# X-ray Scattering in polymer science: From heterogeneous systems to nanostructures

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CSIC

**SAXS Workshop**

**Barcelona, 1st October 2014**

IEM

# Outline

- ✓ Hierarchical structures and techniques
- ✓ Basics about X-ray scattering and polymers
- ✓ Wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS)
- ✓ Microfocus X-ray scattering (μWAXS y μSAXS)
- ✓ Grazing incidence X-ray scattering (GIWAXS y GISAXS)


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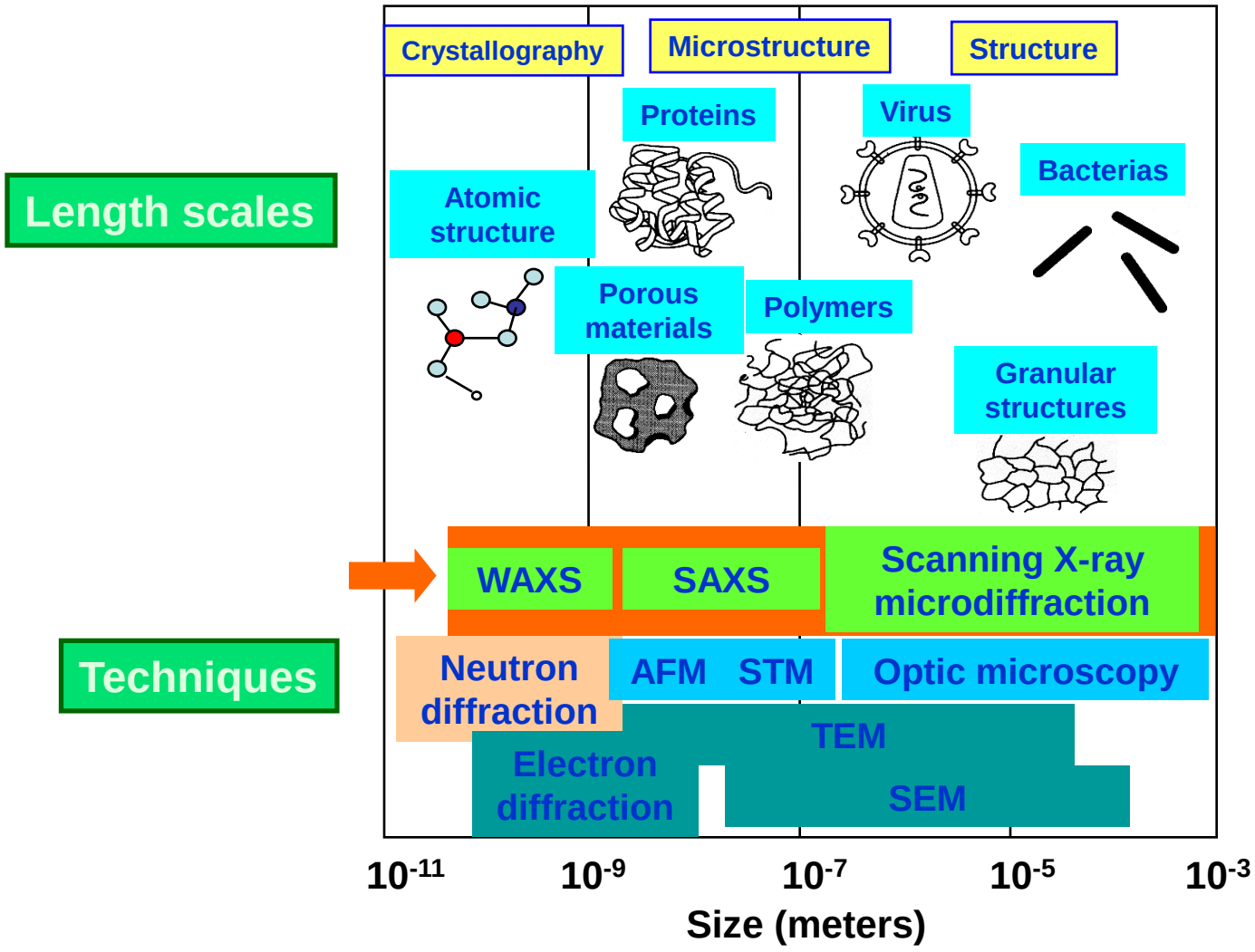
# Hierarchical structures and techniques





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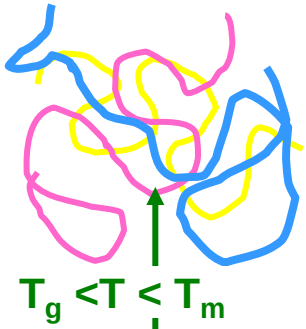
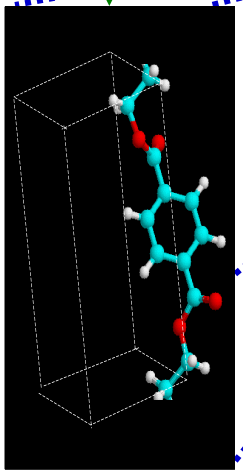
# Hierarchical structures: Polymer crystallization

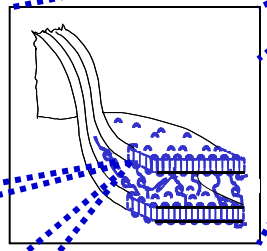


$T_g < T < T_m$



**$5x10^{-10}$ m**

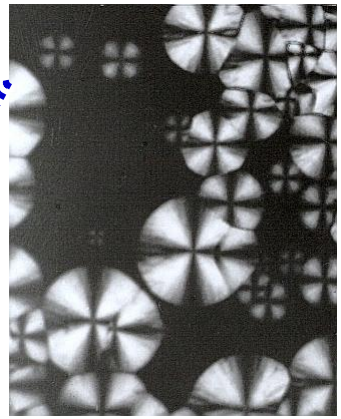
**X-ray scattering (WAXS)**
**Neutron scattering**



**$10^{-8}$ m**

**SAXS; SANS;**

**AFM**



$10^{-5}$ m

**Light scattering**
**Optic microscopy**
**AFM**



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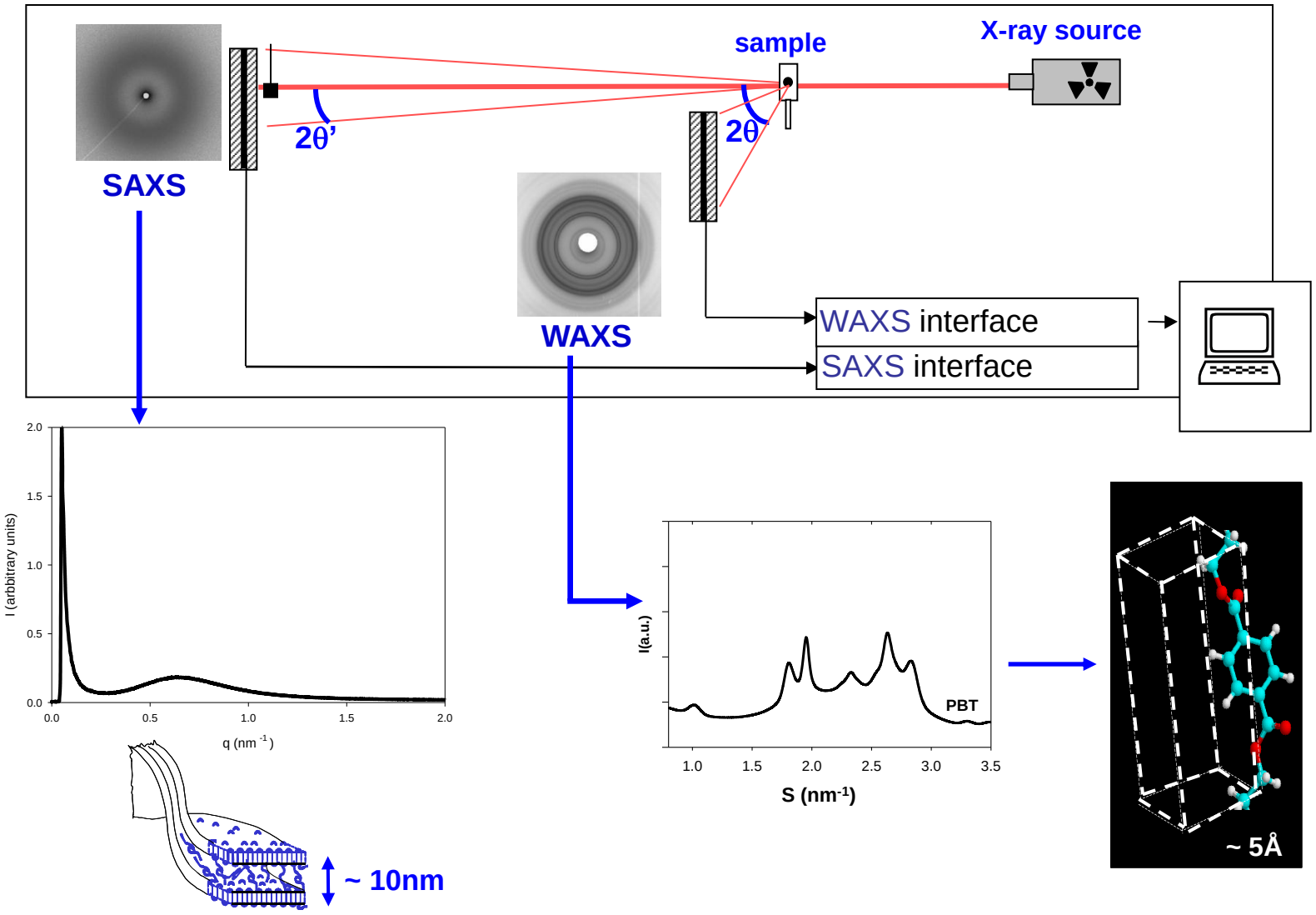
# Wide- (WAXS) and small- (SAXS) angle X-ray scattering



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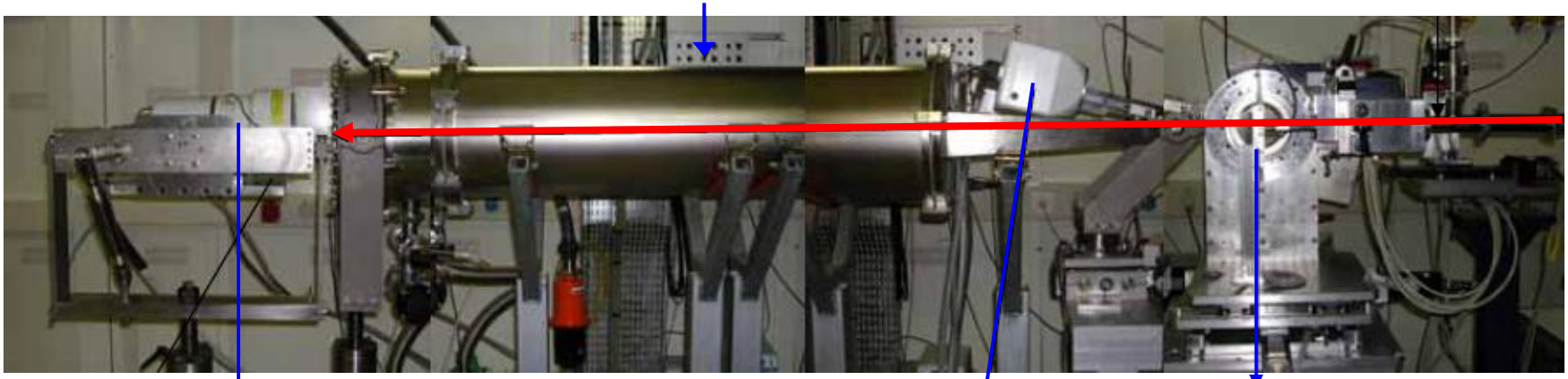
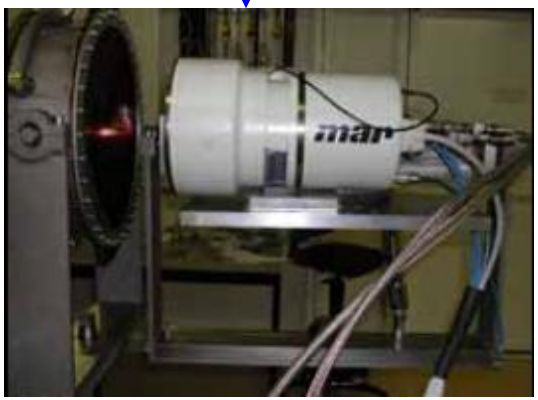
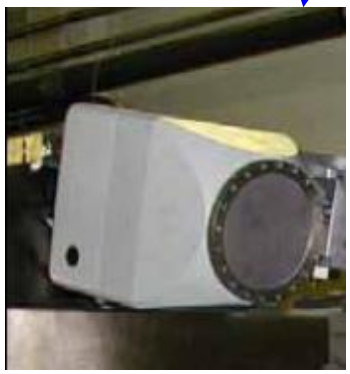
# SAXS-WAXS beamline

