

Estudio Morfológico de Polímeros por medio de Luz Sincrotrón

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**Escuela en Ciencia e Ingeniería de Materiales
(27 de junio al 1 de julio, 2005) , México D.C.**

Estudio de morfología de polímeros por medio de sincrotrón de rayos X y métodos combinados con él

3. Dispersión de Rayos X con luz sincrotrón en materiales poliméricos (dos horas)

- a. Conceptos generales de física de polímeros: estructura y dinámica
- b. Cristalización en polímeros
- c. Caracterización de la estructura en polímeros mediante dispersión de rayos X a ángulos altos y bajos con resolución temporal.
- d. Cristalización de polímeros en medios confinados: mezclas poliméricas
- e. Transformaciones de fase en cristales líquidos poliméricos.
- f. Estructura en materiales compuestos poliméricos basados en nanotubos de carbono.

Brevísima Bibliografía

1. B. Chu, B.S. Hsiao, Chem. Rev. 2001, 101, 1727-1761
2. A. Nogales, I. Sics, T. A. Ezquerra, Z. Denchev, F. J. Balta Calleja, B. S. Hsiao, Macromolecules 2003, 36, 4827-4832
3. I. Sics, A. Nogales, T. A. Ezquerra, Z. Denchev, and F. J. Balta –Calleja, Review of Scientific Instruments, 71,4, 2000
4. A. Nogales, T. A. Ezquerra, Z. Denchev, I. Sics, F. J. Balta-Calleja, J. of Chemical Physics, 115, 8, 2001
5. C. Alvarez, I. Sics, A. Nogales, Z. Denchev, S.S. Funari, T.A. Ezquerra, Polymer 45 (2004) 3953–3959.

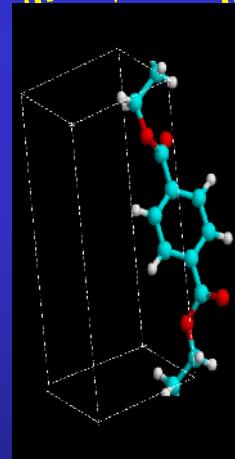
Resultados obtenidos por:

Aurora Nogales
Mari Cruz García
Alejandro Sanz
Cristiana Alvarez
Igors Sics
Daniel Rueda
Tiberio Ezquerra

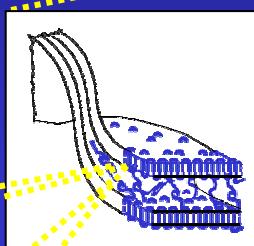
Cristalización de Polímeros: Jerarquía Estructural



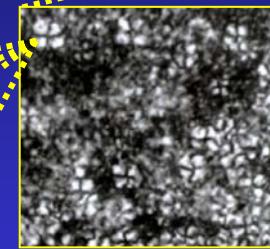
$$T_g < T < T_m$$



$5 \times 10^{-10} \text{ m}$
X-ray Diffraction
Neutron Diffraction



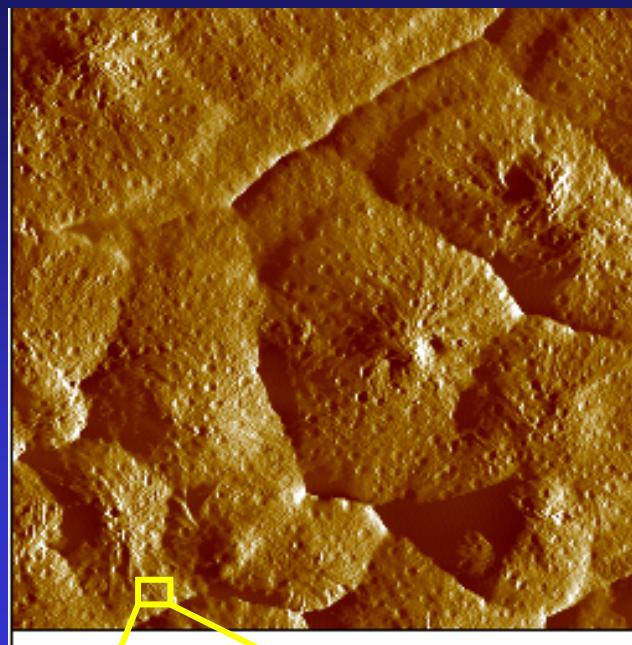
SAXS
SANS
AFM



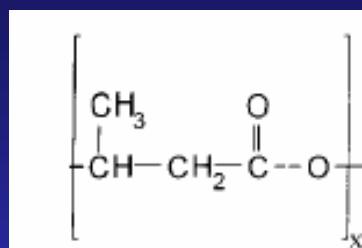
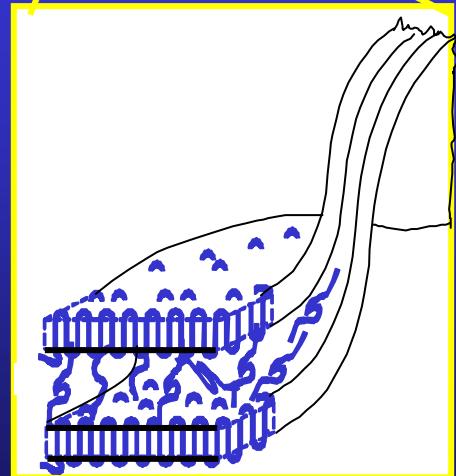
10^{-5} m
Light Scattering
Optical Microscopy
AFM



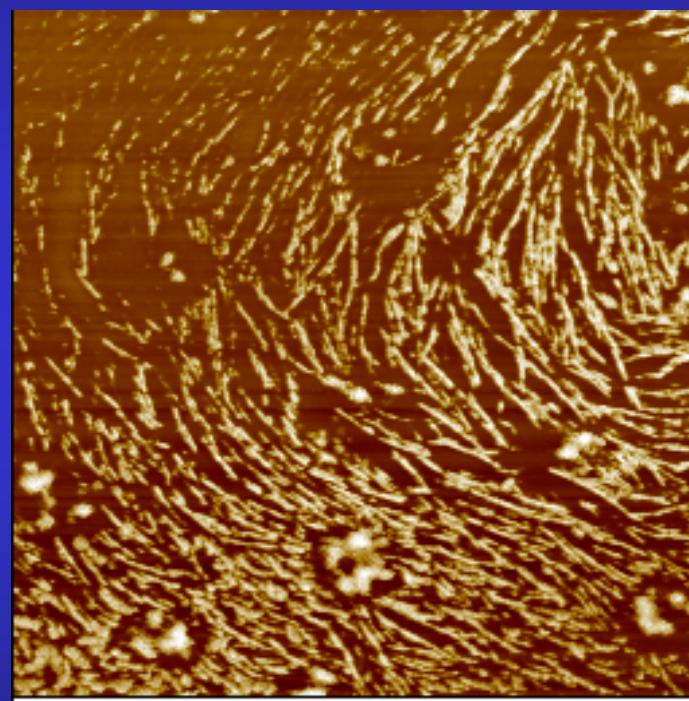
10^{-1} m
Eyes



0 10.0 μm



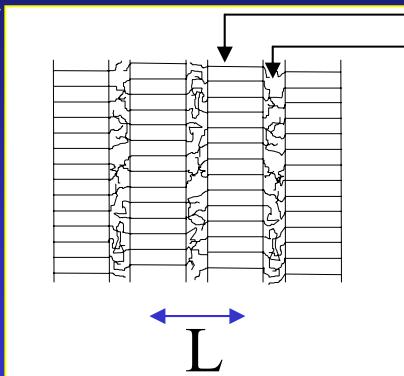
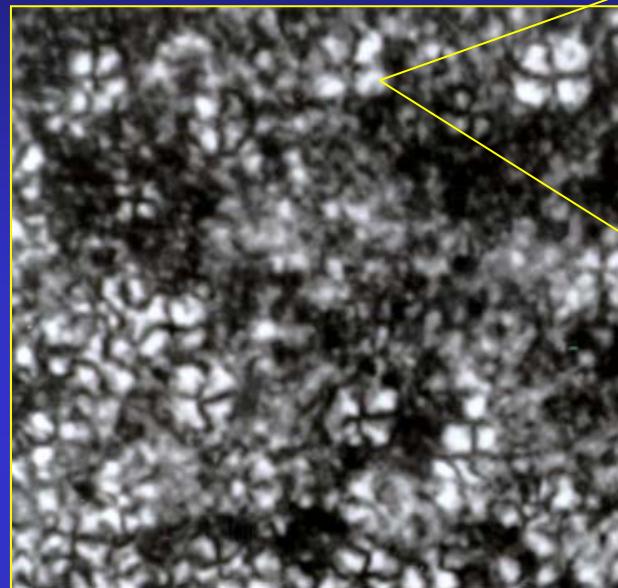
PHB-AFM



0 1.00 μm

M.J. Capitán, D.R. Rueda IEM-CSIC

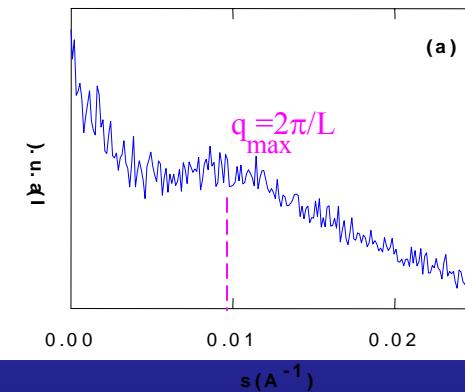
Técnicas Experimentales



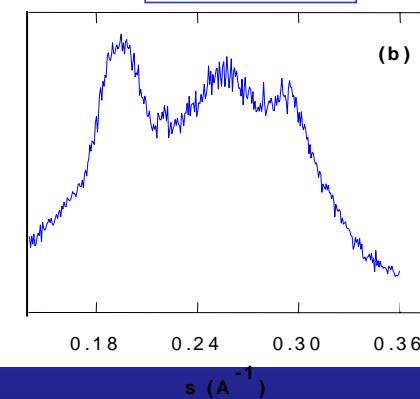
Fase cristalina
Fase amorfa

Estructura

SAXS



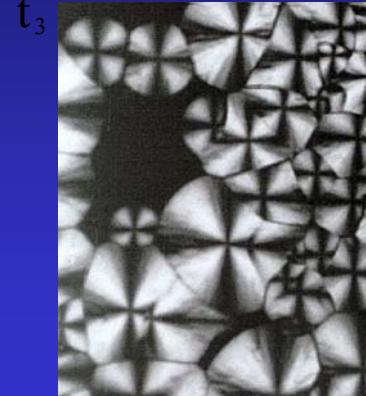
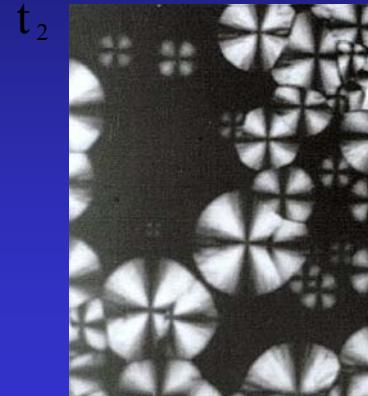
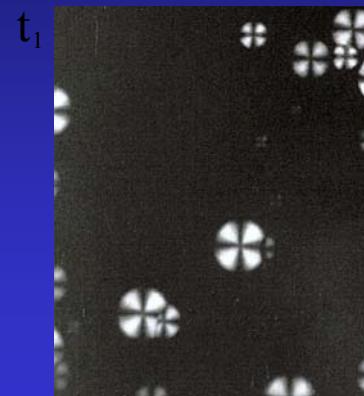
WAXS



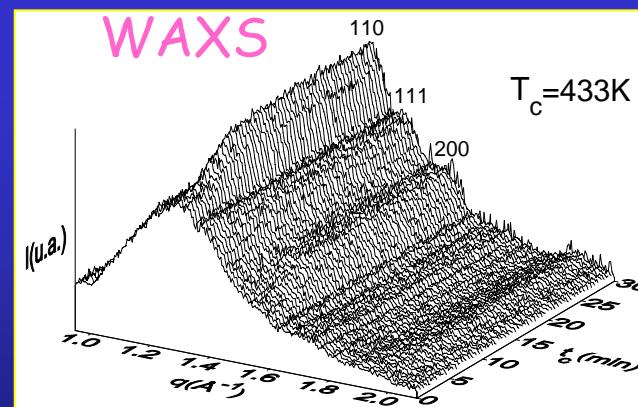
¿Porqué luz Sincrotrón?

Procesos Dinámicos

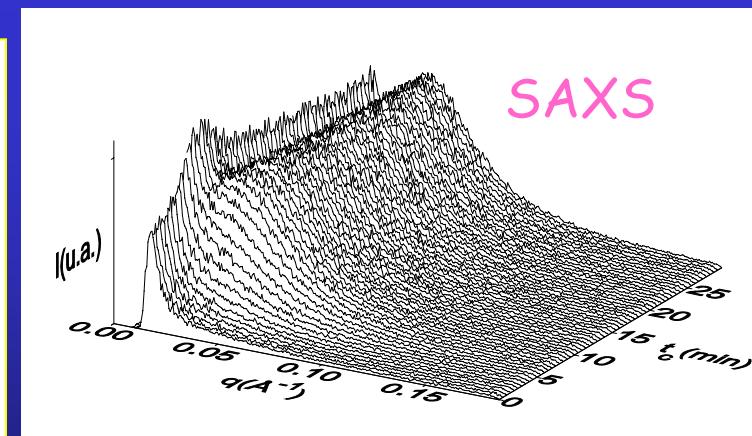
tiempo



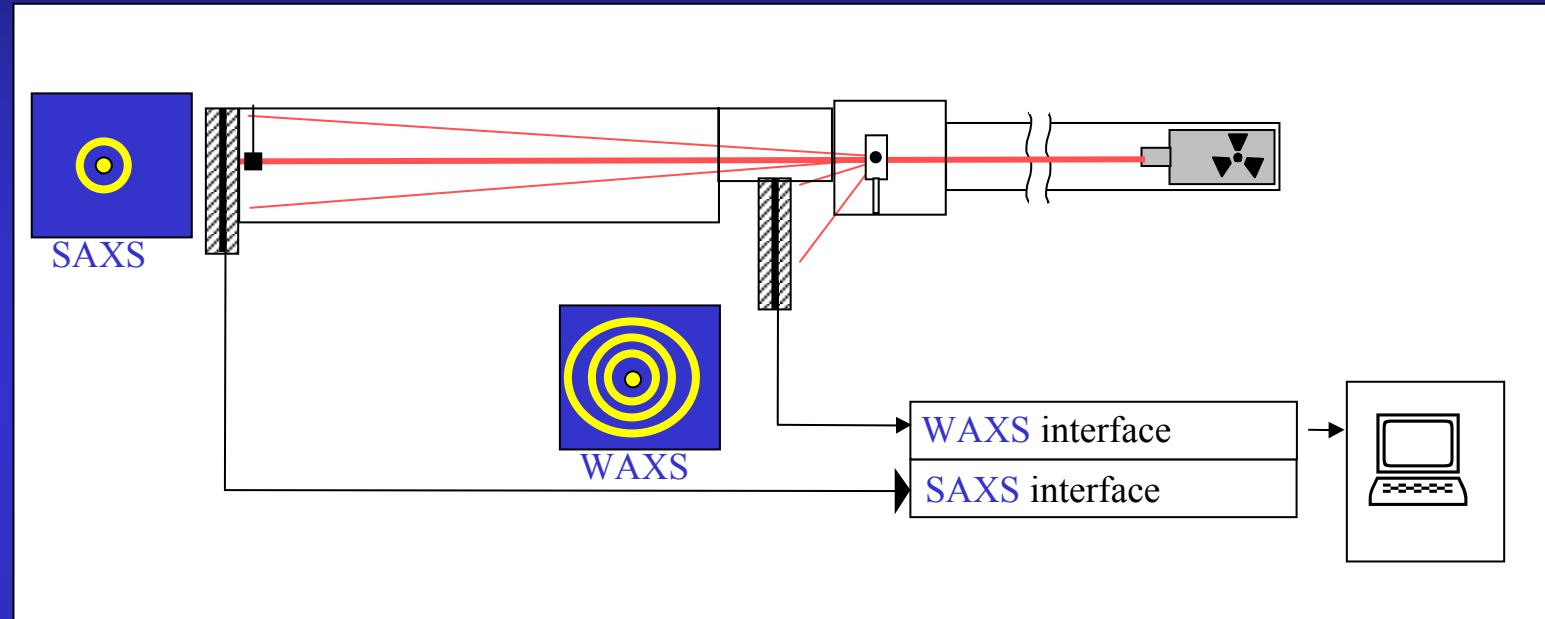
WAXS



SAXS



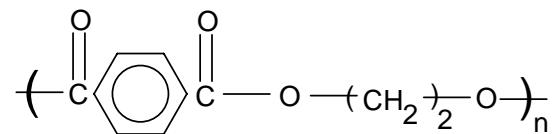
Esquema del sistema experimental



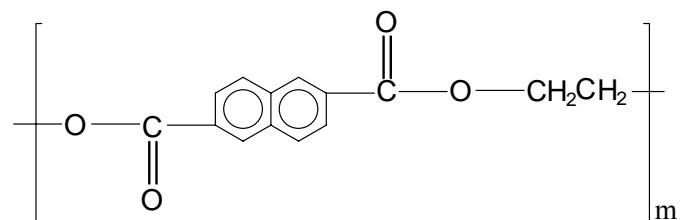
$$\text{Ley de Bragg} \quad d = \lambda / (2 \sin \theta)$$

