SCIENCE USING IR SYNCHROTRON LIGHT
A USER'S PERSPECTIVE
Basel, 1-2 February 2011

IR Workshop on Spectro-Microscopy

Synchrotron IR Microspectroscopy:

A powerful tool for Polymer Science

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Outline

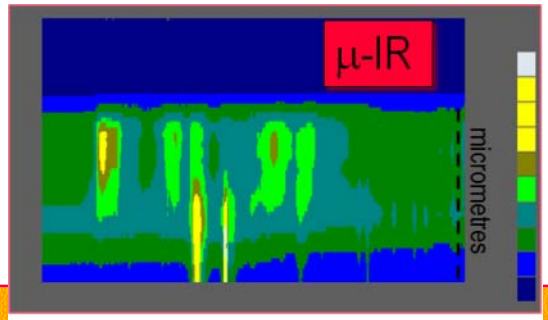
- Introduction
  - *Microscopic imaging in polymeric materials*
  - *The synchrotron IR microspectroscopy advantage*
- Some examples in polymeric materials
  - *Heterogeneous polymer systems*
- Future developments
  - *Wider, smaller & faster!*
- Conclusions
- Acknowledgements

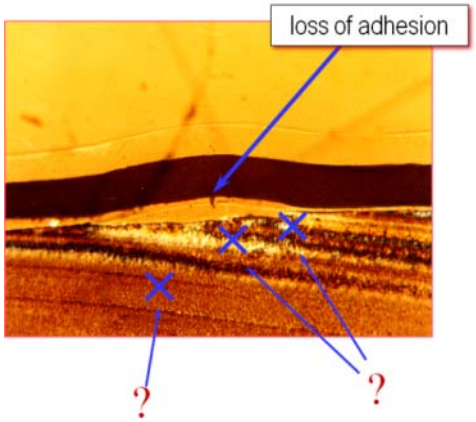
Introduction

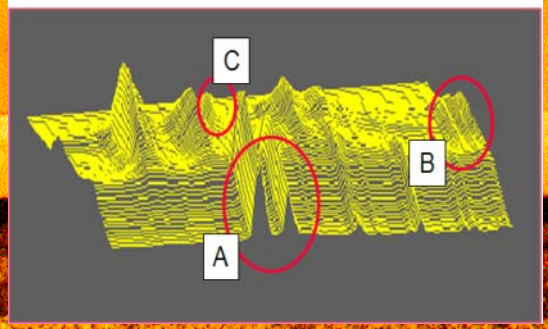
- Polymers in everyday life
  -  Essential for almost all our daily needs
  -  Playing with polymers
  -  Safety and Polymers
- Polymers are fine when they work…
  - But when they don't…   
  - *Example Problem:* Paintwork on cars

Cross-section of a car bumper / fender

MULTILAYER
POLYMERIC SYSTEM







varnish / lacquer

black paint

matrix polymer

POLARIZED OPTICAL MICROSCOPY

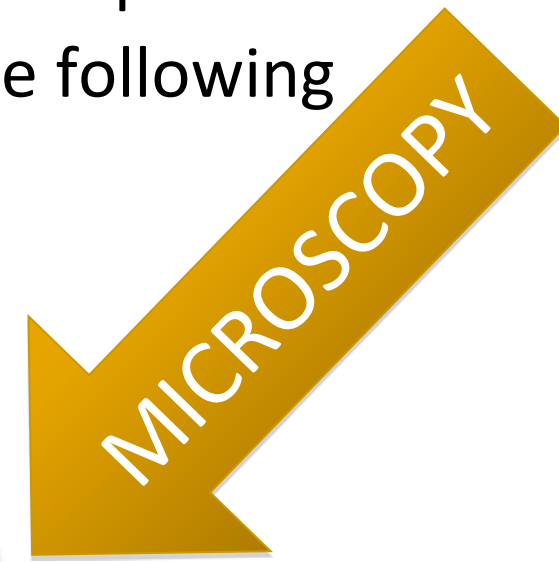
structural variations

How do we solve these problems?

- Almost all polymeric materials are “heterophase”
- Need for understanding and control the following parameters:
  - COMPOSITION
  - STRUCTURE
  - MORPHOLOGY
  - ORIENTATION

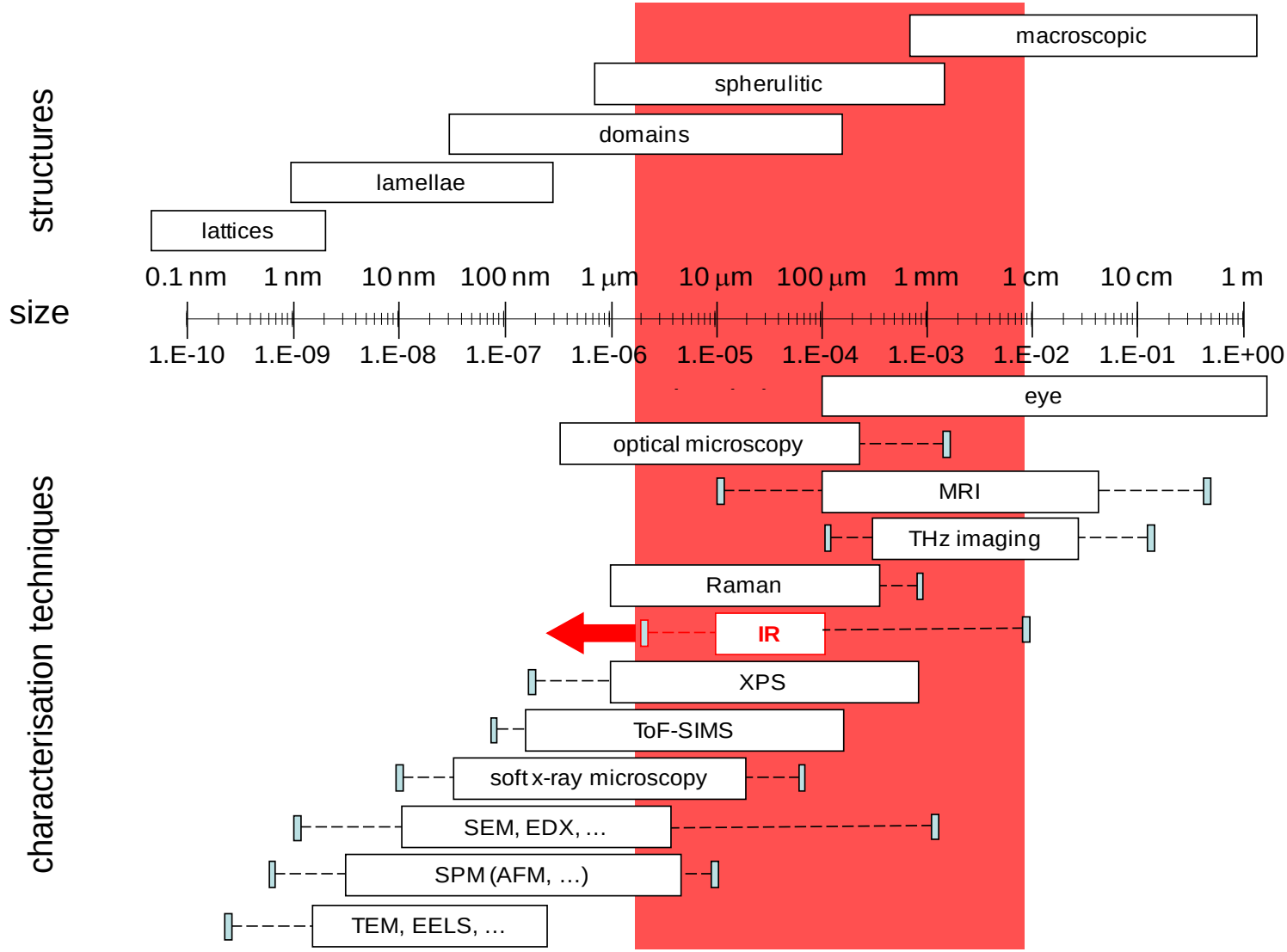
  } TYPES OF HETEROGENEITY

- Materials design
  - Control of “Architecture”
  - MODIFICATION
- CONTROL OF PROPERTIES



CARACTERIZATION OF DOMAINS

Tools for microscopic imaging



Why infrared?