Vacuum chamber

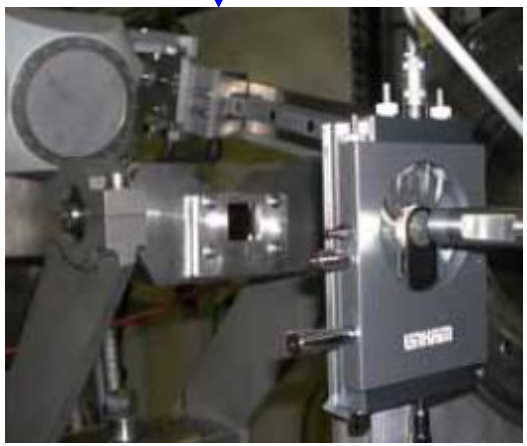




Detector SAXS



Detector WAXS



Sample environment



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# Applications of X-ray scattering


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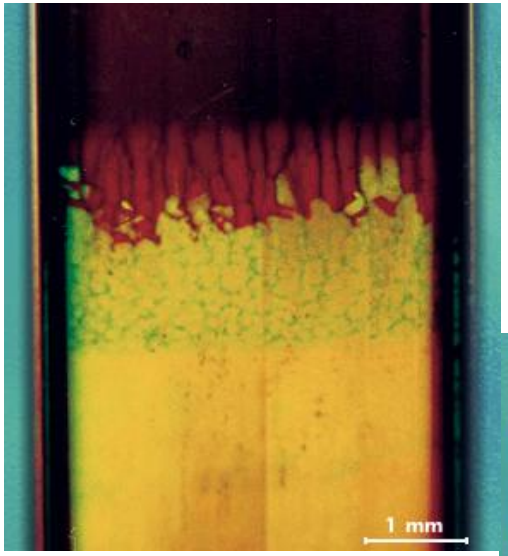
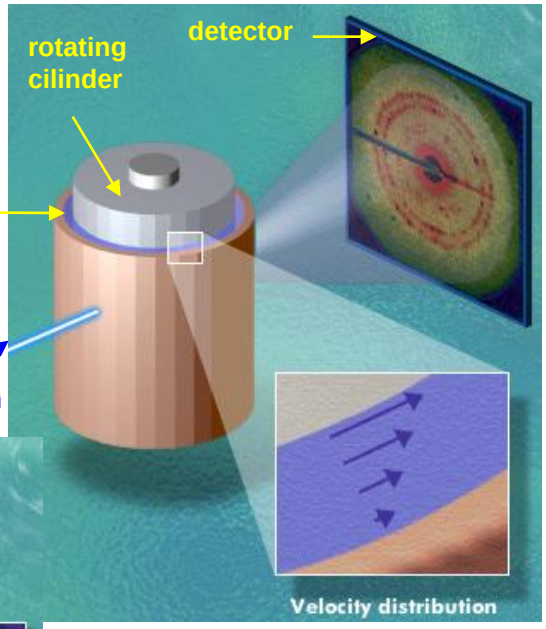
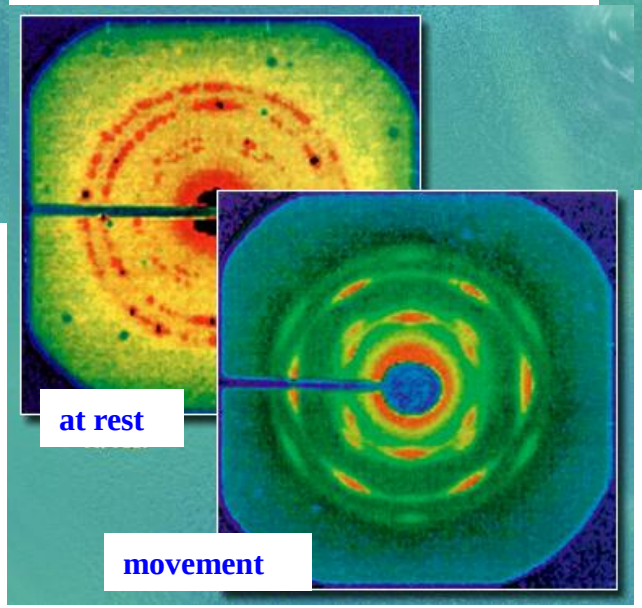
# Colloidal systems

**PS in methanol**



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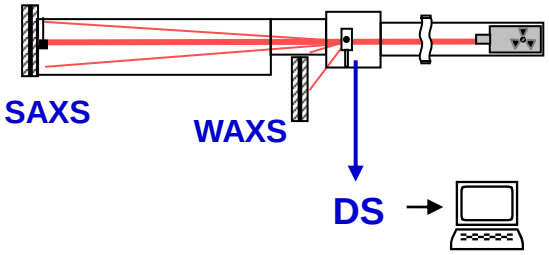
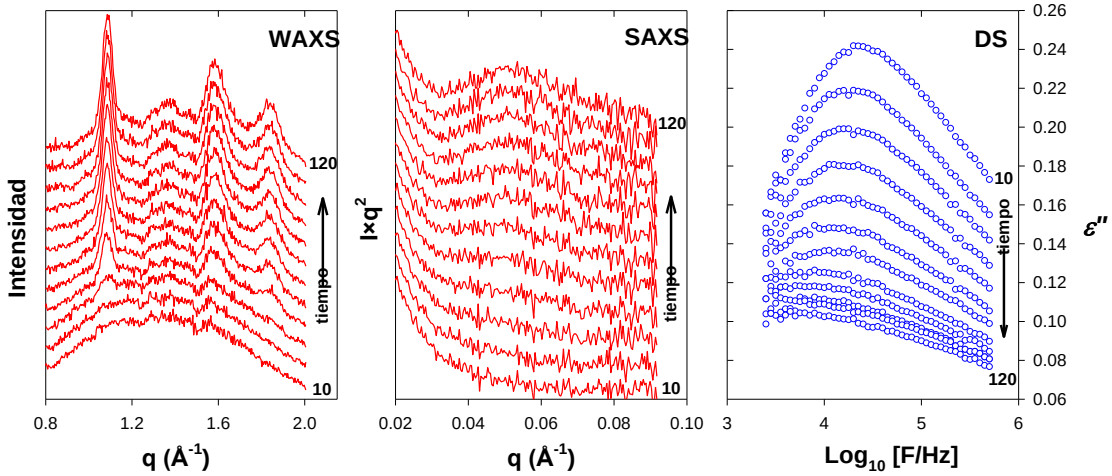
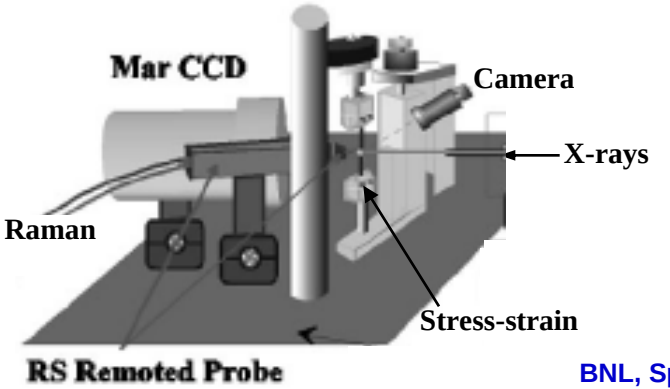
# Simultaneous techniques




I Sics *et al, Rev. Sci. Instrum. 71,1733 (2000)*

**Structure** ⟷ **Dynamics**



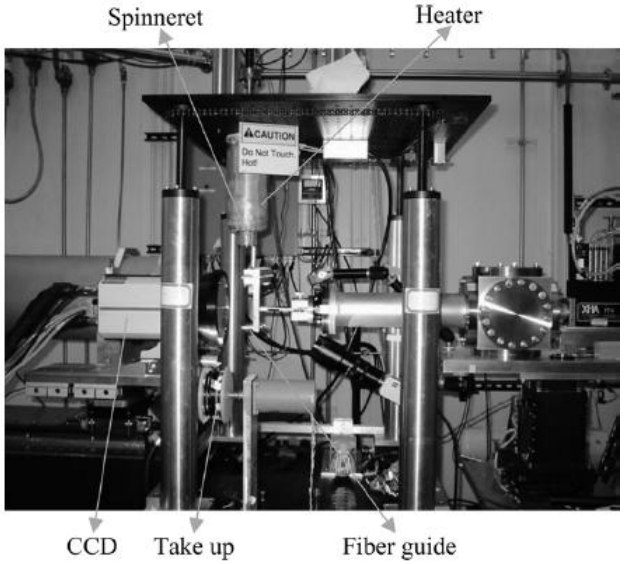




**BNL, Spring-8**

**Uniaxial deformation SAXS/WAXS + Raman** ➡

**Complementary information about the structural evolution of molecular chain in the amorphous phase, mesophase and crystalline phase.**

S. Ran *et al, Rev. Sci. Instrum. 74, 3087 (2003)*




**Processing SAXS/WAXS**

**BNL**

S. Ran *et al, Colloid Polym. Sci. 282, 802 (2004)*



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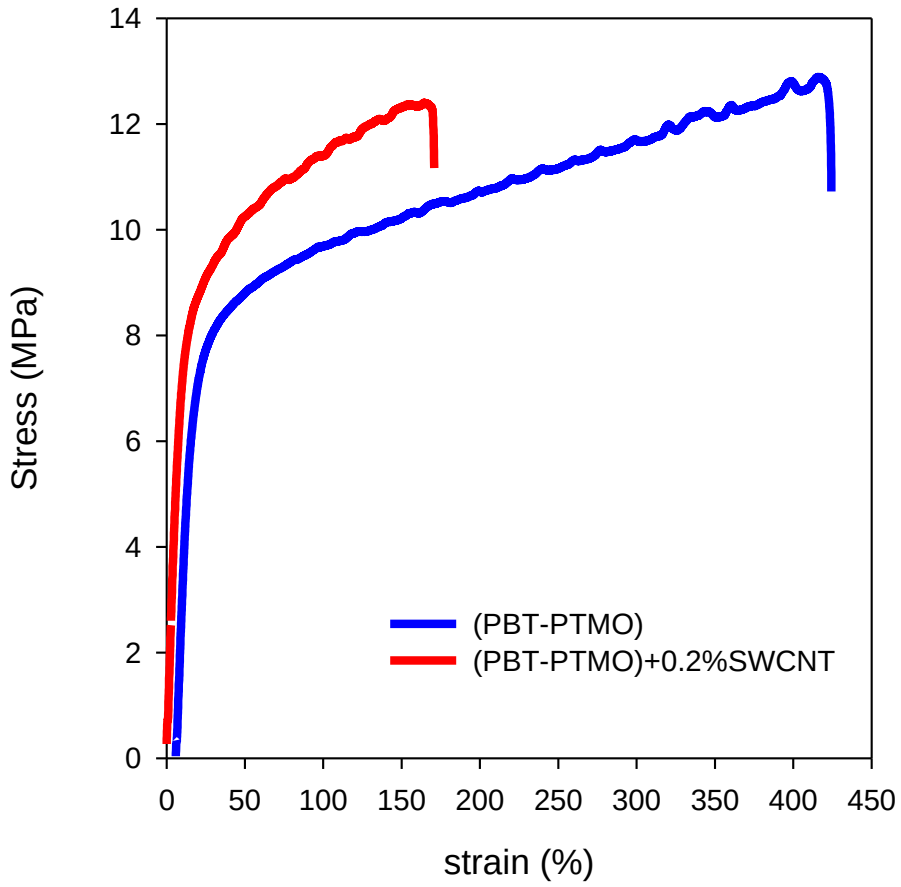
# Uniaxial deformation + SAXS-WAXS




**Young's Modulus:**

**(PBT-PTMO): 75.8 MPa**

**(PBT-PTMO)+SWCNT: 87.6 MPa**

**Yield Strength:**

**(PBT-PTMO): 8.4 MPa**

**(PBT-PTMO)+SWCNT: 9.1 MPa**

**Elongation-to-break:**

**(PBT-PTMO): 420%**

**(PBT-PTMO)+SWCNT: 170%**

**"Deformation behavior during cold drawing of nanocomposites based on single wall carbon nanotubes and poly(ether ester) copolymers" J.J. Hernández, M.C. García-Gutiérrez, *et al.*; *Polymer* 48, 3286 (2007)**