Muestras Poliméricas

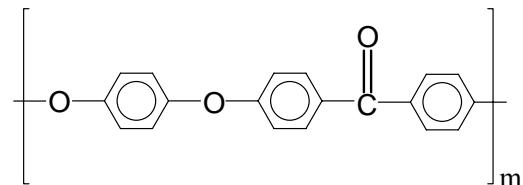
$T_g ({}^\circ C)$



PET 75



PEN 117

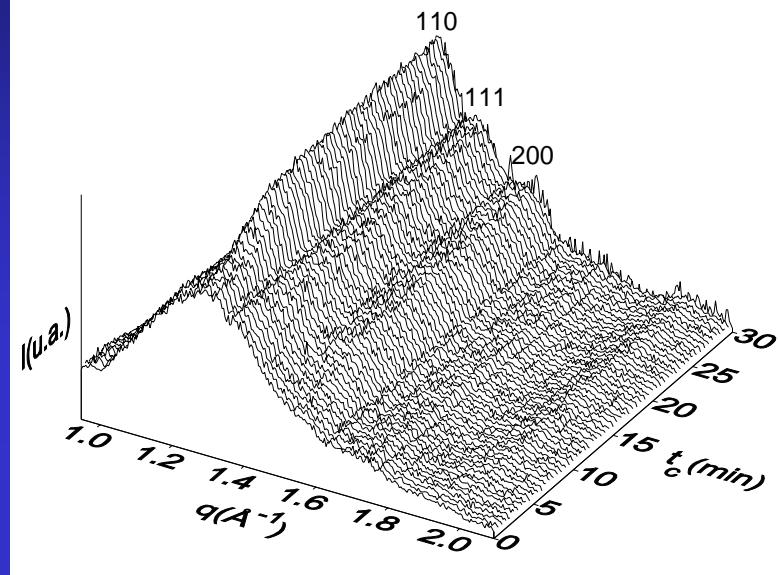


PEEK 145

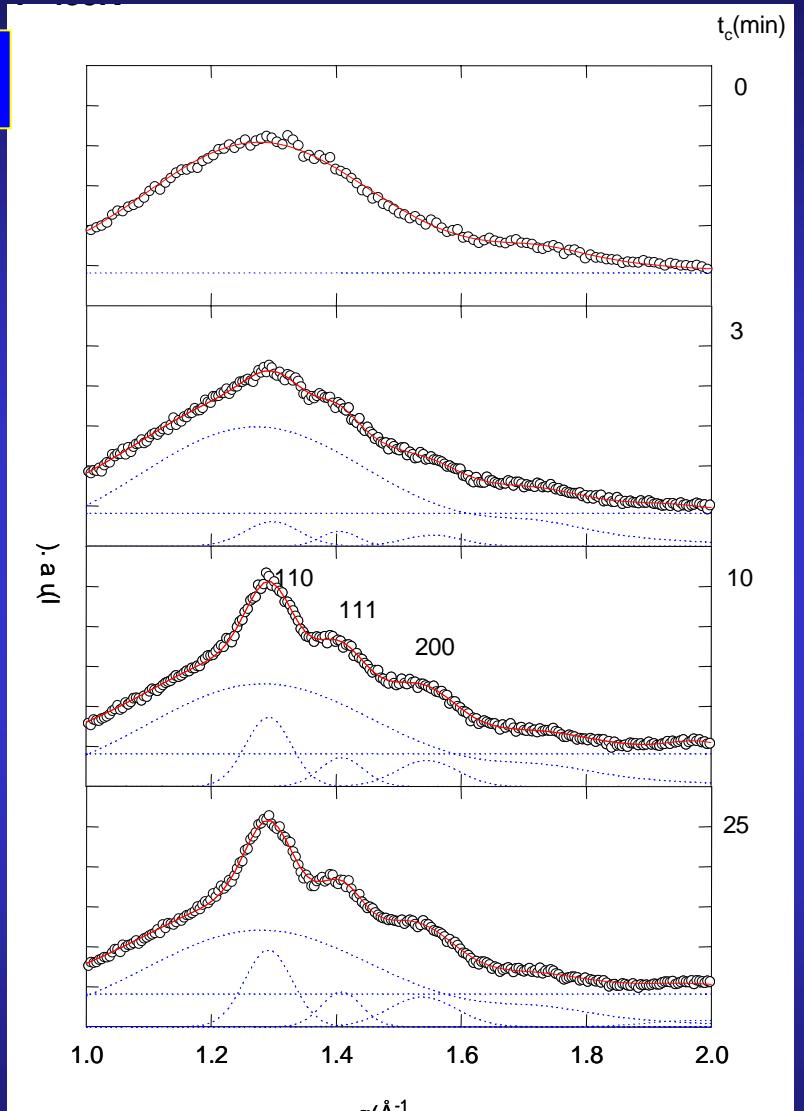


Rayos-X : PEEK

$T_c = 160^\circ C$



$$\text{Cristalinidad} = \frac{\text{Fracción de cristales}}{\text{Fracción total}}$$

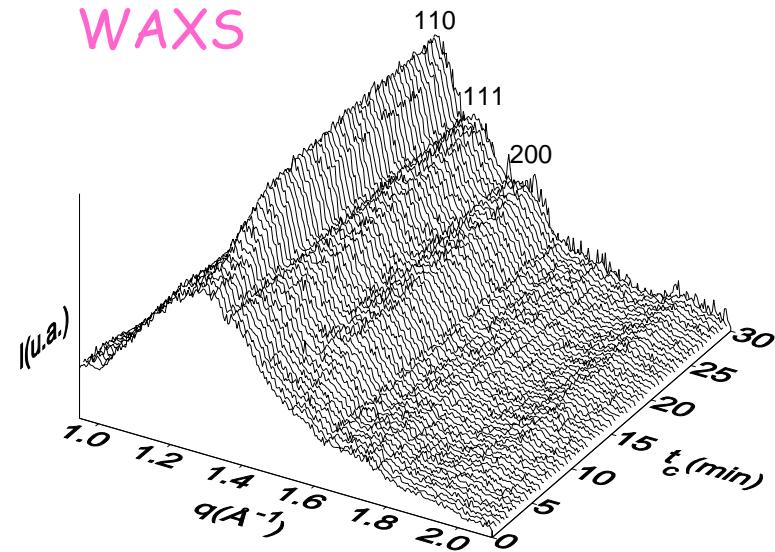


Rayos-X

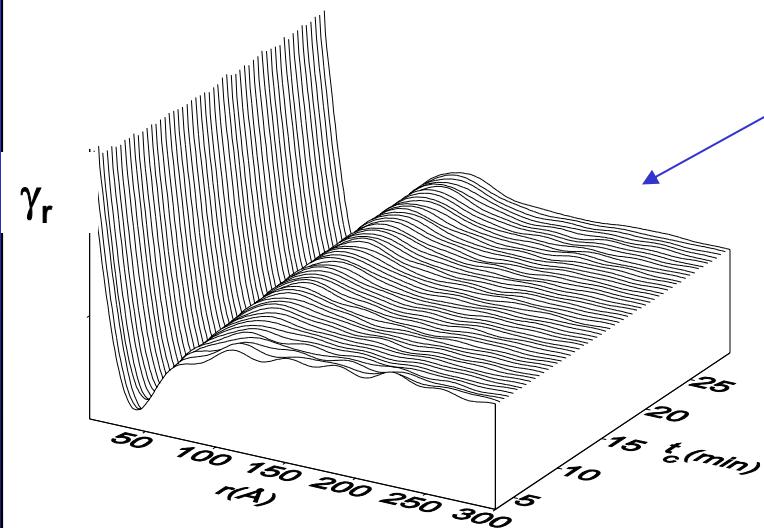
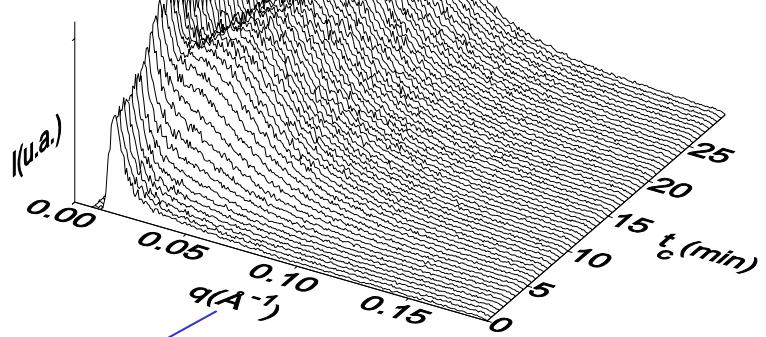
T_c = 160 °C

PEEK

WAXS



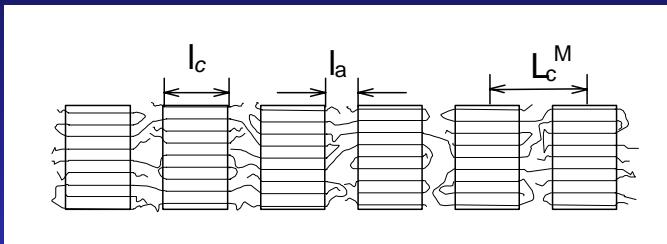
SAXS



$$\gamma(\vec{r}) = \mathfrak{I}^{-1}[\hat{I}(\vec{q})] = \int_V \hat{I} e^{-i\vec{q}\vec{r}} d\vec{q}$$

$$\gamma = \rho * \rho = \int_V \rho_a \rho_{a+r} d\vec{a}$$

Ángulos pequeños en polímeros: función de correlación



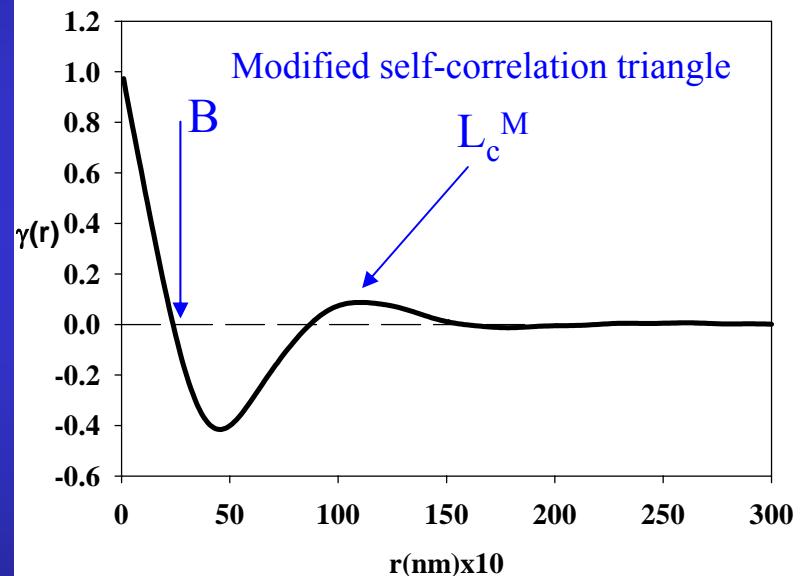
$$\gamma(r) = \int_0^{\infty} I_{corr} \cos(qr) dq$$

$$x_1 \cdot x_2 = \frac{B}{L_c^M}$$

$$x_1 + x_2 = 1$$

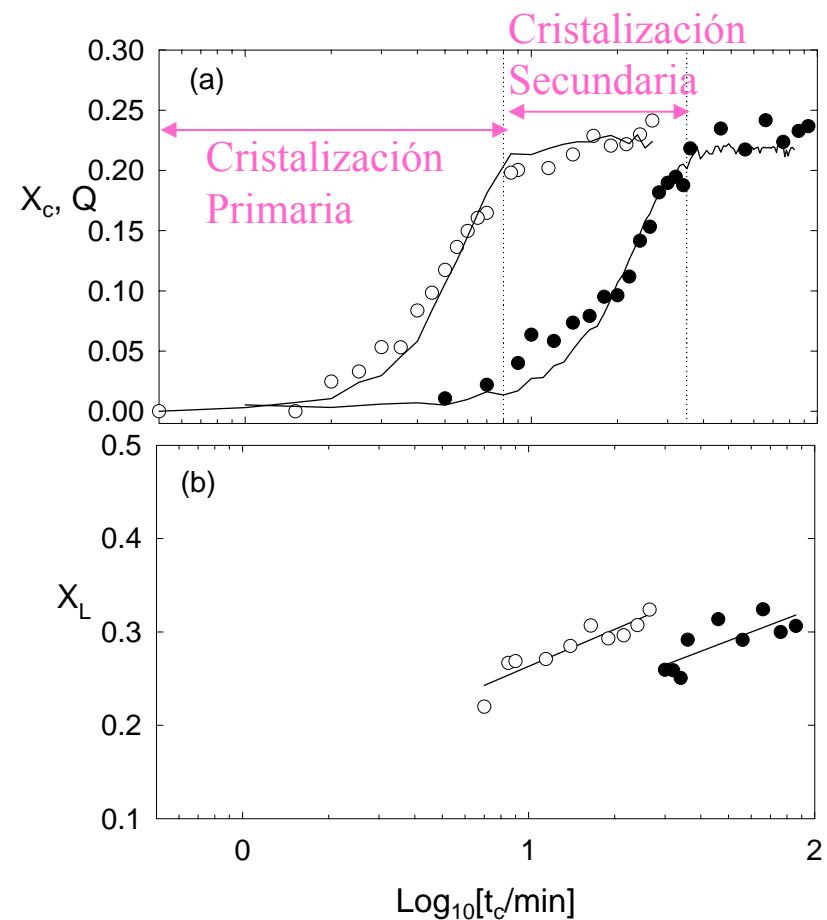
$$l_1 = x_1 \cdot L_c^M$$

$$l_1 + l_2 = L_c^M$$



Rayos-X

PEEK



$$X_c = X_s \cdot X_L \cdot X_{cL}$$

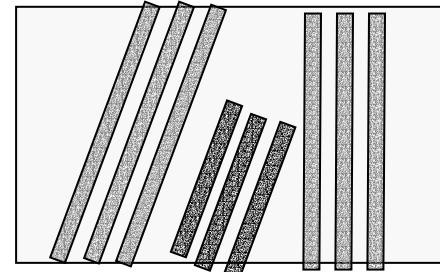
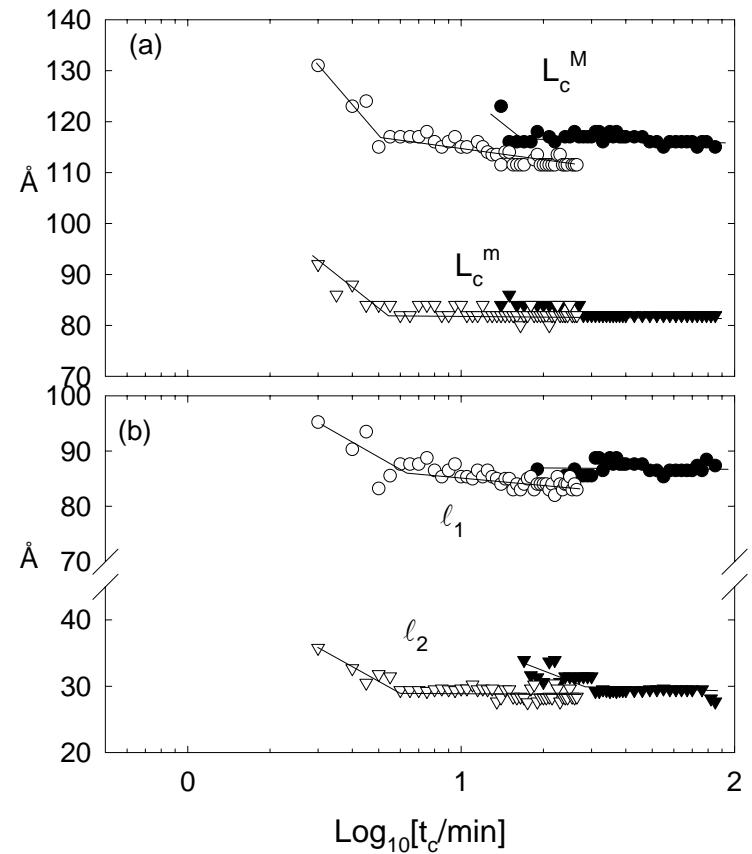
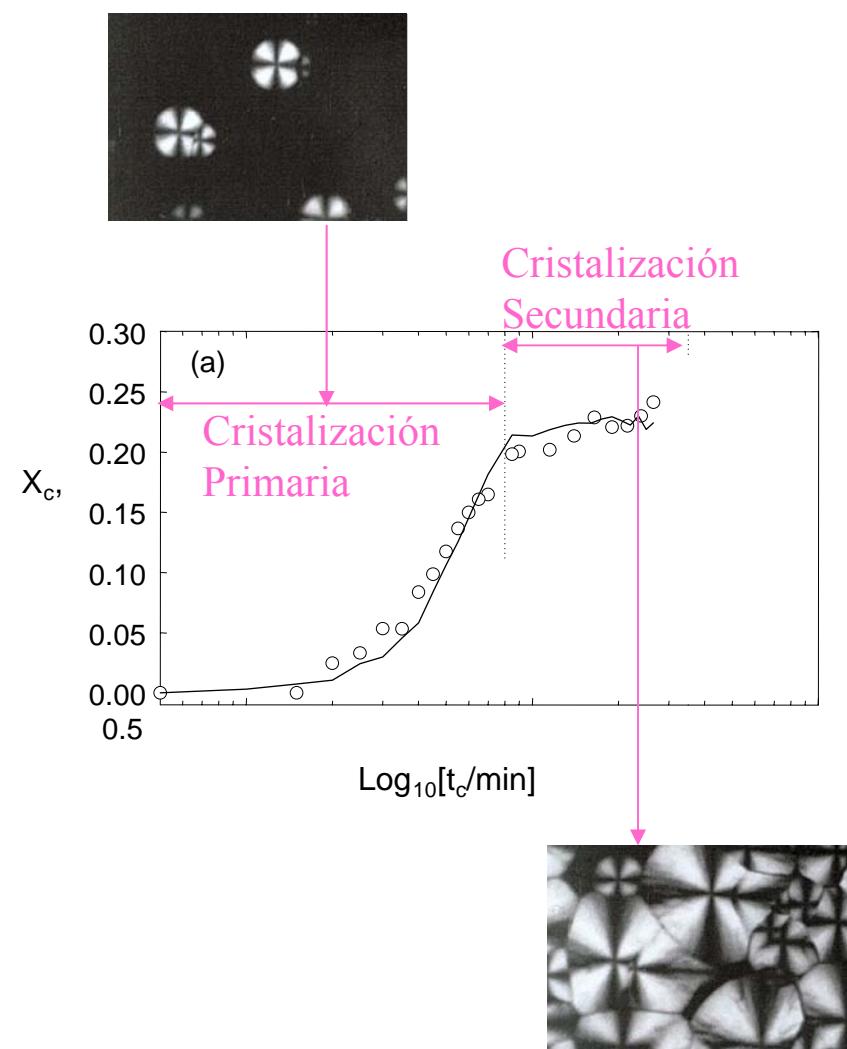
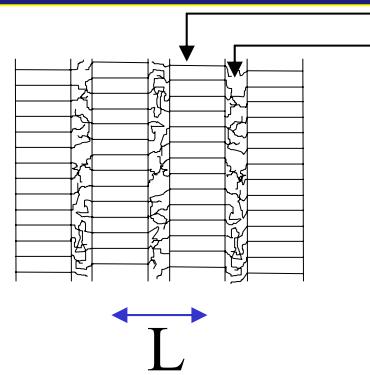
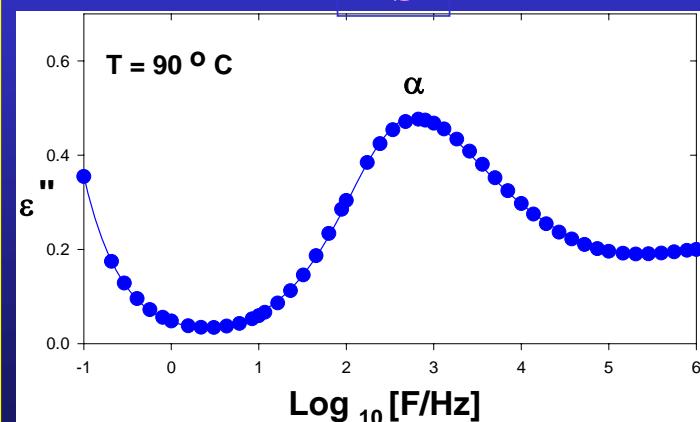
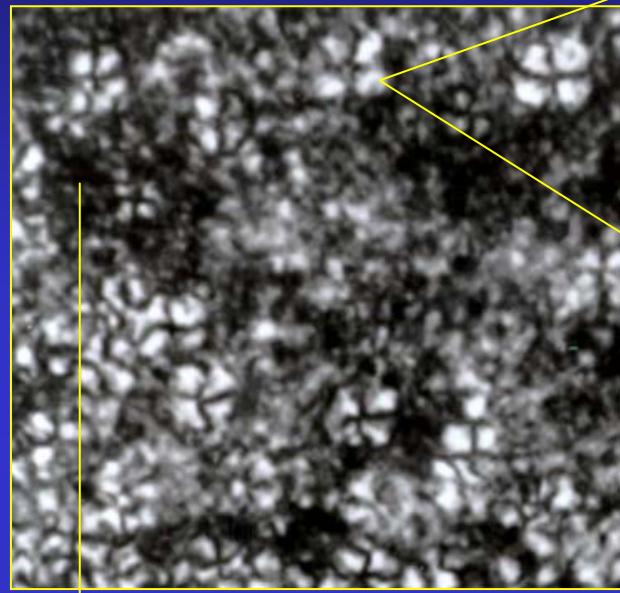