- IR spectroscopy
  - Powerful molecular characterization technique
  - High information content
  - Non-destructive
  - Versatile sampling
  - Well-understood
- IR microspectroscopy
  - Spatially resolved spectra
  - Small sample / small volume analysis
  - Chemical and structural mapping

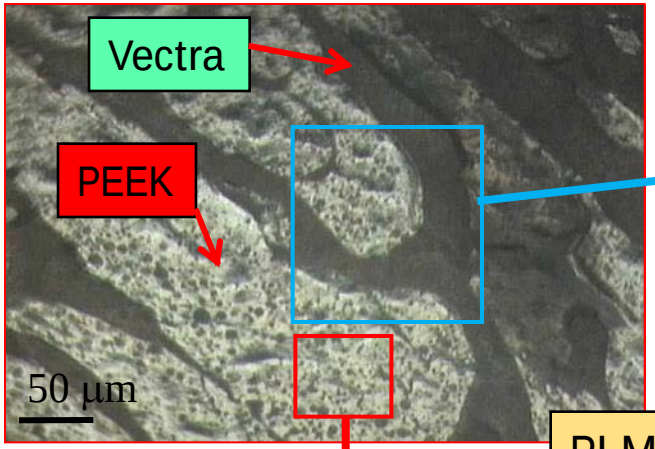
Infrared microspectrosocopy has been around for some time....

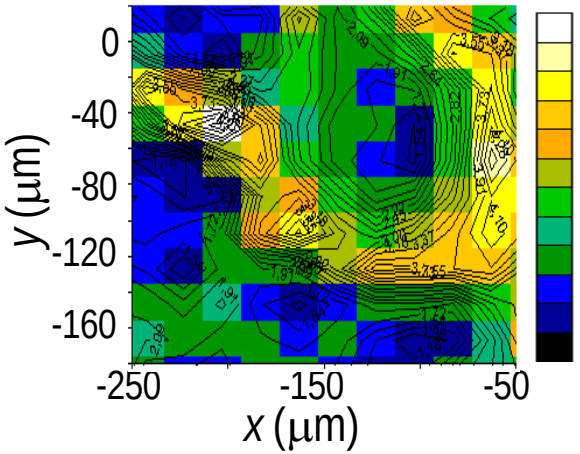
Aperture-limited domain characterization

(Pixel size)

Example: Polymer blend

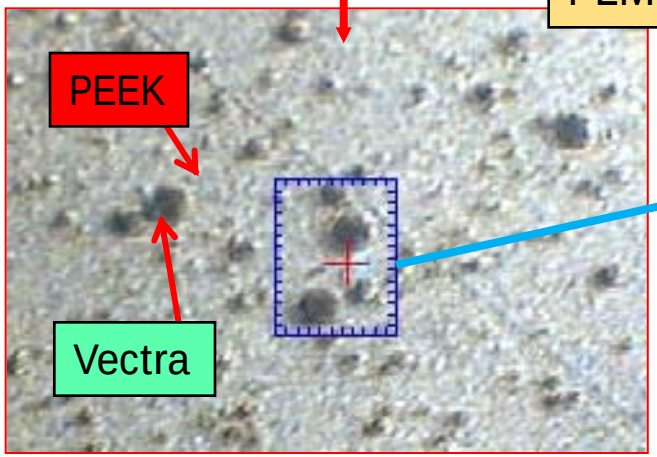
Coalescence and phase inversion





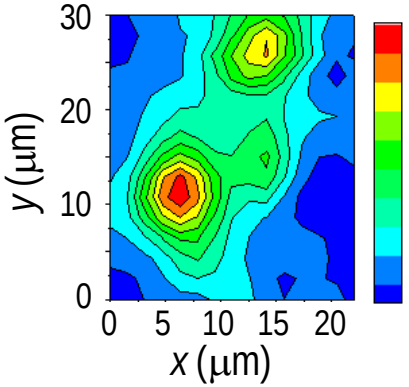
Aperture 20 x 20 μm (Conventional microscope)

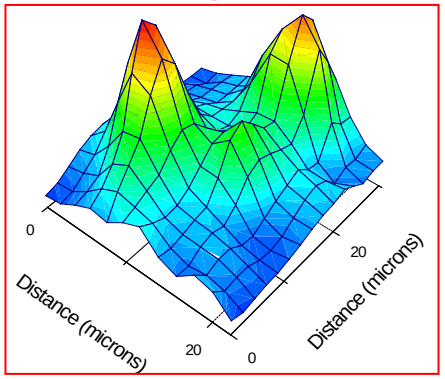
PLM



Aperture 6 x 6 μm (oversampled 3 x 3 μm)

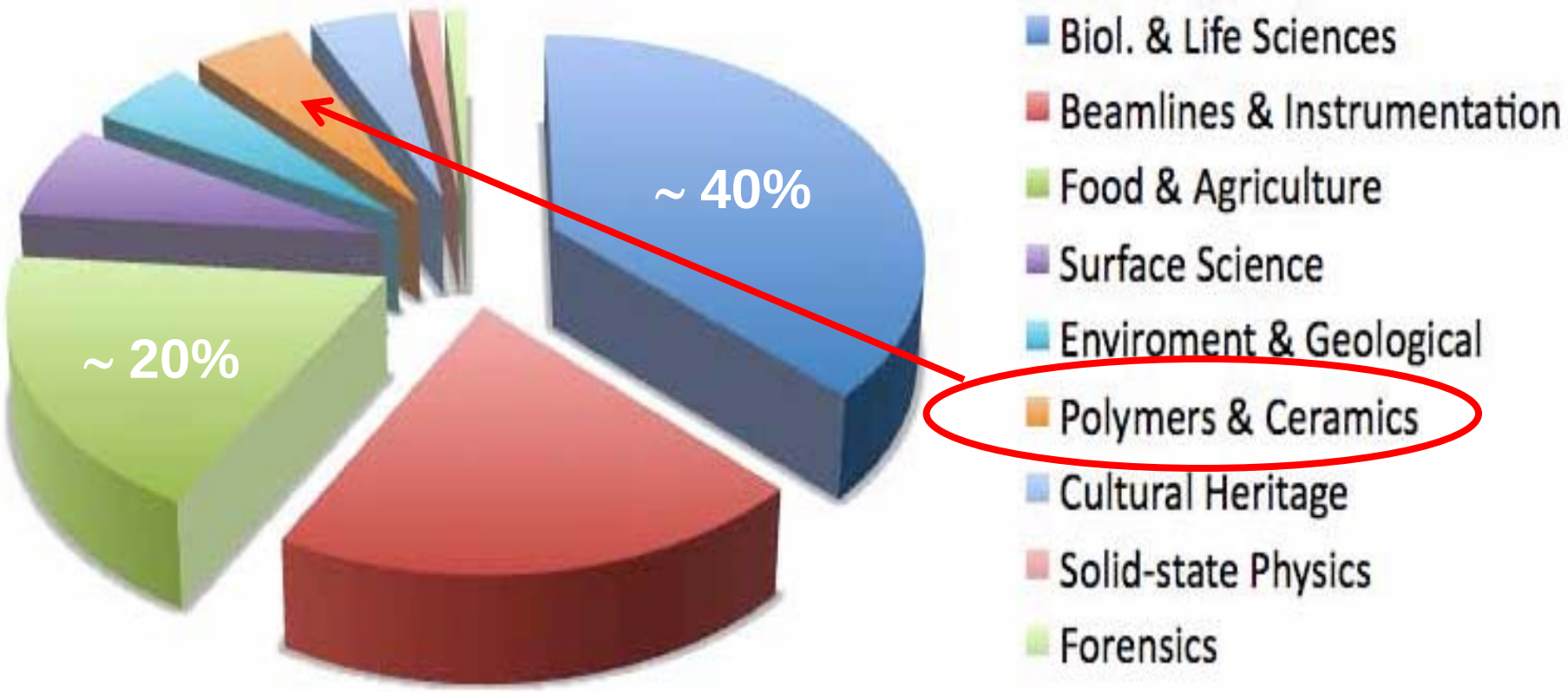
Synchrotron source required!