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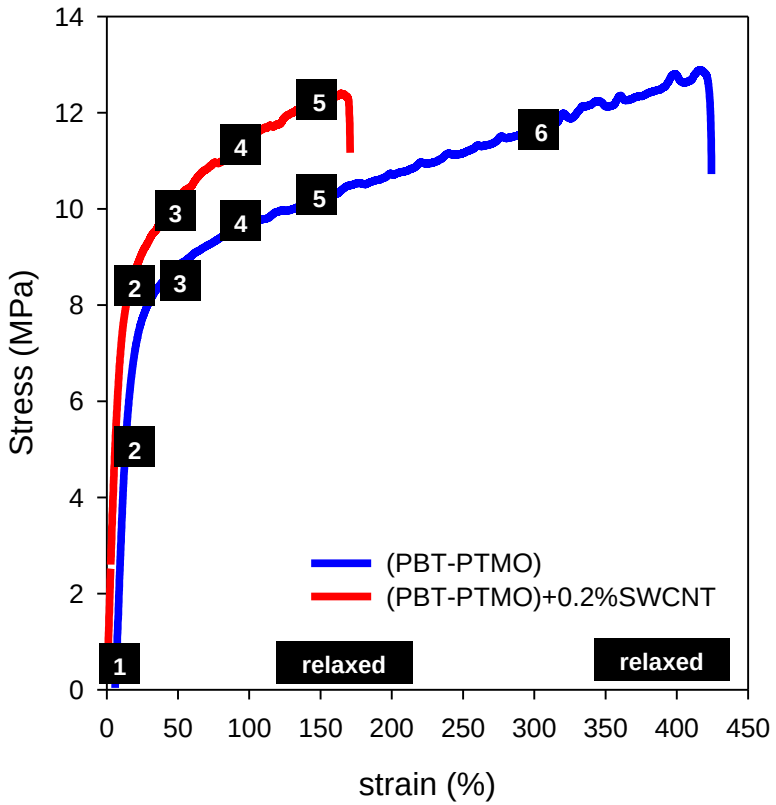
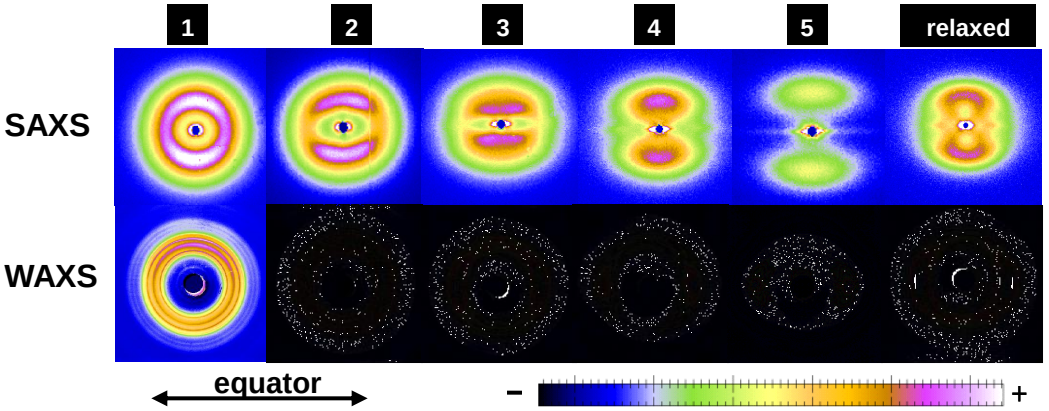
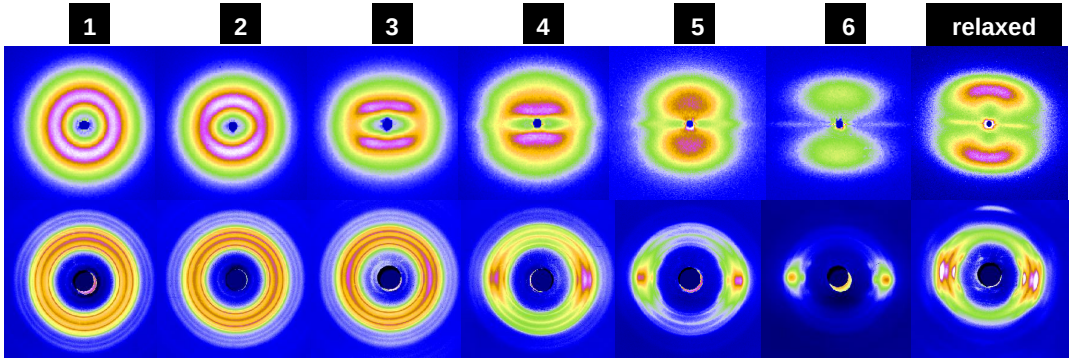
# Uniaxial deformation + SAXS-WAXS




(PBT-PTMO)+SWCNT




(PBT-PTMO)



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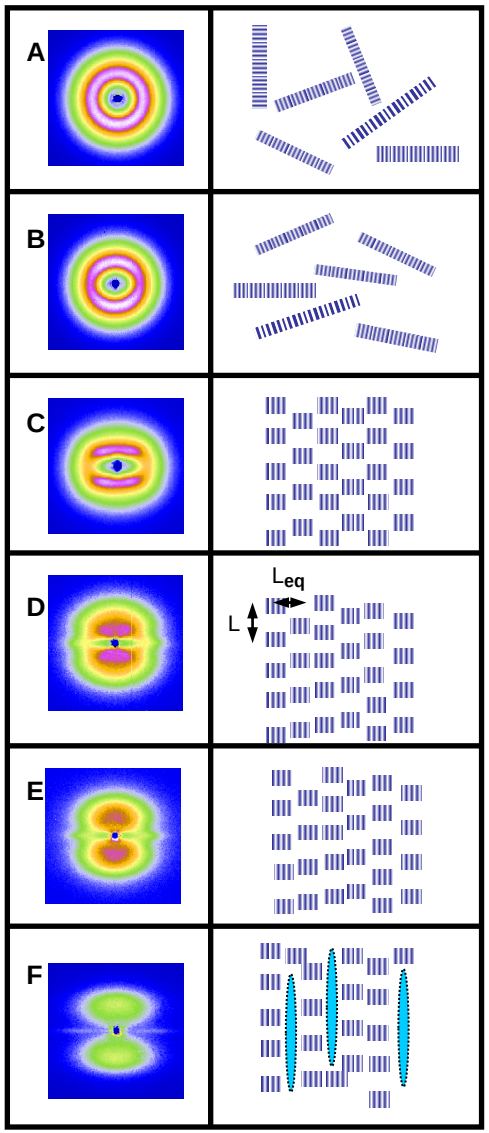
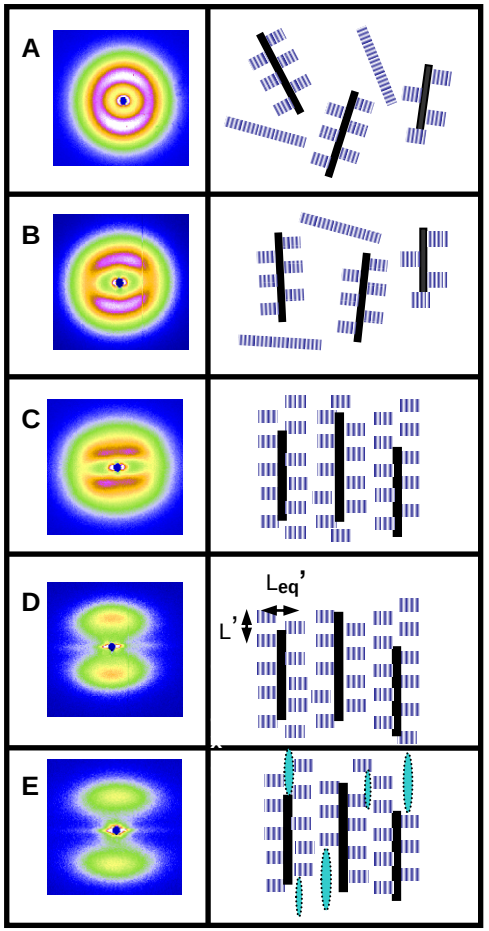
# Uniaxial deformation + SAXS-WAXS

**Copolymer**




**Nanocomposite**




$L > L'$

$L_{eq} < L_{eq}'$



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# X-ray scattering with microfocus


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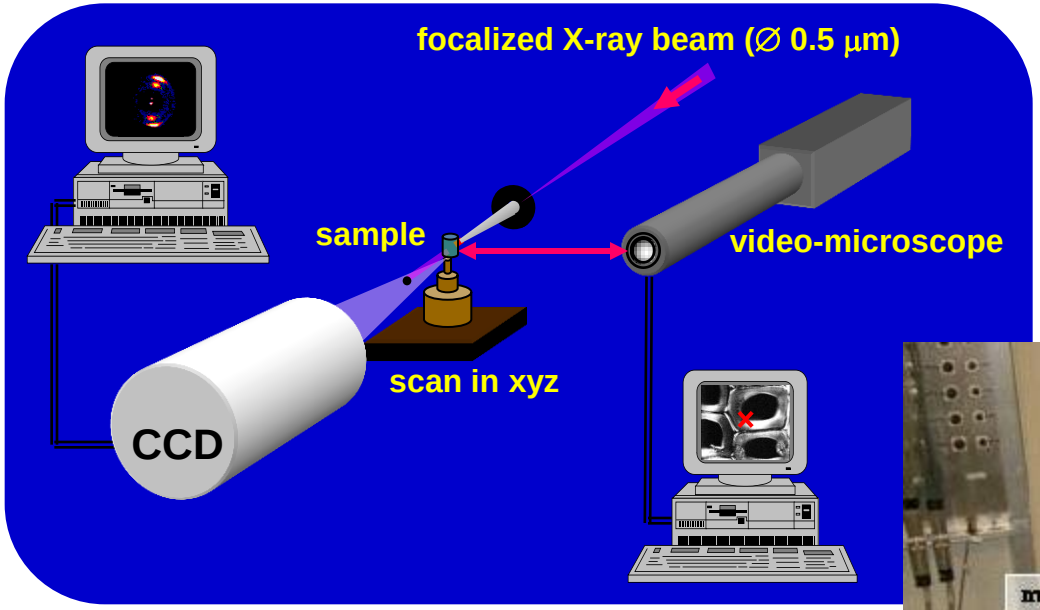
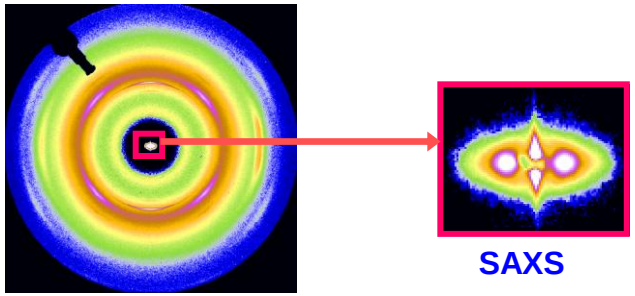
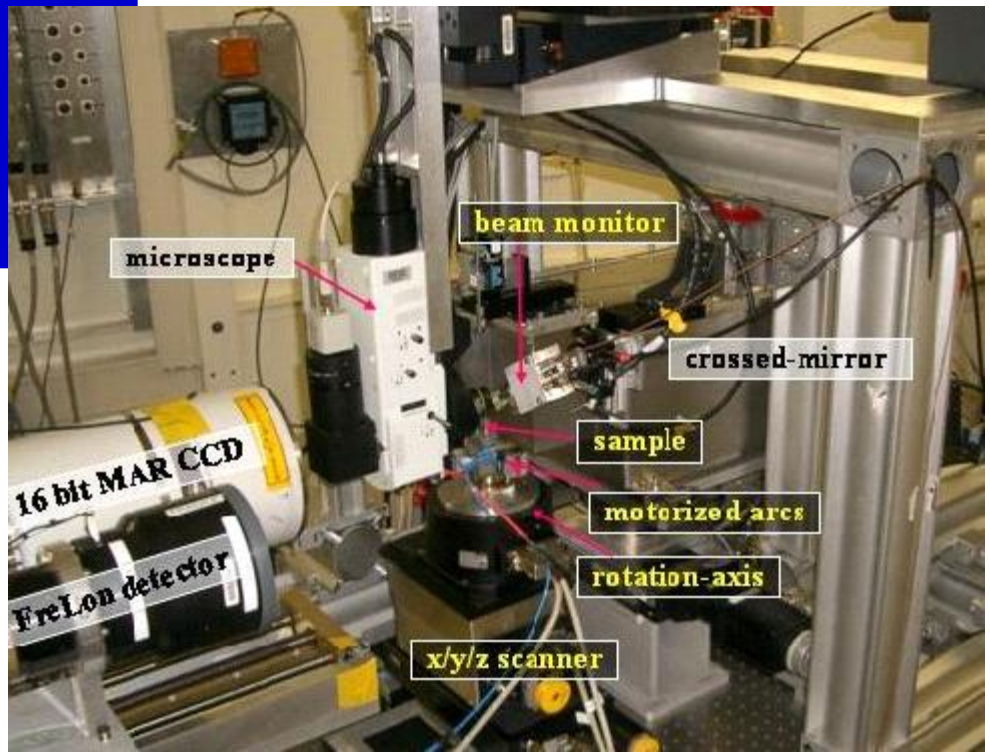
# X-ray scattering with microfocus