Fig. 2

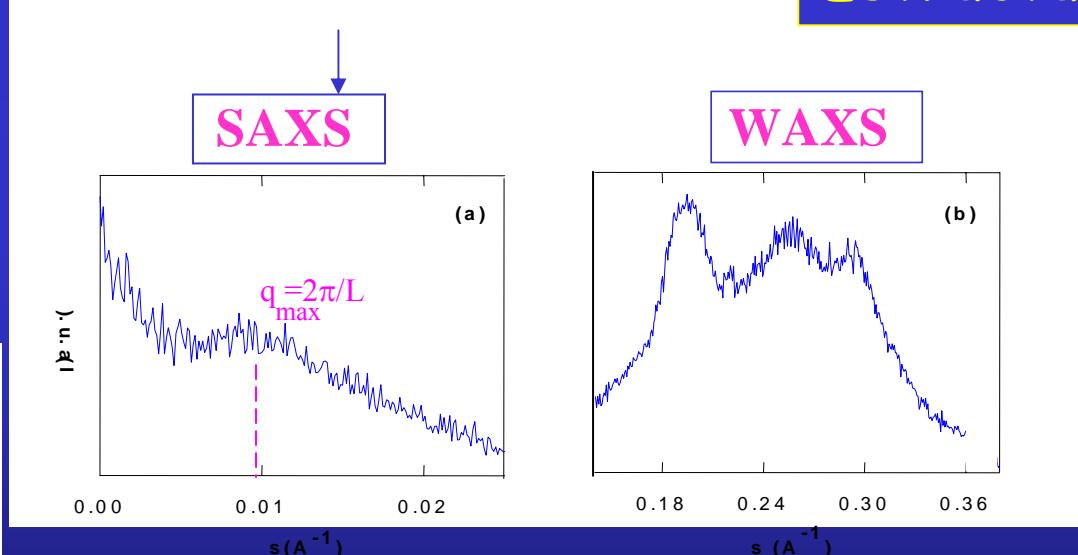


Técnicas Experimentales



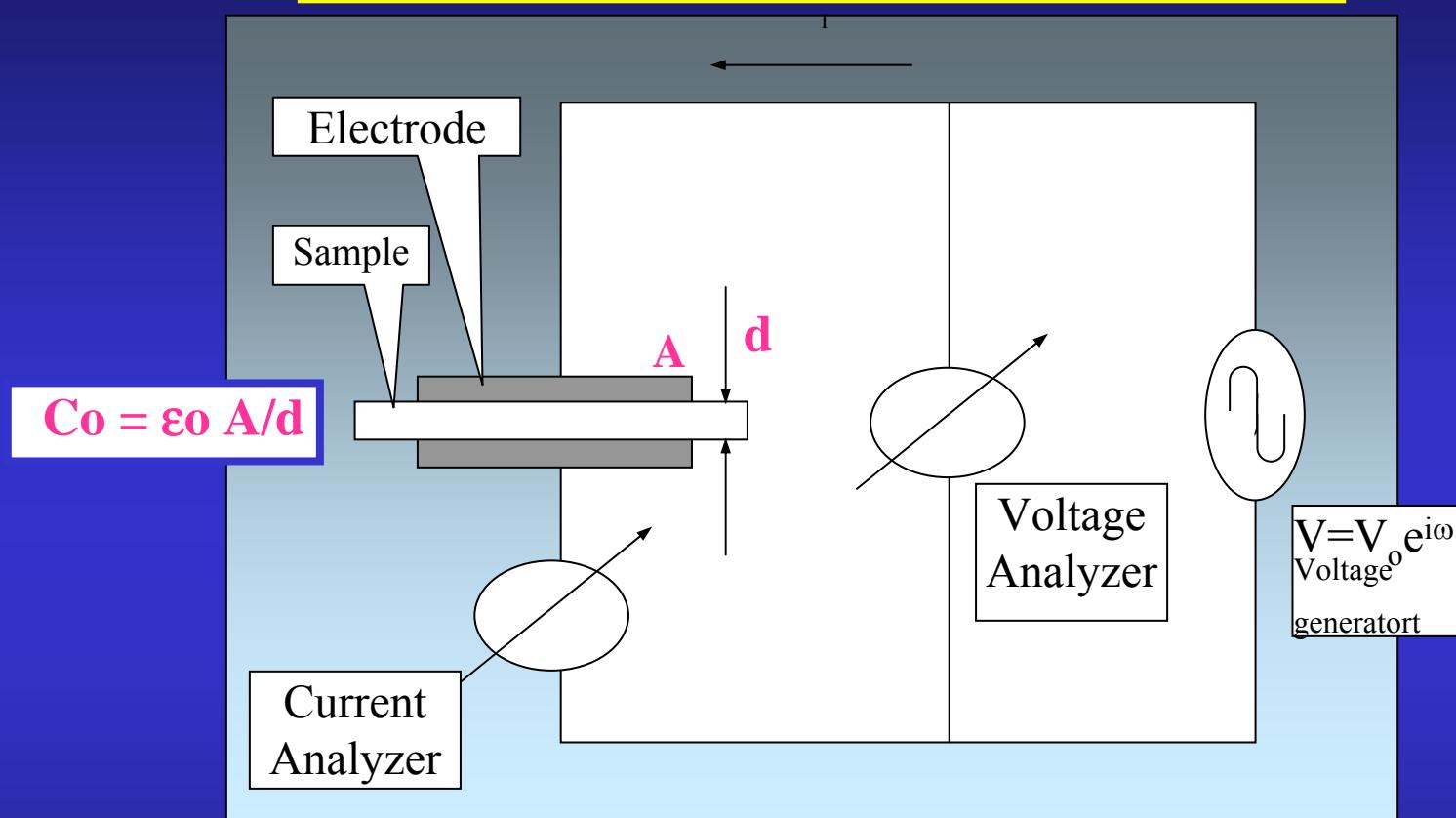
Crystalline Phase
Amorphous Phase

Estructura



Dinámica

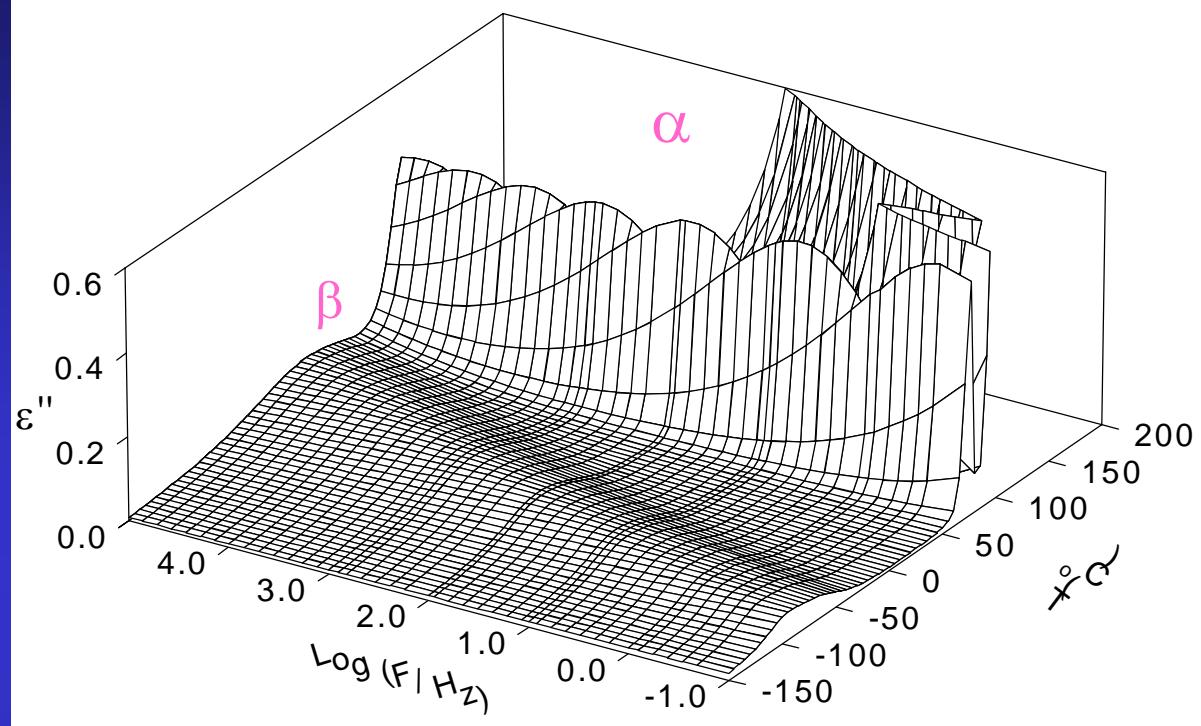
Espectroscopía Dielectrica



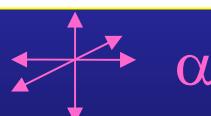
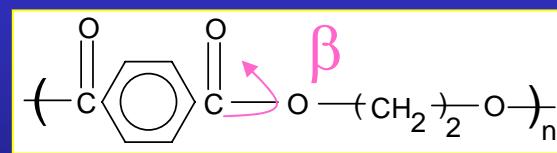
$$I_c = i \omega C_0 \epsilon' V$$

$$I_r = \omega C_0 \epsilon'' V$$

DS- medida

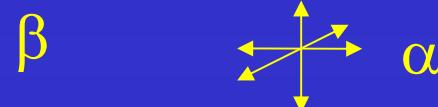
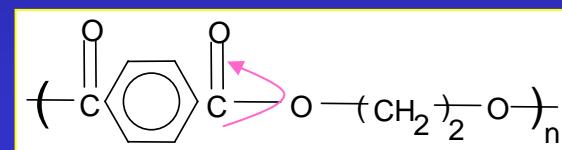
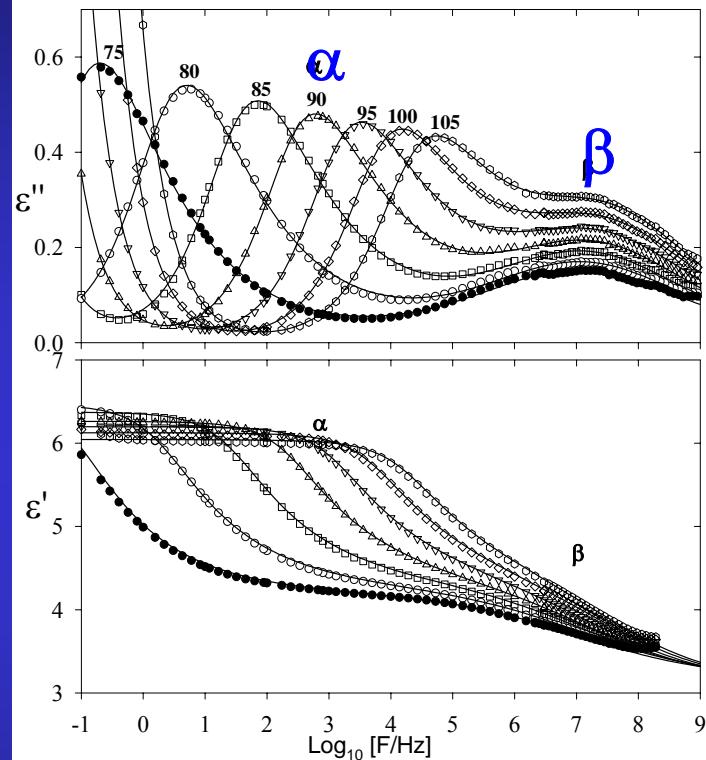


