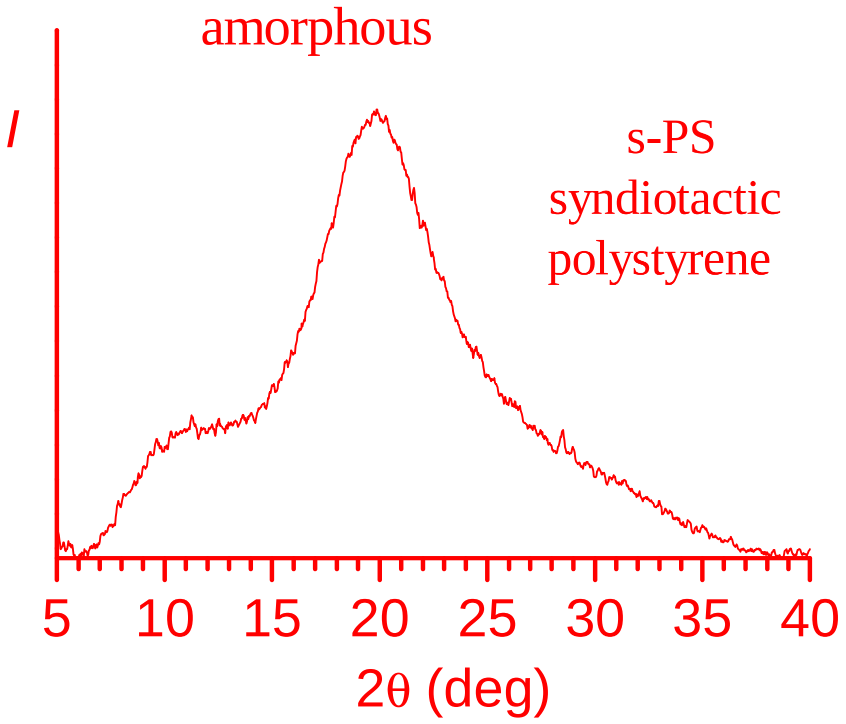




Unoriented PE

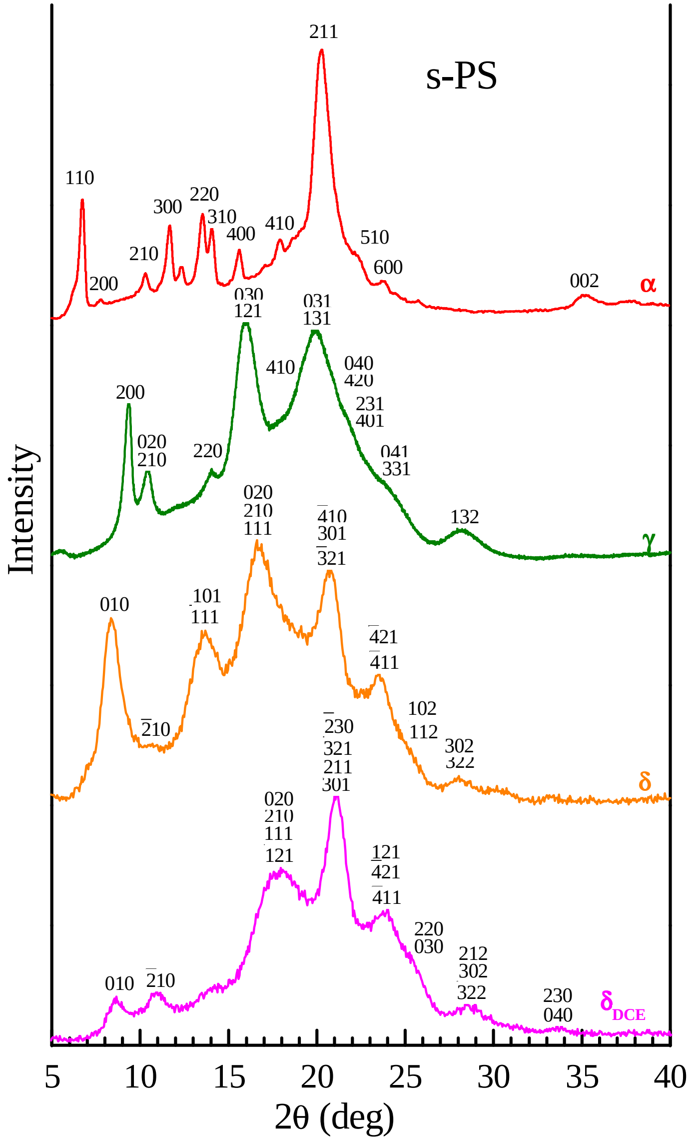
X ray diffraction of semicrystalline and amorphous polymer



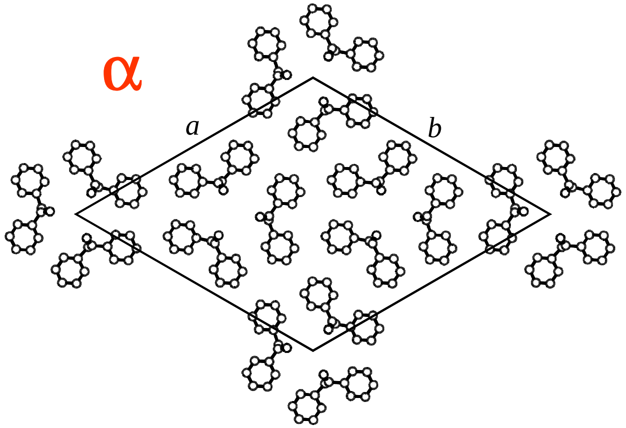


1) Identification of crystalline phases of polymers

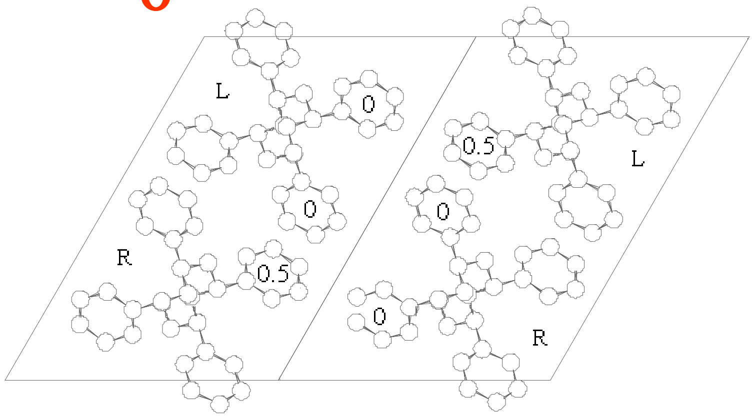
Position and Relative intensities are the fingerprint of crystalline phases of polymer



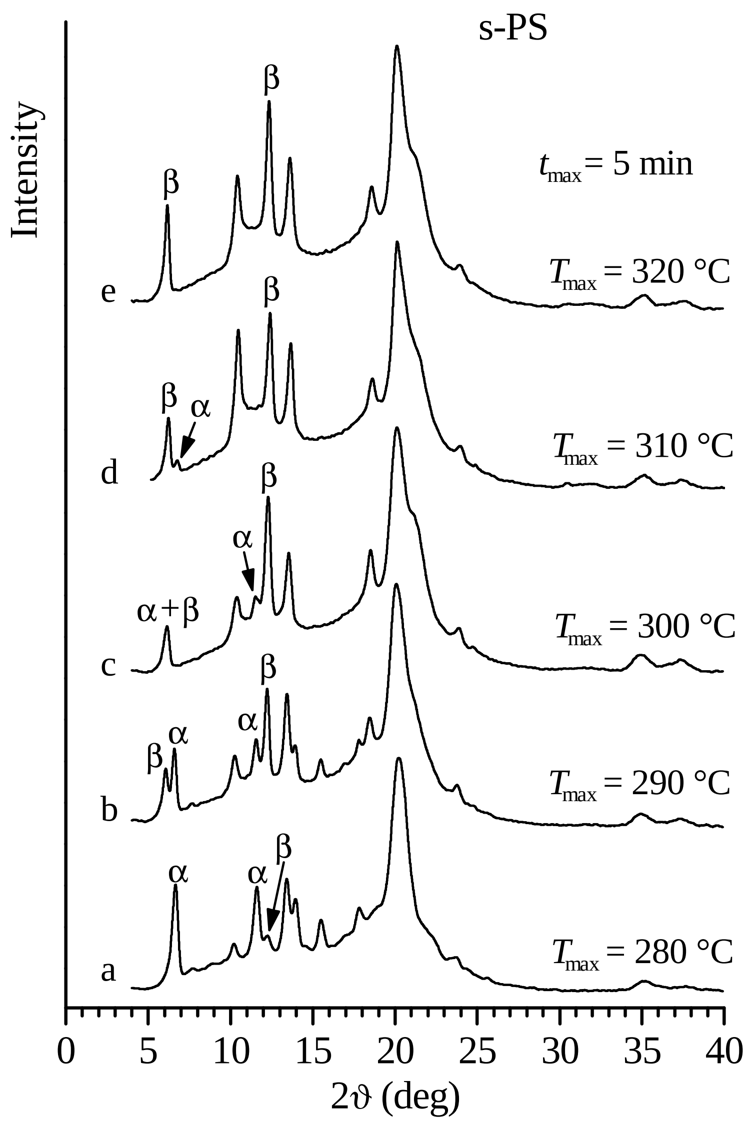
α

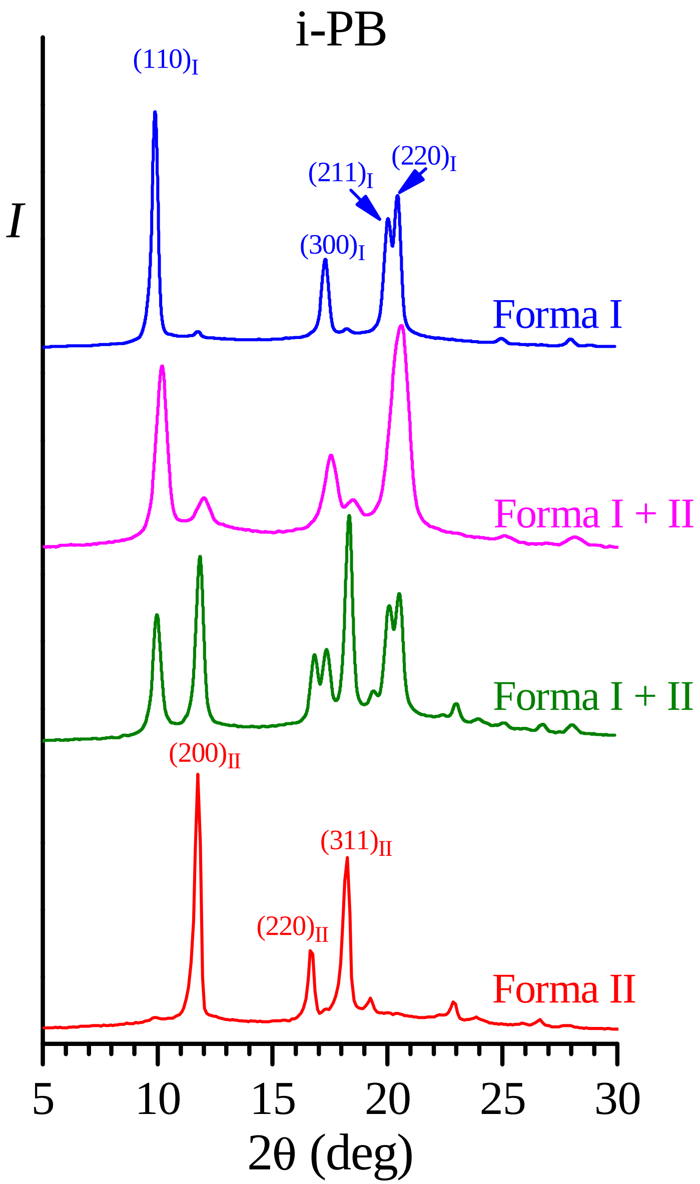


δ



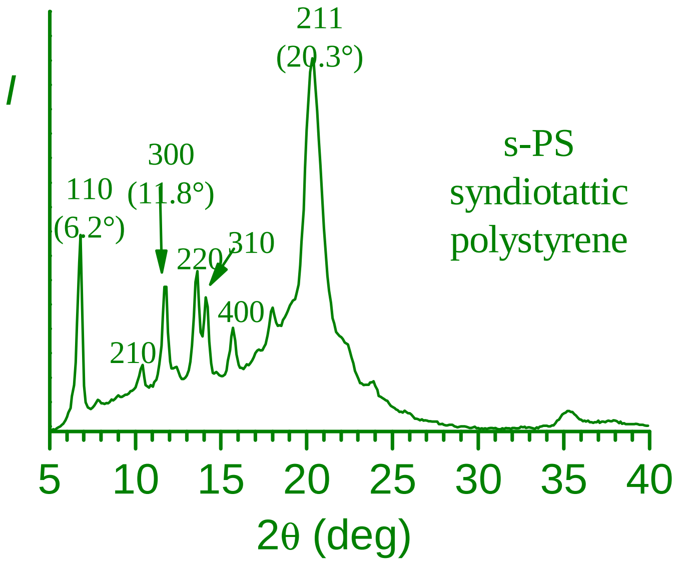
Identification of crystalline phases of polymers also if they are present in mixture.