Synchrotron IR microspectroscopy

Multidisciplinary Scientific Impact

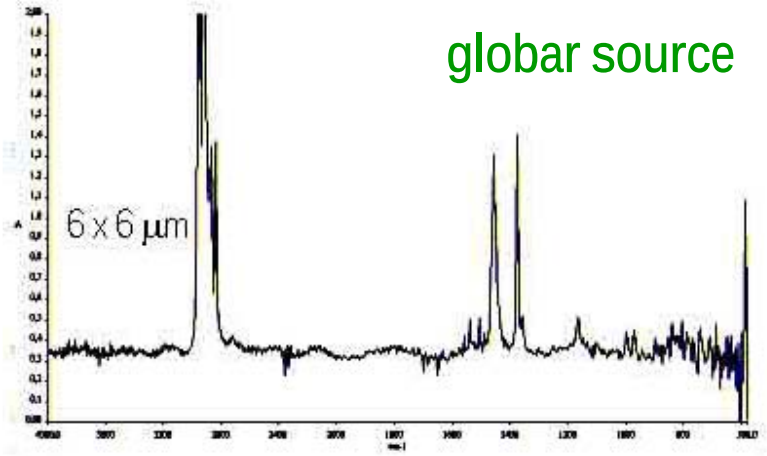


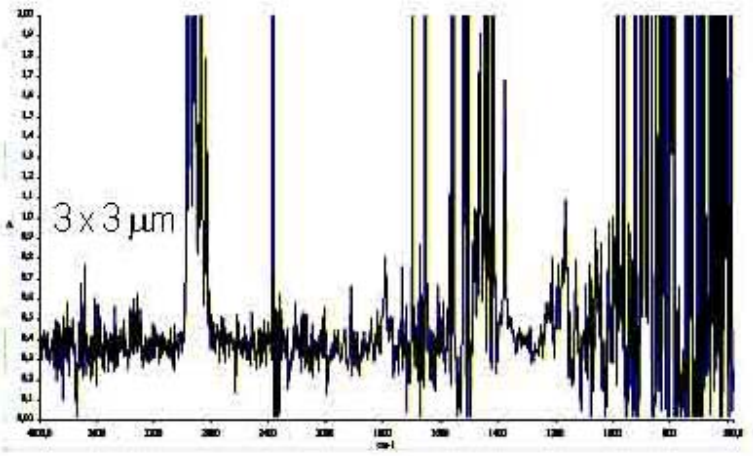
Last 270 SCI publications (to 2008)

It works for polymers too…

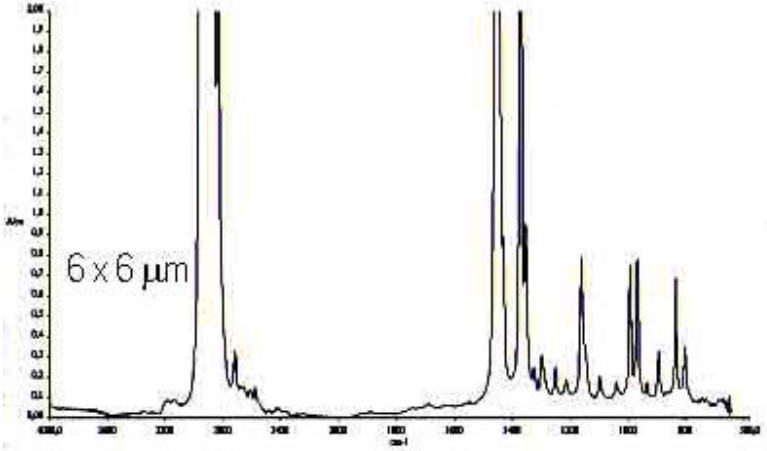
ISOTHERMALLY CRYSTALLISED POLYPROPYLENE FILM

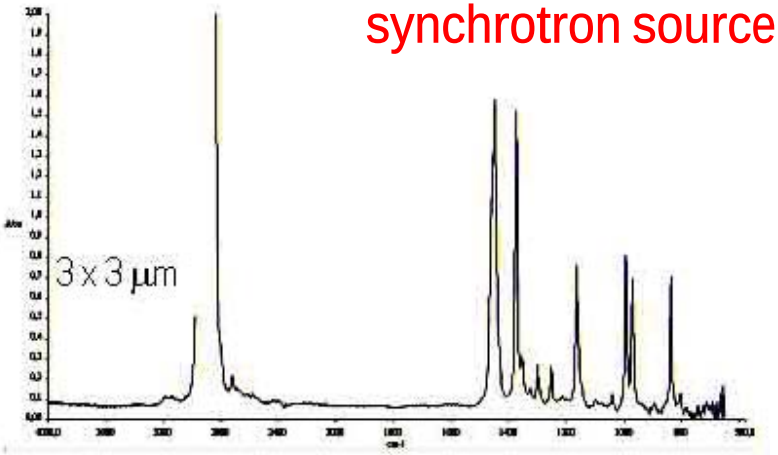
globar source





synchrotron source





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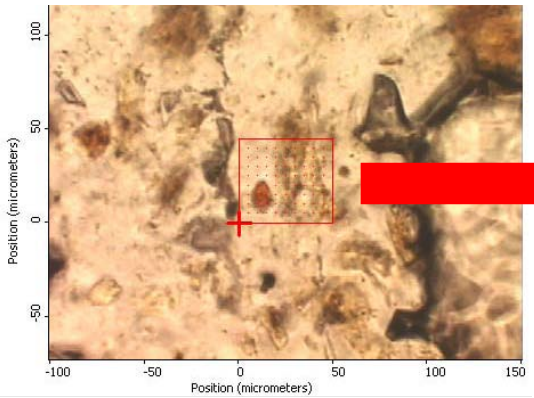
Heterogeneous polymer systems

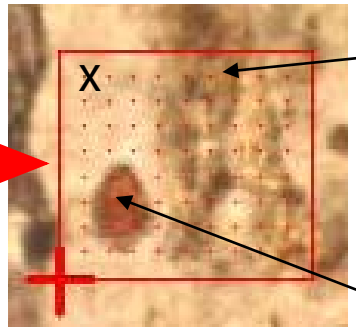
- Composition
  - *Polymer composites and blends*
- Structure & Morphology
  - *Polymorphism*
  - *Transrystallinity*
  - *Crystalline superstructure*
- Modification
  - *Laser microperforated biopolymers*

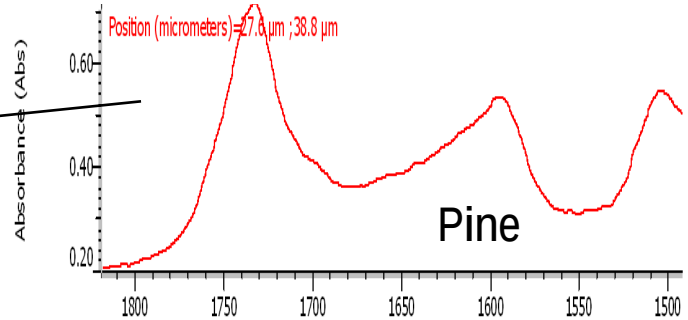
Wood – Polymer Composites

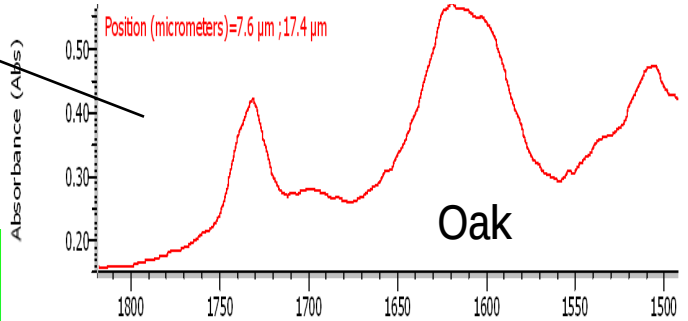
Colaborators
Rebeca BOUZA
Zulima MARTIN
Gonzalo SANTORO

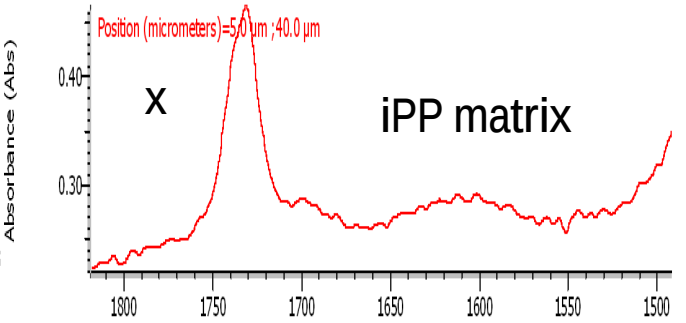
Distinguish between different types of wood partcles