Scanning set-up @ ID13 (ESRF)





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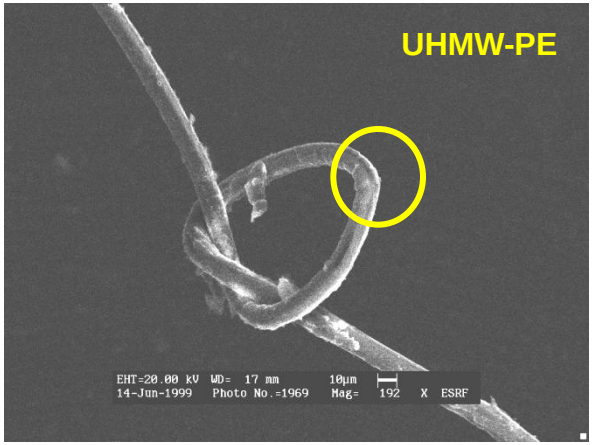
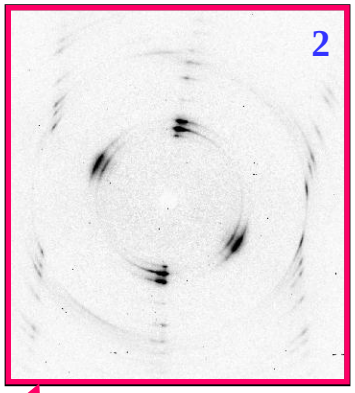
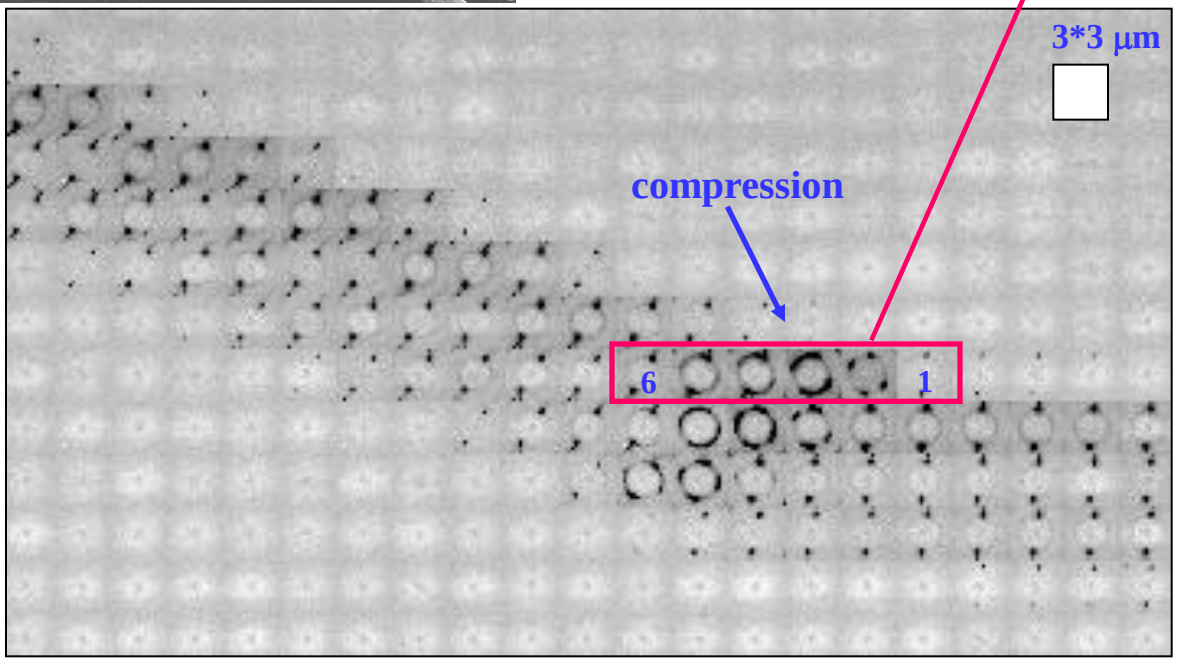
# Mechanisms of deformation




C. Riekel, M.C. García-Gutiérrez, *et al.*; *Anal. & Bioanal. Chem.* 376, 594 (2003)



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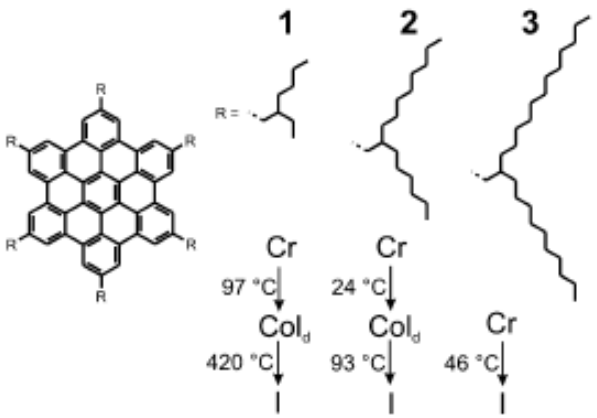
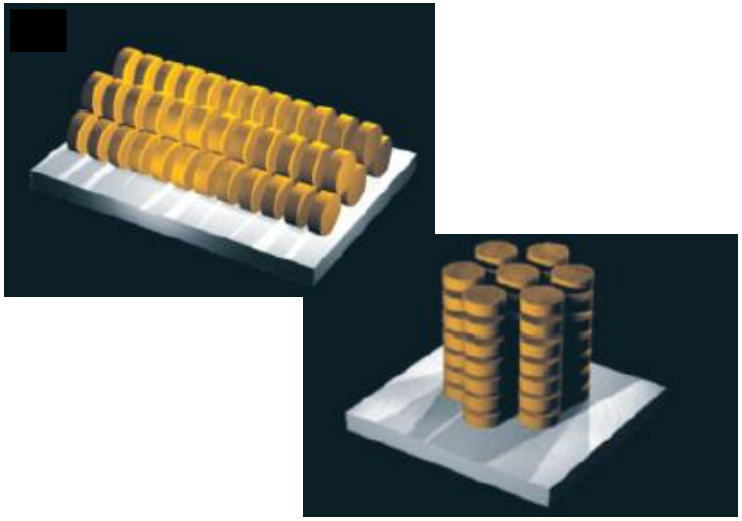
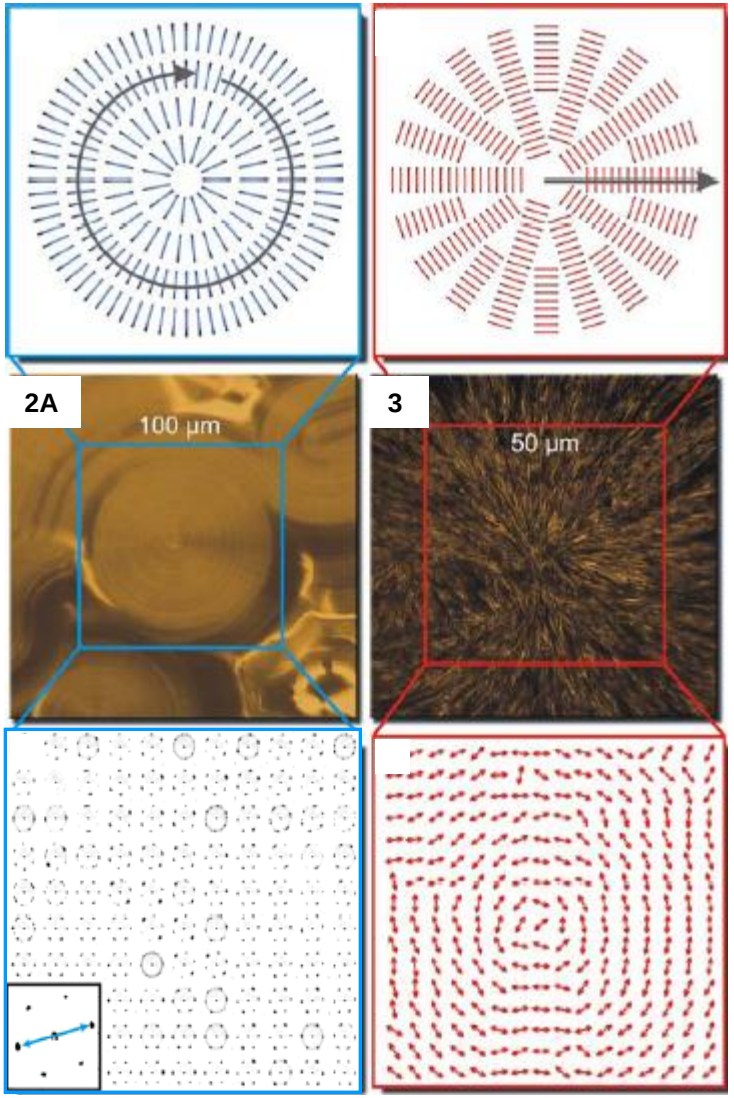
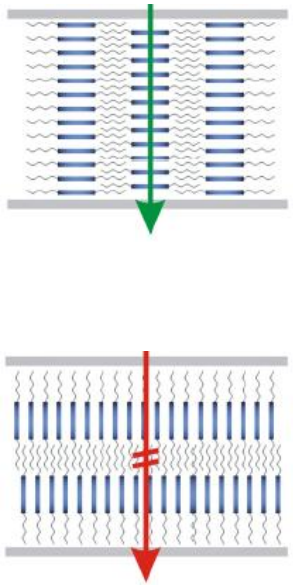
# Discotic Liquid Crystals: Charge-carrier pathways for organic electronics





M. Kastler *et al. Adv. Mater.* 18, 2255 (2006)



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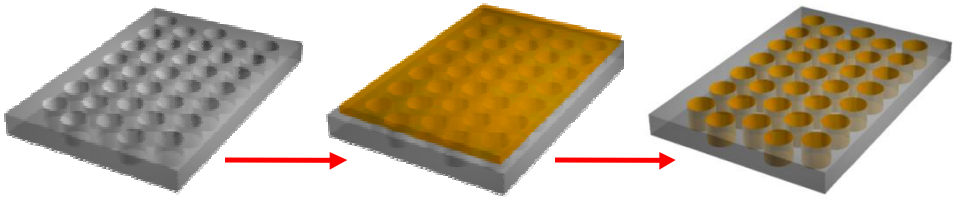
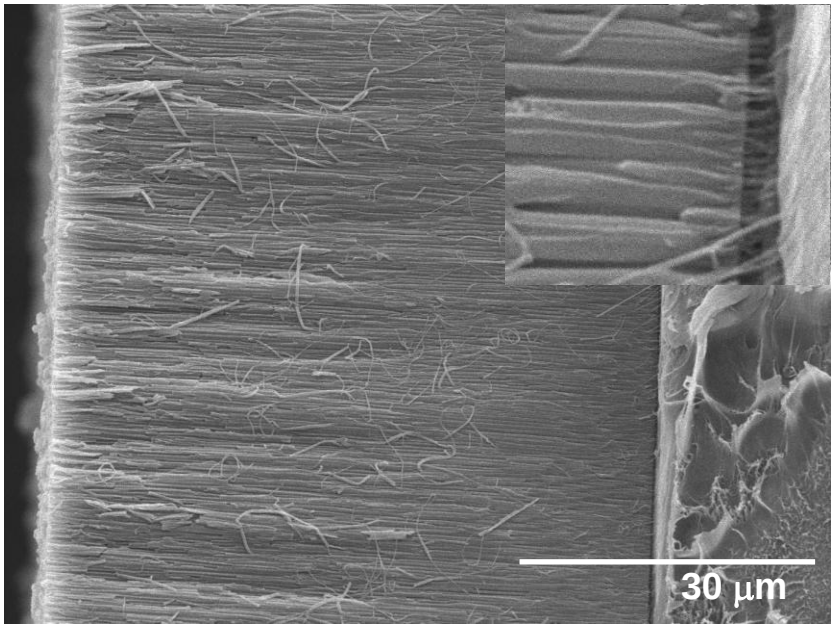
# Confinement effects in polymer nanofibers