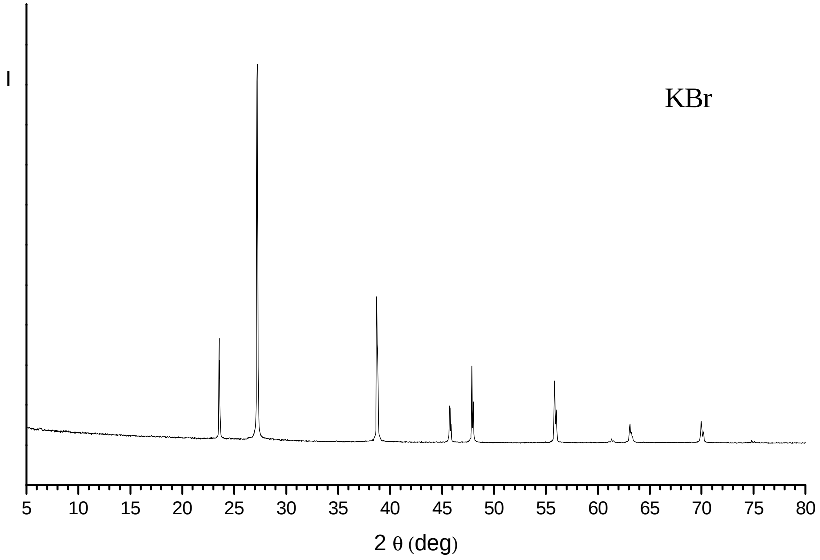


X ray diffraction of semicrystalline polymer and inorganic compound

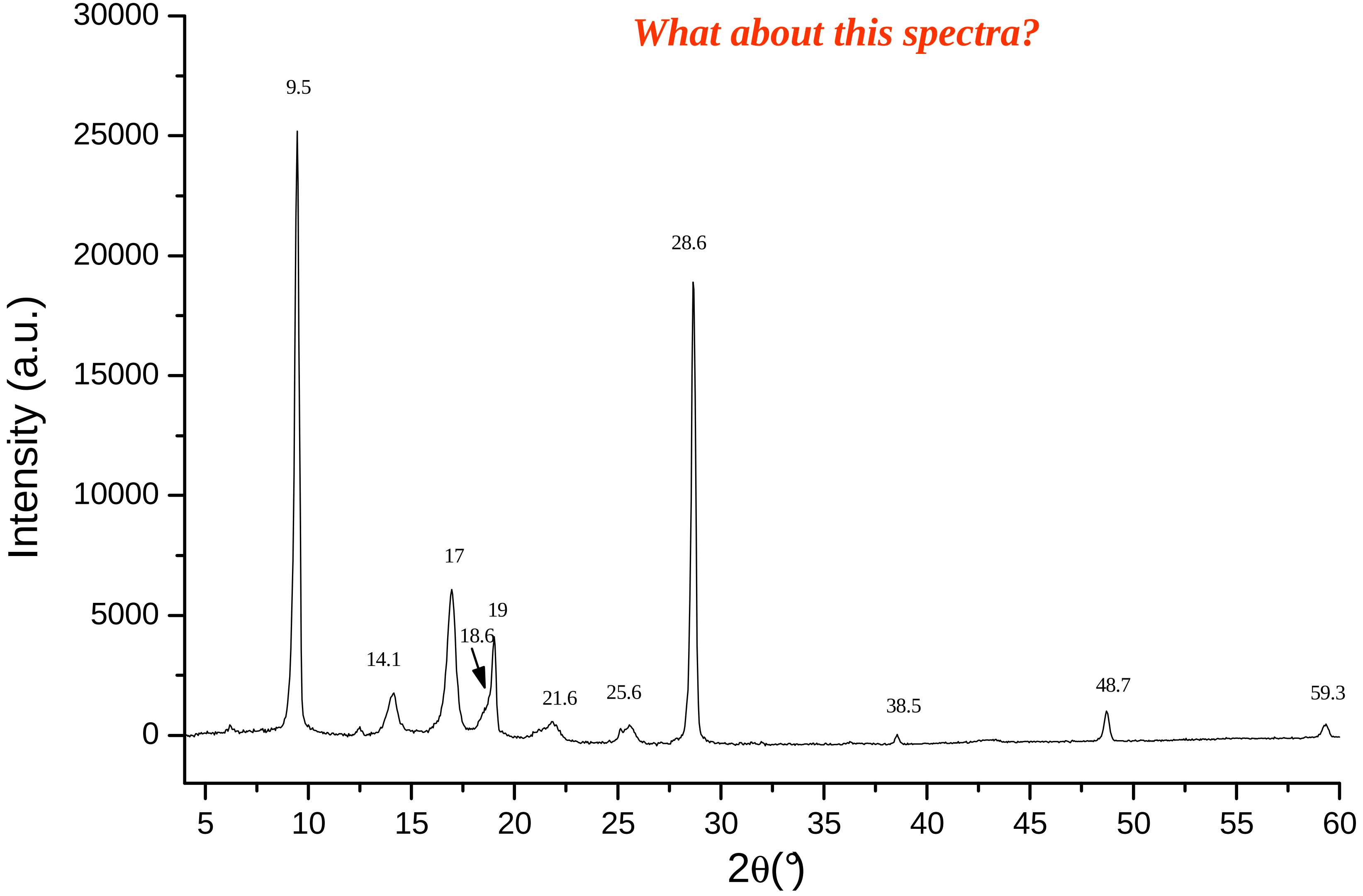
Polymer



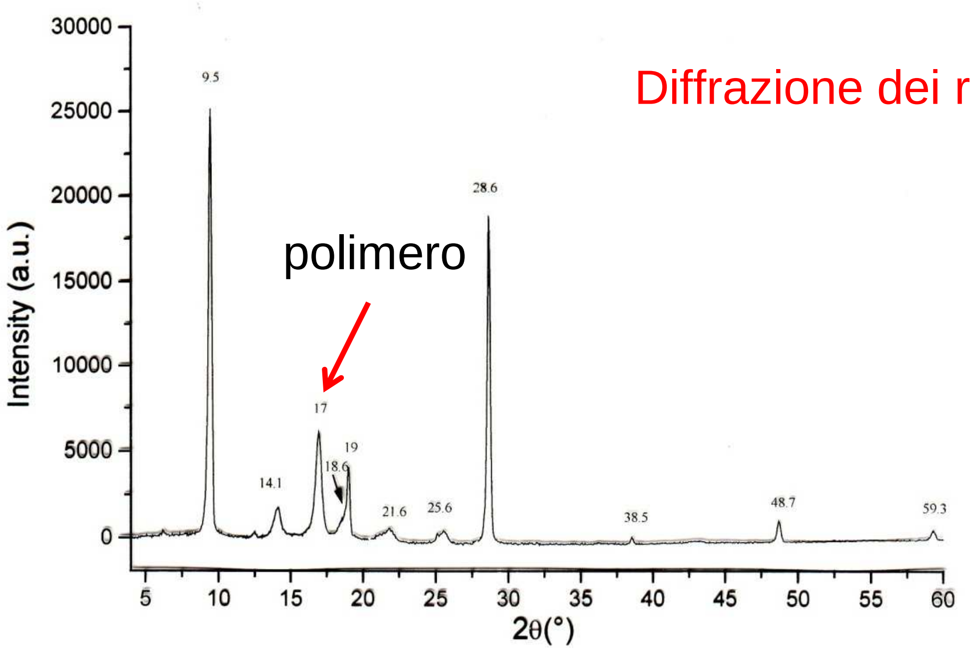
inorganic compound



What about this spectra?

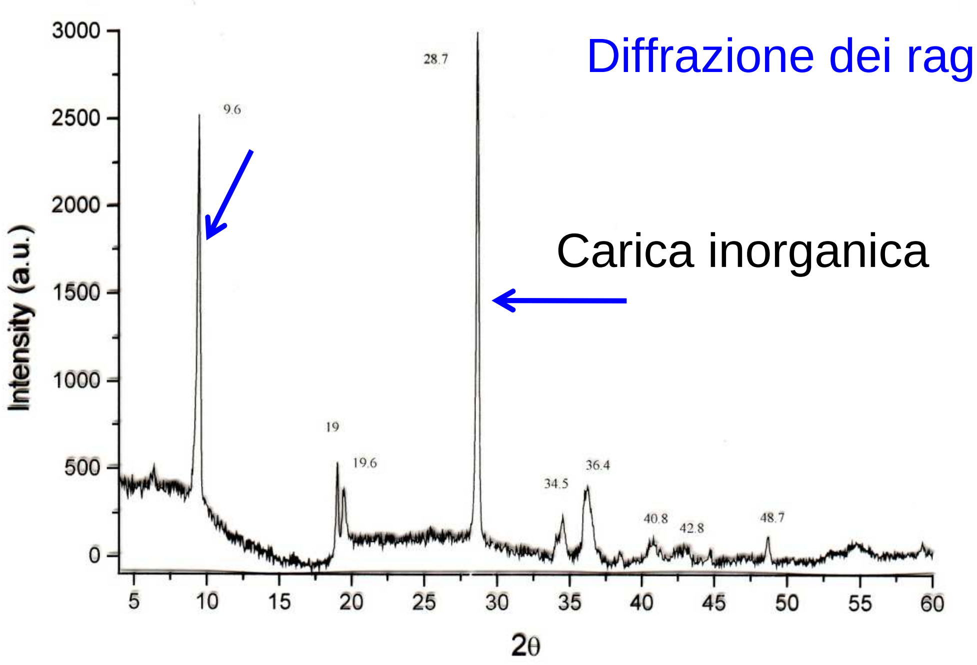


Diffrazione dei raggi X del campione prima TGA



polimero

Diffrazione dei raggi X del campione dopo TGA



Carica inorganica

The peak positions, intensities, widths and shapes provide important information about the structure of the material

- amorphous / crystalline
- (polymer, inorganic/organic compound)
- crystalline phases

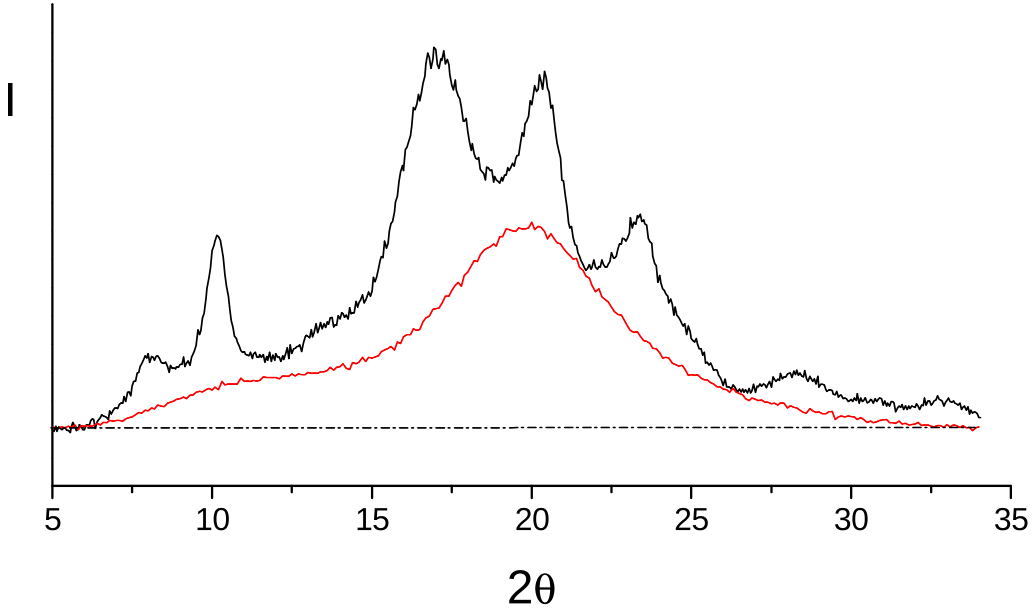
2)XRD a primary technique to determine the **degree of crystallinity** in polymers.

The determination of the degree of crystallinity implies use of a two-phase model, i.e. the sample is composed of crystals and amorphous and no regions of semi-crystalline organization.

$$\boxed{I = I_{\text{crystalline}} + I_{\text{amorphous}}}$$

degree of crystallinity : X_c

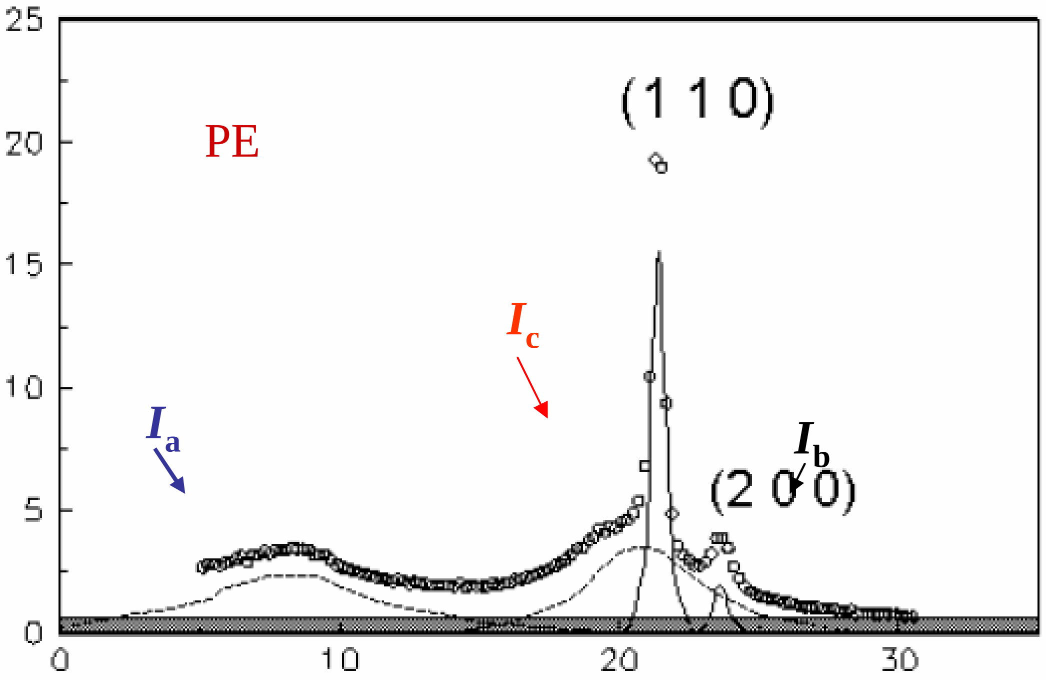
$$\boxed{X_c = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}}}$$



2) XRD : determination of **degree of crystallinity** in polymers.

The diffraction profile is divided in 2 parts: peaks are related to diffraction of crystallites, broad alone is related to scattering of amorphous phase.

The assumption is that the areas are proportional to the scattering intensities of crystalline and amorphous phases



I_a = diffracted intensity of amorphous phase

I_b = diffracted intensity of *background*

I_c = diffracted intensity of crystalline phase

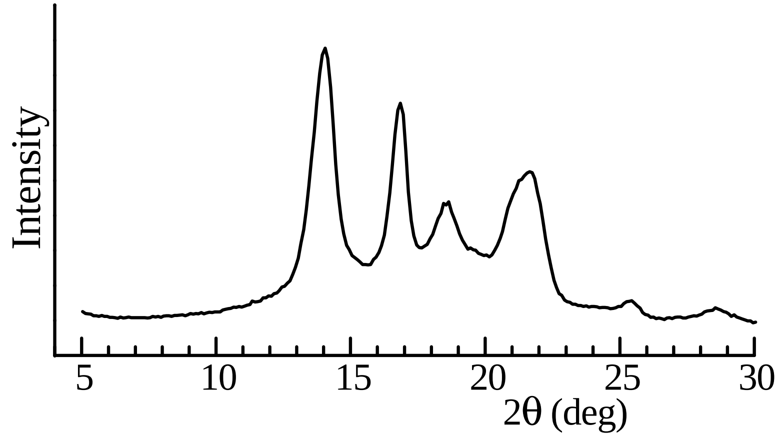
$$x_c = \frac{A_{cr}}{A_{cr} + KA_{am}}$$

K is a constant related to the different scattering factors of crystalline and amorphous phases. For relative measures $K = 1$.