PET



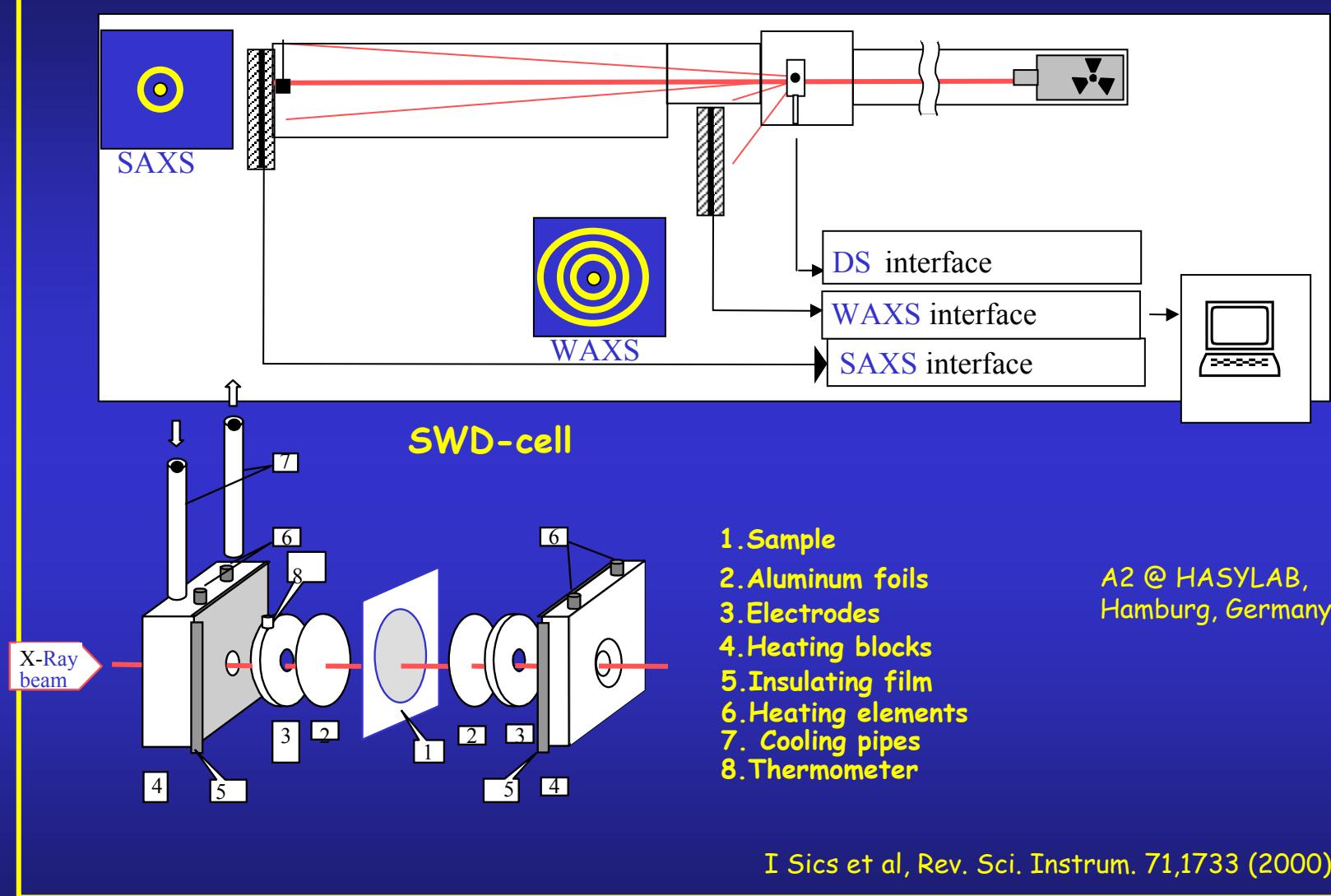
DS- medidas

PET

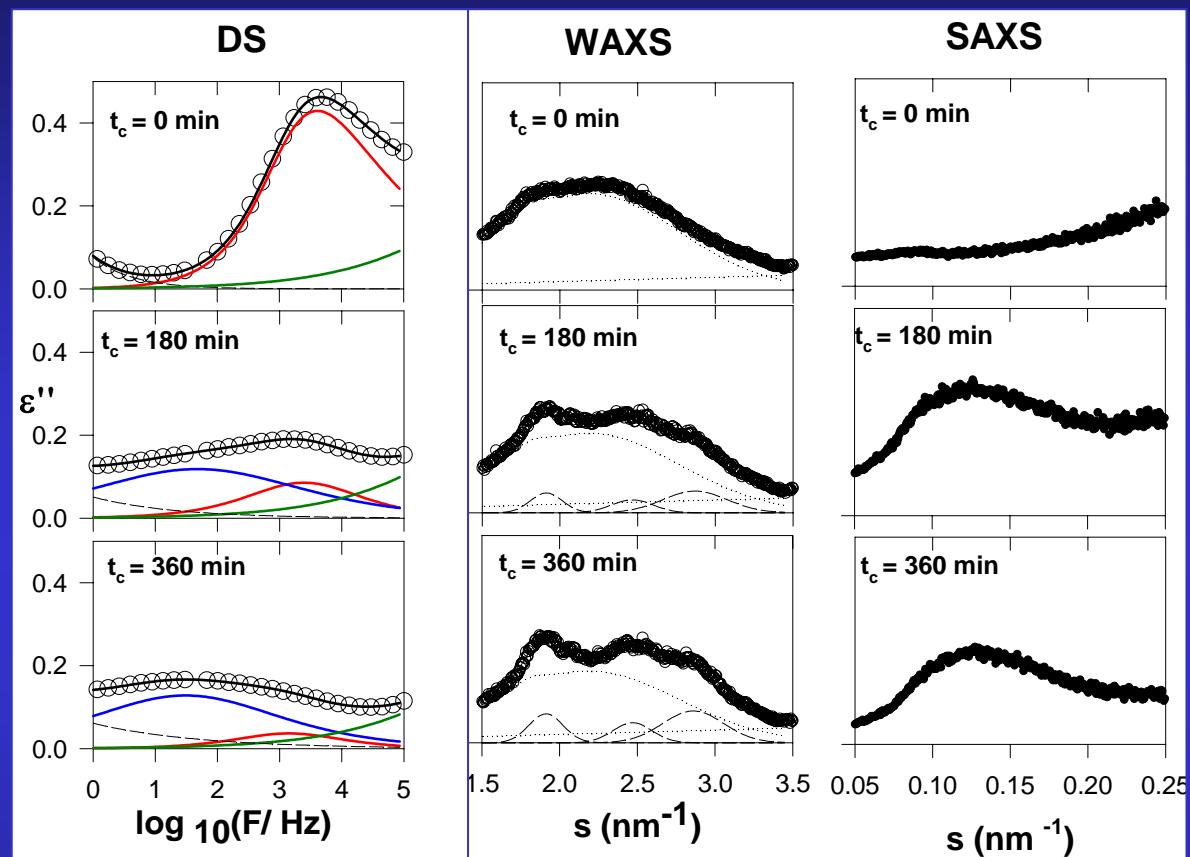


$$\epsilon^* = (\epsilon_\infty)_\beta + \sum_{x=\alpha,\beta} \frac{(\epsilon_0 - \epsilon_\infty)_x}{\left[1 + (i\omega\tau_x)^{b_x} \right]^{c_x}}$$

Esquema del sistema experimental SWD

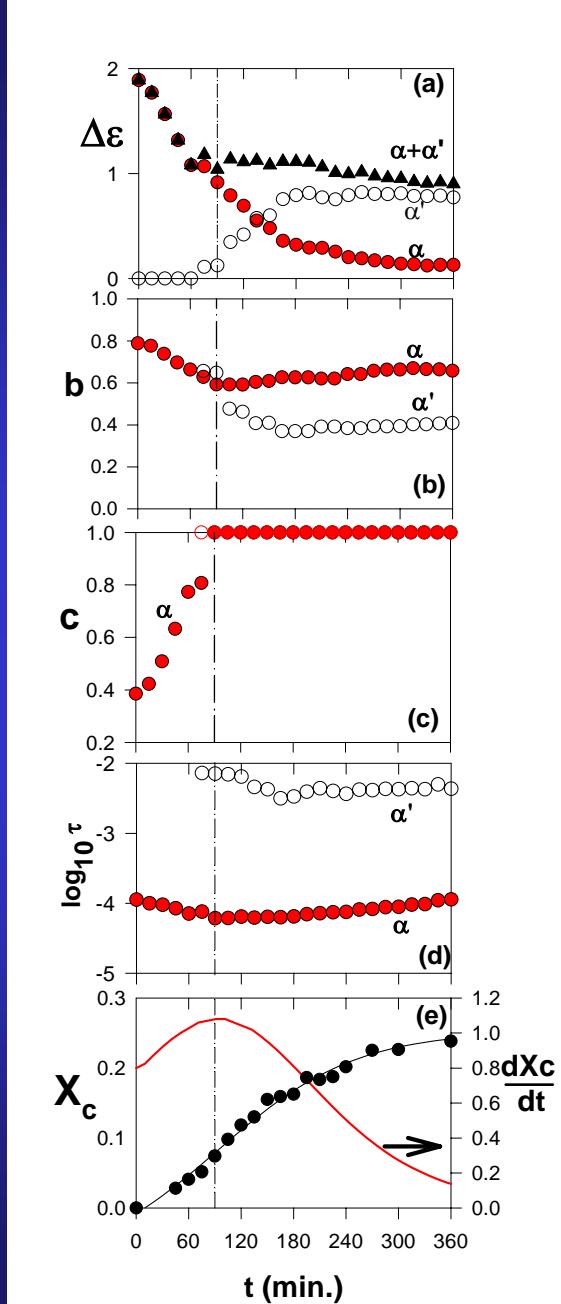


PET @ 96 °C

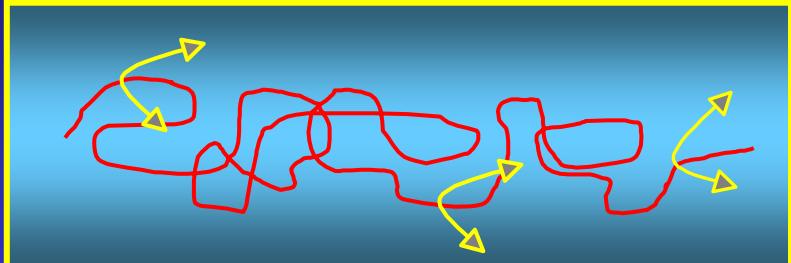


$$\varepsilon^* = \varepsilon_\infty + \frac{(\Delta\varepsilon)_a}{\left[1 + (i\omega\tau_{HN})^b\right]^c} + \frac{(\Delta\varepsilon')_a}{\left[1 + (i\omega\tau'_{HN})^{b'}\right]^{c'}} + \frac{(\Delta\varepsilon)_\beta}{\left[1 + (i\omega\tau_{HN})^b\right]} - i \frac{\sigma_{dc}}{\varepsilon_0 \Omega^n}$$

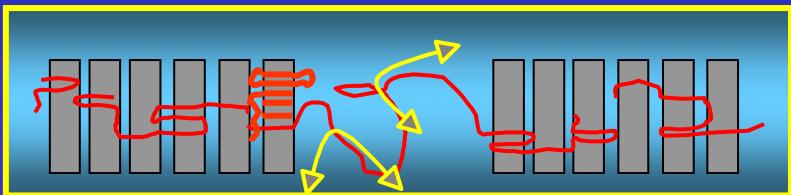
PET @ 96 °C



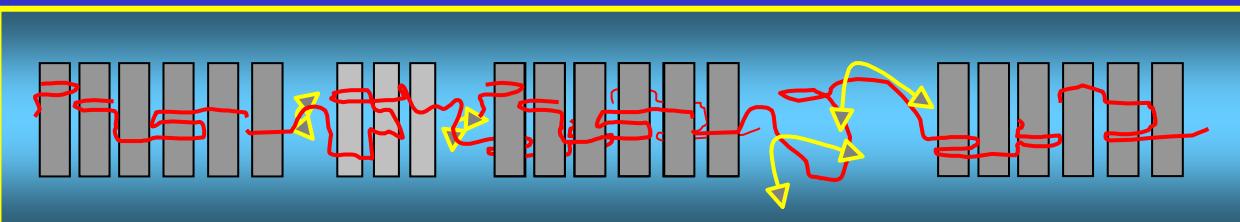
Modelo



(a) Estado amorfo



(b) cristalización primaria

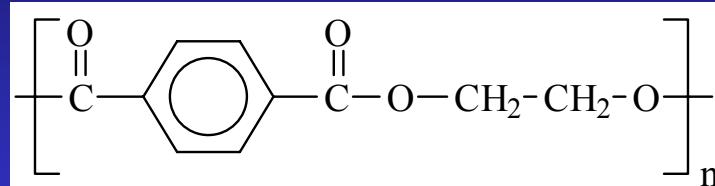


(c) cristalización secundaria

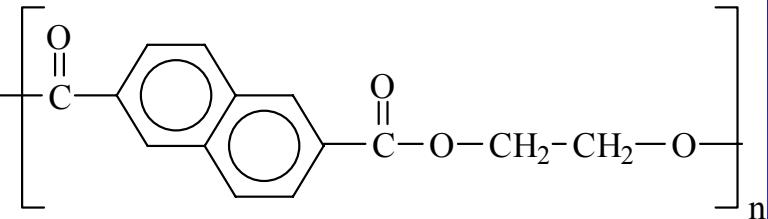
- Lin J., Shenogin S., Nazarenko S. Polymer 2002; 43:4733
- Ivanov D.A., Pop T., Yoon D.Y., Jonas A.M. Macromolecules 2002; 35: 9813

Transesterificación de mezclas poliméricas

Poly(ethylene terephthalate)
PET



Poly(ethylene-2,6-naphthalene dicarboxylate)
PEN

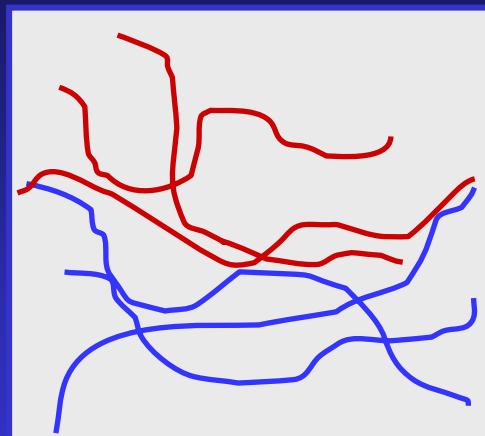


Properties *

	PET	PEN
Glass Transition (°C)	75	117
Melting Temperature (°C)	255	265
Tensile Modulus (Kg/mm ²)	1700	2000
Tensile Strength (kg/mm ²)	50	83
O ₂ Permeability at 20 °C (cm ³ mm m ⁻² d ⁻¹ bar ⁻¹)	1.16-1.55	0.31
CO ₂ Permeability at 20 °C (cm ³ mm m ⁻² d ⁻¹ bar ⁻¹)	5.81-9.86	2.40

* Handbook of thermoplastic polyesters,
S. Fakirov Ed. ,vol.2, cap. 19, Wiley-VCH, Germany, 2002

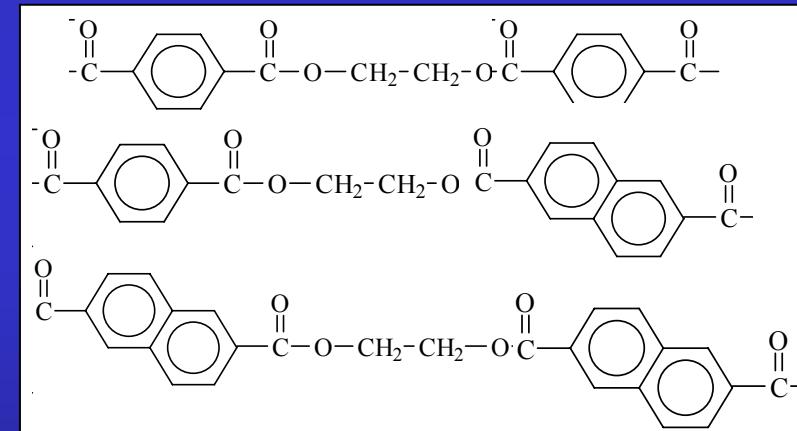
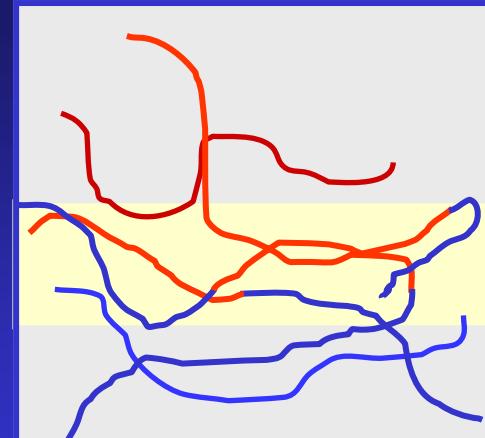
PET/PEN son inmiscibles



Transesterificación

$T > T_m \uparrow 300^{\circ}\text{C}$

t: 1 – 35 min.



T-E-T

T-E-N

N-E-N

Molido Criogénico

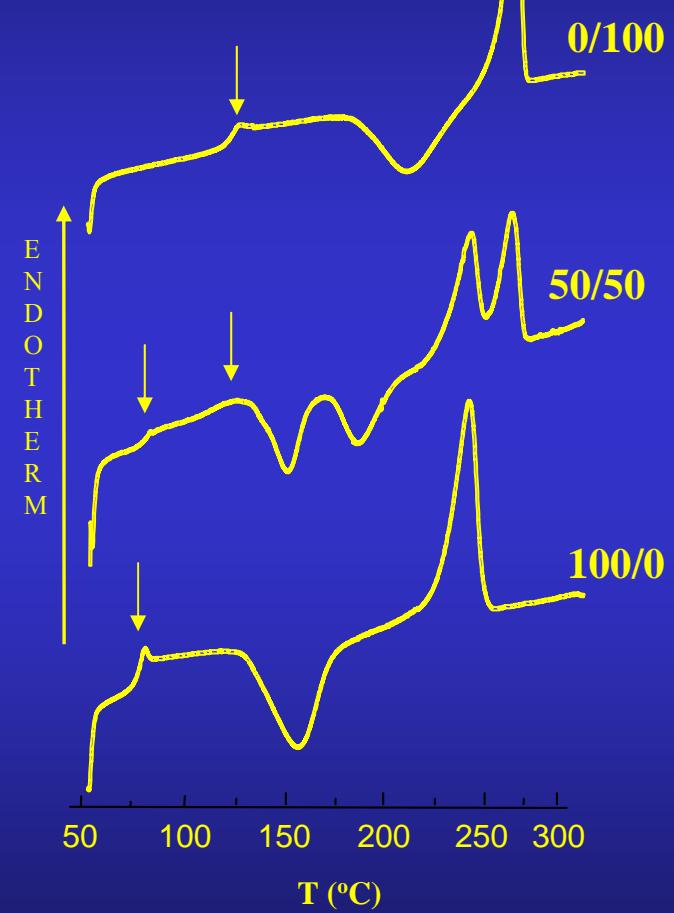
Molido de la granza a temperatura de N₂ líquido