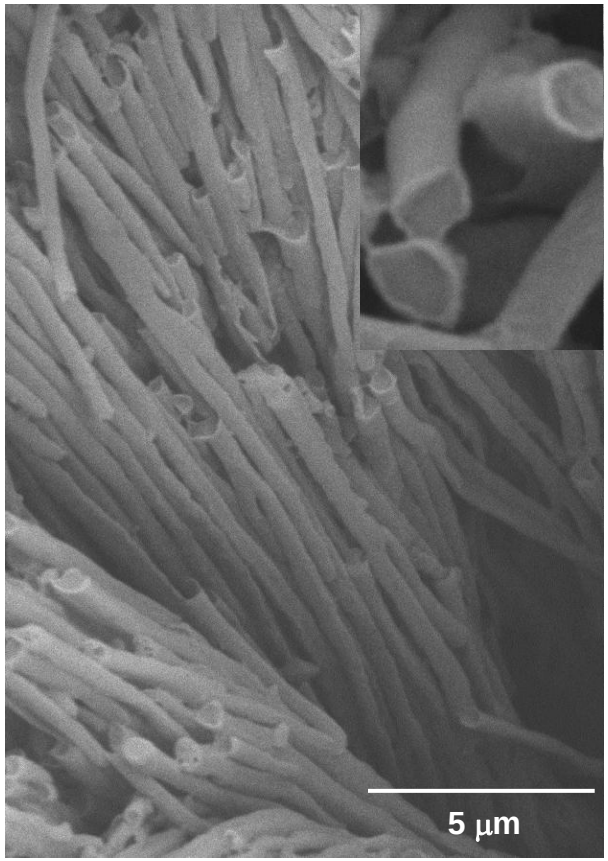
**AAO Membrane + solution (30wt% PVDF-Dimethylacetamide)**



**SEM**




**PVDF nanofibers**




**"Confinement-induced one-dimensional ferroelectric polymer arrays" M.C. García-Gutiérrez, *et al.*; *Nano Letters* 10, 1472 (2010)**



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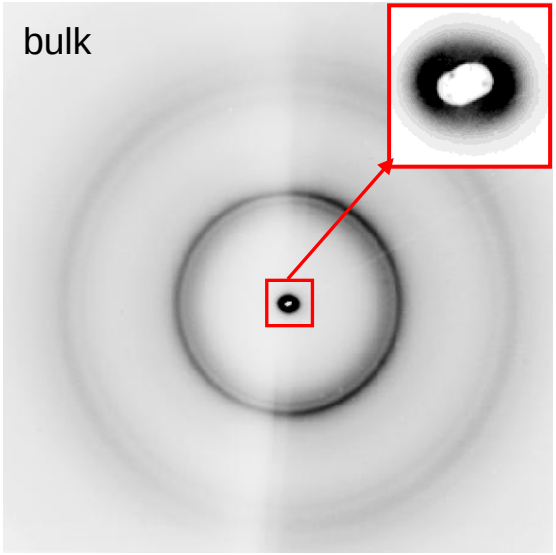
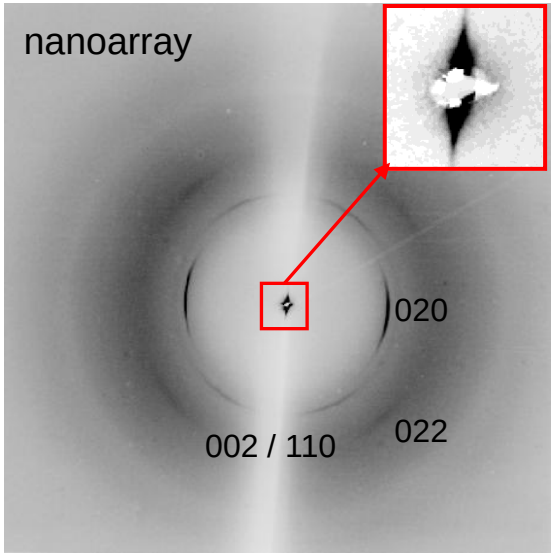
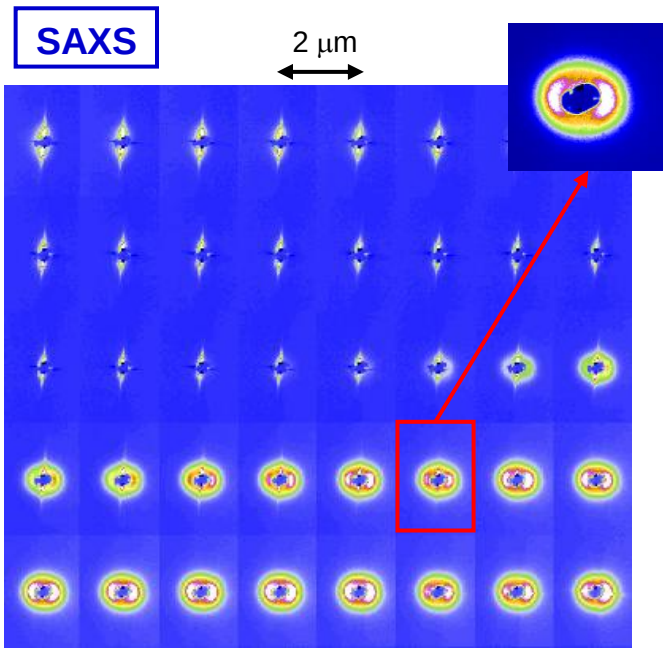
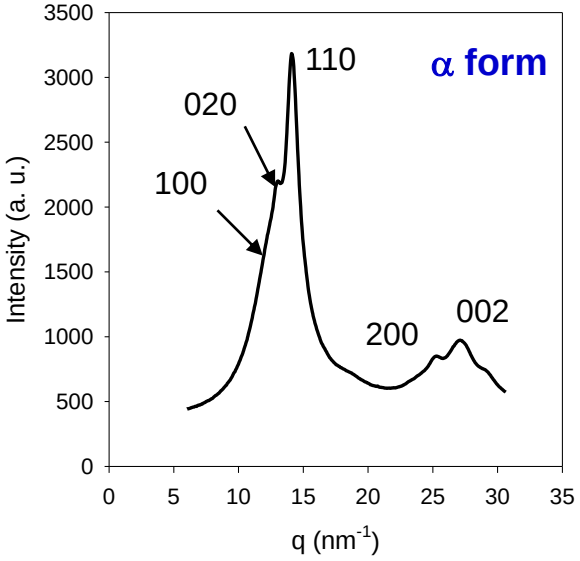
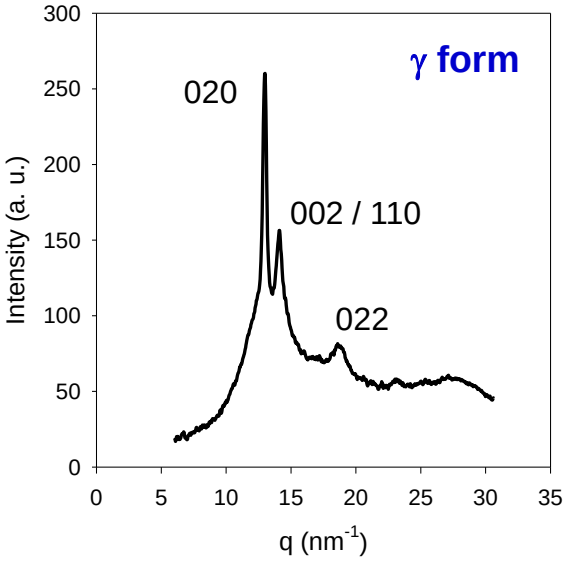
# Confinement effects in polymer nanofibers

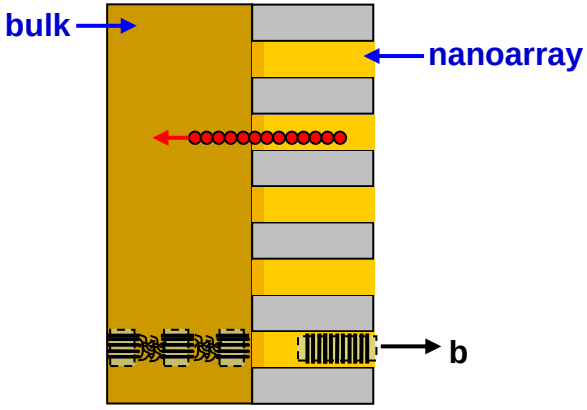


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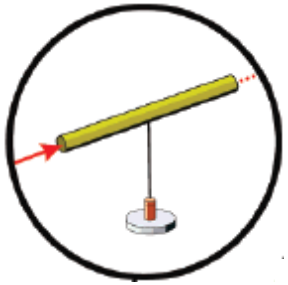
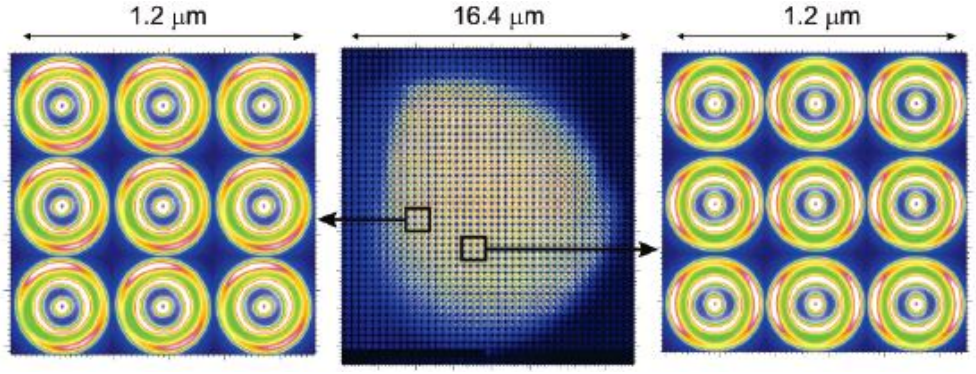
# Other applications

**"Probing the internal structure of high-performance fibers by on-axis scanning diffractometry" R. Davies *et al. Macromolecules* 40, 5038 (2007)**

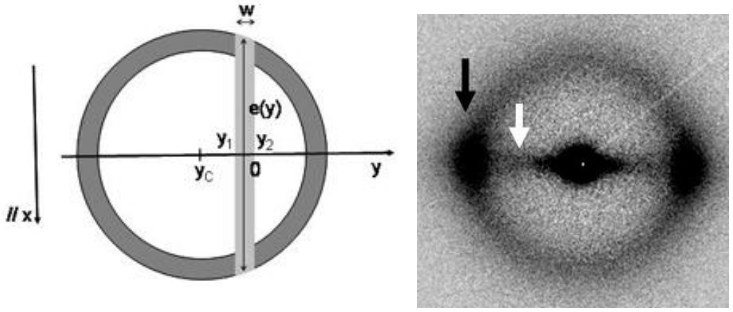


**Tamaño de haz = 500nm**

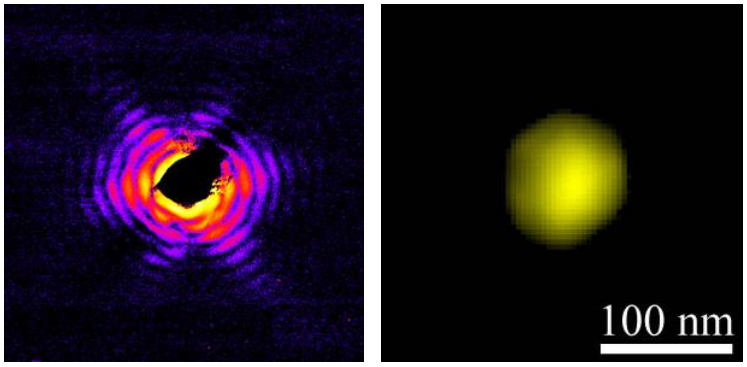



**Beam size< 100 nm**

**"X-ray microdiffraction study of SWCNT alignment across a fiber" V. Pichot *et al. EPL* 79, 46002 (2007)**




**"Coherent X-ray diffraction imaging with nanofocus illumination" C.G. Schroer *et al. PRL* 101, 090801 (2008)**



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# Grazing incidence X-ray scattering