3) Microstructure: Crystallite size in polymers

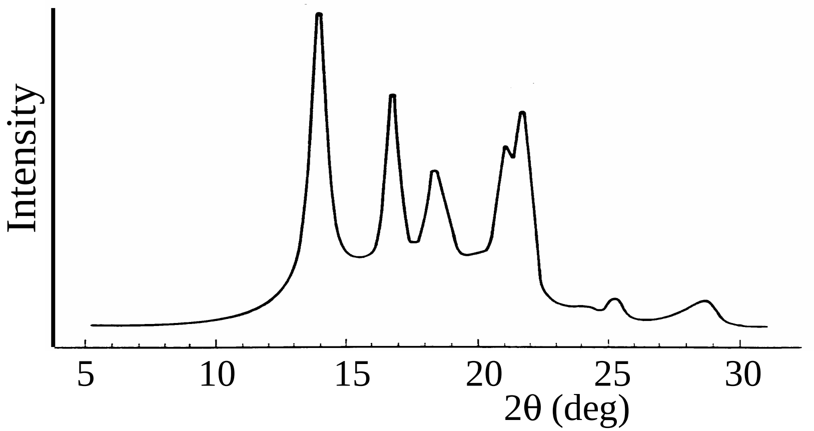
The half-width of peaks is related to crystallite dimensions.

Half-width large correspond to smaller crystallites

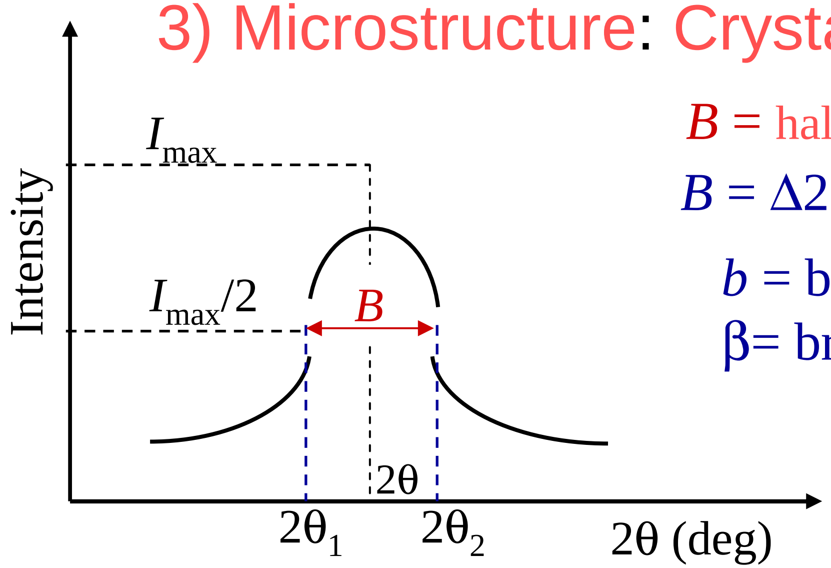


Contribution to broadening can be due to lattice distortion, structural disorder as well as instrumental effects.

Half-width narrow correspond to bigger crystallites



3) Microstructure: Crystallite size in polymers



B = half-width of peaks

$B = \Delta 2\theta = 2\theta_2 - 2\theta_1$ $\qquad \beta = B - b$

b = broadening instrumental

β= broadening due to crystallites dimensions

b can be measured by the half-width of a peak of crystalline compounds low molecular weight.

Crystallite size in polymers :

$$L_{hkl} = \frac{K\lambda}{\beta \cdot \cos\theta}$$ Scherrer's Equation

L_{hkl} = crystallite dimensions (in Å) along the direction perpendicular to the crystallographic plane *hkl*.

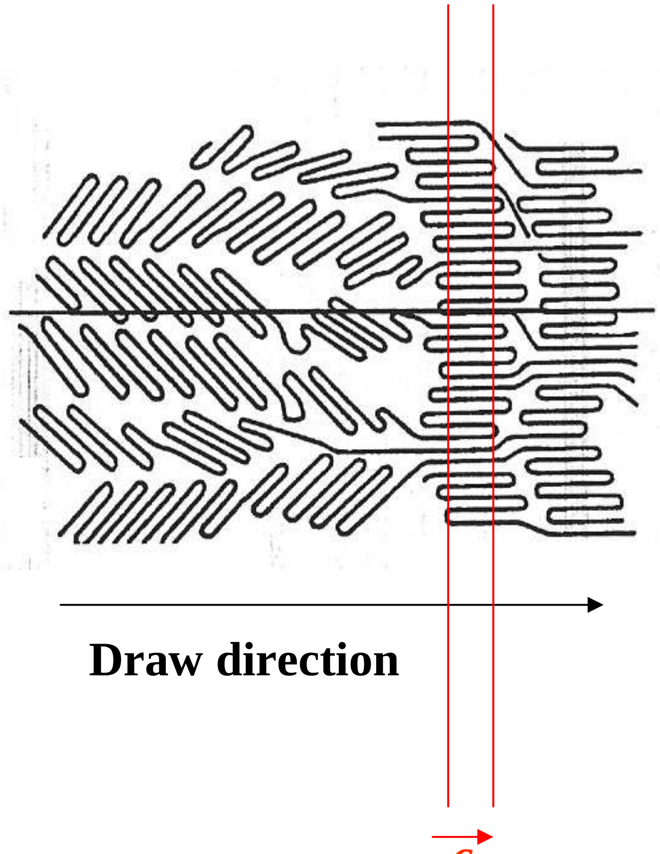
β = half-width of peak related to the crystallographic plane *hkl* (rad).

K = constant (usually $K = 0.89$)

θ = diffraction angle of the *hkl reflection*.

λ = wavelength used ($\lambda_{Cuk\alpha} = 1.5418$ Å.)

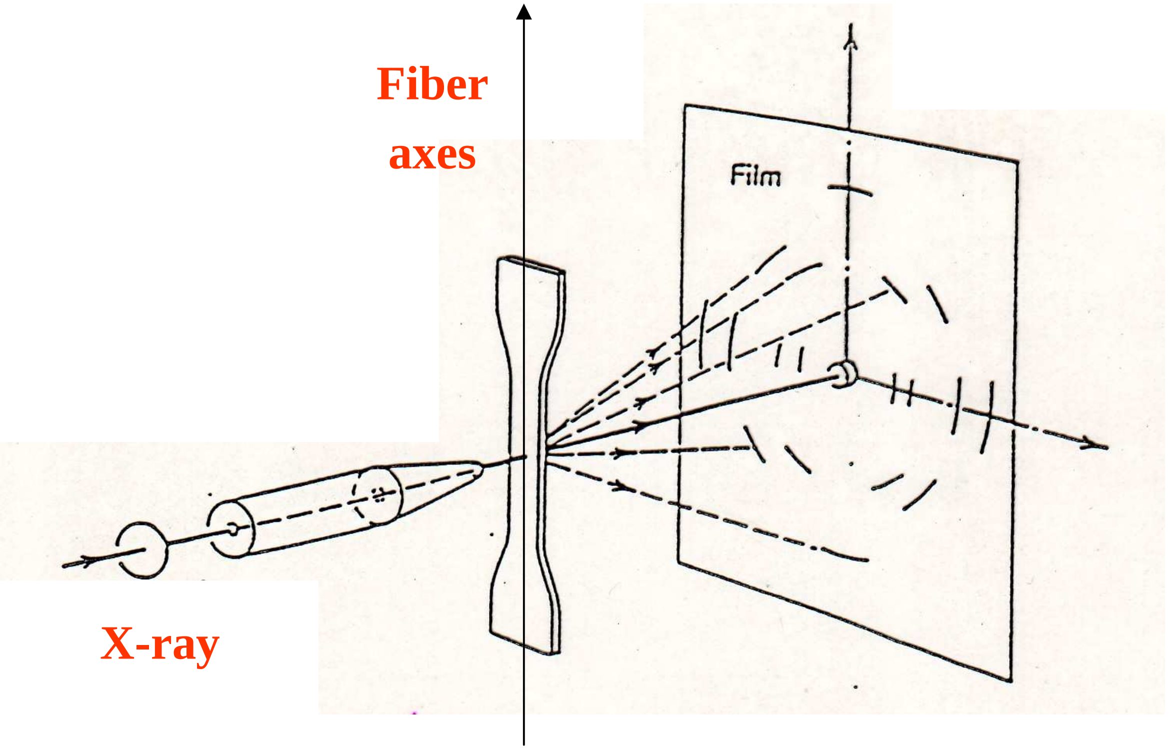
4)Orientation: Polymers, due to their long chain structure,are highly susceptible to orientation



Draw direction

c

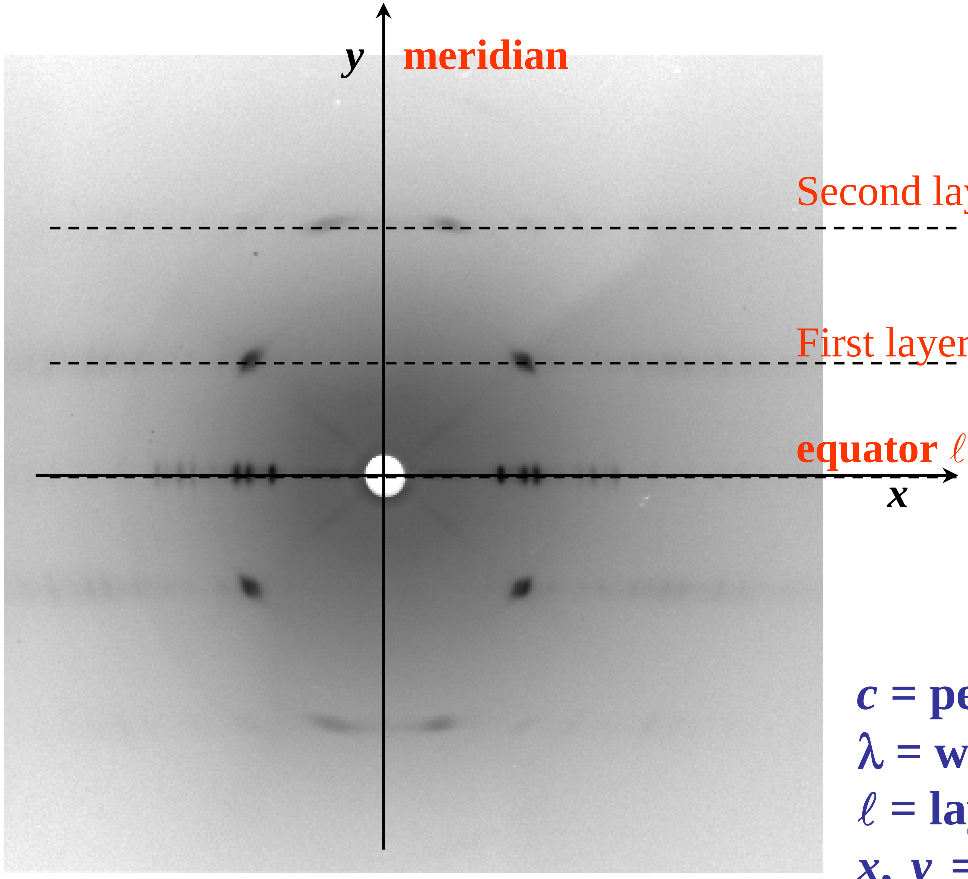
fiber



Fiber axes

X-ray

X-ray diffraction of oriented polymer: fiber pattern



i-PP fiber

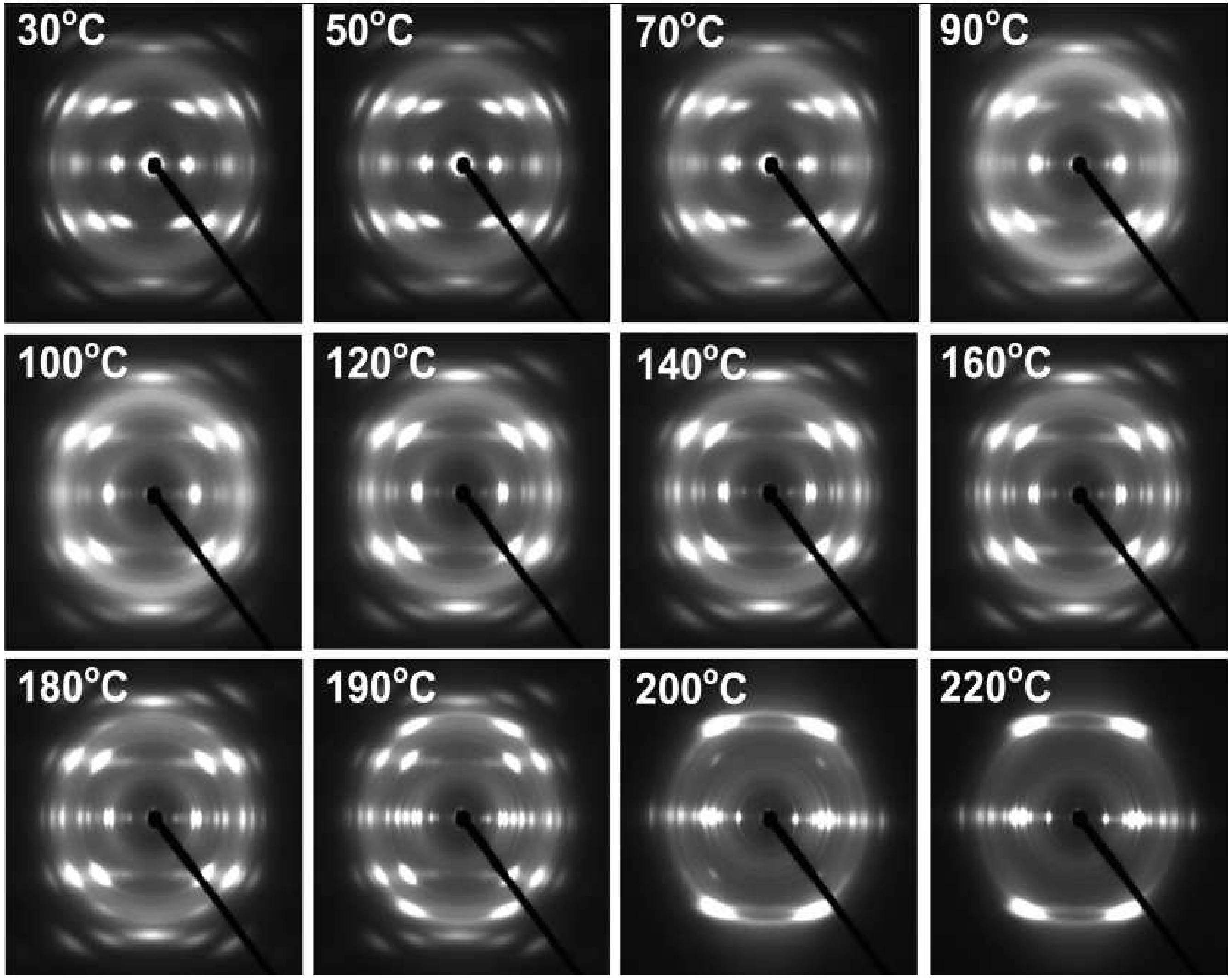
$$\cos 2\theta = \cos\left(\frac{360x}{2\pi R}\right)\cos\left(\tan^{-1}\frac{y}{R}\right)$$

$$c = \frac{\ell\lambda}{sen(\tan^{-1}(y/R))}$$

c **= periodicity along the chain axes**
λ = wavelength used (CuK$_\alpha$ = 1.5418 Å)
ℓ = layer
x**,** ***y*** **= distance of reflections from the center along equatorial and meridian lines**
R **= chamber radius**