transreacciones iniciales se minimizan

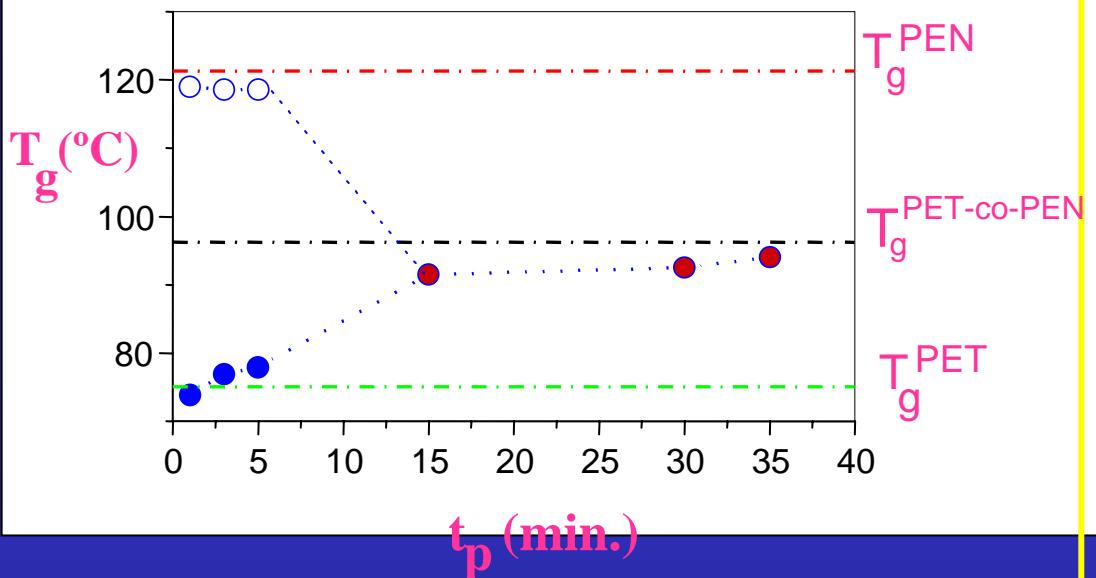
Propiedades térmicas

PET/PEN wt. %

$t_p = 3 \text{ min.}$

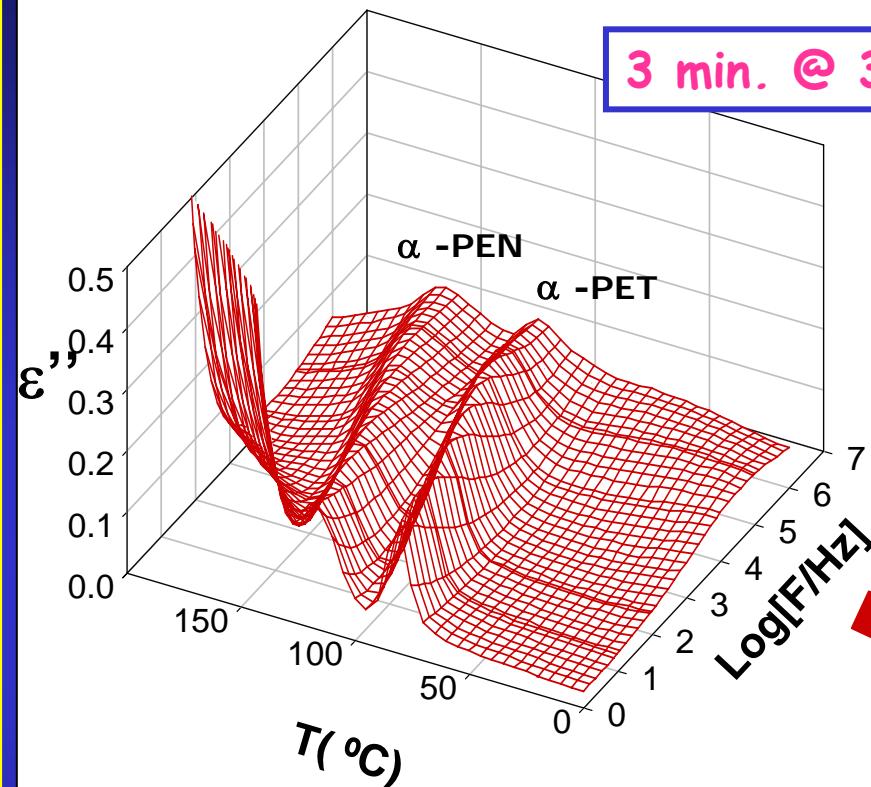


PET/PEN 50/50 wt. %

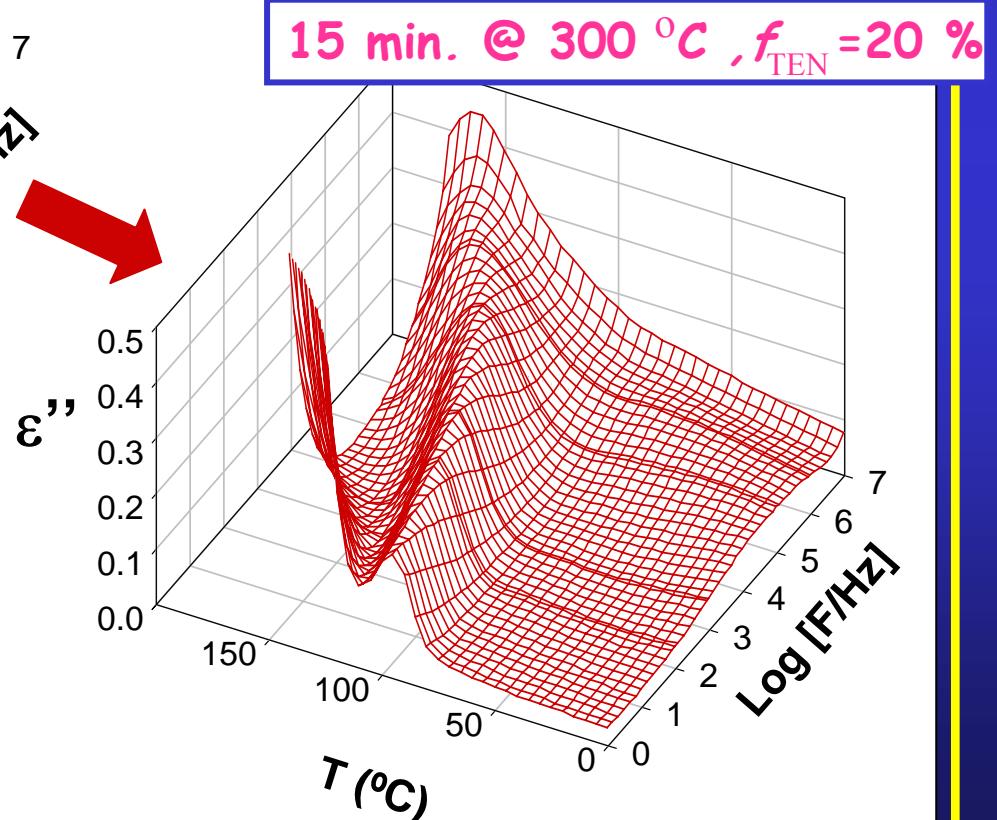


PET/PEN 50/50 wt. %

DS-medidas

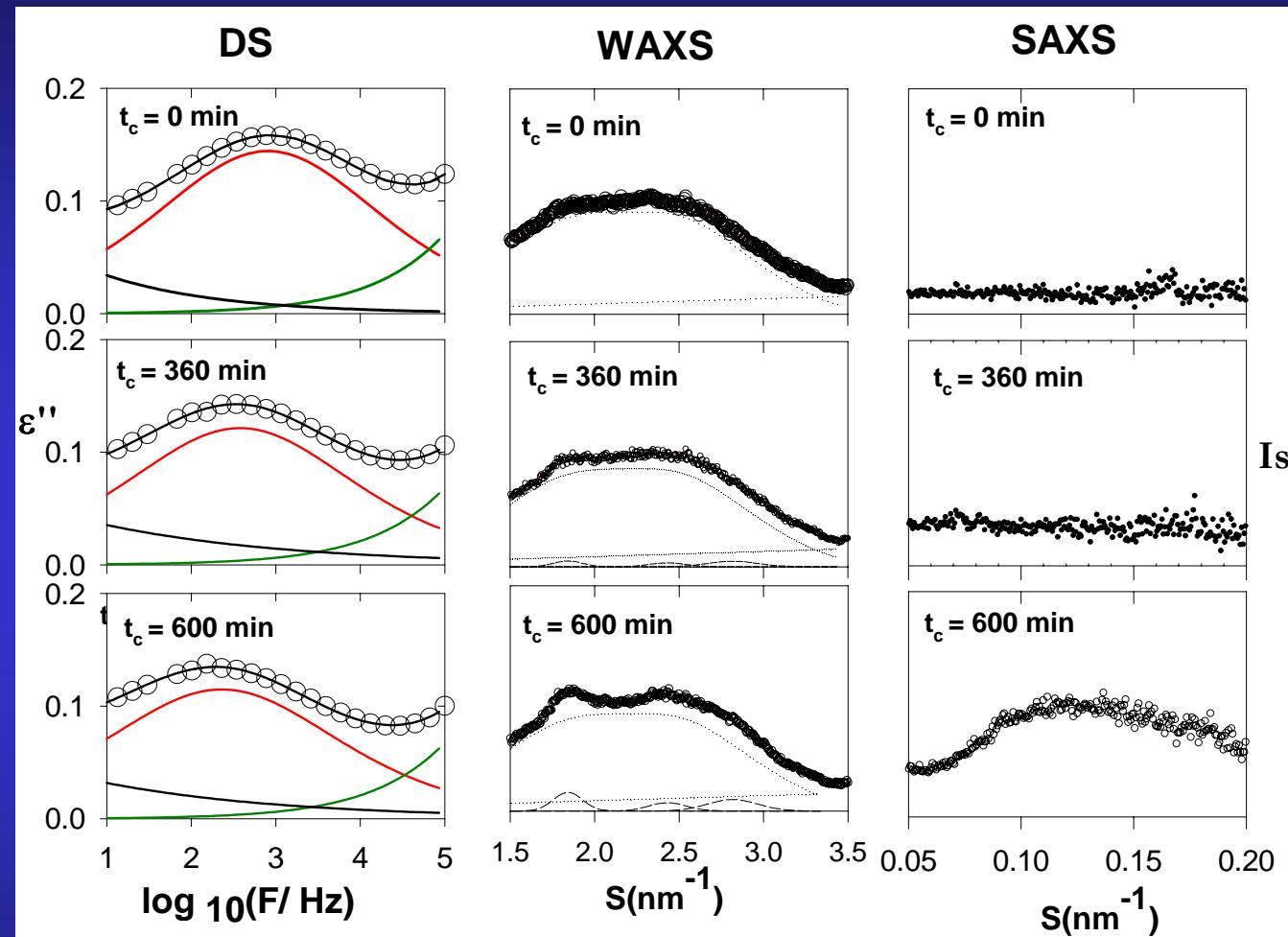


3 min. @ $300\text{ }^{\circ}\text{C}$, $f_{\text{TEN}}=11\text{ }\%$



15 min. @ $300\text{ }^{\circ}\text{C}$, $f_{\text{TEN}}=20\text{ }\%$

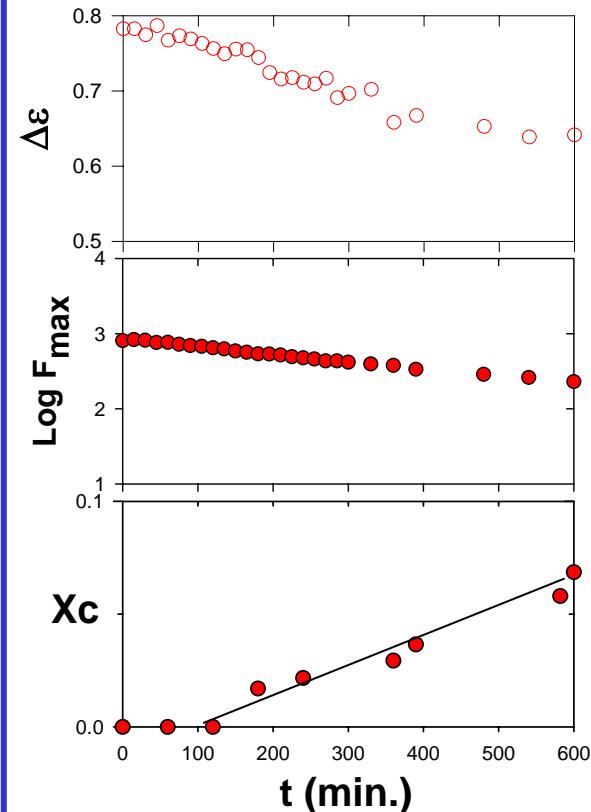
PET/PEN 50/50 @ 96 °C , $f_{\text{TEN}} = 11 \%$



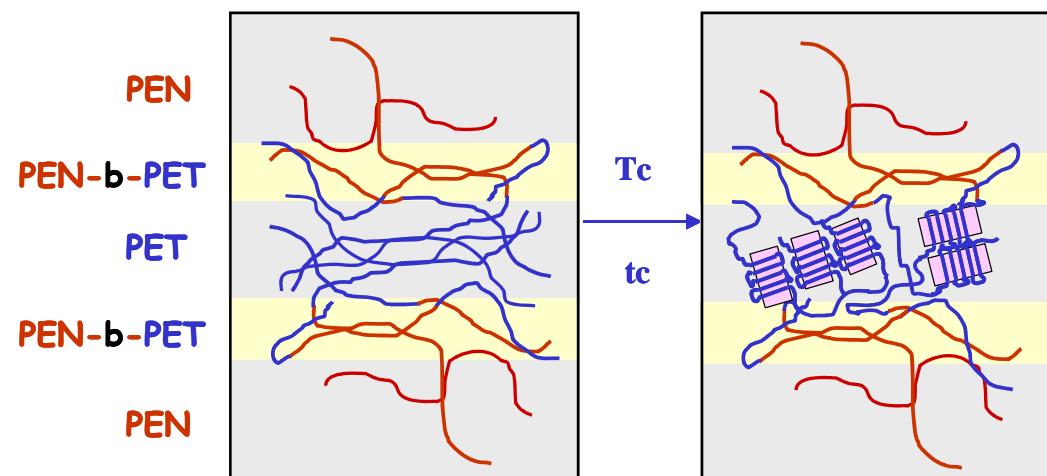
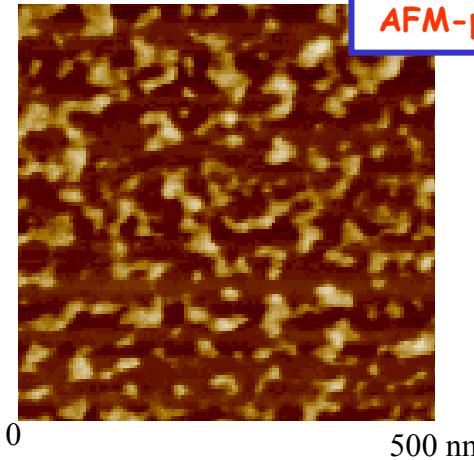
$$\varepsilon^* = \varepsilon_\infty + \frac{(\Delta\varepsilon)_a}{\left[1+(i\omega\tau_{HN})^b\right]^c} + \frac{(\Delta\varepsilon')_d}{\left[1+(i\omega\tau_{HN})^{b'}\right]^{c'}} + \frac{(\Delta\varepsilon)_\beta}{\left[1+(i\omega\tau_{HN})^b\right]} - i \frac{\sigma_{dc}}{\varepsilon_0 \omega^n}$$

PET/PEN mezclas ligeramente transesterificadas

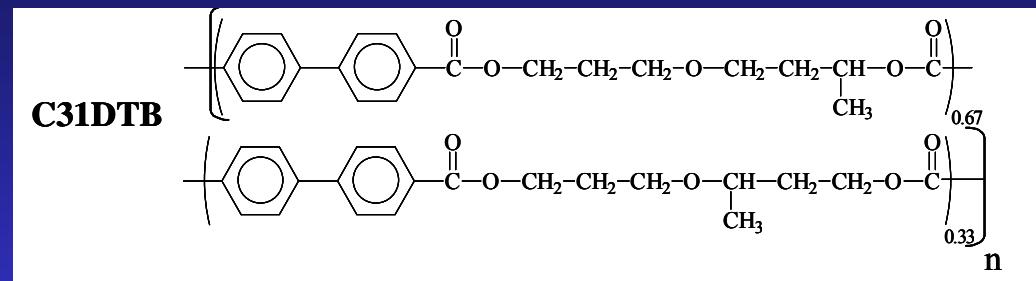
PET/PEN 50:50, $f_{TEN} = 11\%$



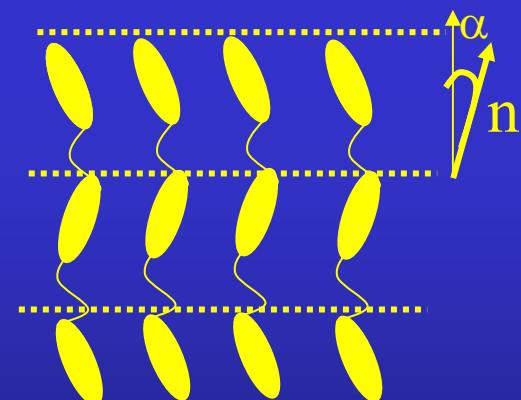
annealing at 120°C, 14 hours



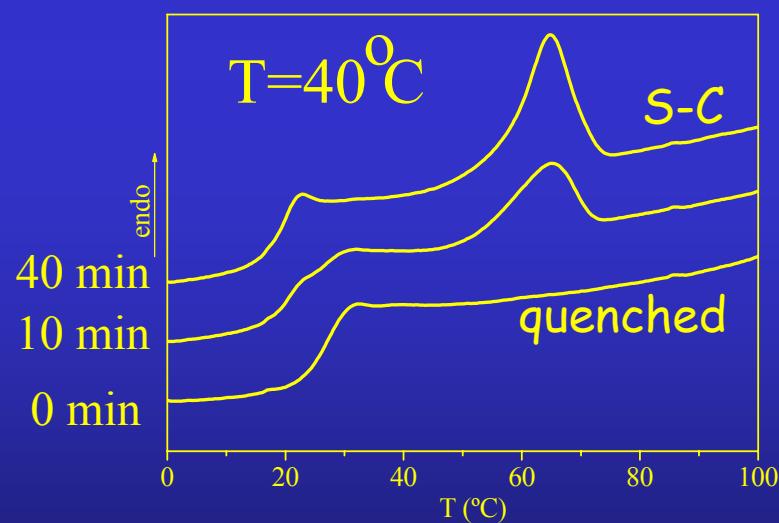
Ordenamiento en Cristales líquidos Poliméricos*