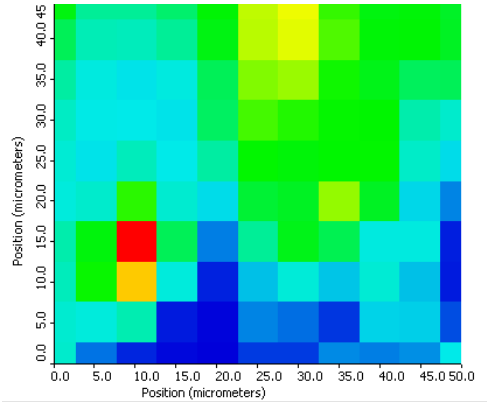






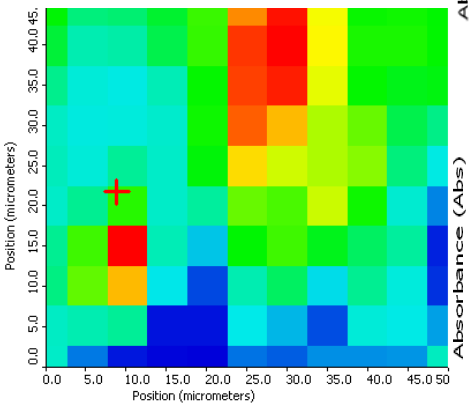


1620 cm^{-1}

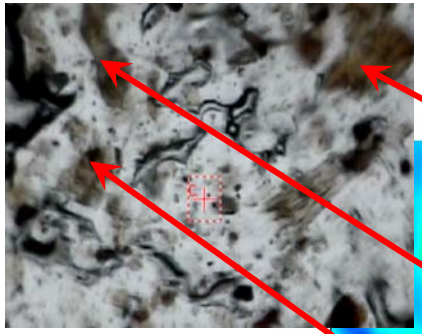


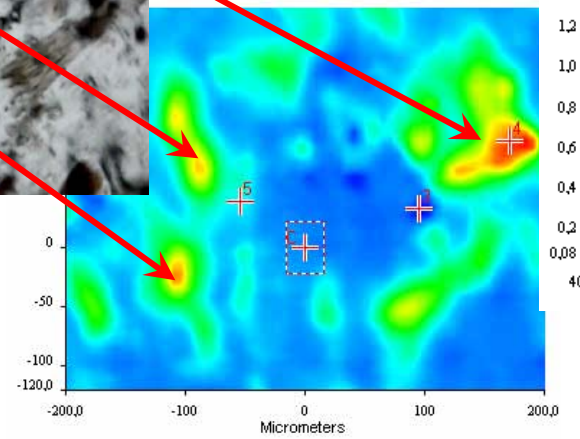
Intensity maps

1595 cm^{-1}



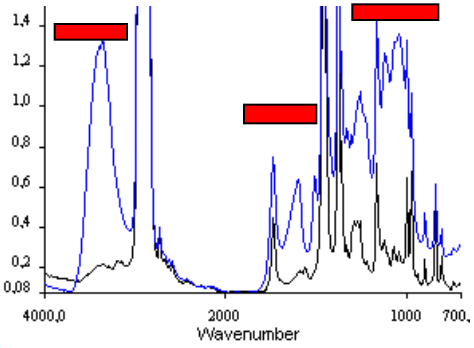
Composite: 90% PP / 10% Woodflour (5% MAH)



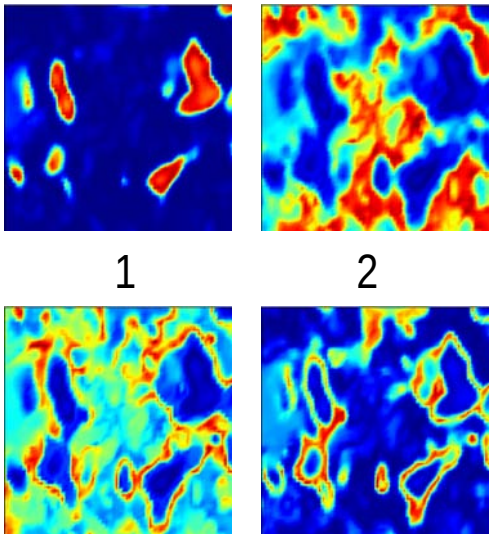


IR functional groups map (univariate)

High S/N IR spectra

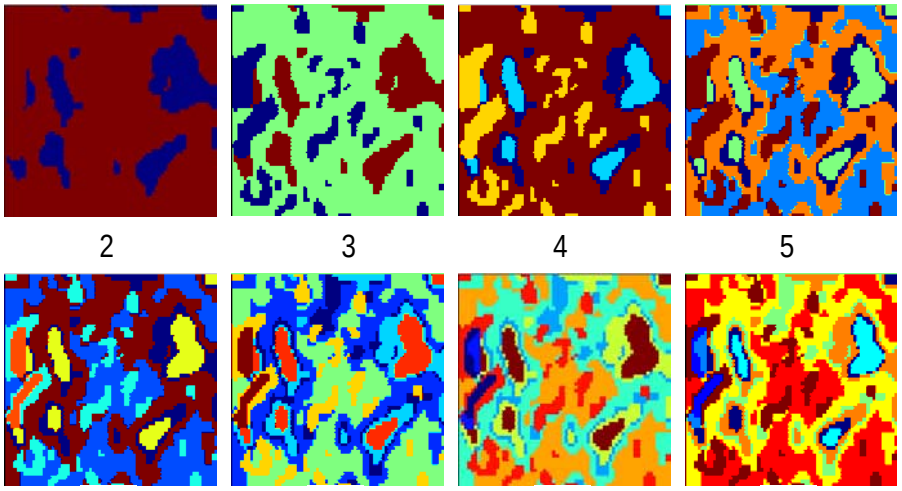


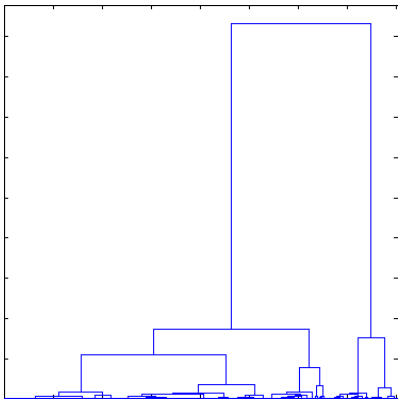
Fuzzy C-Means Cluster Analysis



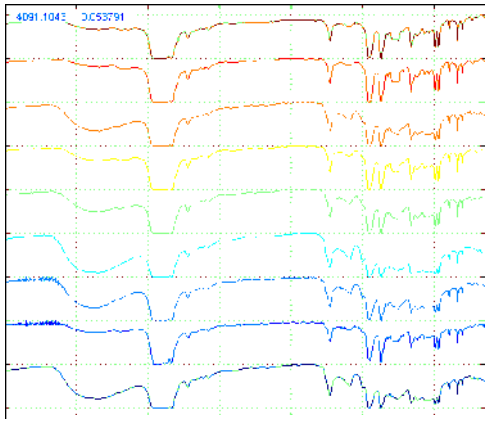
Chemometrics
(multivariate)