X-ray diffraction of fibers annealed at different T

Distance from layers correspond to *c* axes



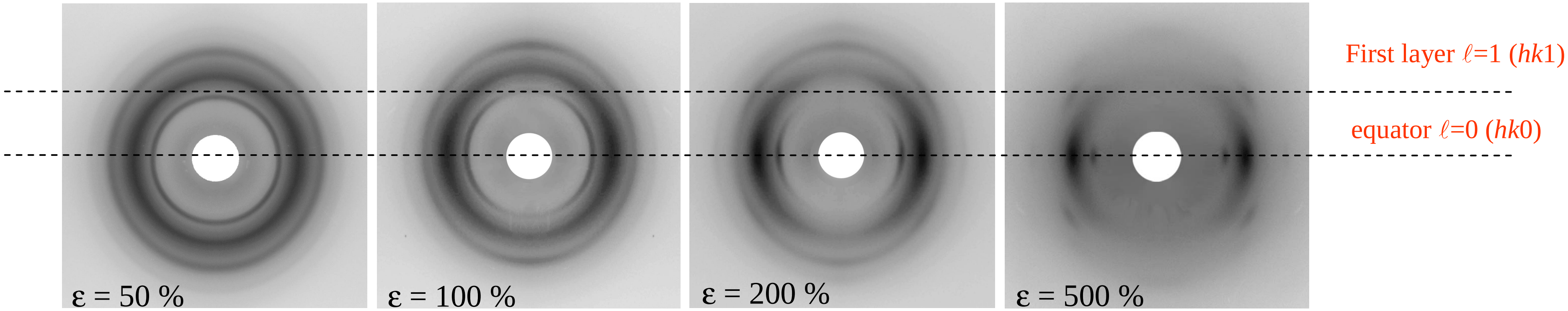
Helical conformation

$c=7.8$ Å

Trans-planar conformation

$c=5.1$Å

Oriented sPP fiber stretched at different ε



$$\varepsilon=100(L\mathrm{f}-L\mathrm{i})/L\mathrm{i}$$

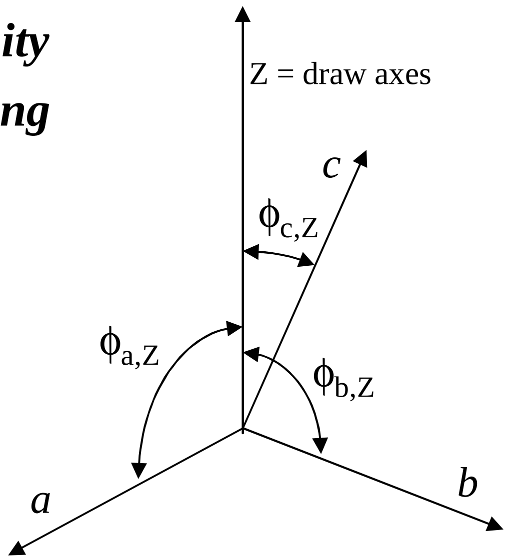
Lf = final length

Li = initial length

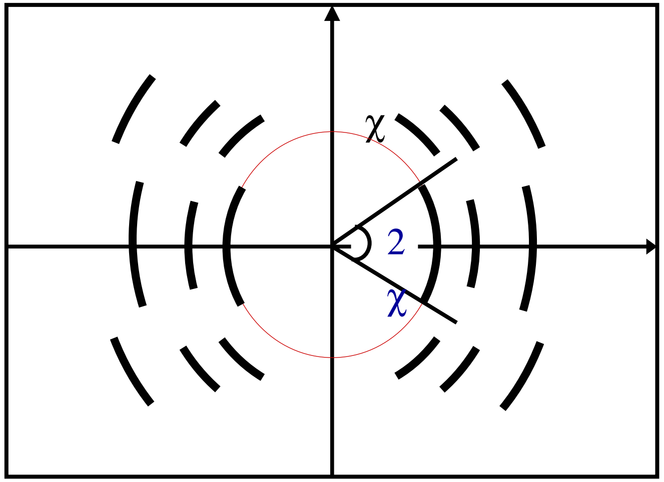
The degree of orientation can be determined from the intensity distribution of the corresponding diffraction on the Debye ring by using the Hermans' Orientation Function

$$\boxed{f_\phi = \frac{1}{2}\left(3\left\langle \cos^2\phi \right\rangle - 1\right)}$$

Average cosine squared value of ϕ angle



Azimutal scan: measuring the intensity at 2θ constant, by varying the χ angle.



	Orientation with respect to draw direction		
parameter	parallel	random	perpendicular
$<\cos^2\phi>$	1	1/3	0
f	1	0	-1/2

If the radiation is perpendicular to the fiber axes

$$\cos^2\phi_{hkl} = \cos^2\chi_{hkl}$$

$$<\cos^2\chi_{hkl}> = \frac{\int_0^{\pi/2} I(\chi)\, sen\chi\, \cos^2\chi\, d\chi}{\int_0^{\pi/2} I(\chi)\, sen\chi\, d\chi}$$

If $\chi = 0$ for meridian reflection (00ℓ)

$<\cos^2\phi_{00\ell}> = 1$ e $f_c = \mathbf{1}$

The fiber is perfected oriented: $f_c = 1$

Types of Orientation in polymers

	Types of ORIENTATION		GEOMETRY	
	(Heffelfinger & Burton)[1]	PREFERRED ORIENTATION	Crystallographic elements	Reference elements
1	Random	-	-	-
2	Axial	Crystallographic Axes parallel to reference axes	*c*	draw axes
3	Planar	Crystallographic Axes on a reference plane	*c*	film plane
4	Planar-axial	Crystallographic plane Parallel to a reference axes	(100)	draw axes
5	Uniplanar	Crystallographic plane Parallel to a a reference plane	(100)	film plane
6	Uniplanar-axial	Crystallographic Axes parallel to reference axes and a Crystallographic plane Parallel to a a reference plane	*c* (100)	draw axes film plane

C. J. Heffelfinger, R. L. Burton *J. Polym. Sci.* 47, 289 (1960).

Uniplanar orientation: sps film

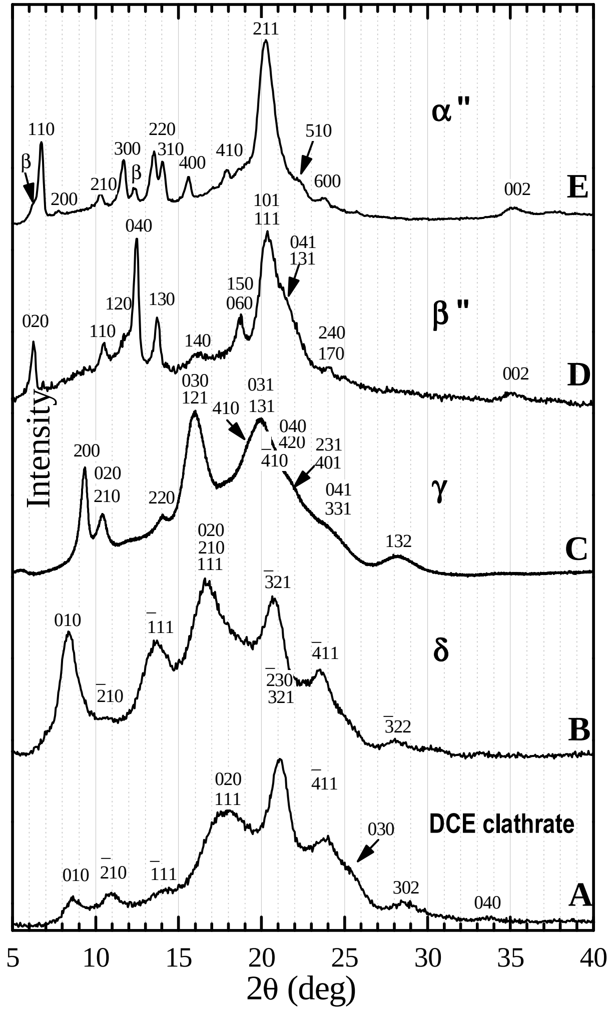


Figure 1

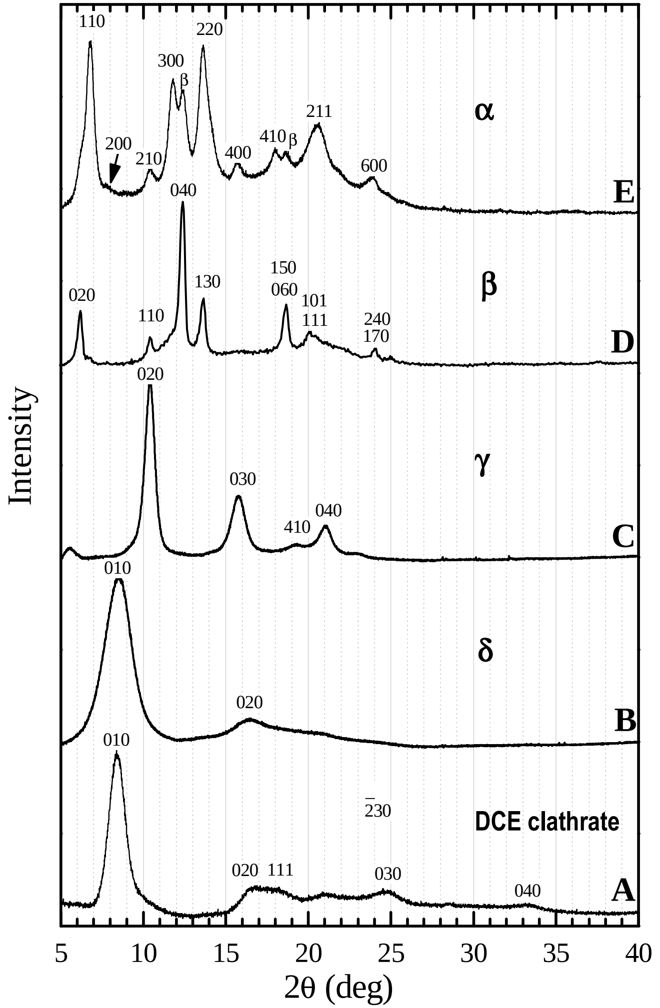
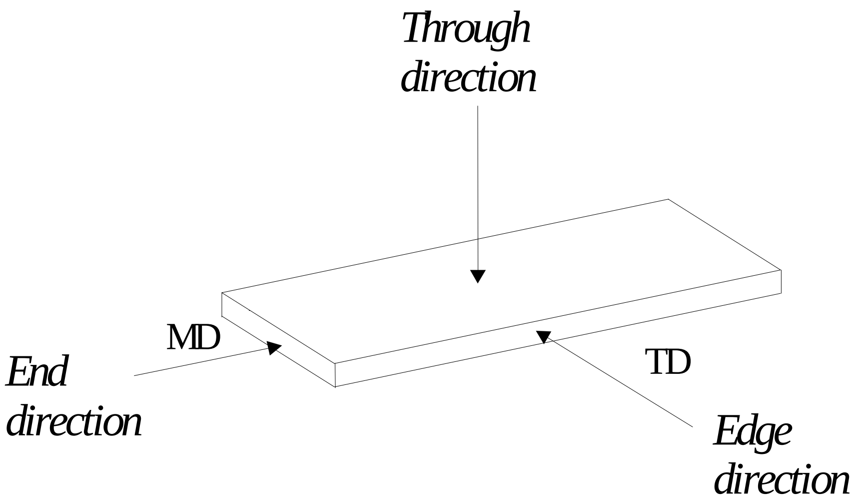
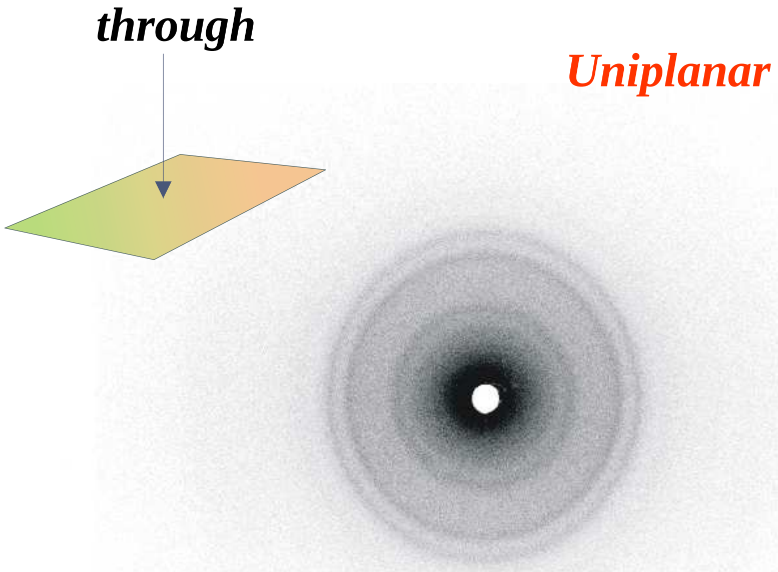