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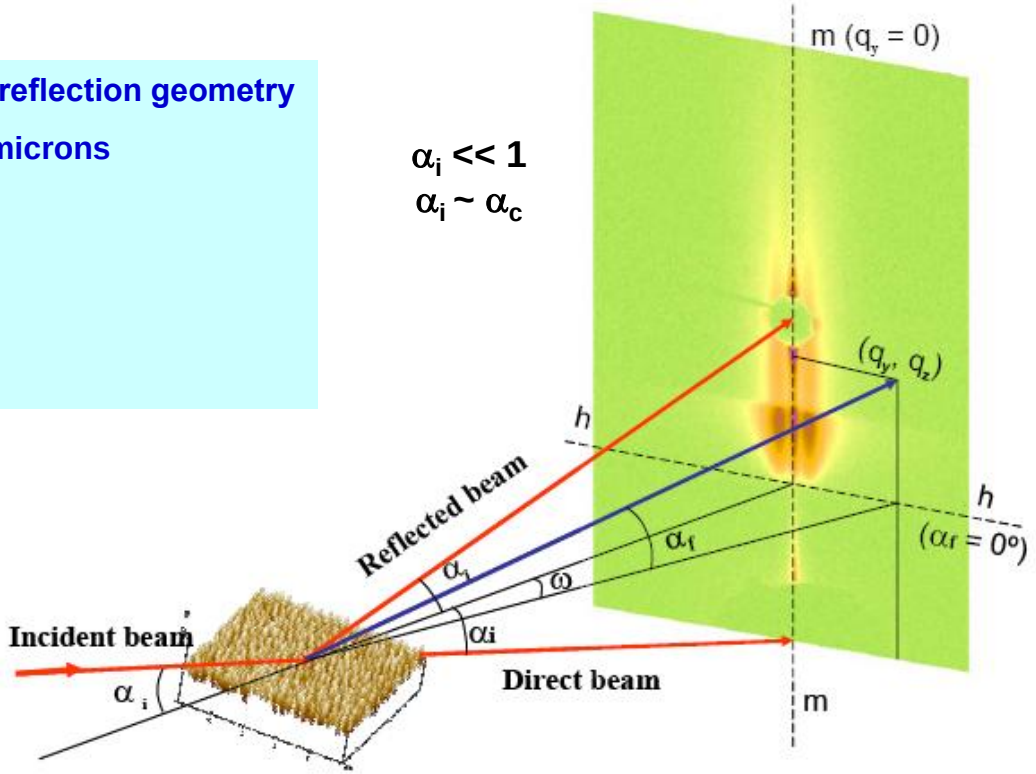
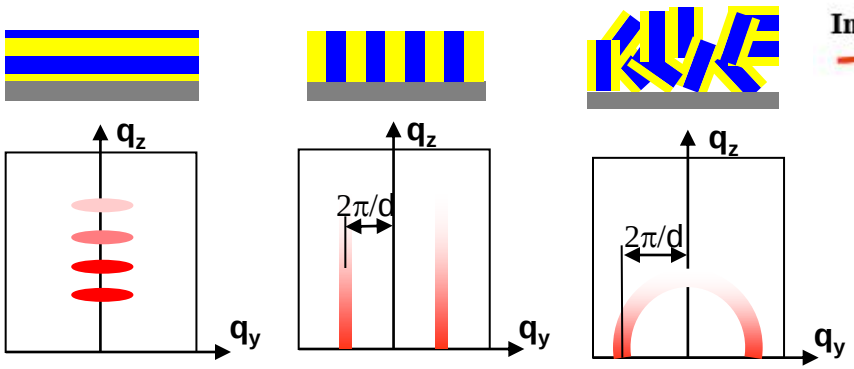
# Grazing incidence X-ray scattering

- GIWAXS/GISAXS → similar to WAXS/SAXS but in reflection geometry
- Length scales range: from Angstroms to several microns
- Structure and morphology: size, shape and order
- Depth sensibility (buried structures)
- Average of illuminated area (~ $cm^2$)
- Real time experiments

$\alpha_i << 1$

$\alpha_i \sim \alpha_c$




$q_z = 2\pi/\lambda \sin(\alpha_i + \alpha_f)$

$q_y = 2\pi/\lambda \sin(\omega)\cos(\alpha_f)$



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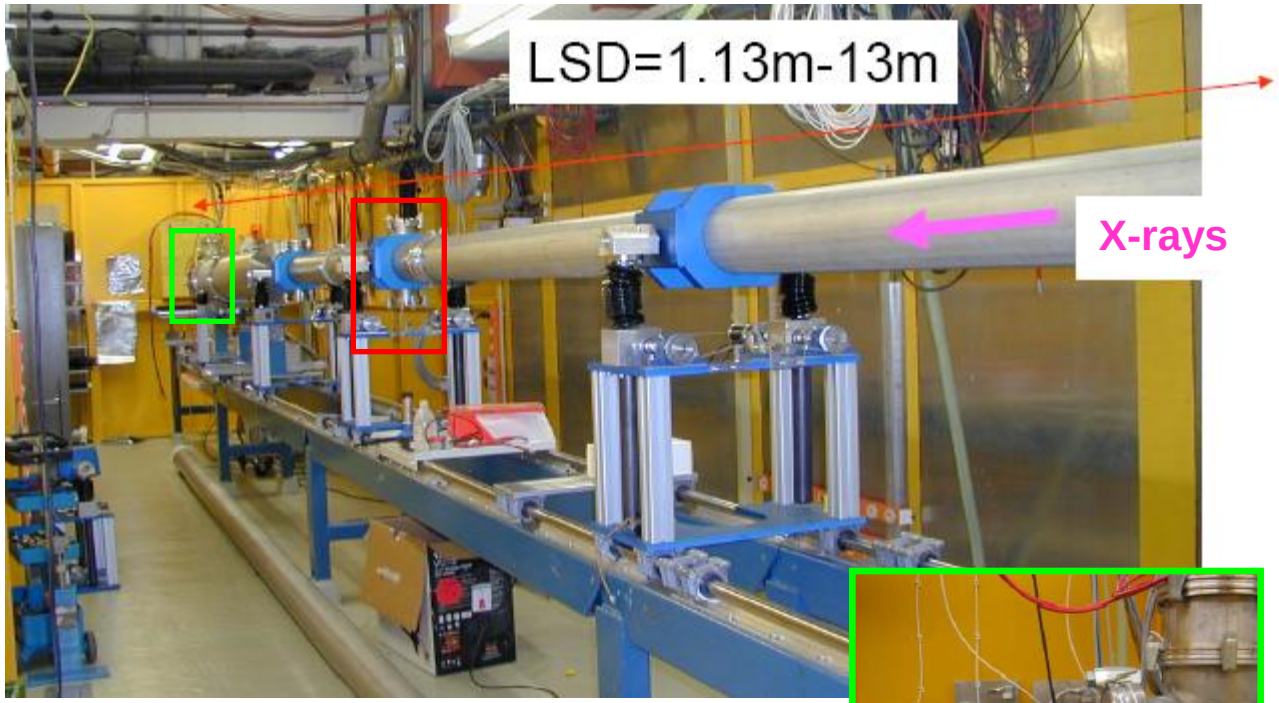
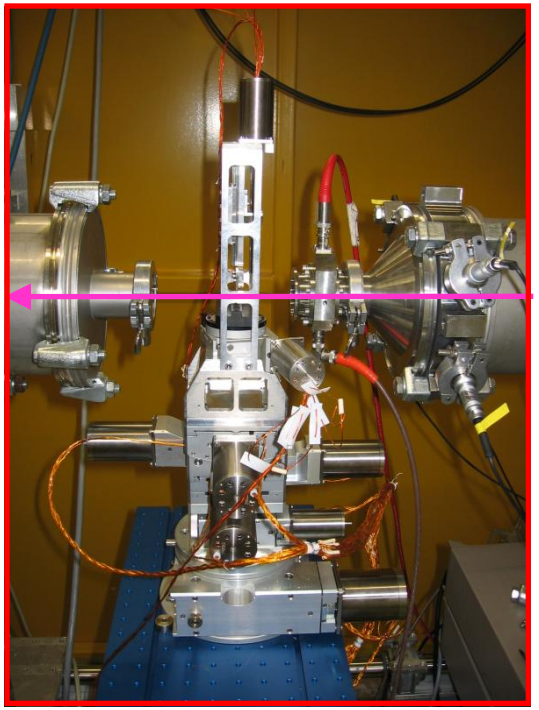
# SAXS and GISAXS beamline

## BW4 beamline @ HASYLAB, Hamburg




Sample environment



Detector

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# Applications of grazing incidence X-ray scattering


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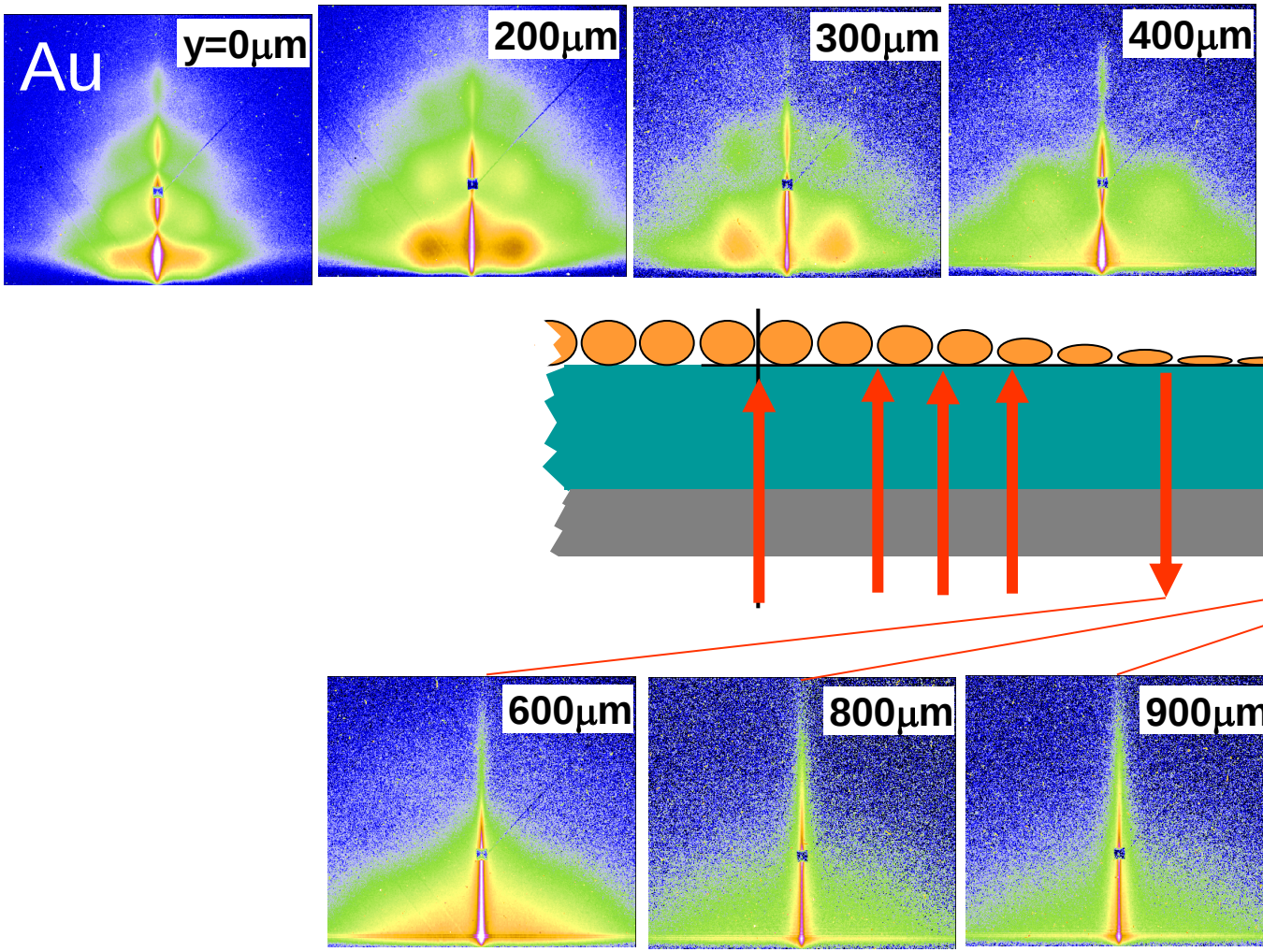
# Sputtered gold nanoparticles on polystirene




"Combinational investigation of the isolated nanoparticle to coalescent layer transition in a gradient sputtered gold nanoparticle layer on top of polystyrene" S. Roth, *et al.*; *Appl. Phys. Lett. 88*, 021910 (2006)