Hierarchical Cluster Analysis





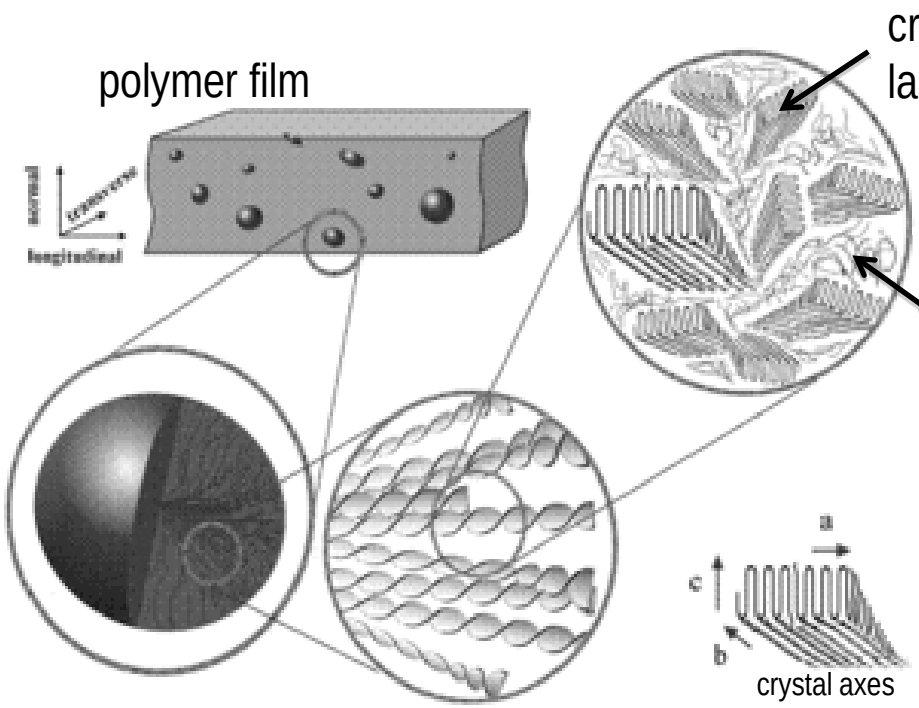
Dendrogram

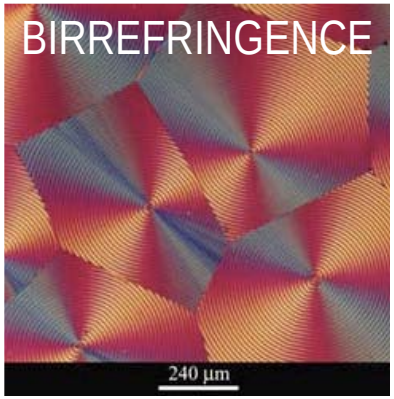


Extraction of mean spectra

Structure and Morphology

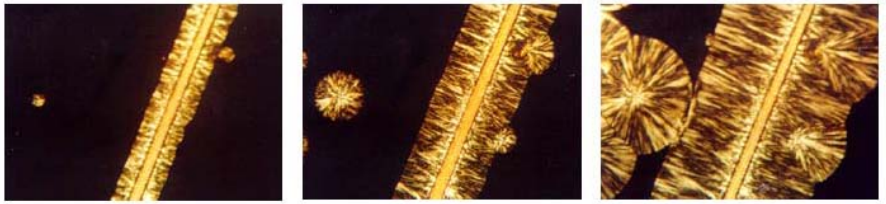
Structural hierarchy





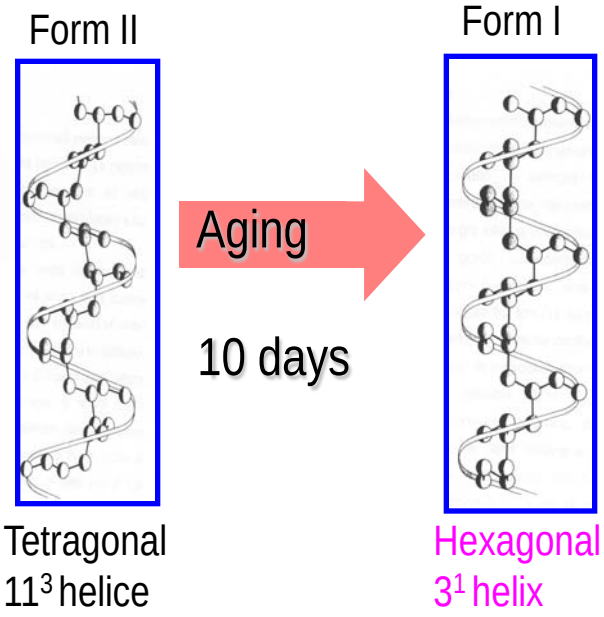
Polarized optical microscopy

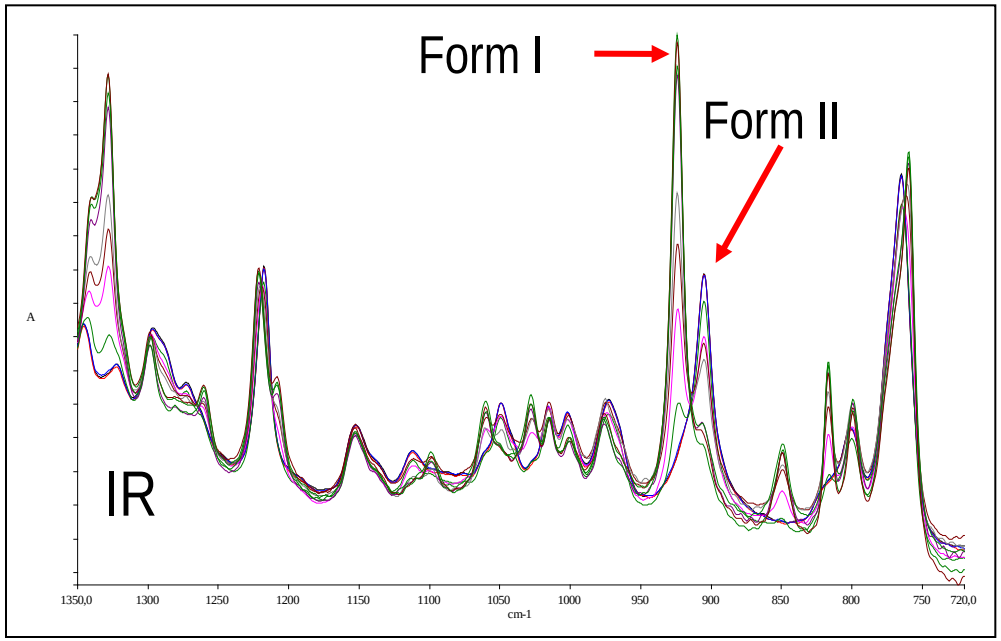
transcrystallinity

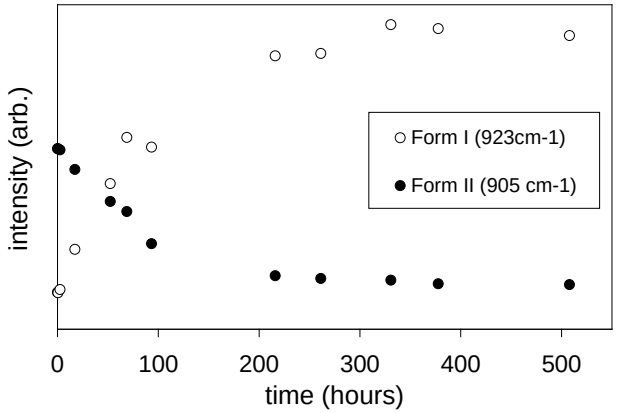


Polymorphism: Isotactic Polybutene

- Change in crystal structure
- Change in conformation
- Nice sensitivity in IR
- Slow transformation (days)

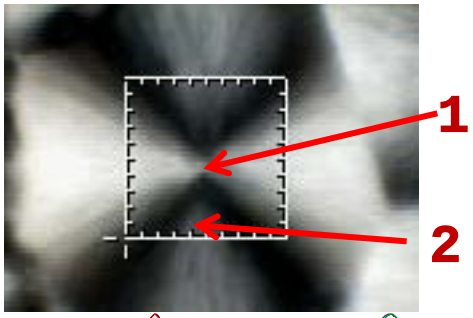






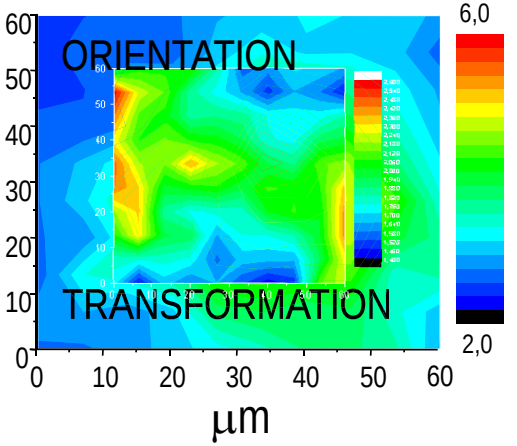
Polymorphism: Isotactic Polybutene

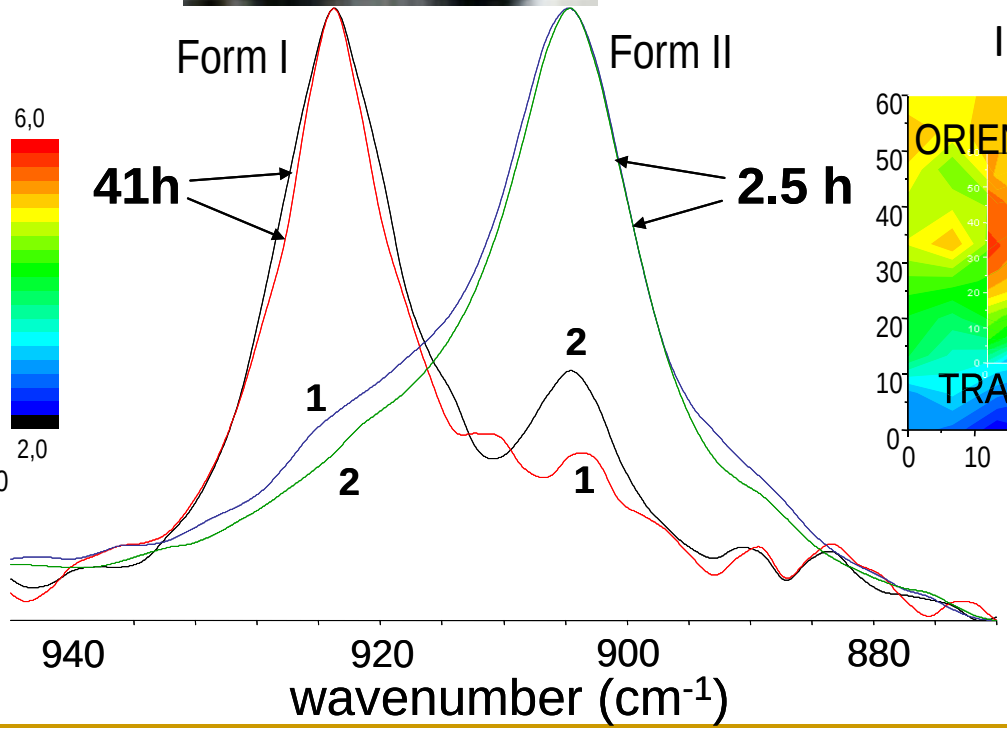
Z = 60 x 60 μm
A = 6 μm



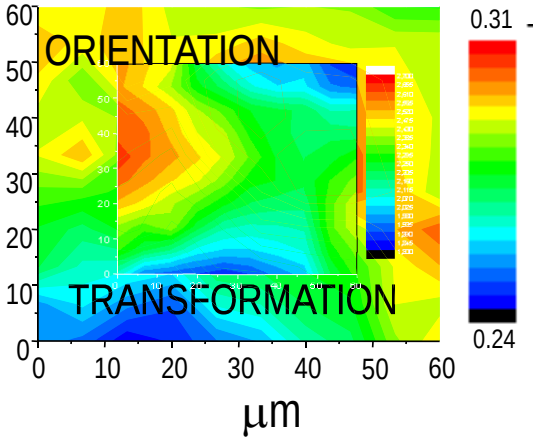
Colaborators
Ana AMATE
Fiorenza AZZURRI
Zulima MARTIN
Carlo MARCO
Gonzalo SANTORO