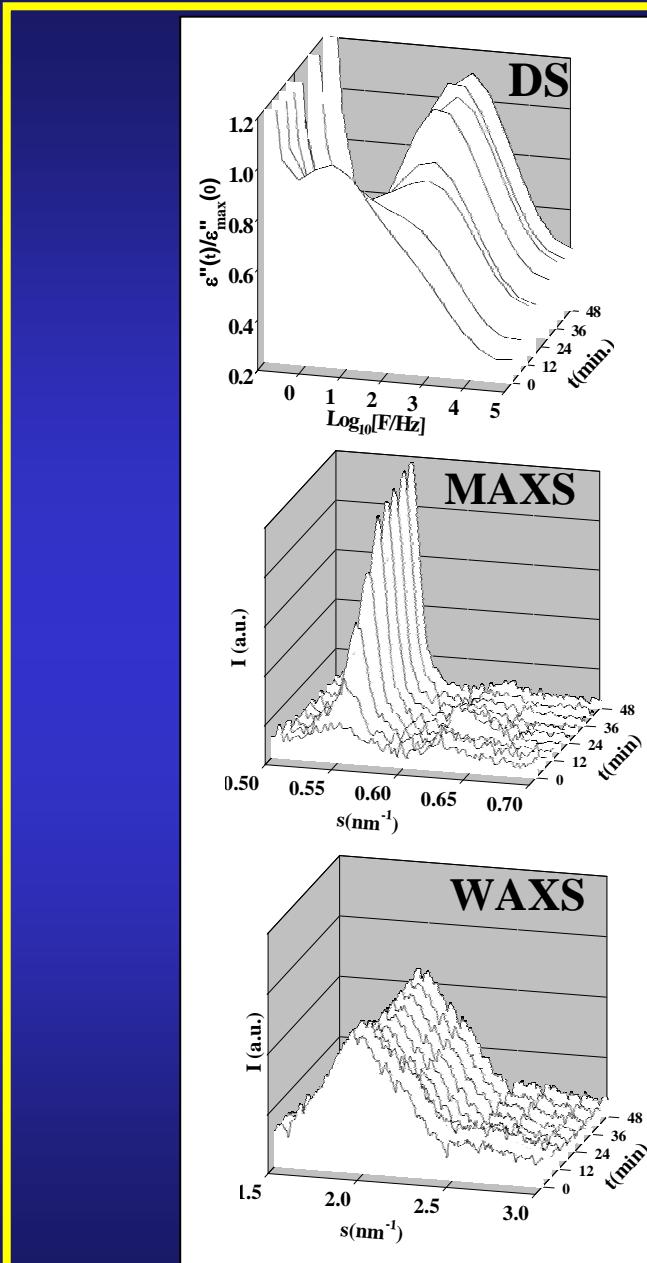
Esméctico-*C*



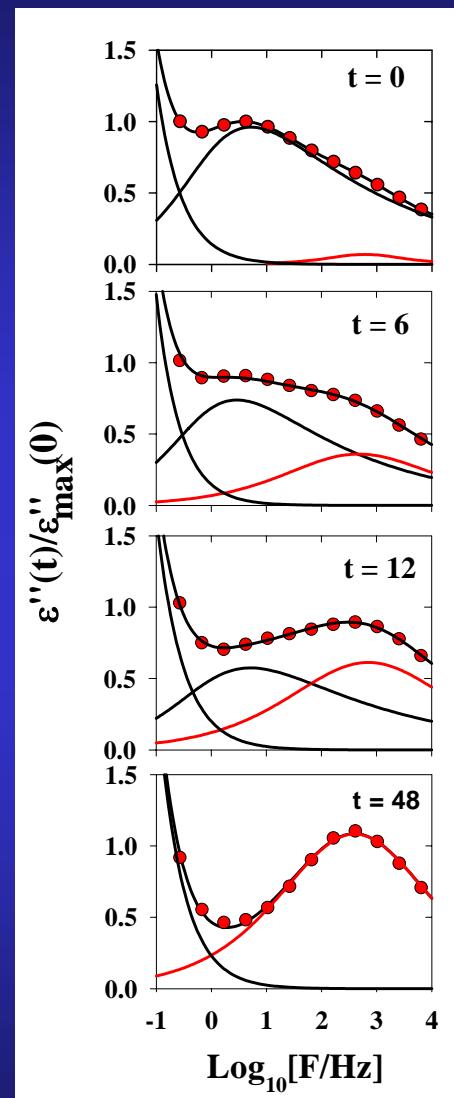
DSC



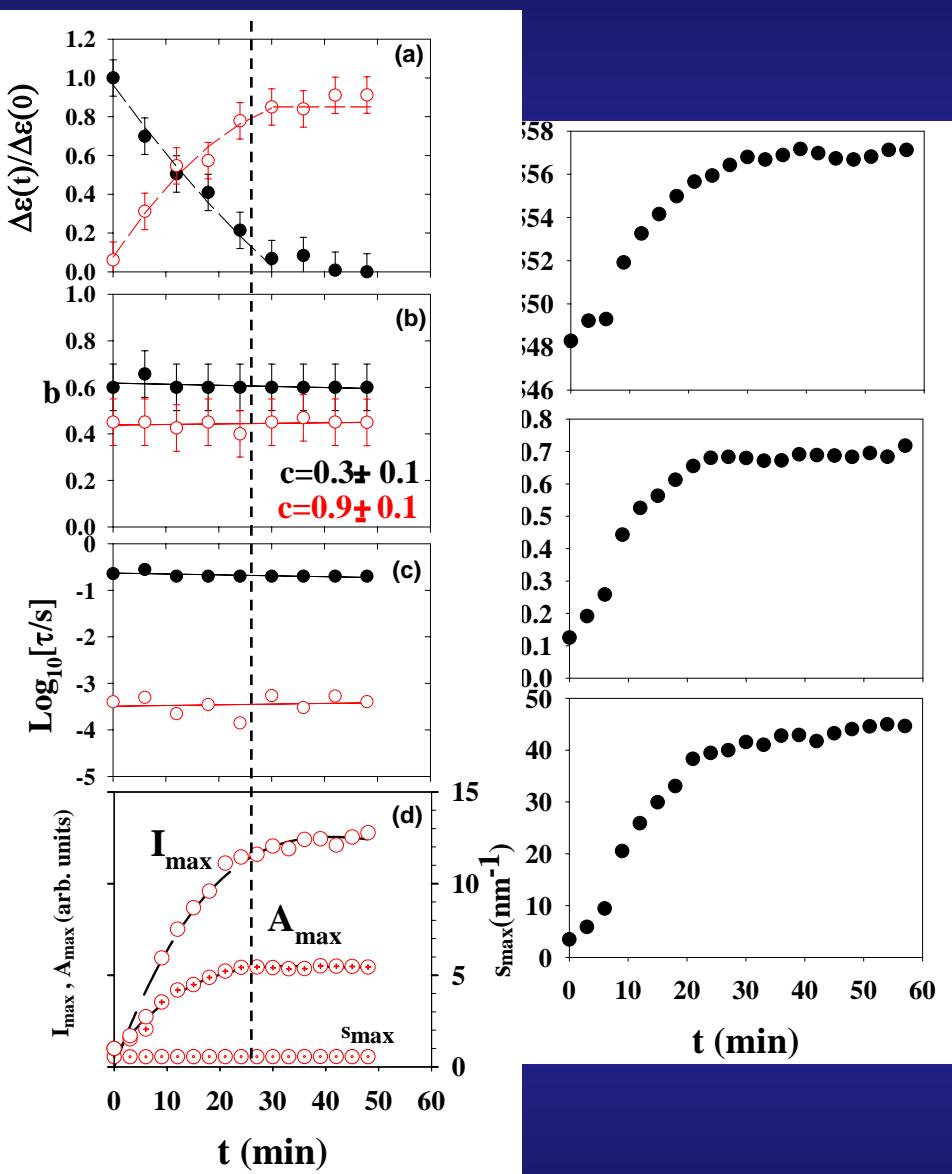
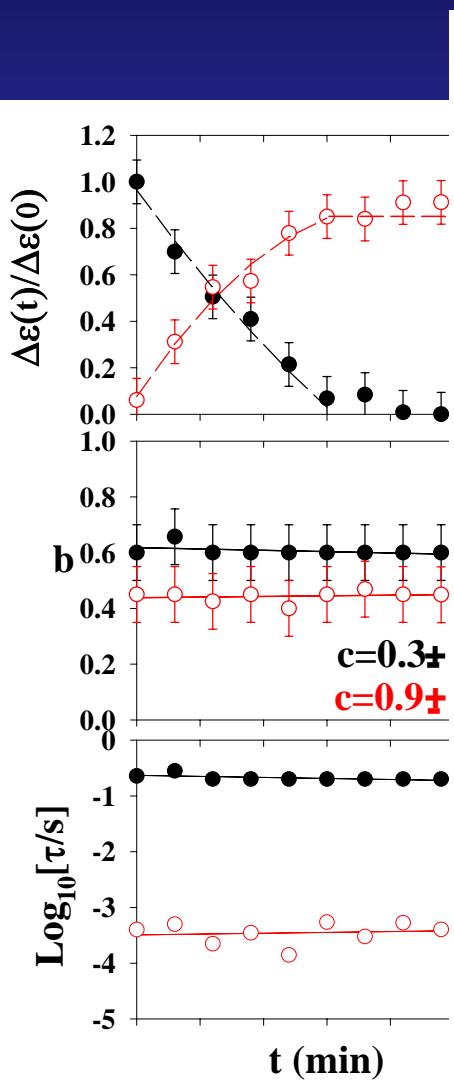
*A. Martínez-Campo, A. Bello, E. Pérez-Tabernero. ICTP-CSIC



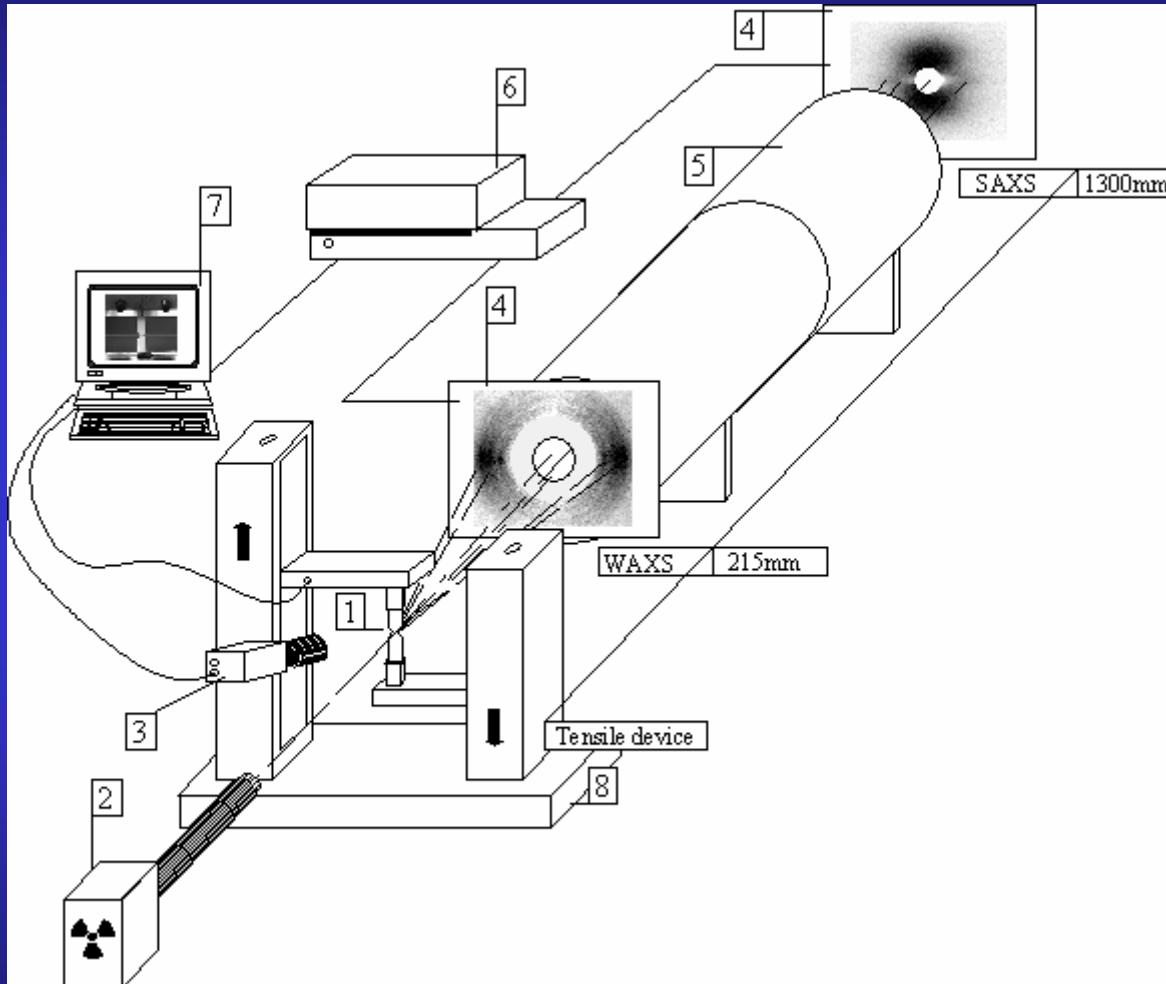
T=35 °C



$T=35^{\circ}C$

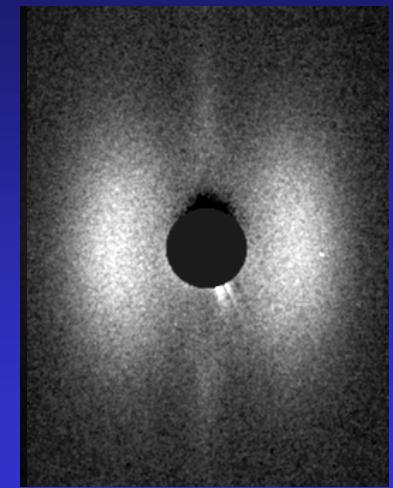
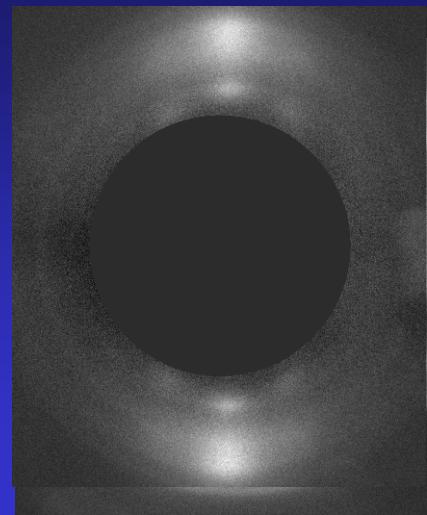
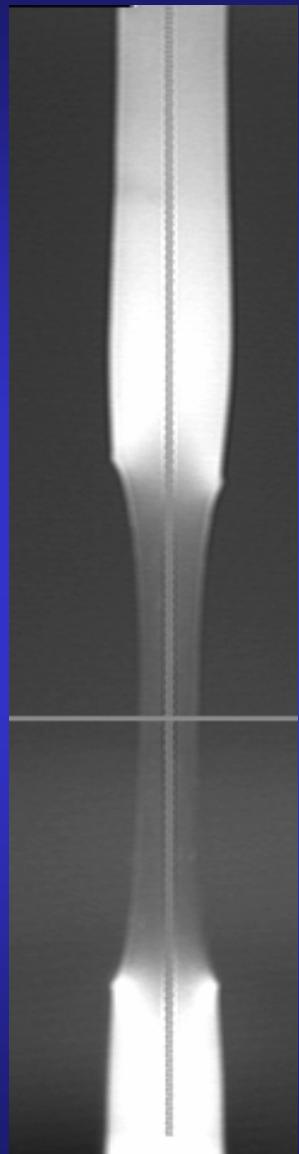
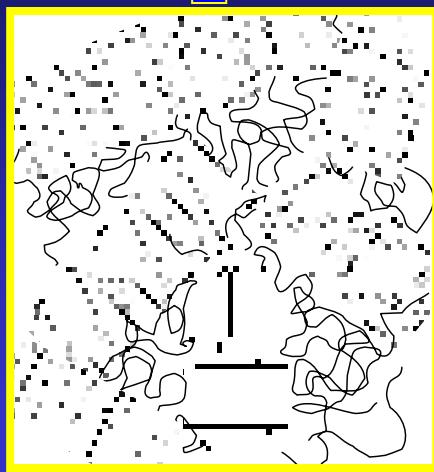


Esfuerzo-Deformación (Stress-Strain)

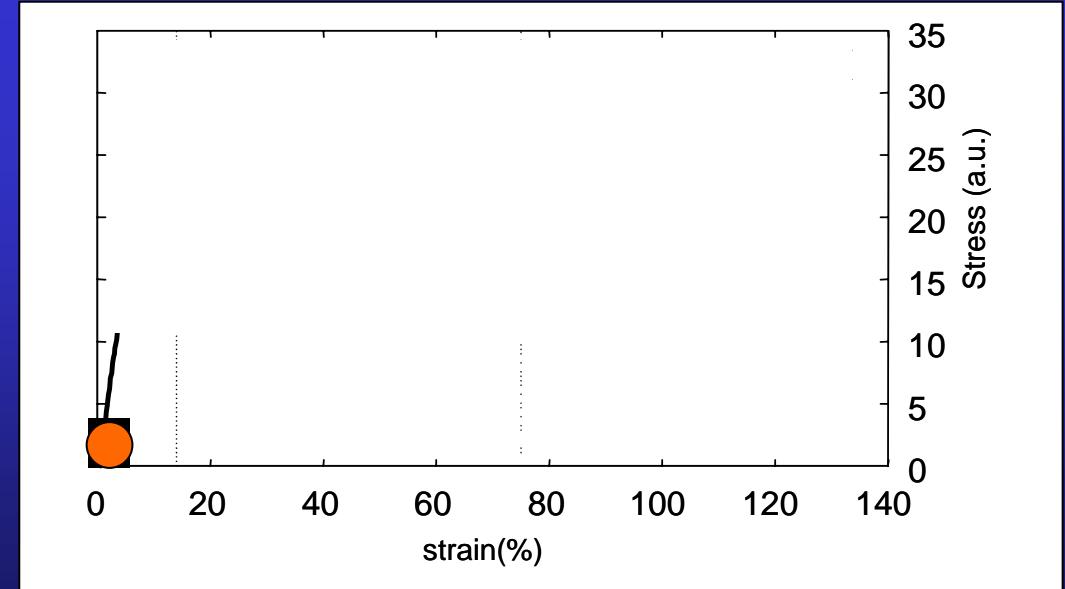
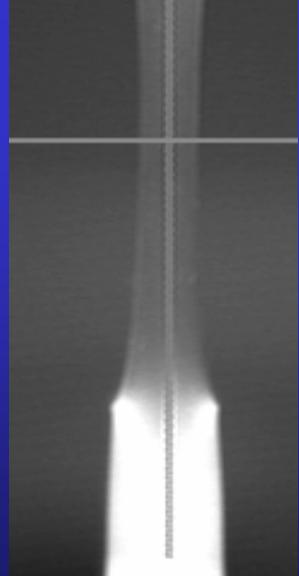
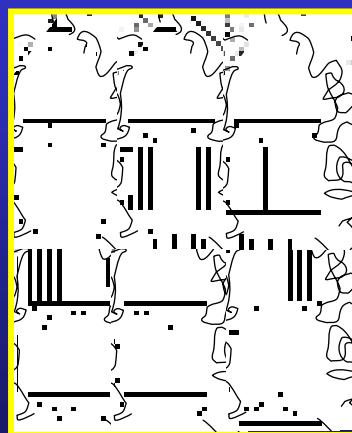


Stress-Strain : Arnitel (PBT-PO4))

1



8



Cristalización anisotrópica en poly(butylene terephthalate) (PBT) inducida por nanotubos de carbono

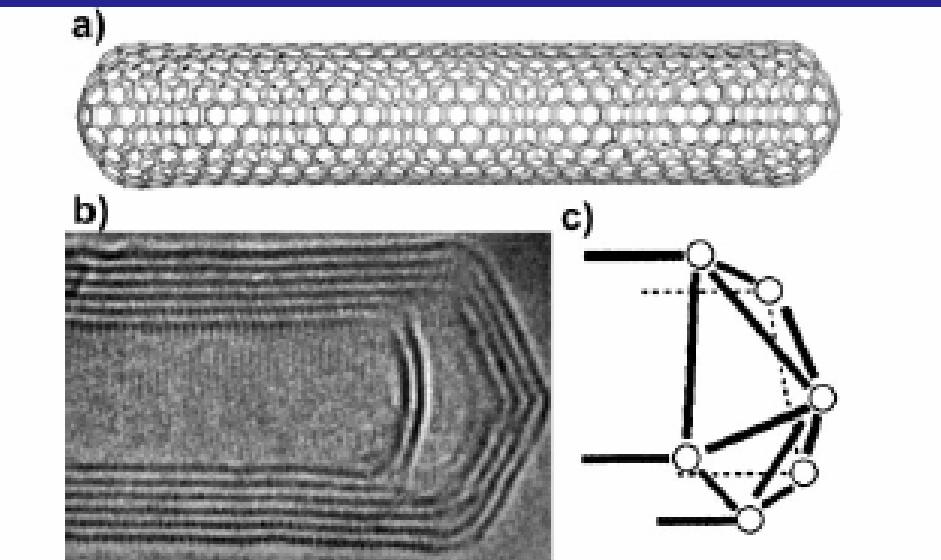


Figure 2 (a) Molecular model of a SWNT (rolled hexagonal carbon lattice) that is capped by six pentagons in each nanotube end; (b) HRTEM image of one end of a MWNT (nested graphene cylinders; courtesy of P.M. Ajayan); (c) model of a nanotube tip exhibiting the locations of the six pentagonal rings (open circles) that permit the hexagonal carbon lattice (graphene sheet) to close; the model resembles that shown in (b) (courtesy of P.M. Ajayan).