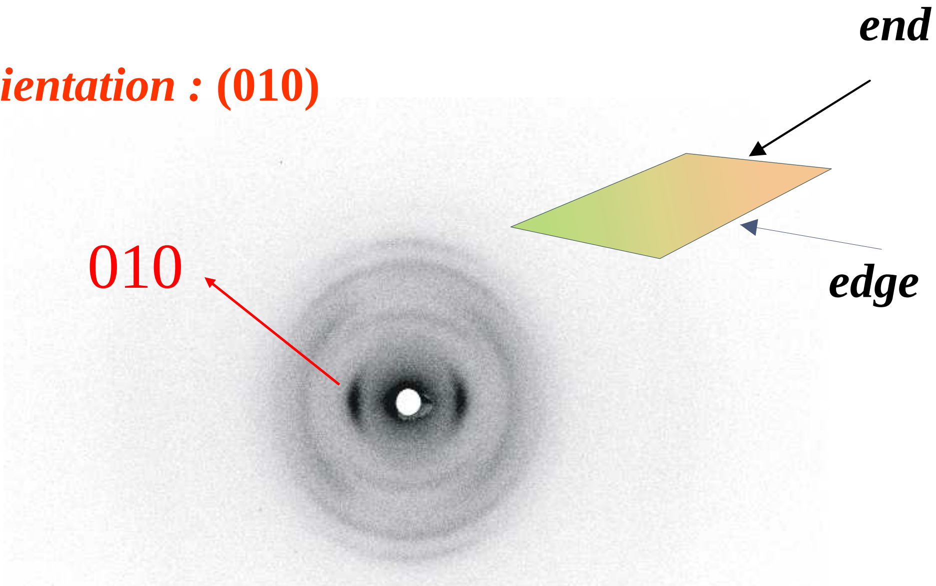
Figure 2

Types of Orientation in polymers



Uniplanar orientation : (010)

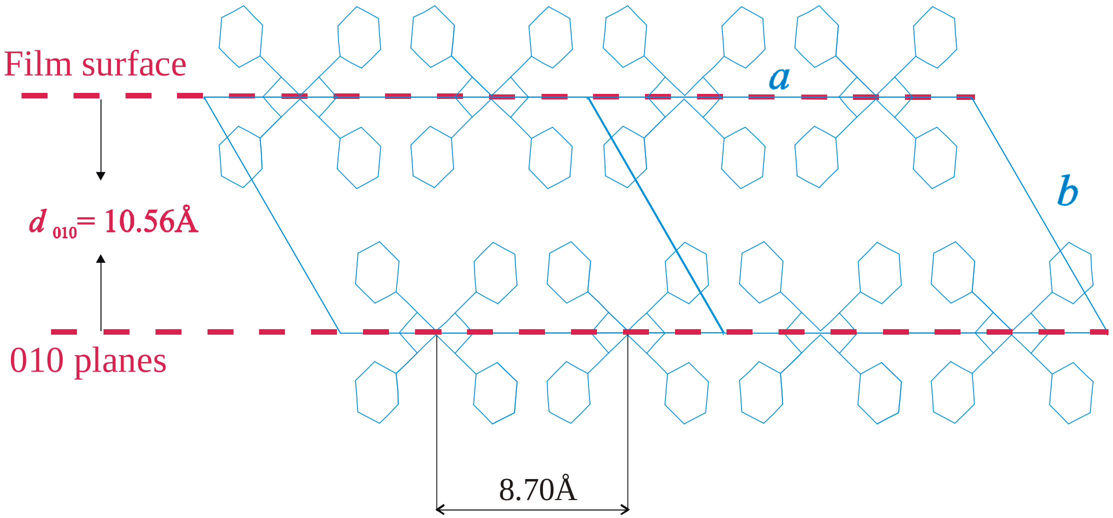




Rizzo, Lamberti, Albunia, Ruiz de Ballesteros, Guerra *Macromol.* 2002, 35, 5854

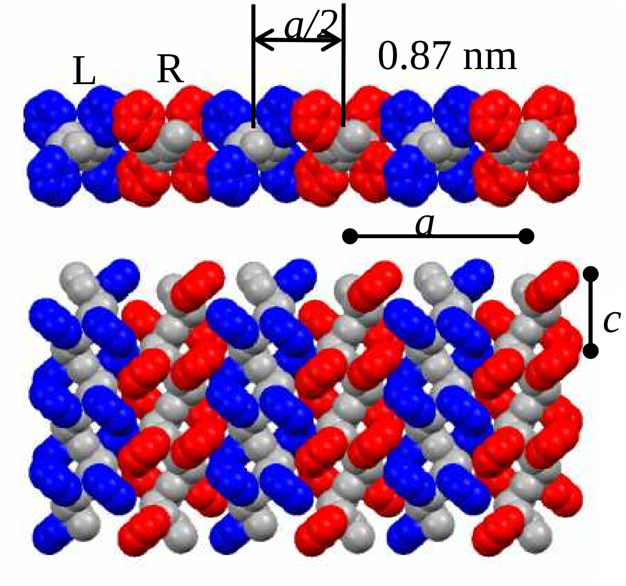
Albunia, Rizzo, Guerra *Chem. Mat.* 2009, 21,3370

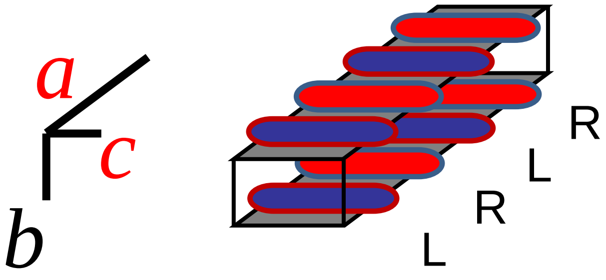
Along the chain projections of packing of δ forms of s-PS showing (010) planes parallel to the film surface

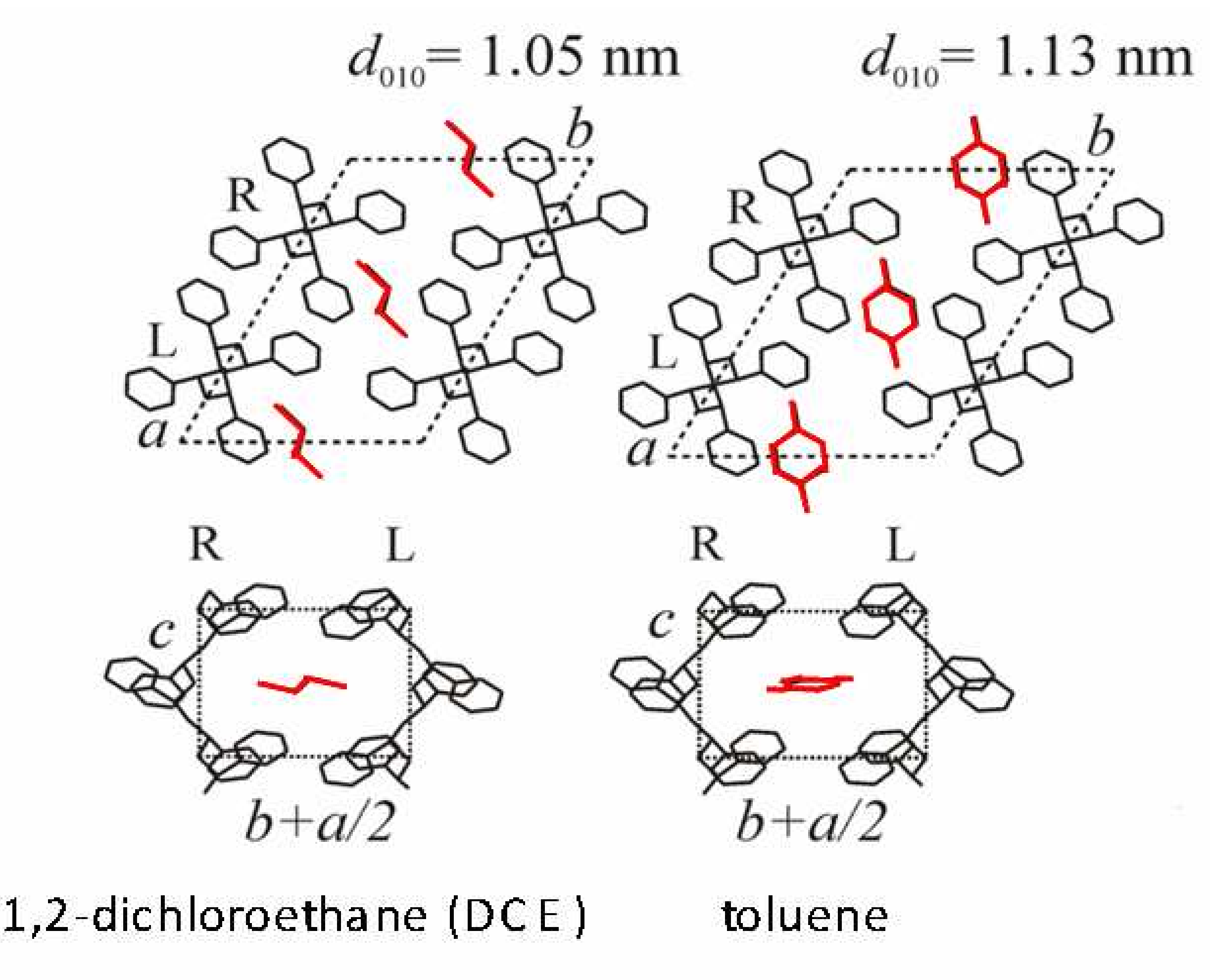


(010) planes correspond to rows of parallel helices with minimum interchain distances (8.70Å) and maximum interplanar distances (10.56Å)

s-PS co-crystals



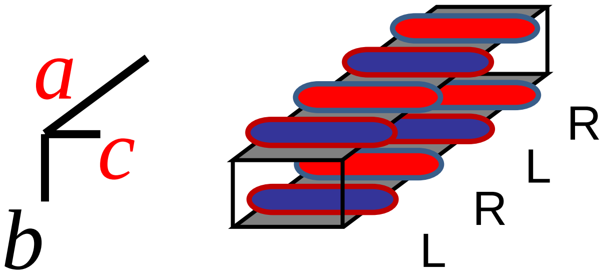




De Rosa, C.; Rizzo, P.; Ruiz de Ballesteros, O.; Petraccone, V.; Guerra G. *Polymer*, **1999**, *40*, 2103.

Chatani, Y.; Shimane, Y.; Inagaki, T.; Ijitsu, T.; Yukinari, T.; Shikuma, H. *Polymer*, **1993**, *34*, 1620.

Unique feature of s-PS: three uniplanar orientations



Solvent induced crystallization on amorphous film

Bp < 110°C

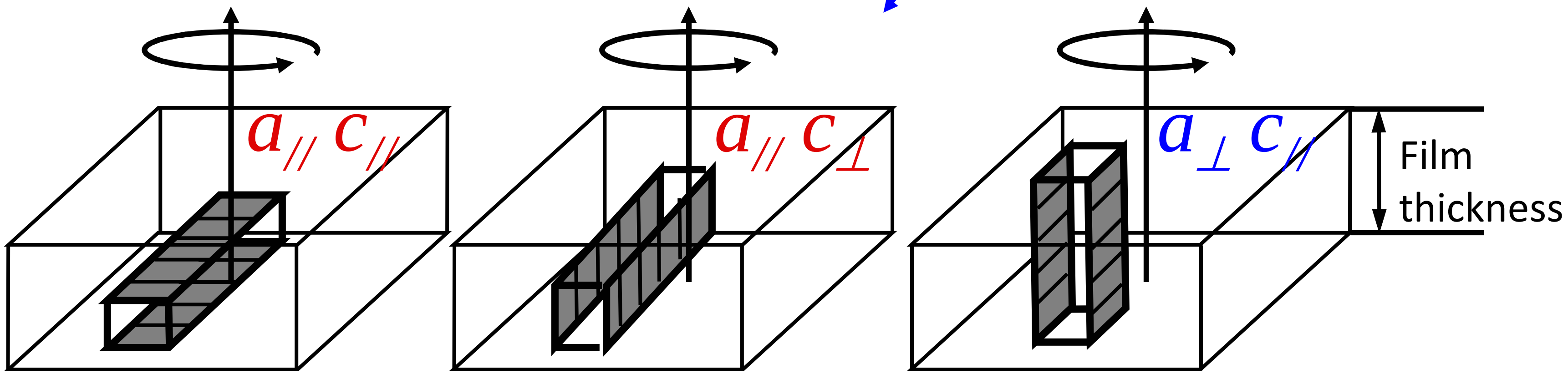
Rizzo, Della Guardia, Guerra

Macromolecules **2004**, *37*, 8043

Bp > 140°C

Rizzo, Spatola, Del Mauro, Guerra

Macromolecules **2005**, *38*, 10089



THF, $CHCl_3$

Rizzo, Lamberti, Albunia, Ruiz, Guerra

Macromolecules **2002**, *35*, 5854

p-xylene, dichloroethane

Rizzo, Costabile, Guerra

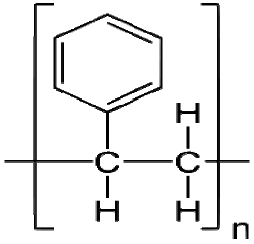
Macromolecules **2004**, *37*, 3071

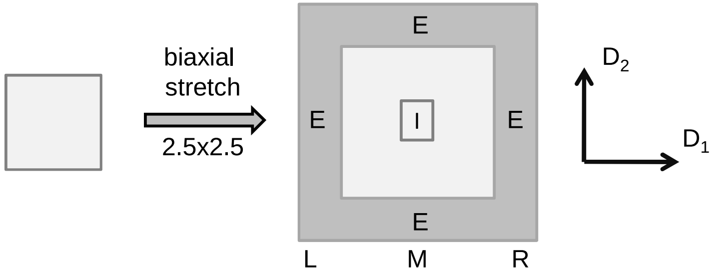
Albunia, Rizzo, Tarallo, Petraccone, Guerra *Macromolecules* **2008**, *41*, 8632