Int (I) / Int (II)



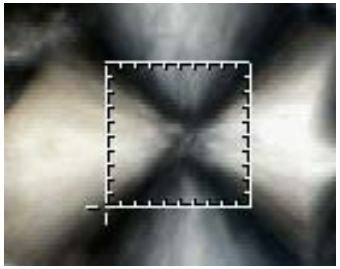


Int (I) / Int (II)

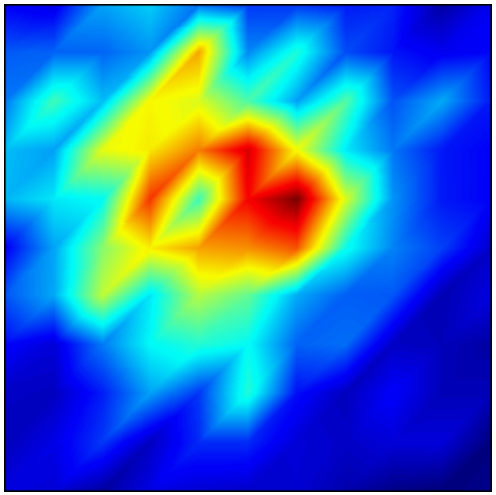


Isotactic Polybutene-1

Z= 60 x 60 μm
A= 6 μm

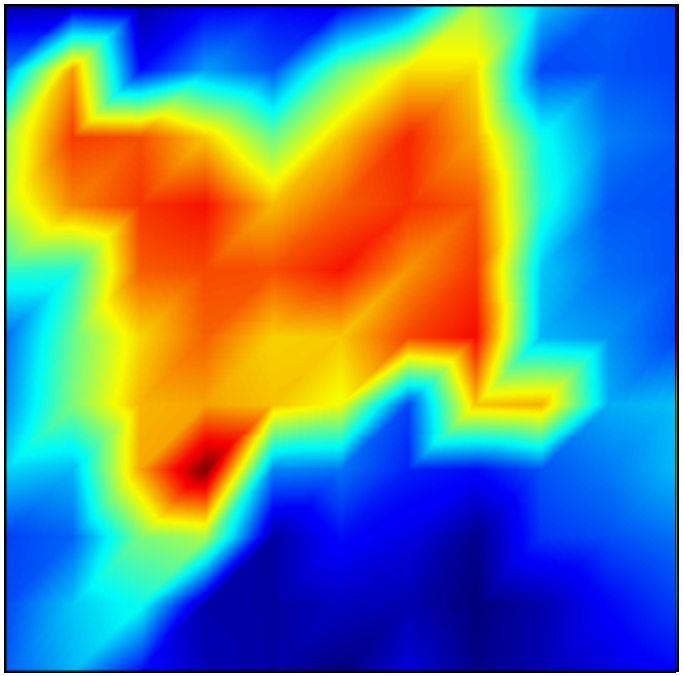


- Relative band intensity map
  - 926 / 905



orientation

Phase transformation

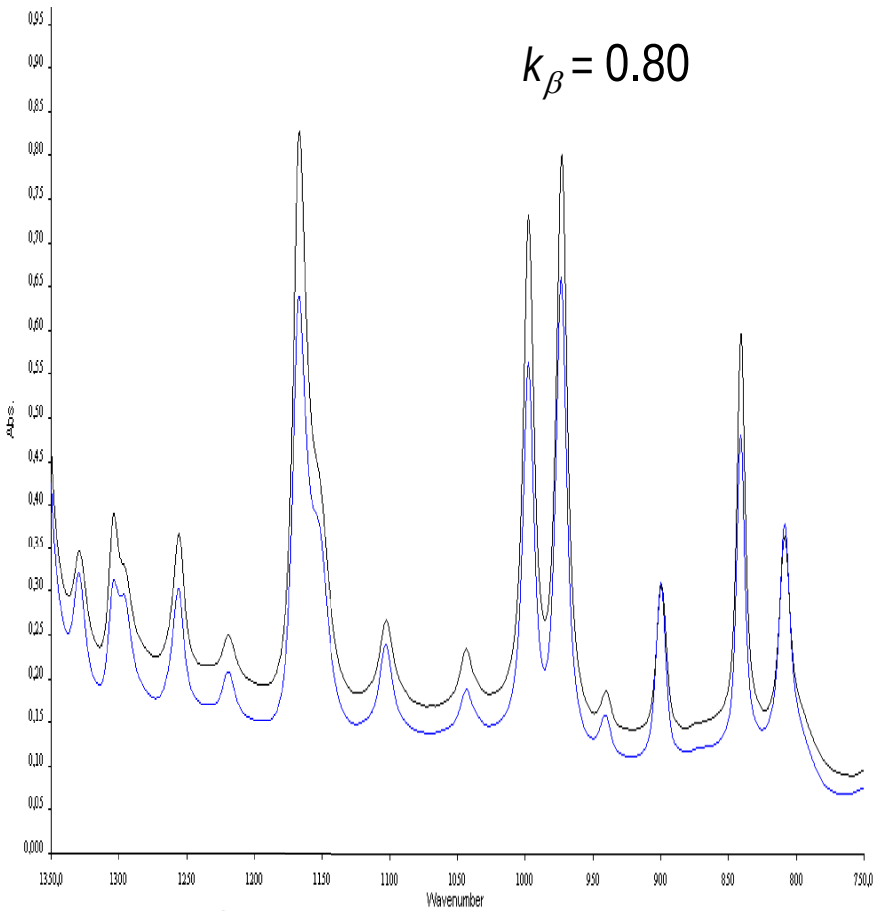


- Multivariate statistics
  - Fuzzy C-means clustering
  - 820 – 1175 cm-1
  - 3 clusters

Polymorfism: Isotactic Polypropylene

Colaborators
Carlo MARCO
Gonzalo SANTORO

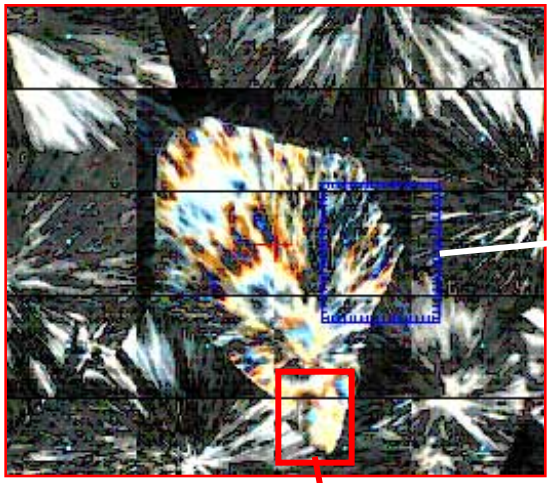
- α (monoclinic)
  - Crystallization from the melt
  - Tm = 170 - 180ºC
- β (trigonal)
  - Crystallization under shear, temperature gradients or nucleating agents
  - Tm = 155ºC
- γ (triclinic)
  - Crystallization under pressure
- δ (smectic)
  - Low order and crystallinity