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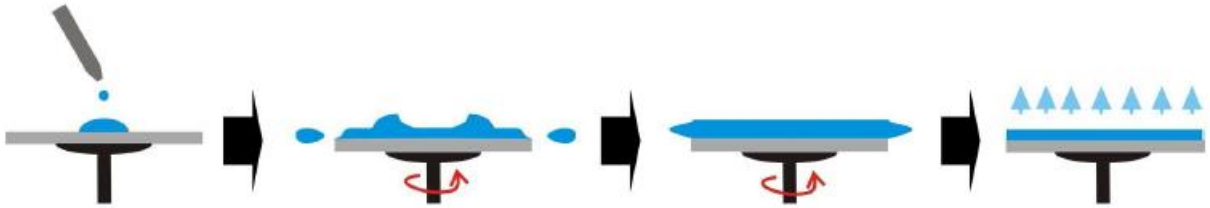
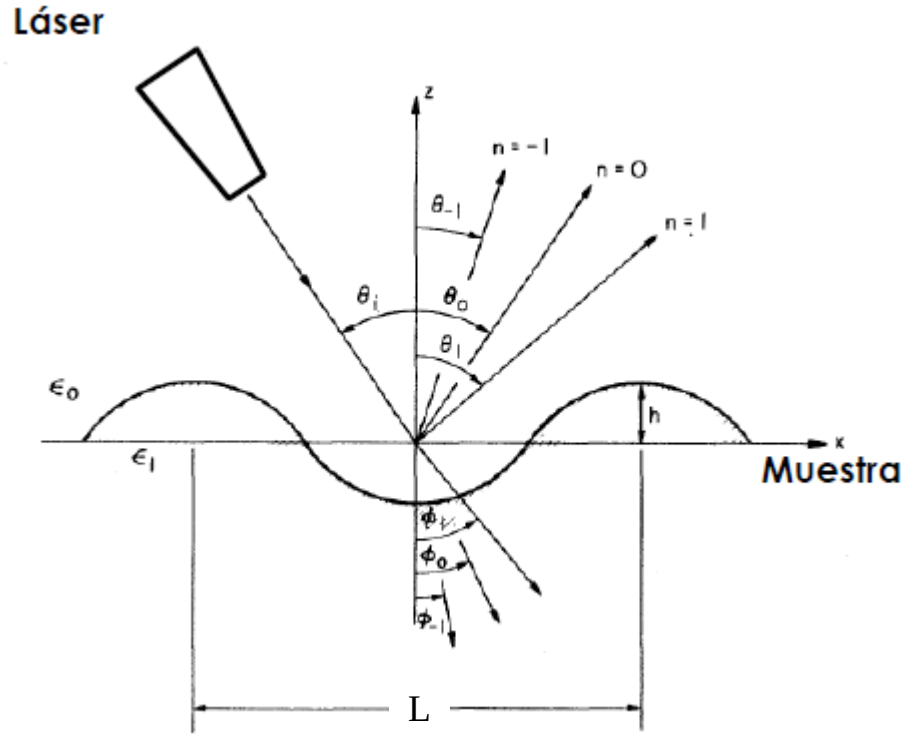
# Laser-Induced Periodic Surface Structures (LIPSS)

**Thin films: Spin-Coating**

Thickness(~nm) : concentration; ω



**LIPSS:** Interference between the incident light and the light dispersed by the surface.




Periodicity: $$L = \frac{\lambda}{n - \sin(\theta)}$$

Laser parameters:

- Wavelength (266 nm)
- Fluence (~ mJ/cm$^2$)
- Number of pulses



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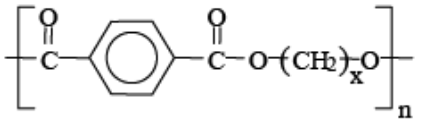
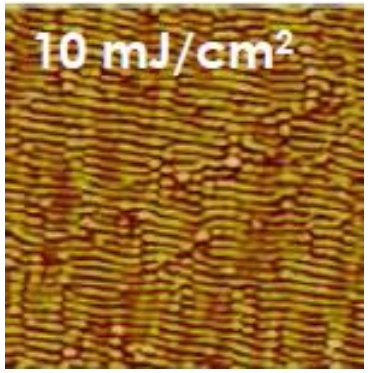
# Laser-Induced Periodic Surface Structures (LIPSS)

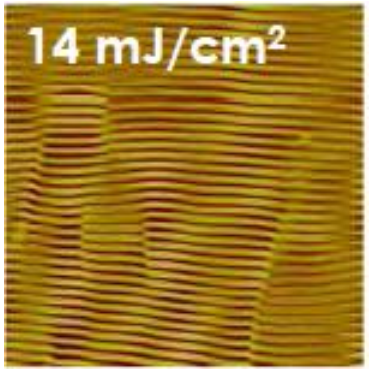
**AFM**

**Poly (trimethylene terephthalate) (PTT), x=3**

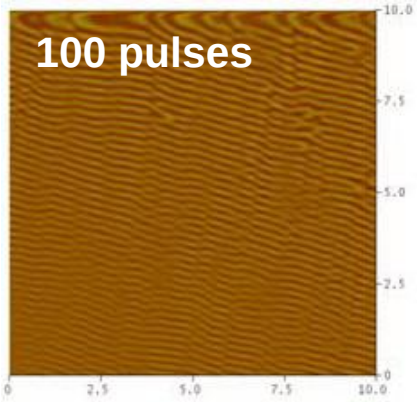


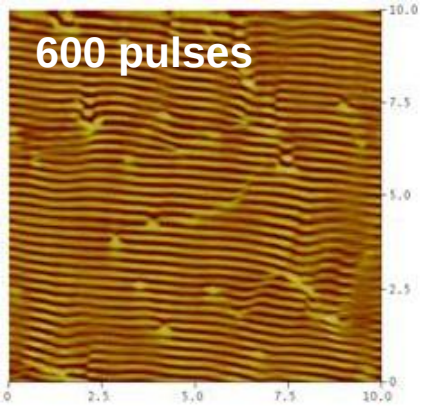
**600 pulses**

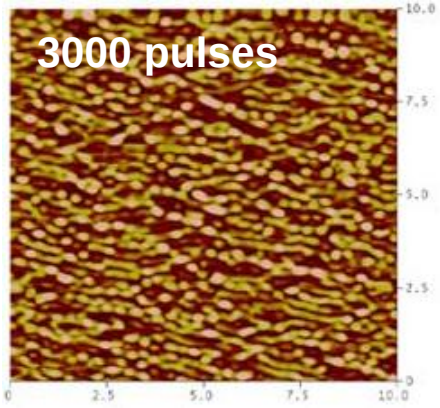




**Fluence: 7 mJ/cm²**




I. Martín-Fabiami, *et al.*; *Langmuir* 28, 7938 (2012)



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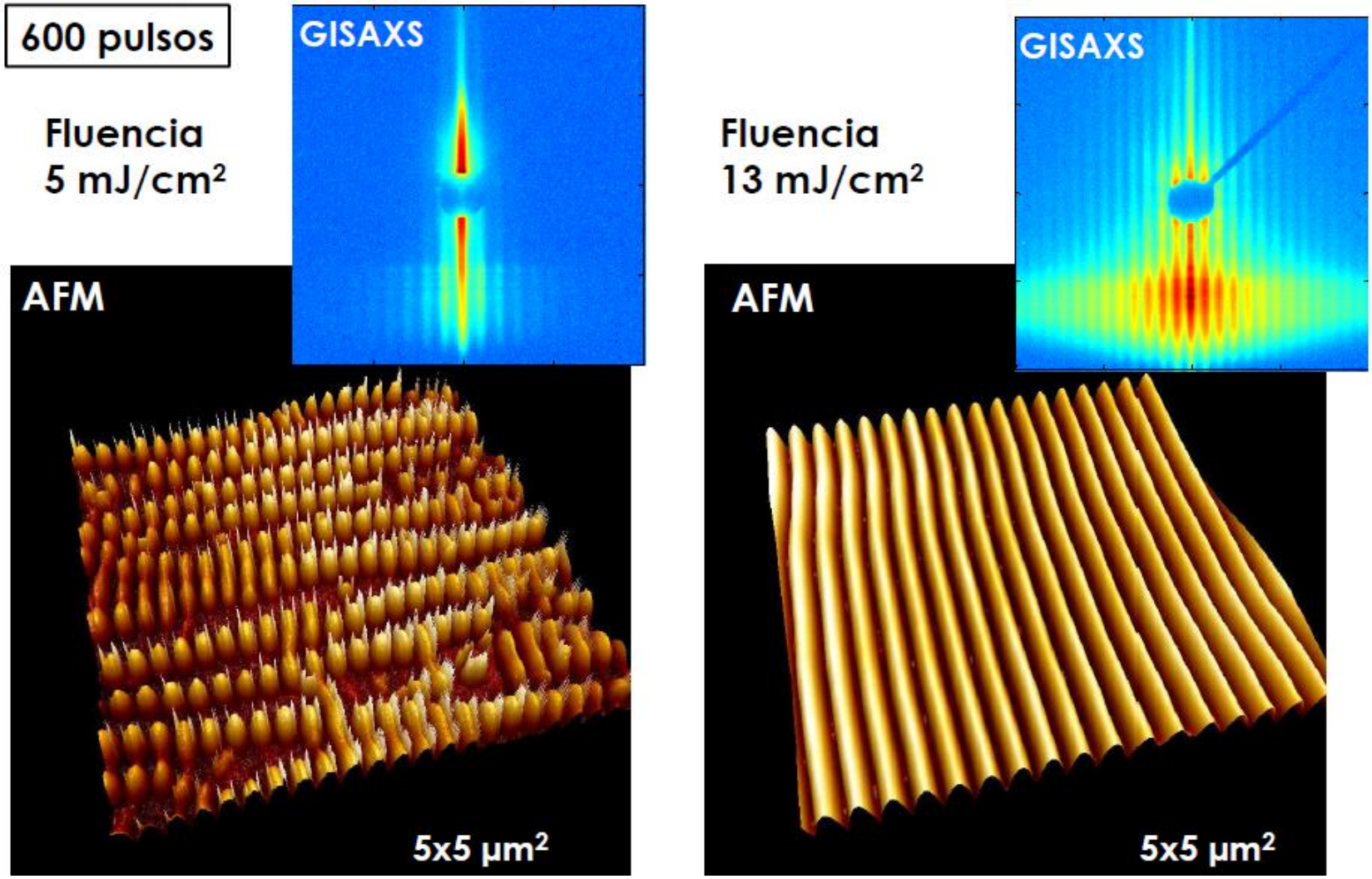
# Laser-Induced Periodic Surface Structures: GISAXS



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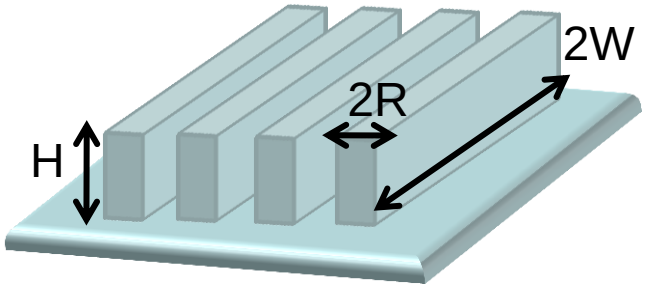
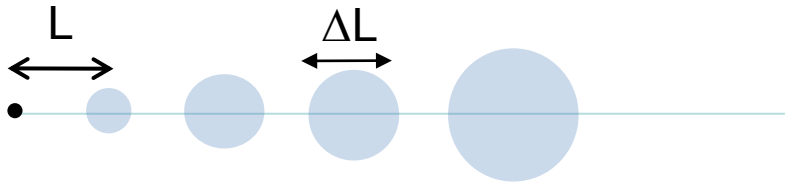
# Simulated GISAXS

H; R; W: Measured by AFM



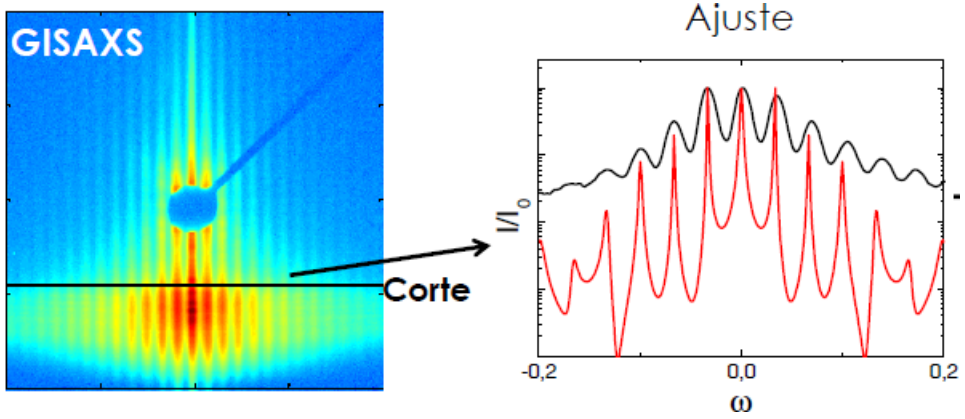

In order to assess the level of order we used a one-dimensional paracrystalline lattice