Mauricio Terrones, Annu. Rev. Mater.Res. 2003, 33:419–501
Advanced Materials Department, San Luis Potosí, SLP, México

Nanocomposite samples

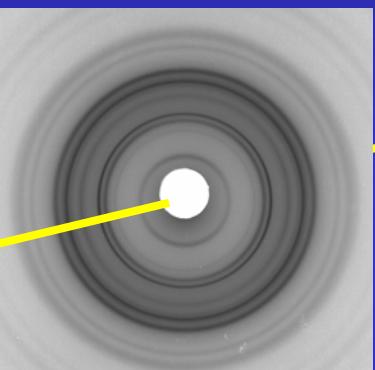
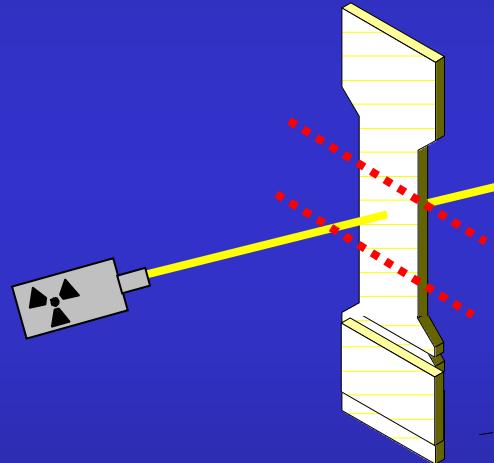
1. Oxidized single wall carbon nanotubes (SWCNT) (CNI Technology Co)
Thickness:0.7-1.2 nm, length: several μm
2. PBT , poly(butylene terephthalate)

Method (Roslaniec Z., Broza G., Schulte K., Composite Interface 2003, 10, 95.) :

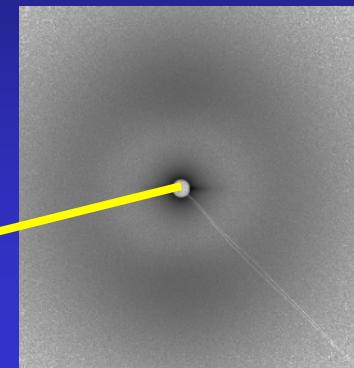
- 1.Mixture with the monomer and subsequent polycondensation
- 2.Pelletized and injection molded into rectangular (2mm thick)
- 3.Compression molded @ 240°C,2 min. and subsequently quenching.



Structure: X-ray scattering



WAXS

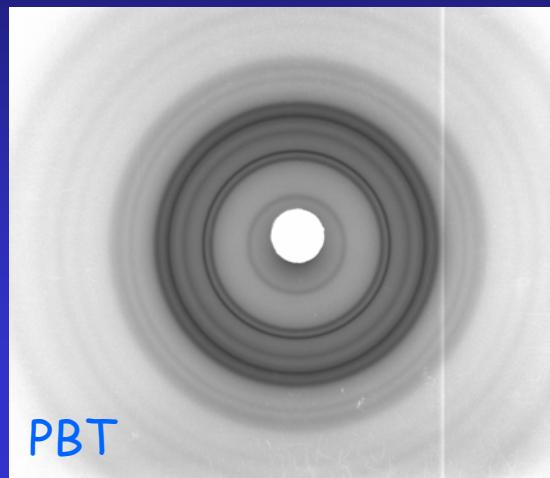


SAXS

- X3A2 beamline @ National Synchrotron Source (NSLS) (USA).
 $\lambda=0.154$ nm. Fuji HR-VM image plates
- ID13 ESRF, Grenoble (France) (Microfocus)

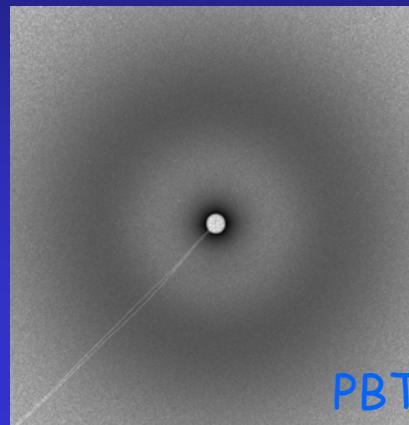
Structure: X-ray scattering

WAXS



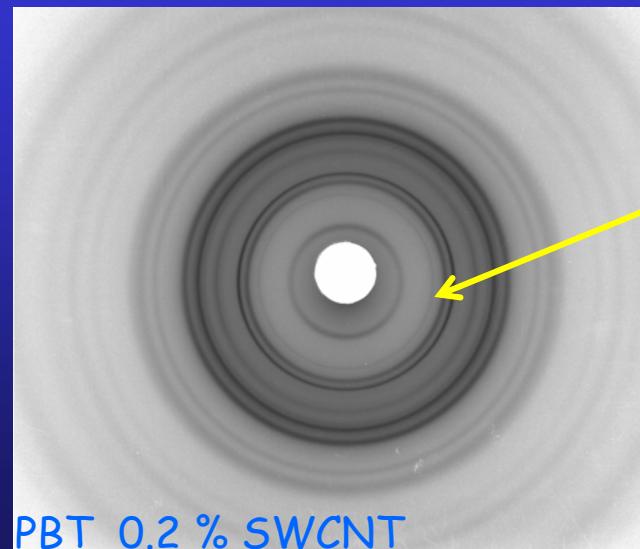
PBT

SAXS

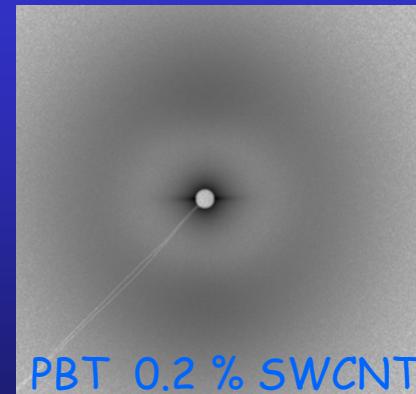


PBT

SWCNT



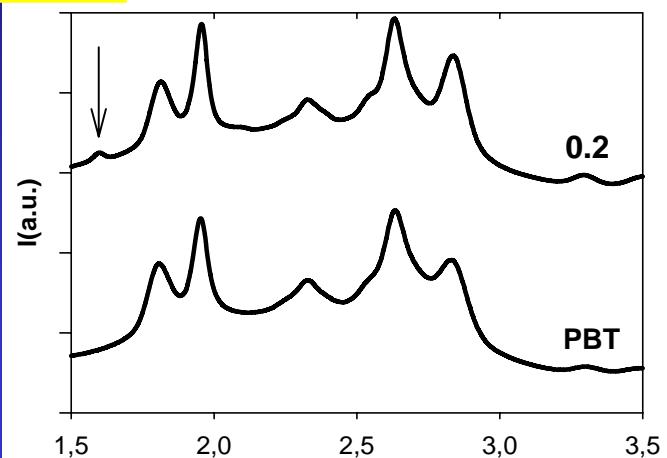
PBT 0.2 % SWCNT



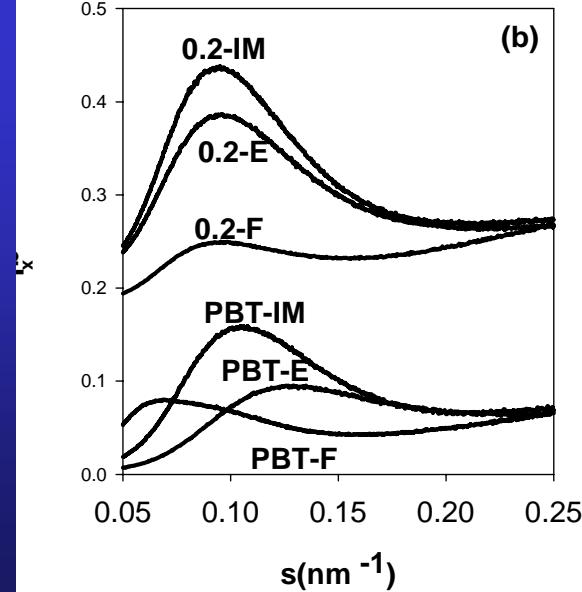
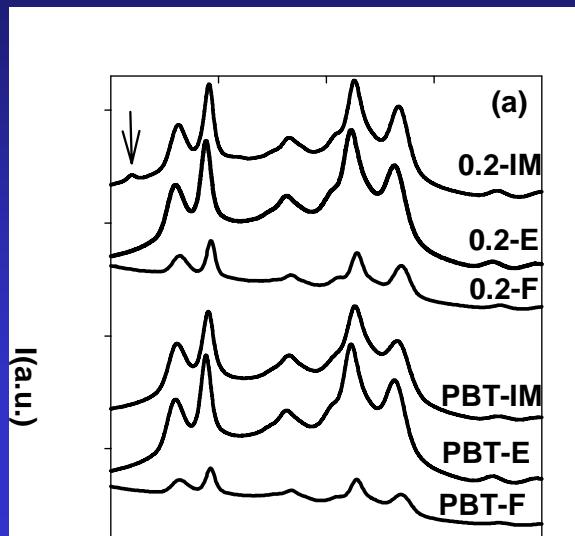
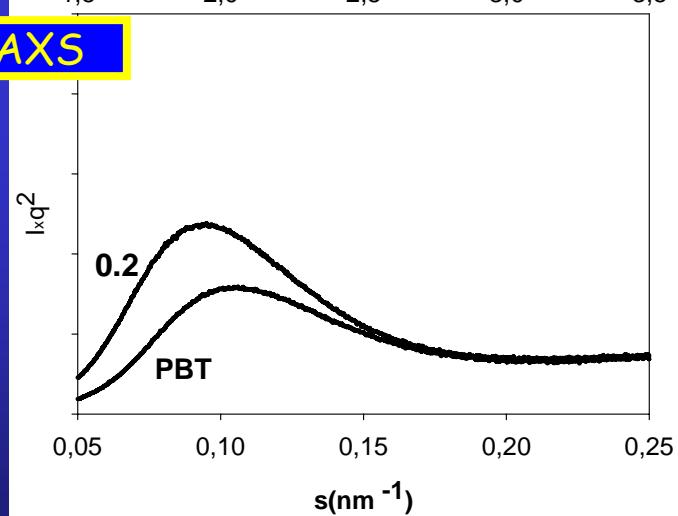
PBT 0.2 % SWCNT