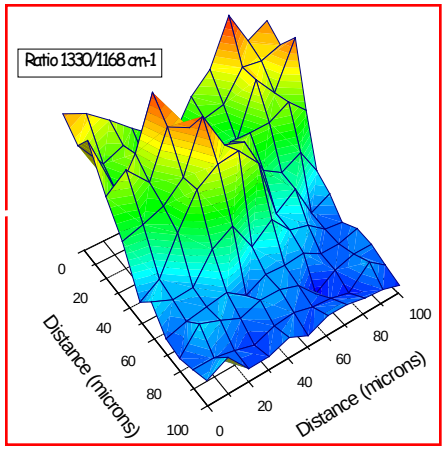


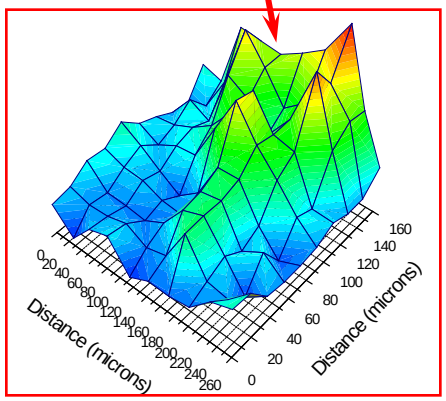
Conformation 3_1 $(TG)_3$

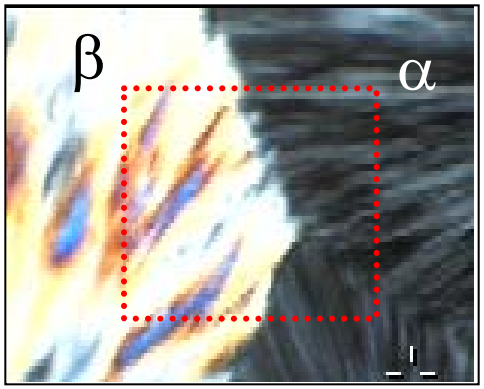
Polymorfism: Isotactic Polypropylene

Detailed microstructure of spherulites

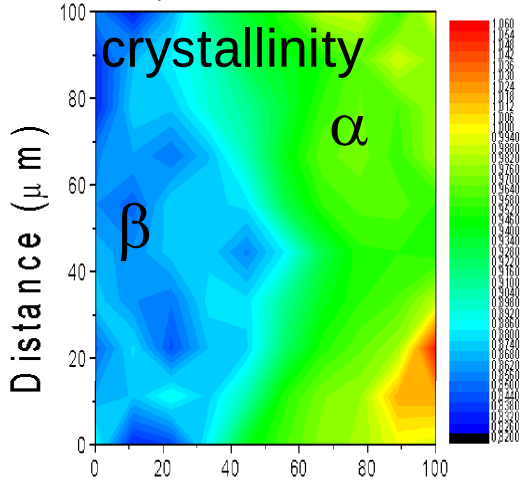


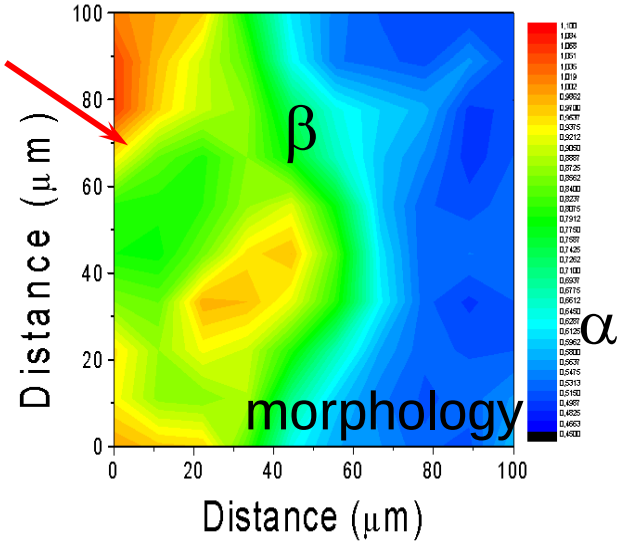




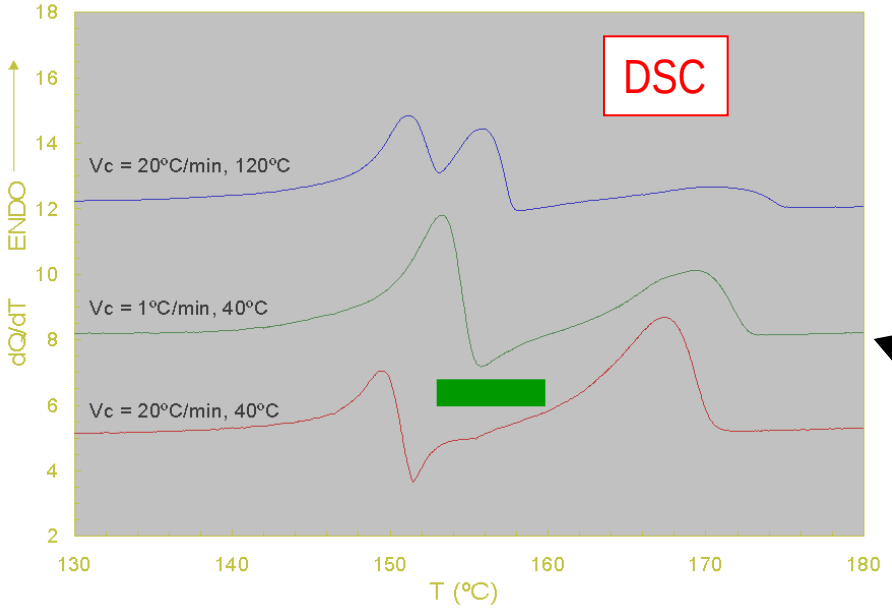


Area = 100 x 100 μm
Aperture
6 x 6 μm





Polimorphism in iPP: Phase transitions



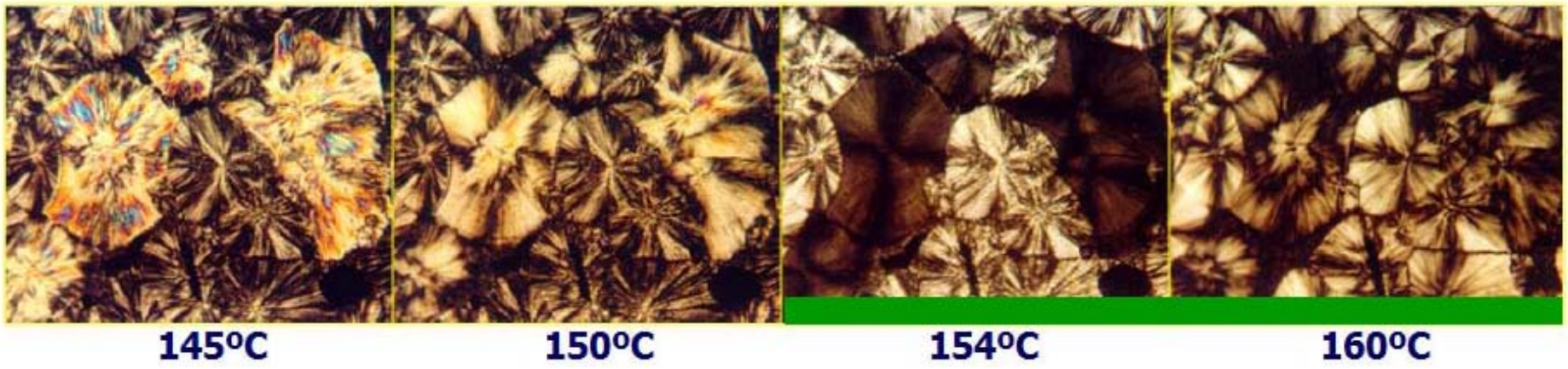
Varga, *et al.*

β - β' transition 120 – 210ºC

Heating rate 1ºC/min