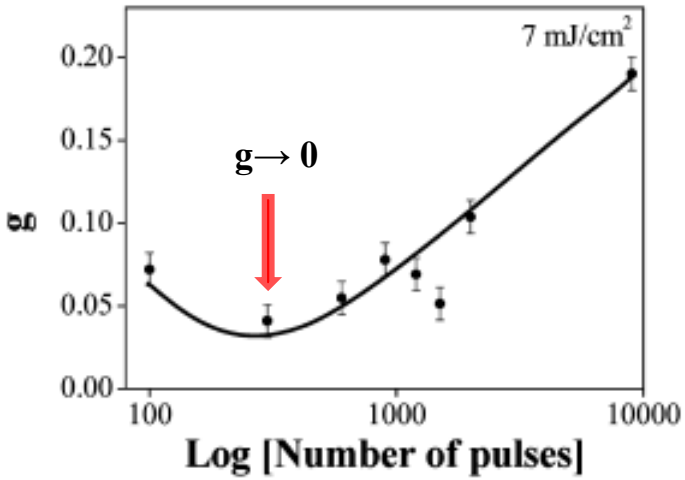



The probability of finding a particle at a distance L is defined by a probabilistic function p(x)

paracrystalline distortion parameter: **g**= ΔL/L

**IsGISAXS** http://www.insp.jussieu.fr/axe2/Oxydes/IsGISAXS/isgisaxs.htm, 2002



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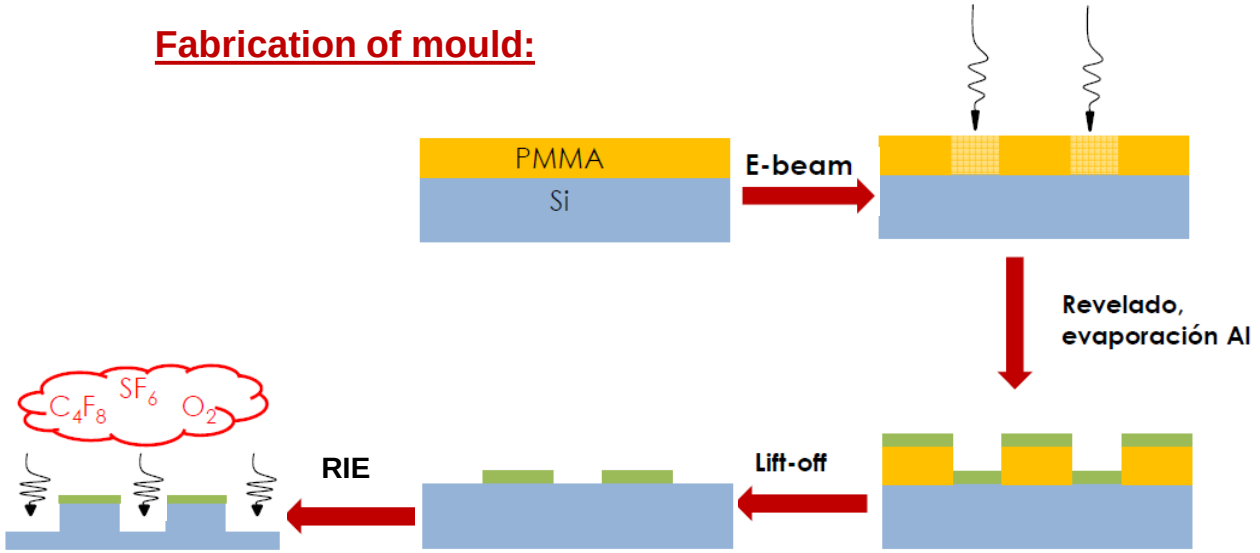
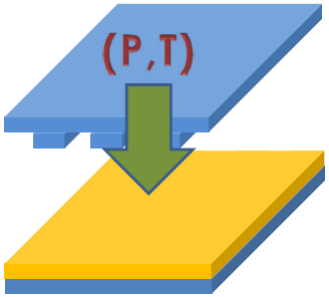
# Nanoimprint lithography (NIL)

**Clean room (IMB-CSIC)**

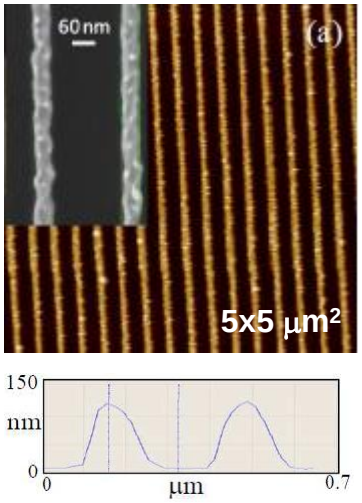
## Fabrication of mould:



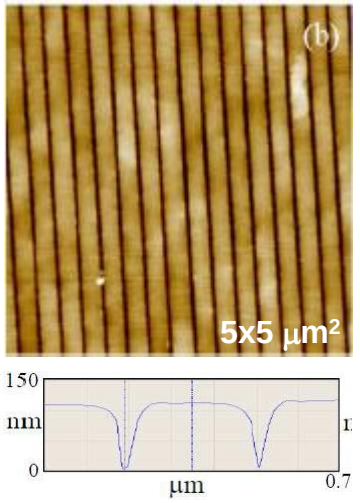

## Nanoimprint:




**Mould**




**NIL**



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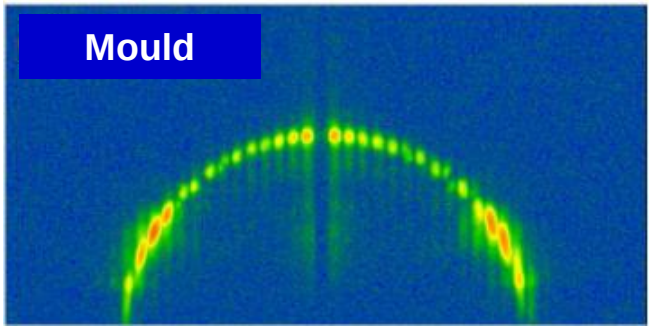
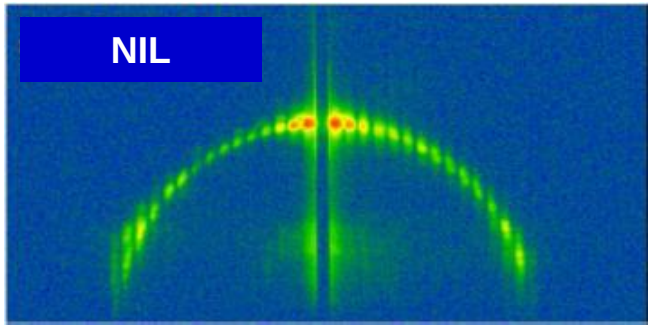
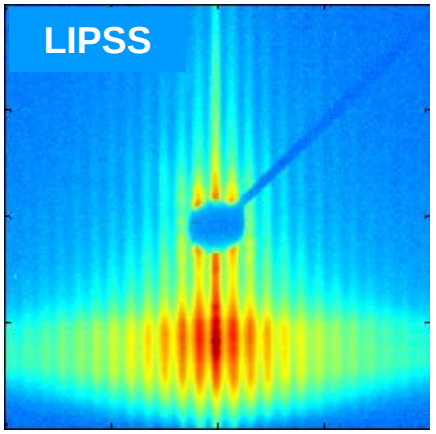
# GISAXS: NIL vs LIPSS

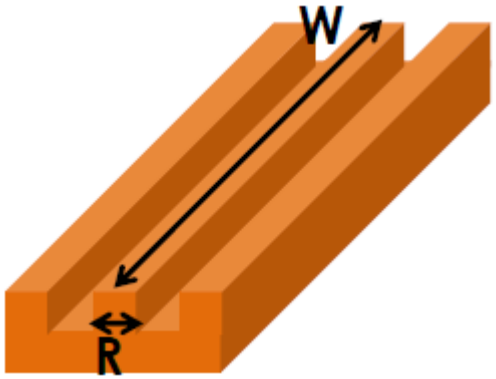
**Experimental GISAXS:**

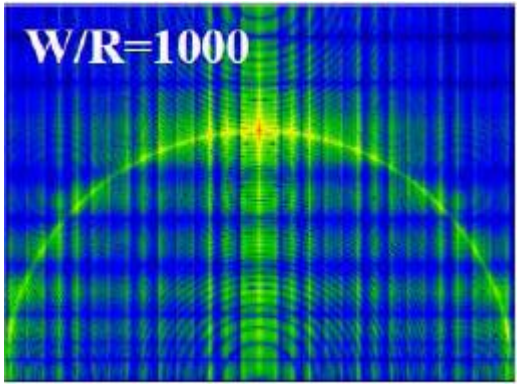


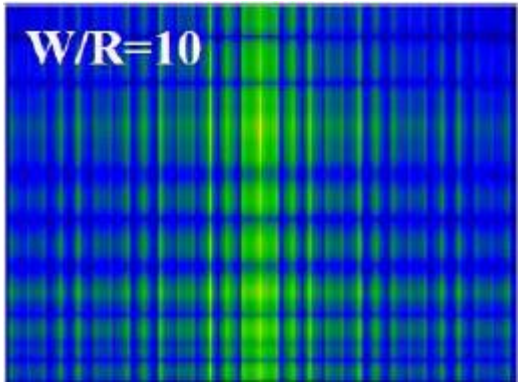




**Simulated GISAXS:**




D.R. Rueda *et al.*; *J. Appl. Cryst.* 45, 1038 (2012)



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# X-ray scattering beamlines in the world


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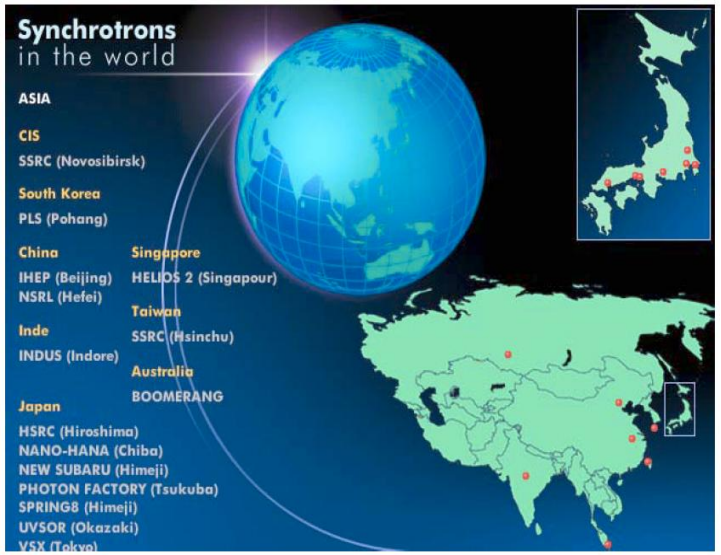
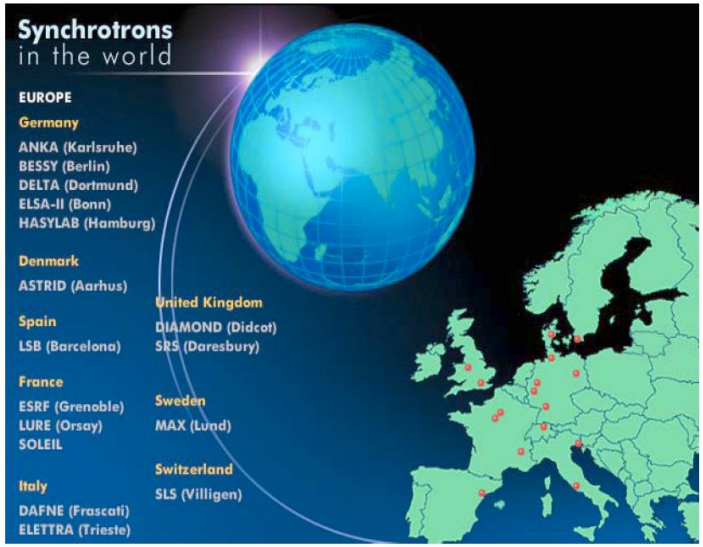
# Líneas de dispersión de rayos X


- **Europe: - ESRF: ID2, ID10, ID13, BM26**
  - **Alba:NCD**
  - **Diamond: I22**
  - **Soleil: SWING**
  - **BESSY: μSpot**
  - **Elettra: BL5.2L**
- **UUEE: - APS: 1-ID, 8-ID, 18-ID**
  - **ALS: 7.3.3**
- **Asia: - Spring-8: BL08B2, BL40B2, BL45XU**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# Bibliography


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- ✓ **Neutrons, X-rays and Light: Scattering Methods Applied to Soft Condensed Matter P. Lindner, T. Zemb Ed., Elsevier: 2002.**
- ✓ **Small Angle X-ray Scattering, O. Glatter, O. Kratky Ed., Academic Press, London (1982).**
- ✓ **Synchrotron Light to Explore Matter, ISBN 3-540-14888-4 © Copyright IMediaSoft® (Bucharest and Meylan) ESRF (Grenoble) and Springer-Verlag (Berlin, Heidelberg) 2001.**
- ✓ **Applications of Synchrotron Light to Scattering and Diffraction in Materials and Life Sciences, T.A. Ezquerra, M.C. García-Gutiérrez, A. Nogales, M.A. Gómez Ed., Lect. Notes Phys. 776 Springer, (Berlin, Heidelberg) 2009.**
- ✓ **AUSE:** http://auseweb.wordpress.com/
- ✓ **ESUO:**http://www.elettra.trieste.it/ELISA/index.php?n=Main.EuropeanSynchrotronUserOrganization