Structure: X-ray scattering

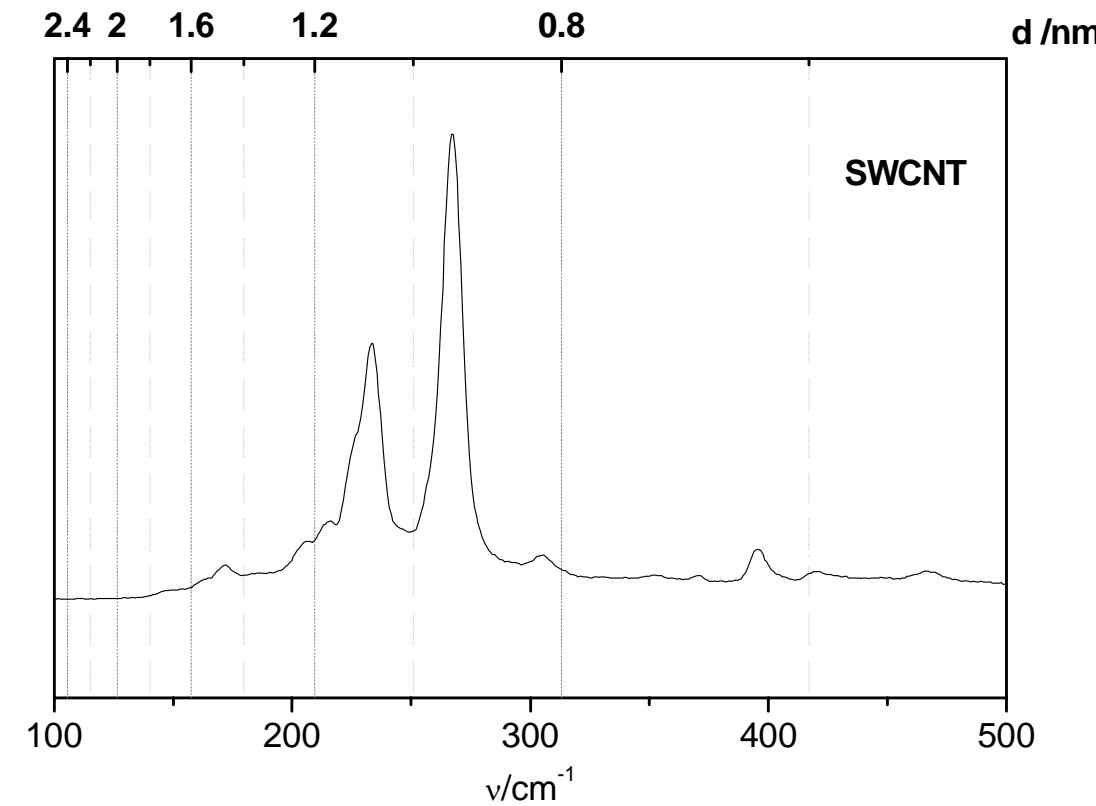
WAXS



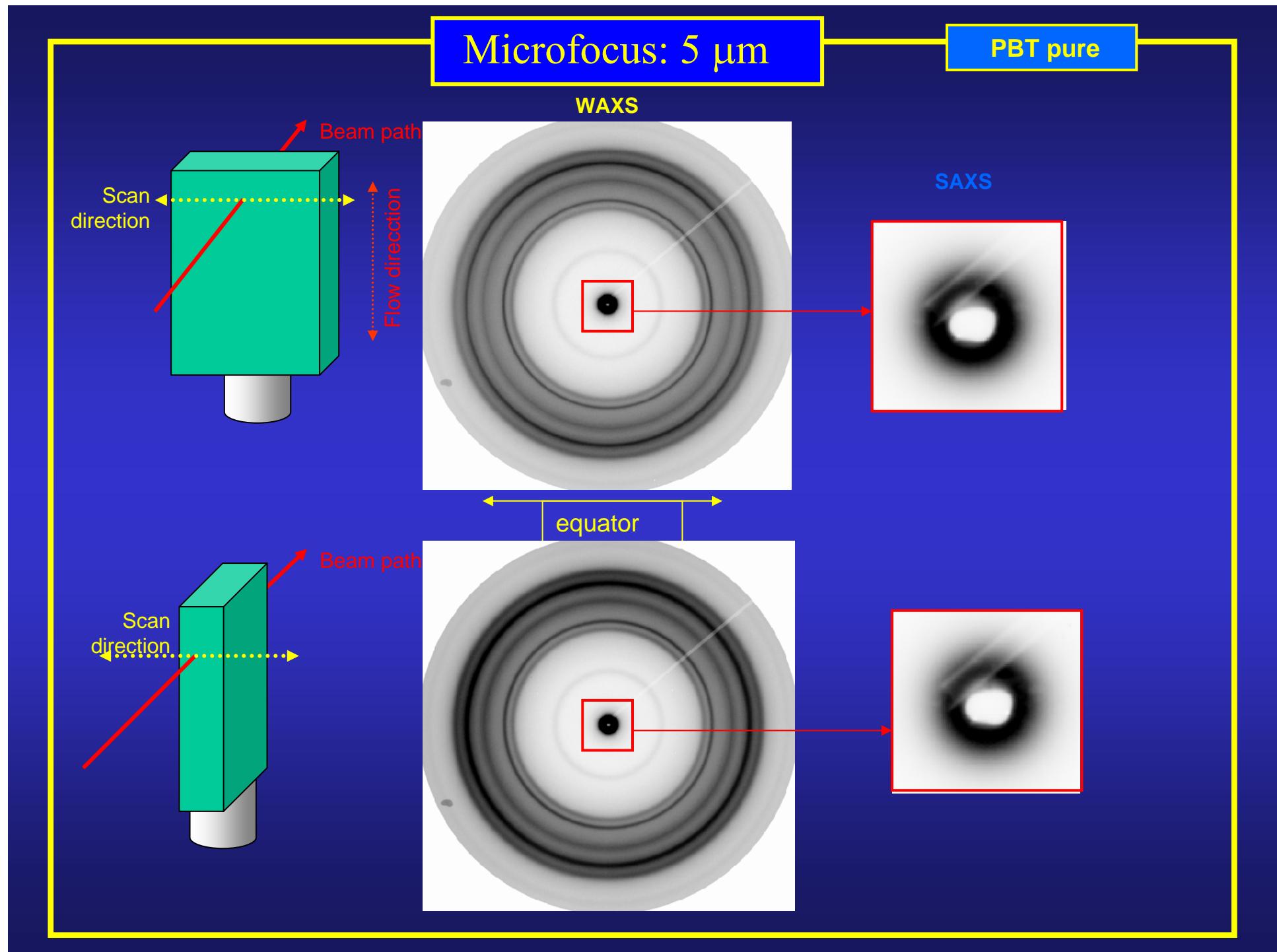
SAXS

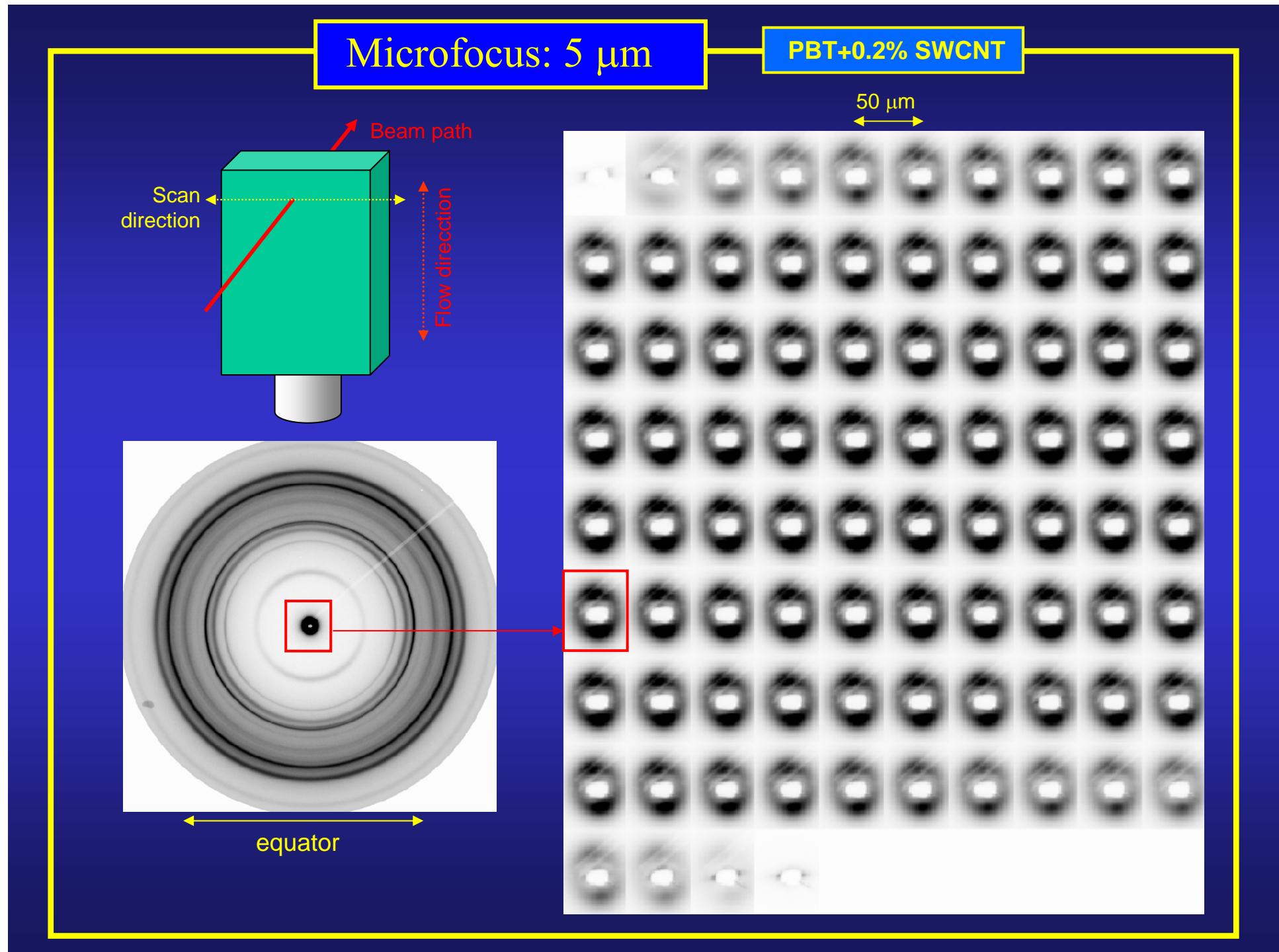


Raman Spectroscopy



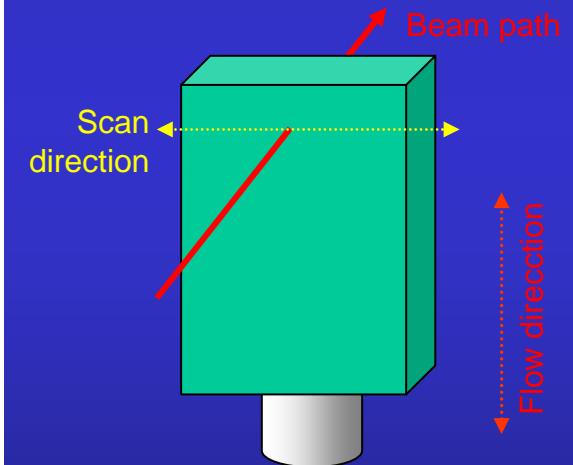
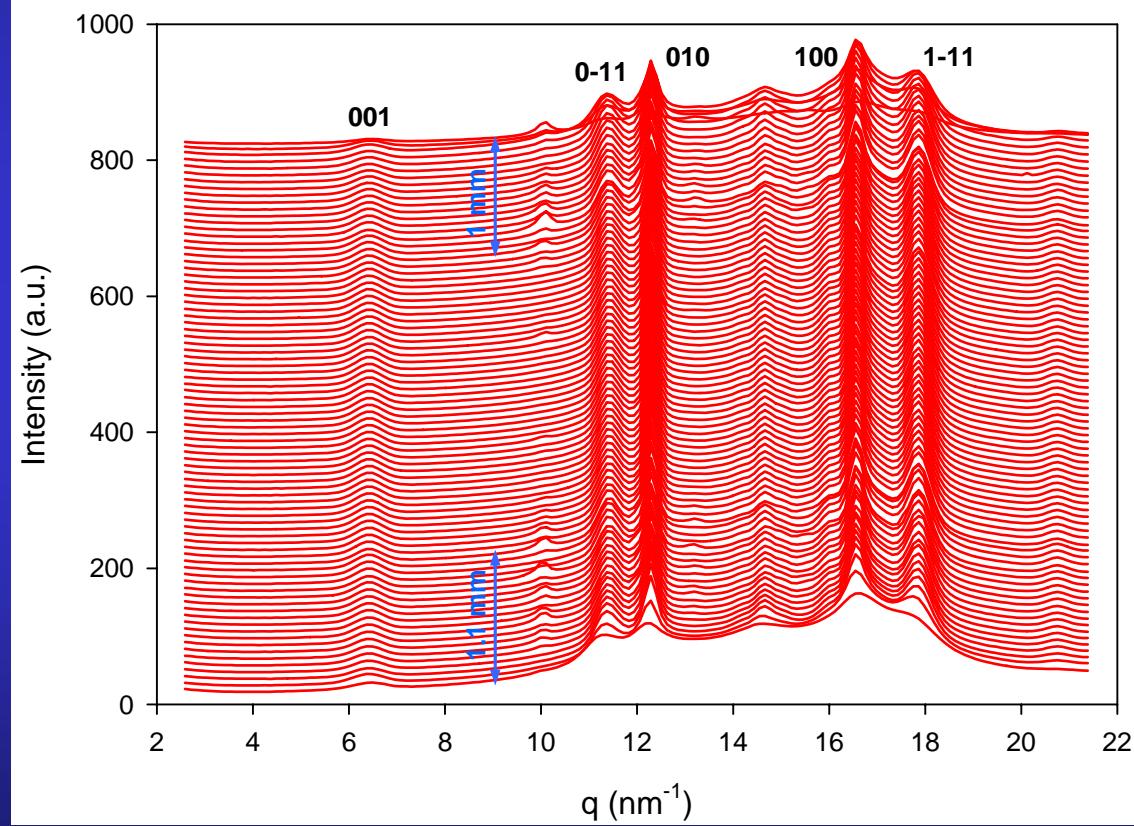
Renishaw Raman Microscope System RM2000 @ 785 nm





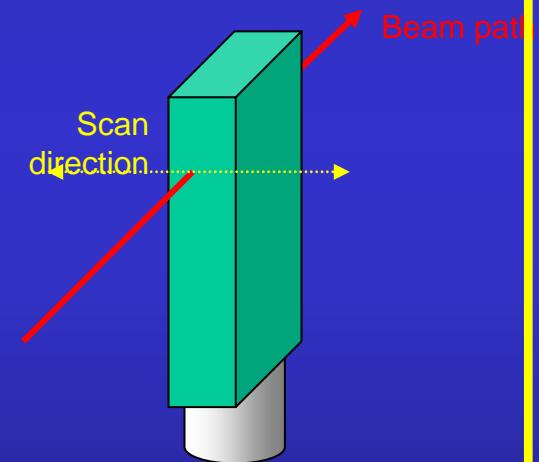
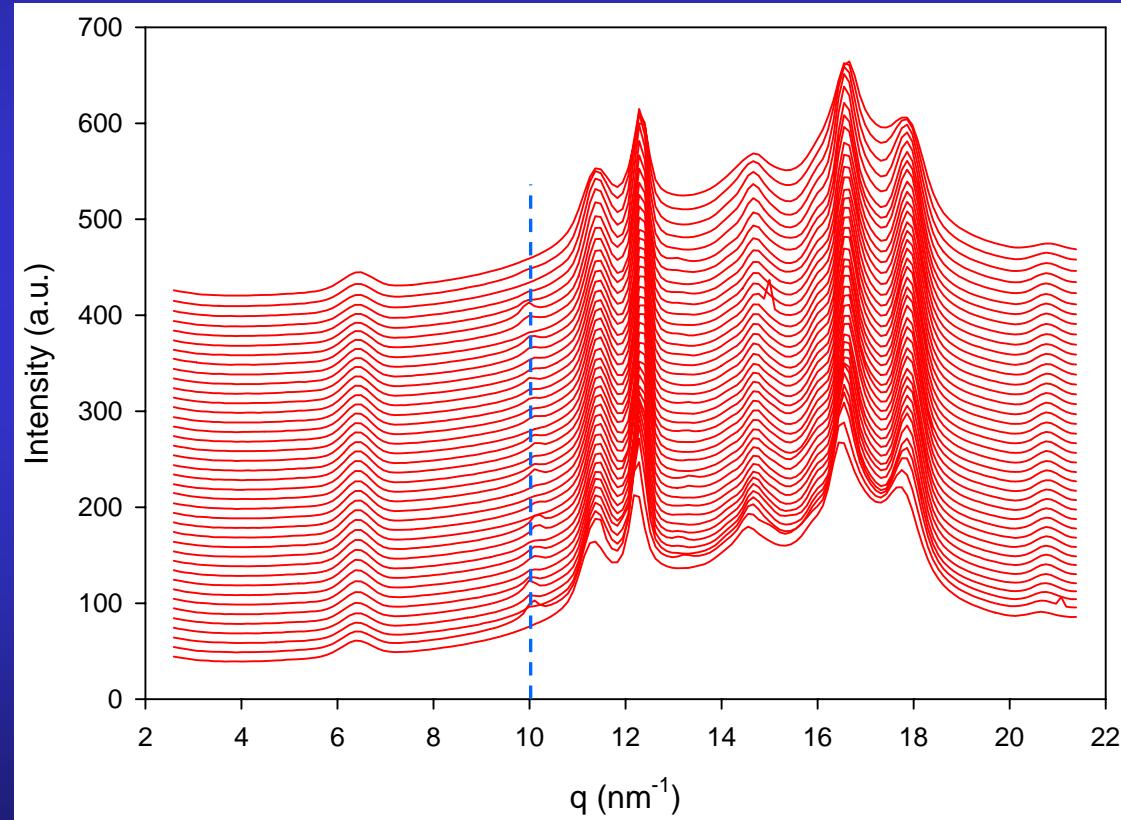
Microfocus: 5 μm

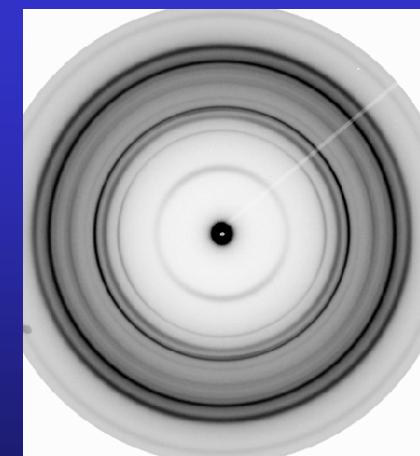
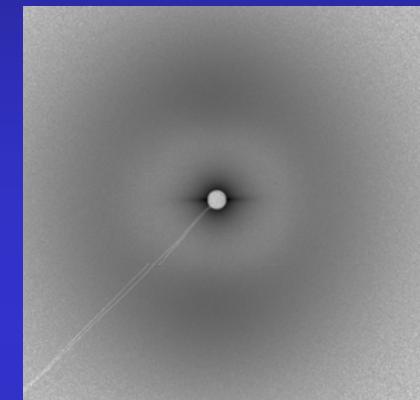
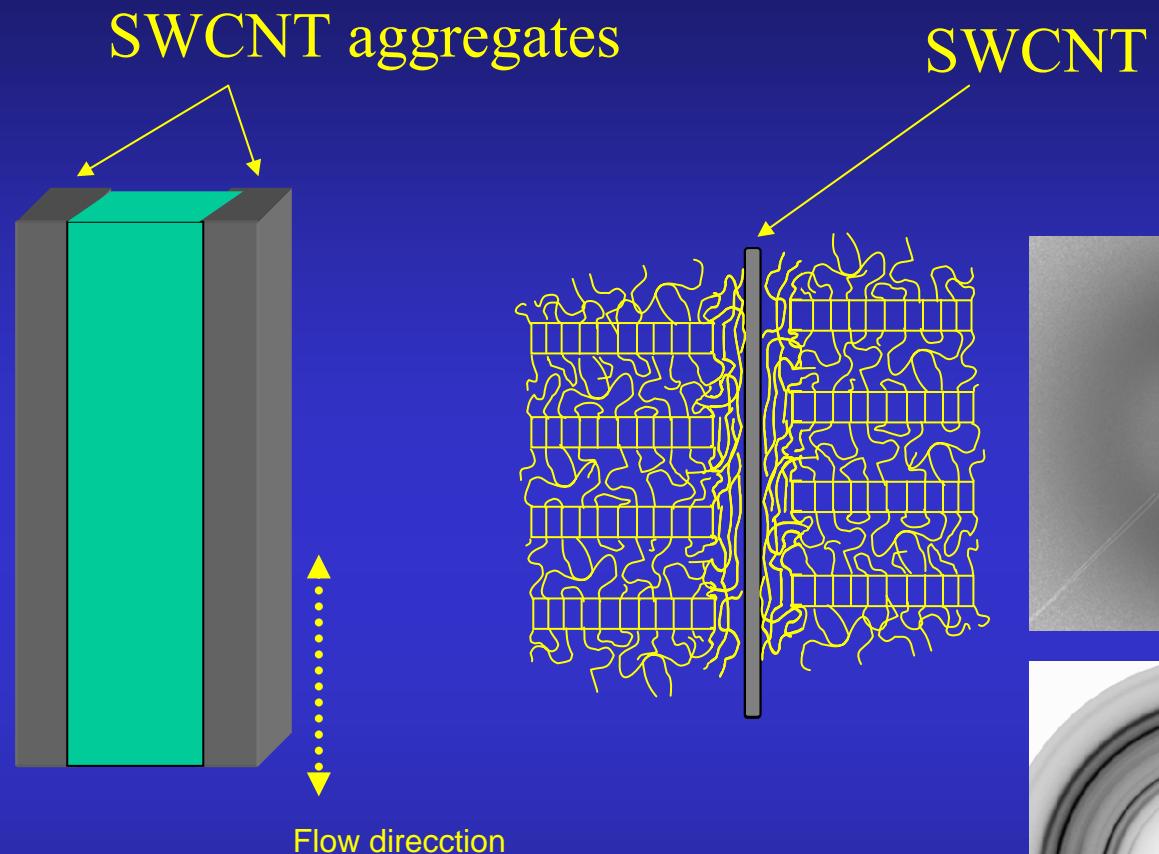
WAXS



Microfocus: 5 μm

WAXS





Brevísima Bibliografía

1. B. Chu, B.S. Hsiao, Chem. Rev. 2001, 101, 1727-1761
2. A. Nogales, I. Sics, T. A. Ezquerra, Z. Denchev, F. J. Balta Calleja, B. S. Hsiao, Macromolecules 2003, 36, 4827-4832
3. I. Sics, A. Nogales, T. A. Ezquerra, Z. Denchev, and F. J. Balta –Calleja, Review of Scientific Instruments, 71,4, 2000
4. A. Nogales, T. A. Ezquerra, Z. Denchev, I. Sics, F. J. Balta-Calleja, J. of Chemical Physics, 115, 8, 2001
5. C. Alvarez, I. Sics, A. Nogales, Z. Denchev, S.S. Funari, T.A. Ezquerra, Polymer 45 (2004) 3953–3959.