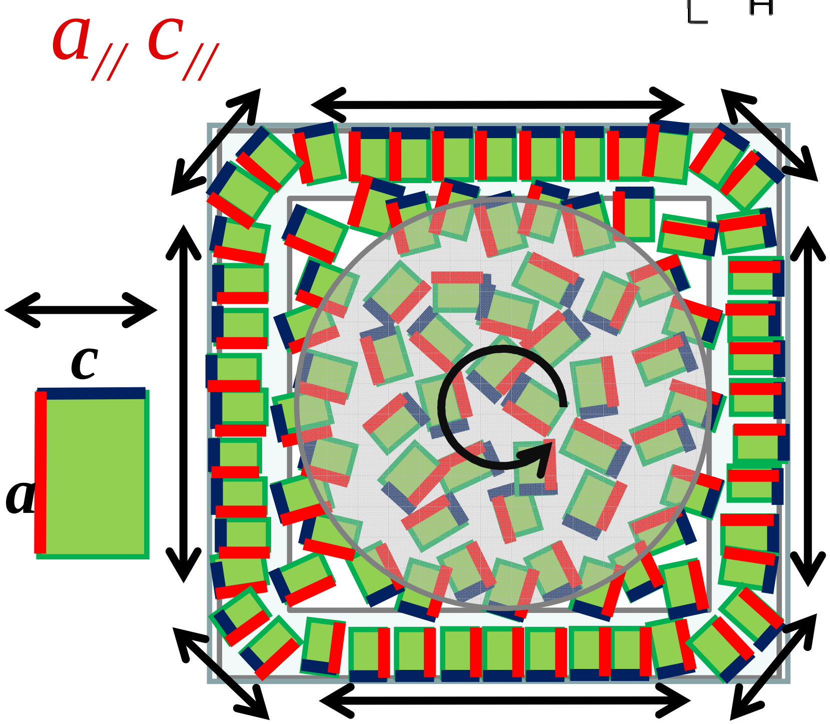
Solution casting; Spin-coating

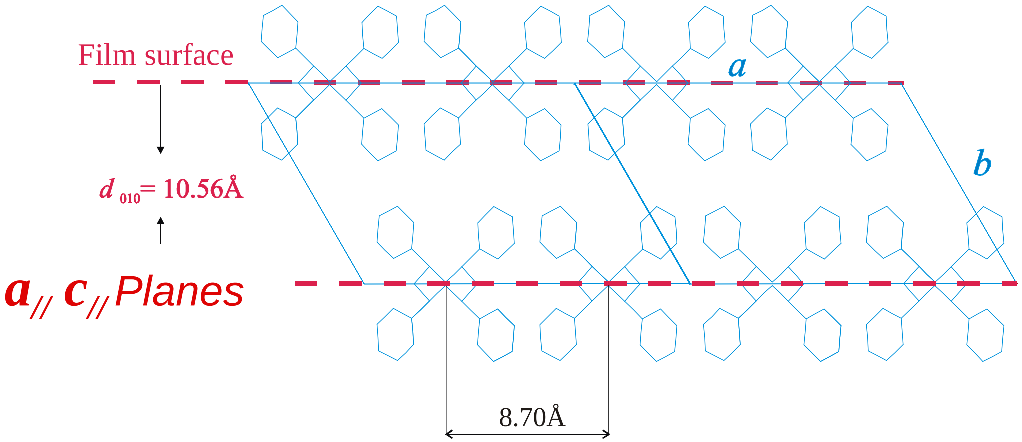
sPS Films: Orientation Upon Biaxial Balanced Drawing

(sPS)syndiotactic polystyrene





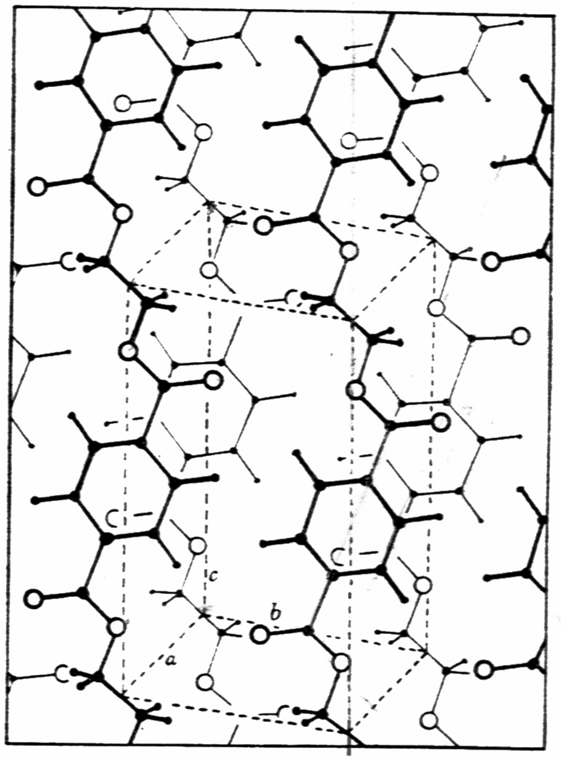


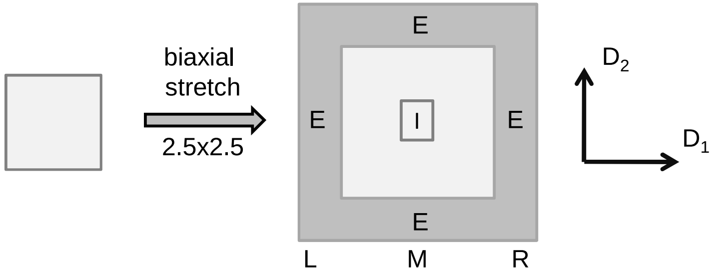


a// c// planes correspond to rows of parallel helices with minimum interchain distances (8.70Å) and maximum interplanar distances (10.56Å)

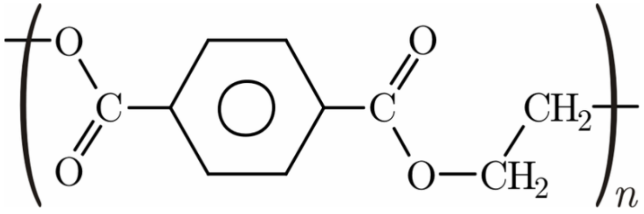
Paola Rizzo, Alexandra R. Albunia Macromolecular Chemistry and Physics* **2011**, 212,1419-26

Uniplanar orientation





(PET) polyethylene terephthalate



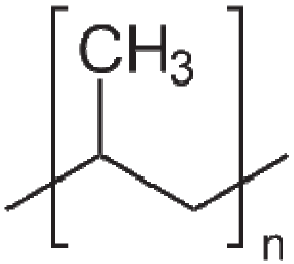
(100) ***uniplanar orientation***

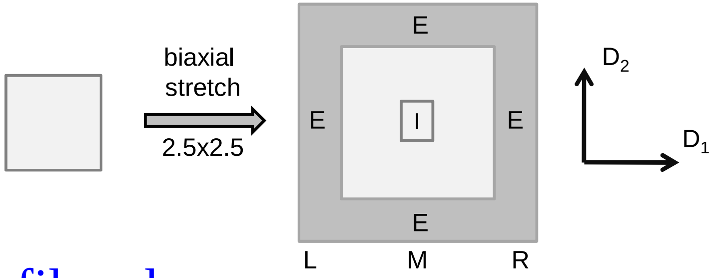
(a=4.56Å b=5.94Å c=10.75Å α=98.5° β=118° γ=112°) triclinic lattice

Bin, Y.; Oishi,K.; Yoshida, K.; Nakashima T.; Matsuo, M.; *J. Polymer*, **2004,** 36,394-402

Uniplanar orientation

(i-PP) polypropylene



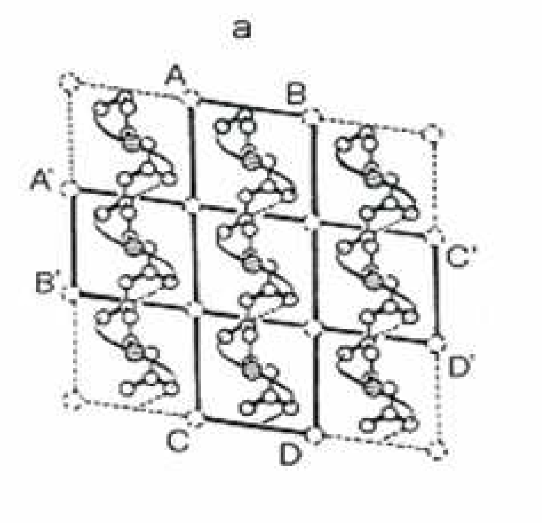


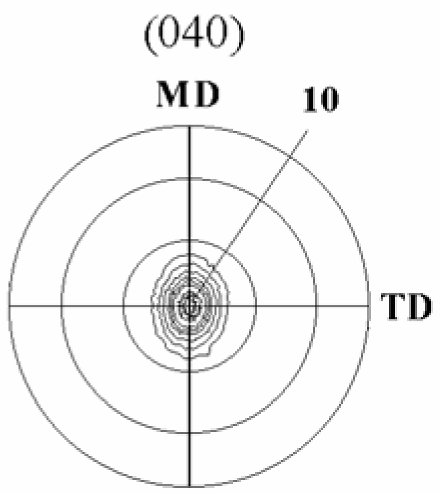
A crystalline plane preferentially parallel to the film plane

Primary slip-plane:
- containing the chain axis
- and having the highest density

a// c// uniplanar orientation

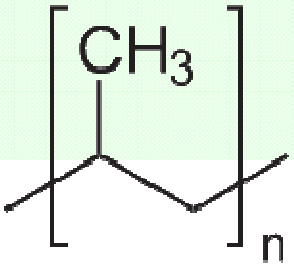
Both *a* and *c* axes parallel to the film plane



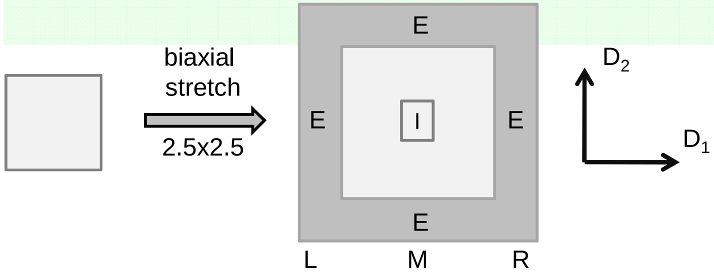


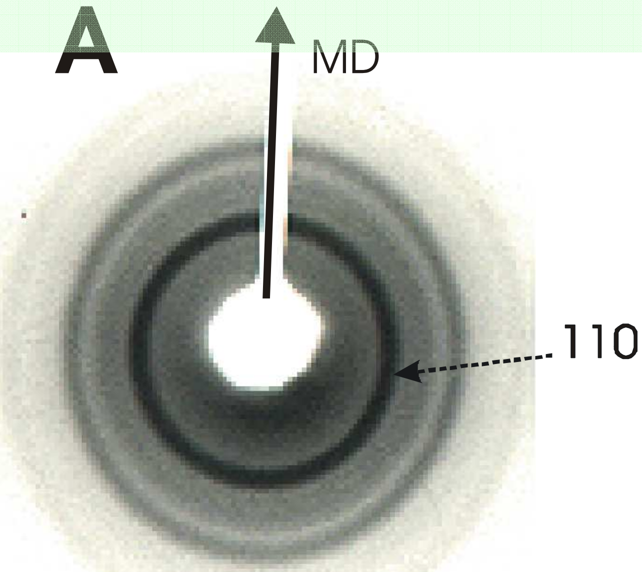
Paola Rizzo, Vincenzo Venditto, Gaetano Guerra, Antonio Vecchione Macromolecular Symposia **2002**, *185*, 53-63.

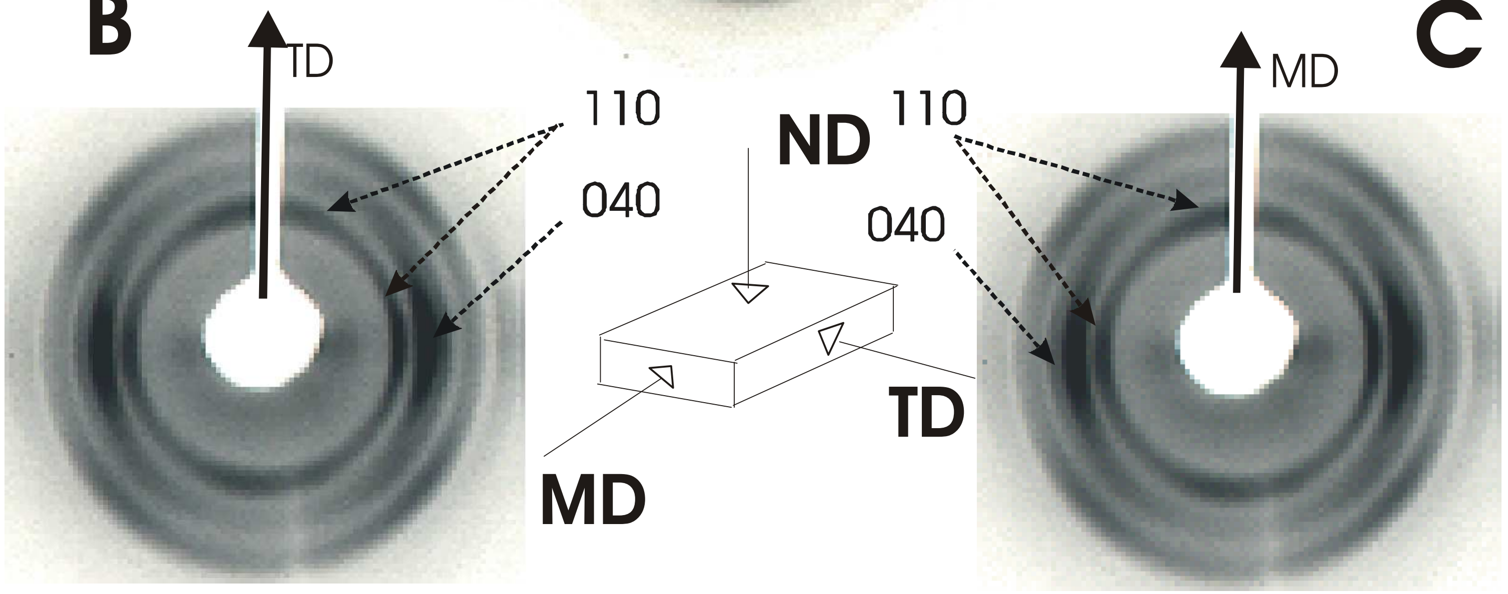
Uniplanar orientation



(i-PP) polypropylene







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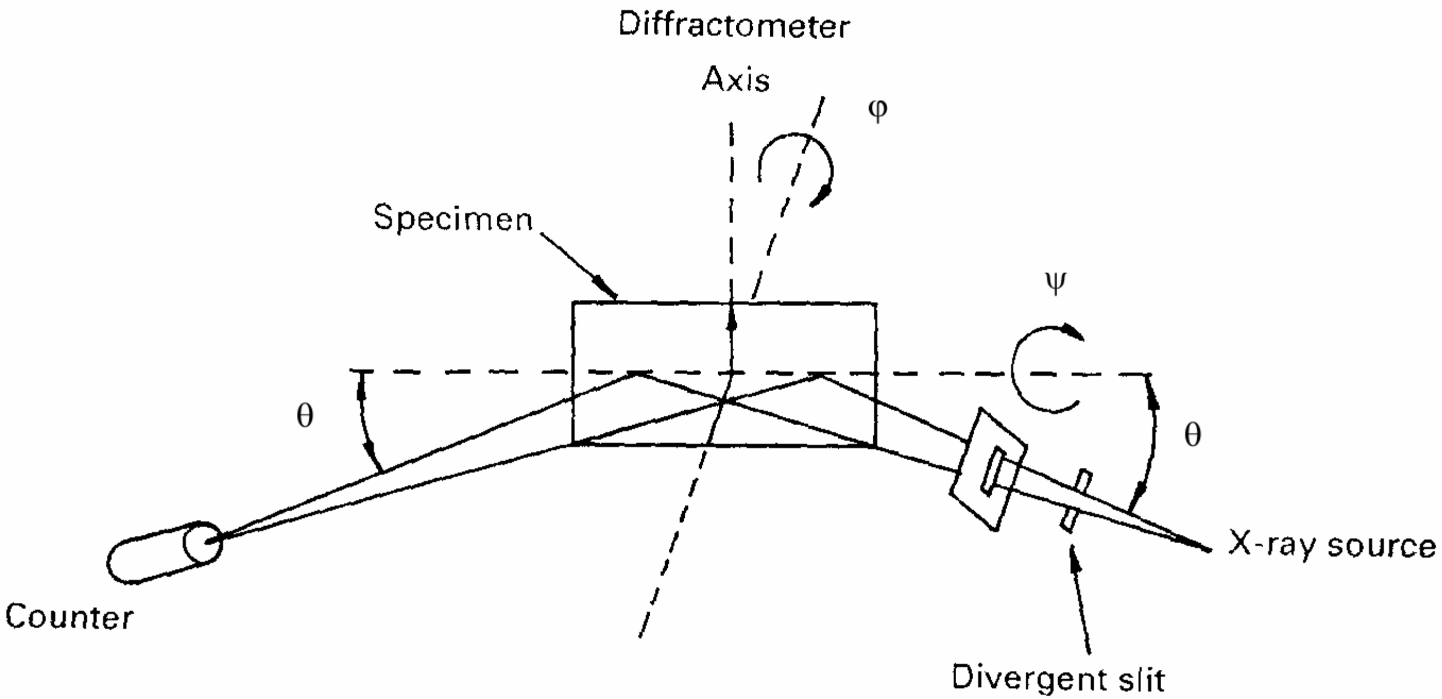
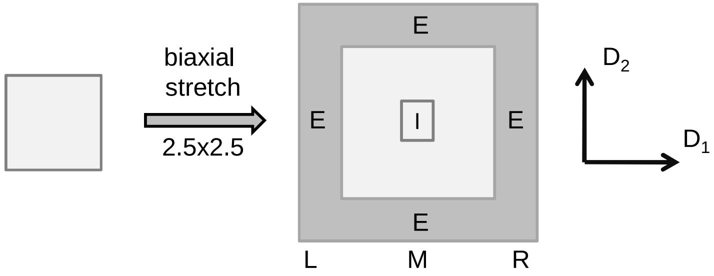
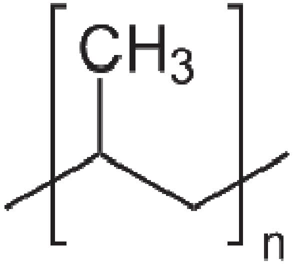


In the Schulz reflection method the goniometer is set at the Bragg angle corresponding to the crystallographic planes of interest. A special specimen holder tilted the sample with the horizontal axis (y rotation axis), while rotating it in its own plane about an axis normal to its surface (j rotation axis) . The y rotation can be varied from 0° to 90°, whereas the j rotation can be varied from 0° to 360°. The pole figures are plotted on a polar stereographic projection using linear intensity scale.

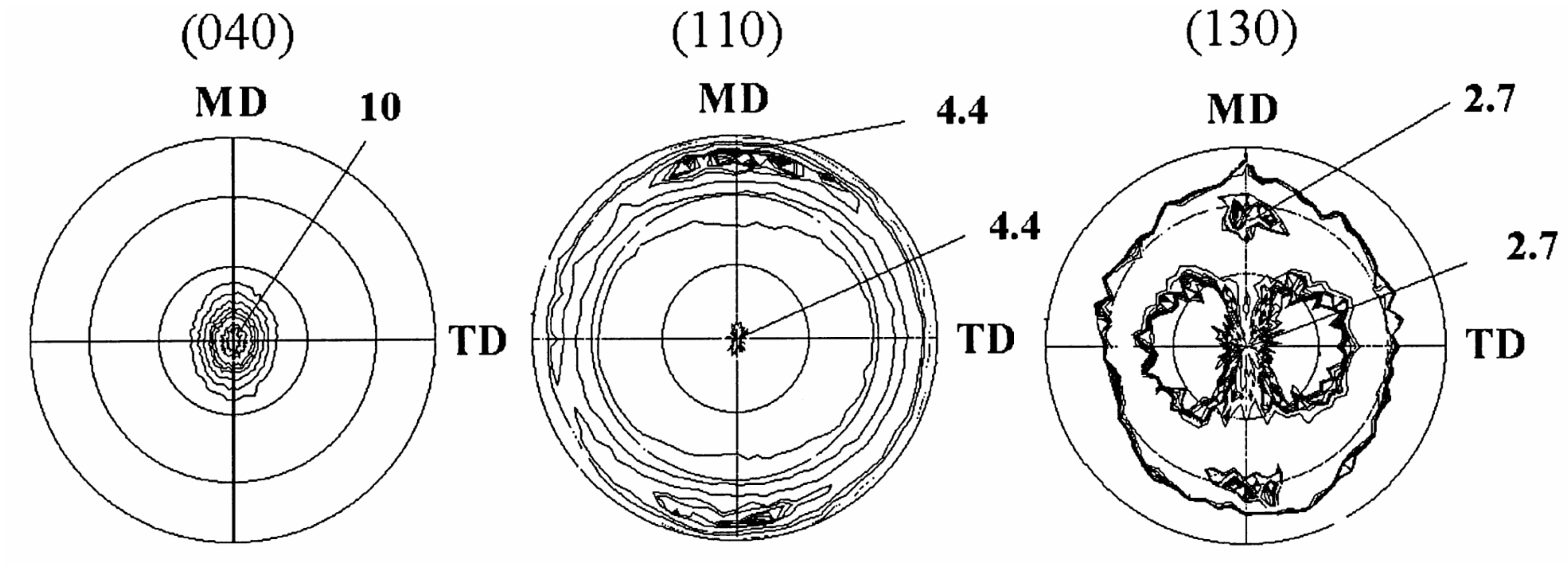
Uniplanar orientation





(i-PP) polypropylene

Iso-intensity lines indicate the relative intensity of the pole related to the maximum diffracted intensity (assumed equal to 10).



The presence on the diffraction rings of the pole figures of the (110) and (130) reflection of intensity maxima along MD indicates some preferential *c*-axis orientation along TD.
It is worth noting that this minor axial orientation, which is related to a not perfect balancing of draw ratios between the two drawing directions.

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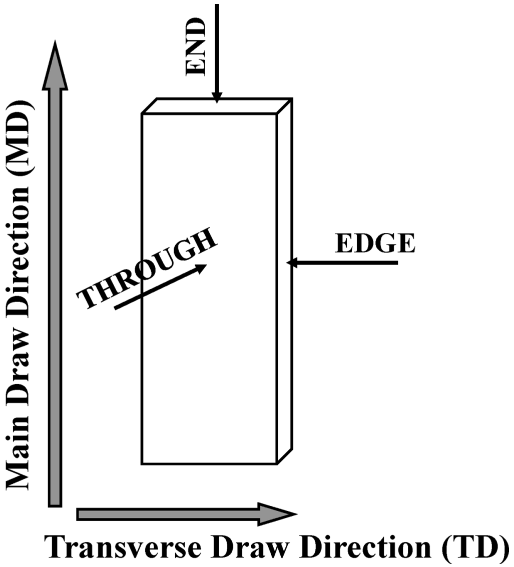
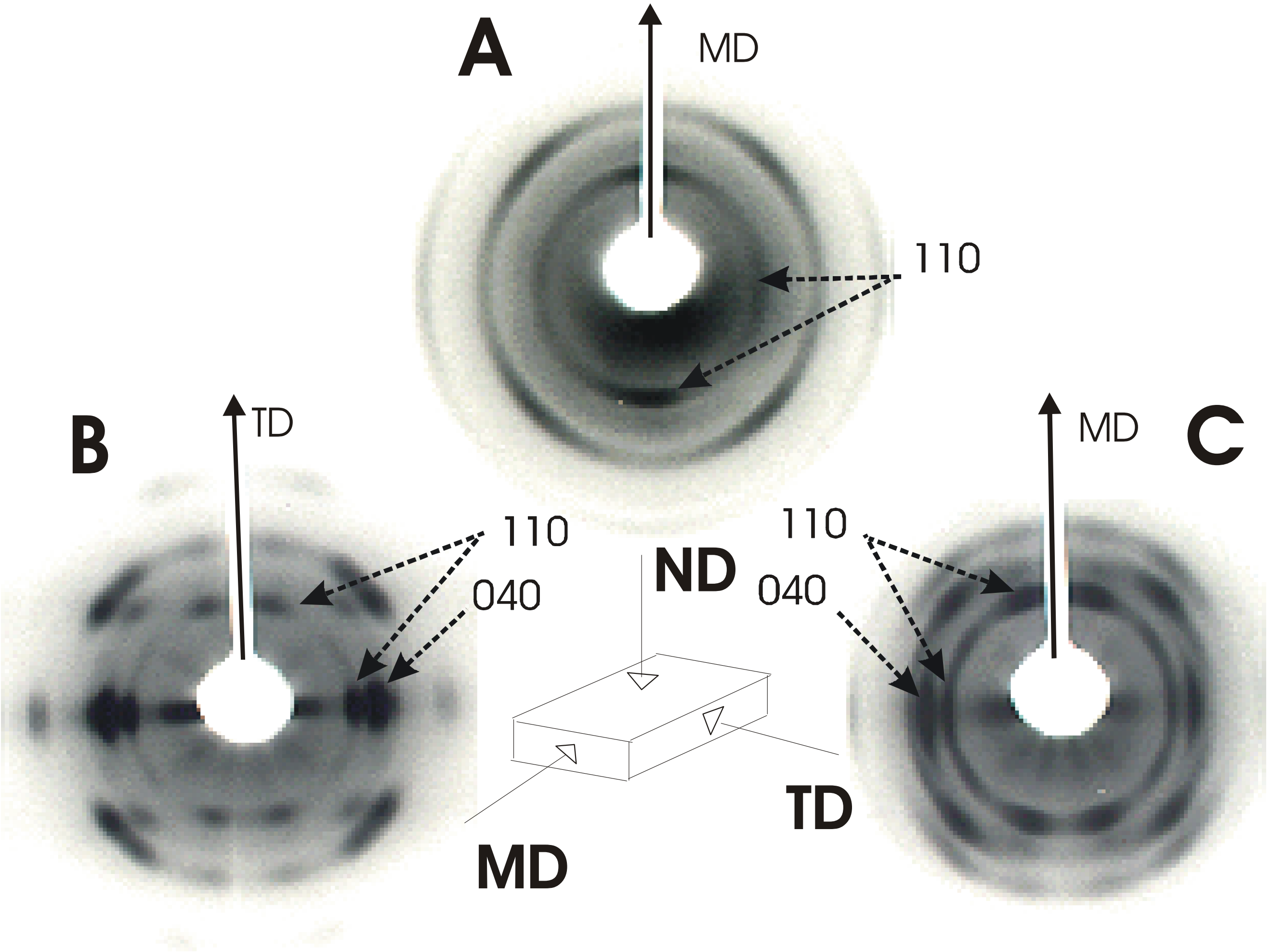
iPP:uniplanar-axial orientation





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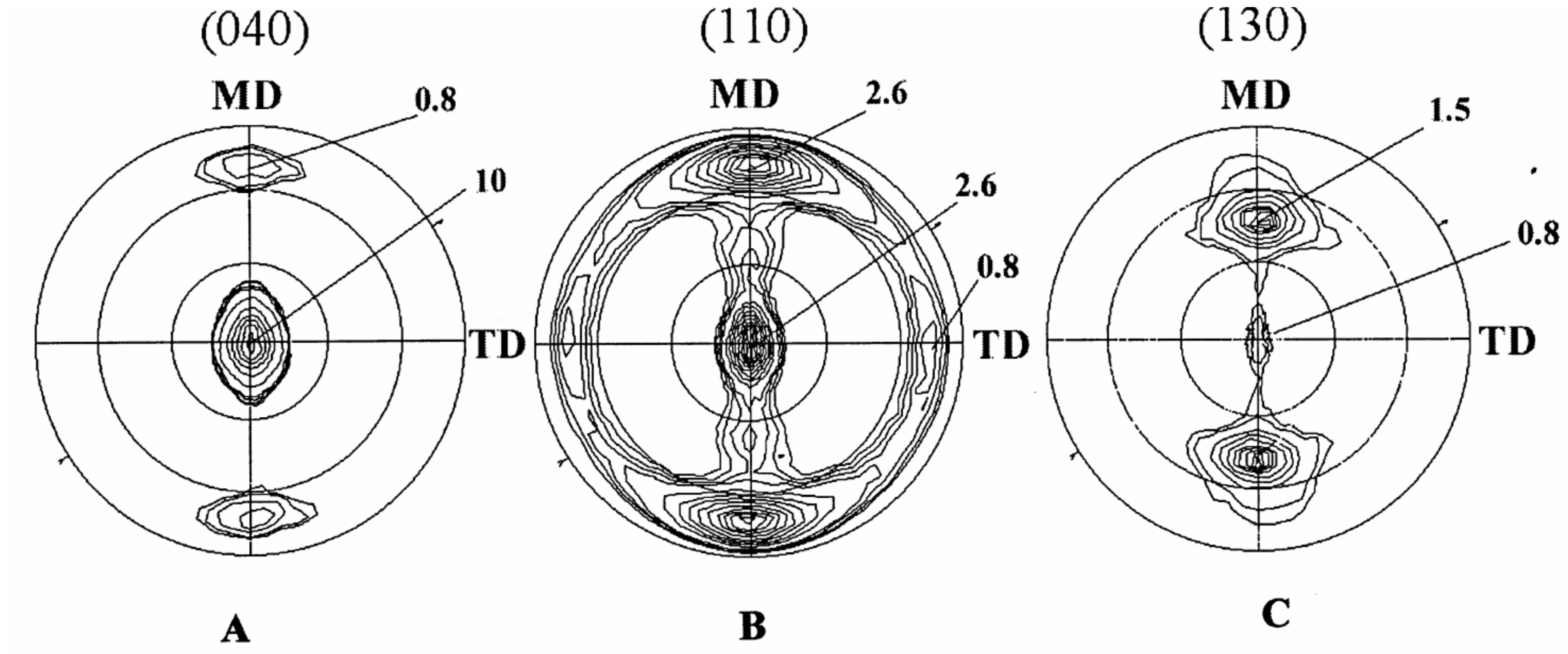
iPP:uniplanar-axial orientation



The pole figure of the (040) reflection shows a strong maximum in ND. Correspondingly, the (110) and (130) pole figures show rings at latitude 72° and 46°, respectively. These rings present more intense maxima along MD and less intense maxima along TD, indicate the occurrence of a bimodal axial orientation, with prevailing orientation along TD.

Crystallites presenting (110) planes parallel to the film surface, associated with a *c*-axis orientation along TD, can account for the two weak reflections at latitude of 72° along MD, which are present on the (040) pole figure

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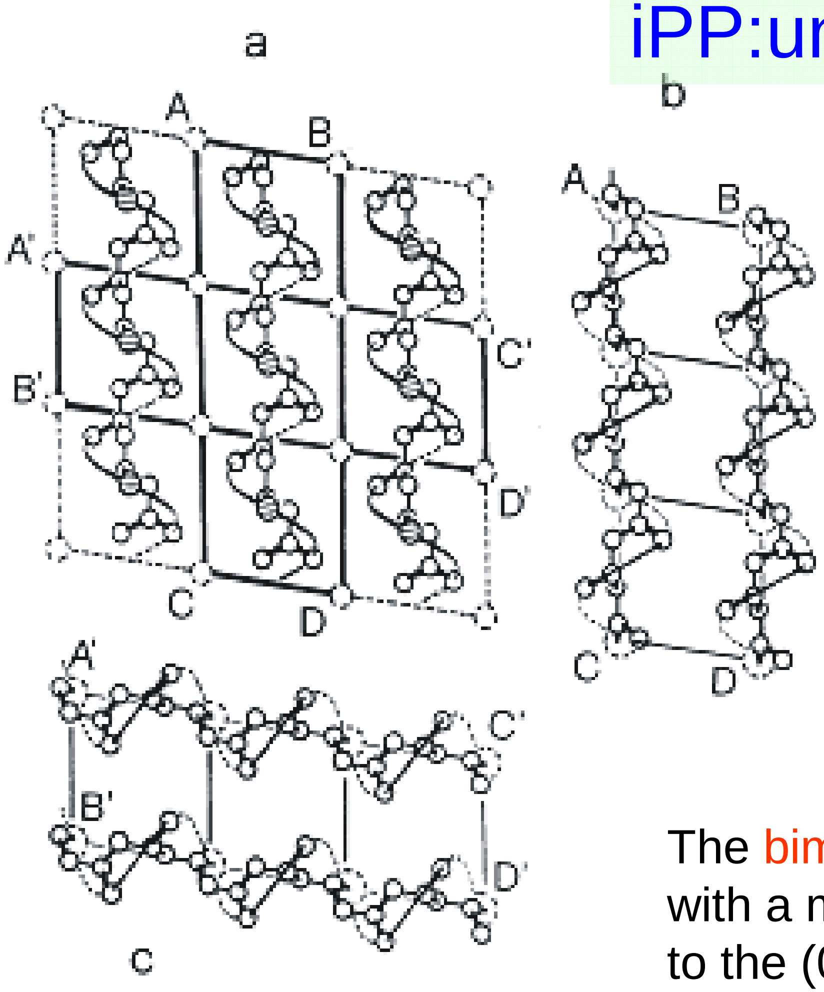
iPP:uniplanar-axial orientation



The bimodal axial orientation, associated with a major uniplanar orientation relative to the (0k0) planes and minor uniplanar orientations relative to the (110) and (130) planes, can rationalize all the diffraction peaks which occur in photographic patterns, like those shown previously

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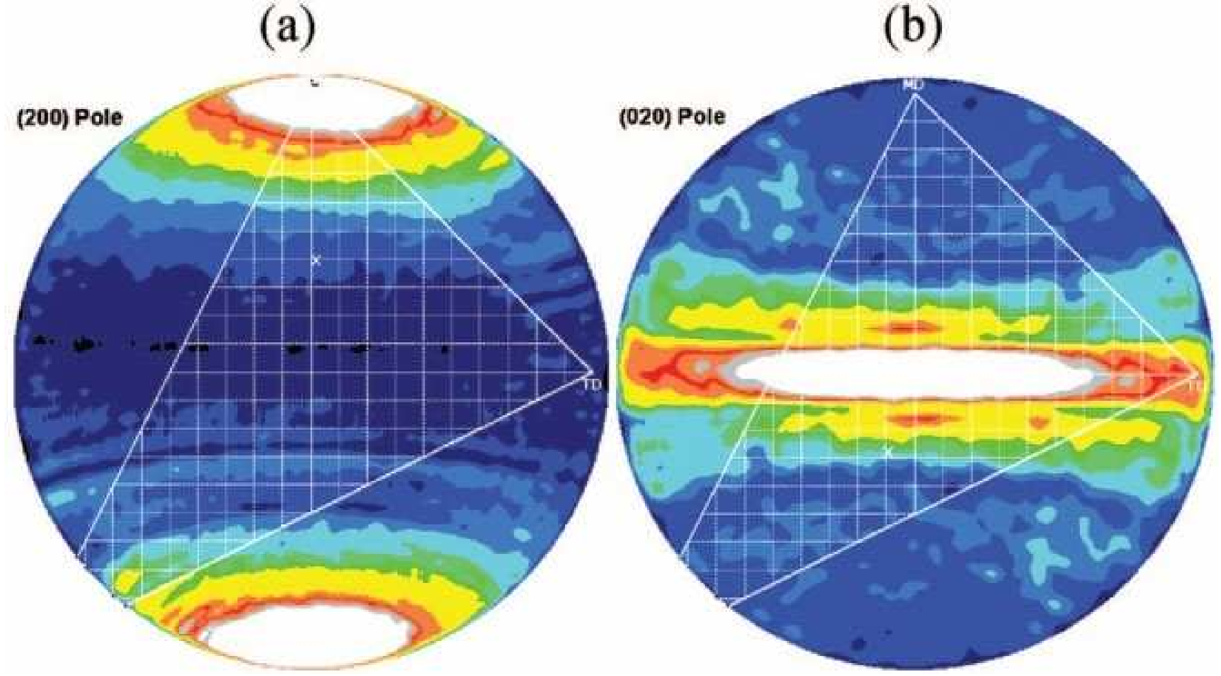
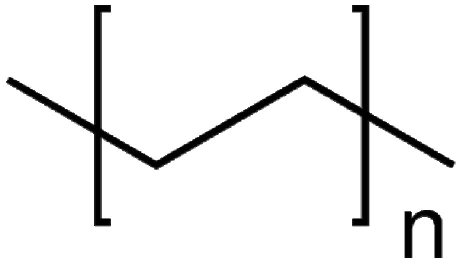
Blown film of PE



(PE) polyethylene

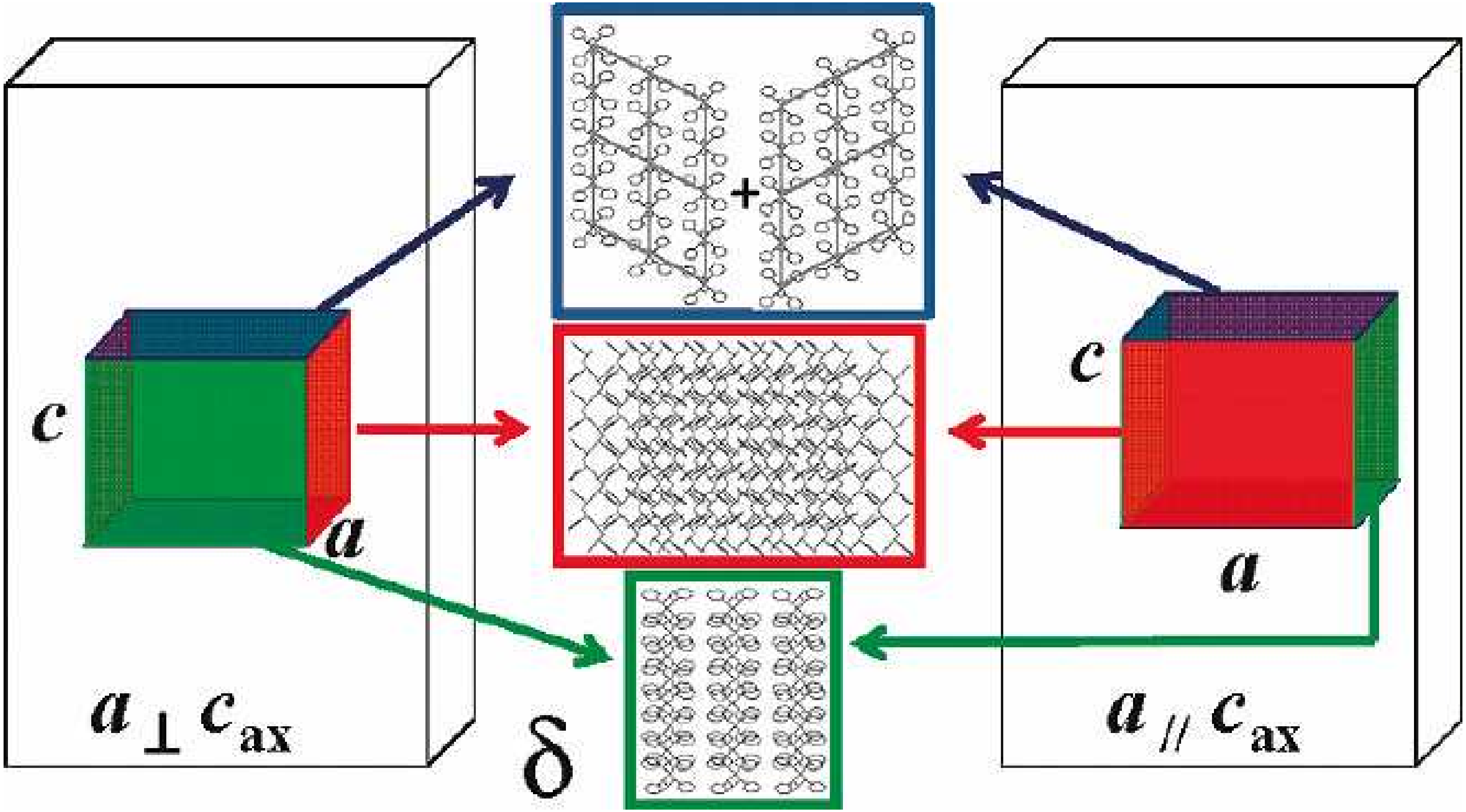


a-axis (200) is preferentially oriented along the MD

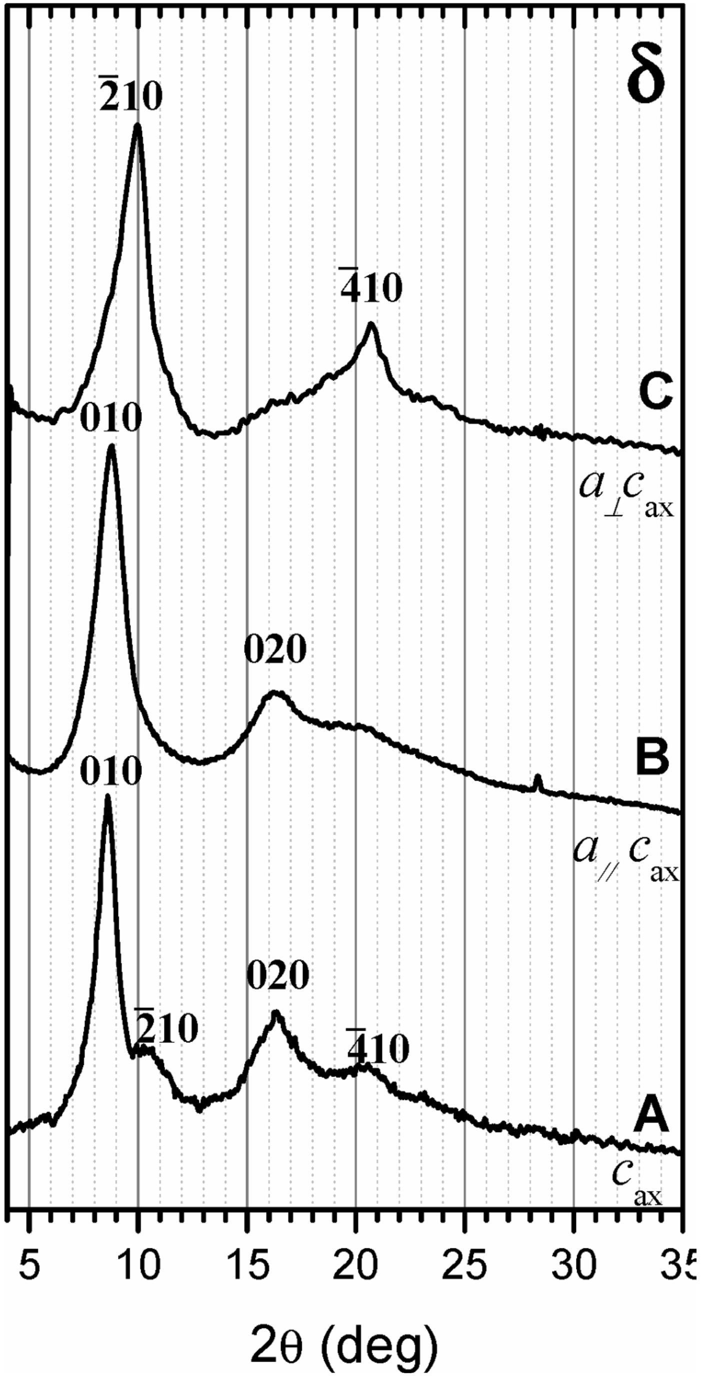
It is evident that the *a*-axis (200) is preferentially oriented along the MD, because poles with highest intensity are concentrated at the north and south ends of the (200) pole figure.
In the (020) pole figure, poles with the highest intensity are concentrated in the center, and spread along the TD. This suggests that *b*-axis is oriented in the ND-TD plane.

Chen, H. Y.; Bishop, M. T.; Landes, B. G.; Chum, S. P.; *J. App. Polym. Sci.*, **2006**, 101, 898-907

sPS:uniplanar-axial orientation



sPS:uniplanar-axial orientation



$a_{\perp}c_{\text{ ax}}$

$a_{//}c_{\text{ ax}}$

c_{ax}

sPS: uniplanar-axial orientation