β - α transition 40 – 210ºC

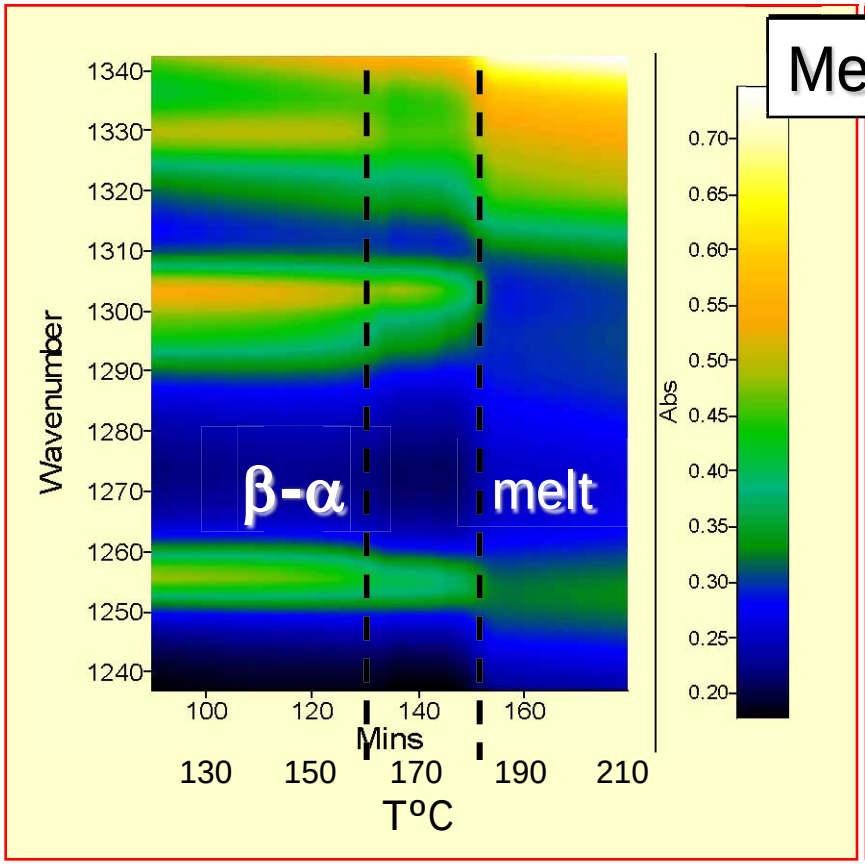
Polarized light microscopy

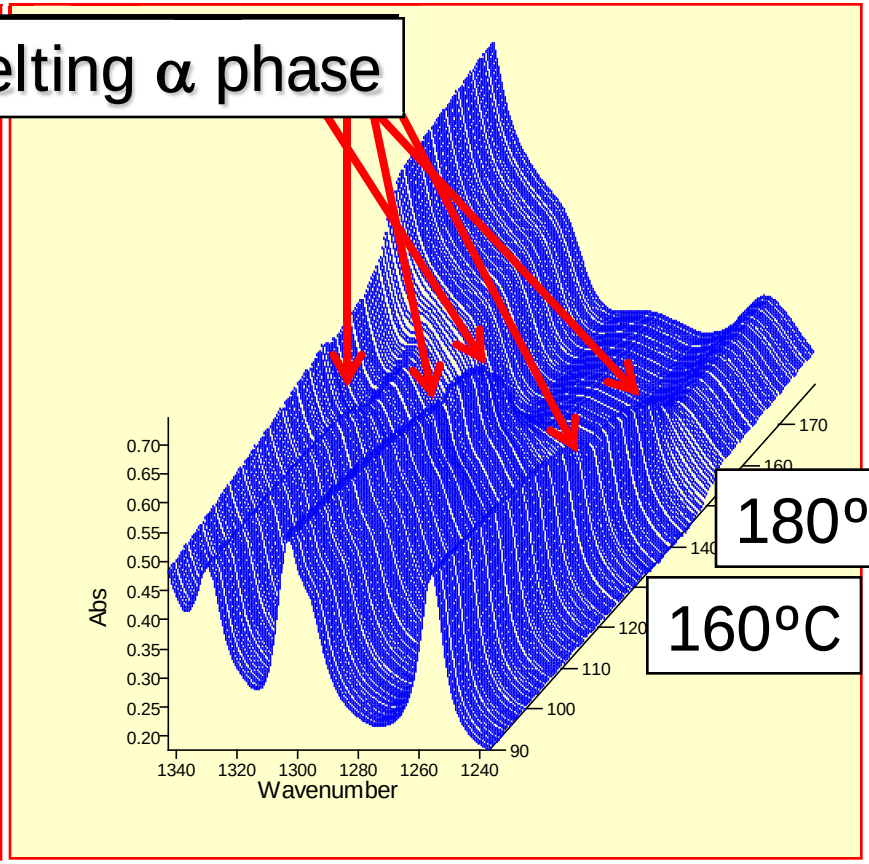


Polimorphism in iPP: Phase transitions

IR measured here

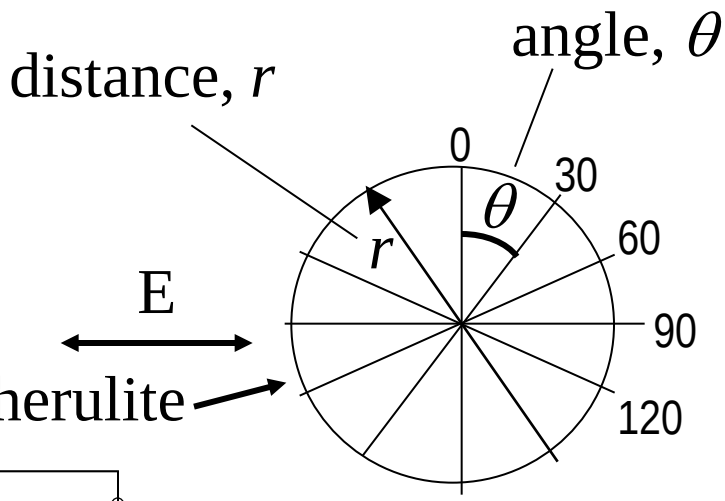
Thermal history: 210ºC ----- 40ºC ---- 210ºC (1ºC/min)

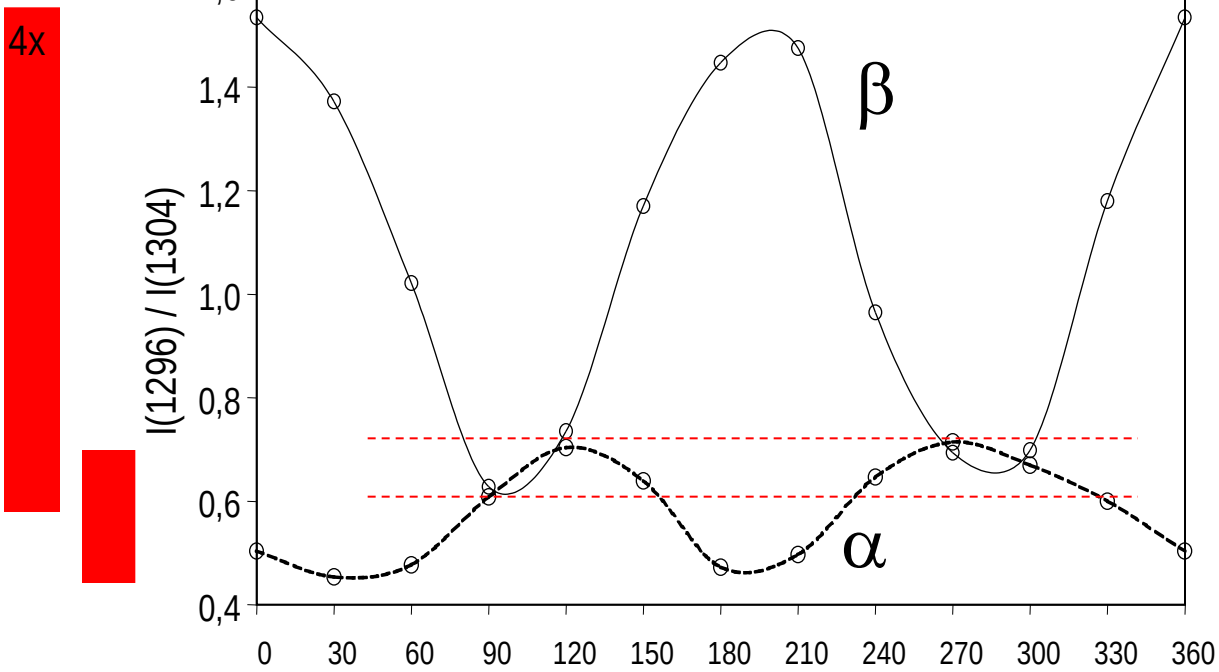


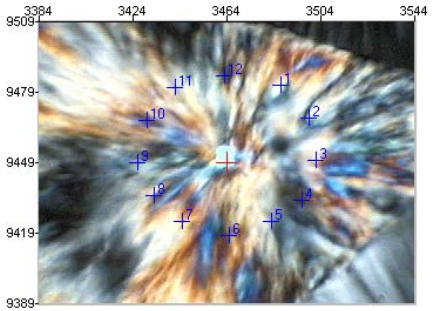


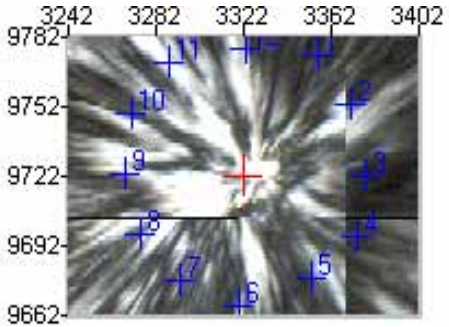
Polimorfism en iPP

- Synchrotron beam highly polarized
- Sensitive to mean orientation of the polymer chains





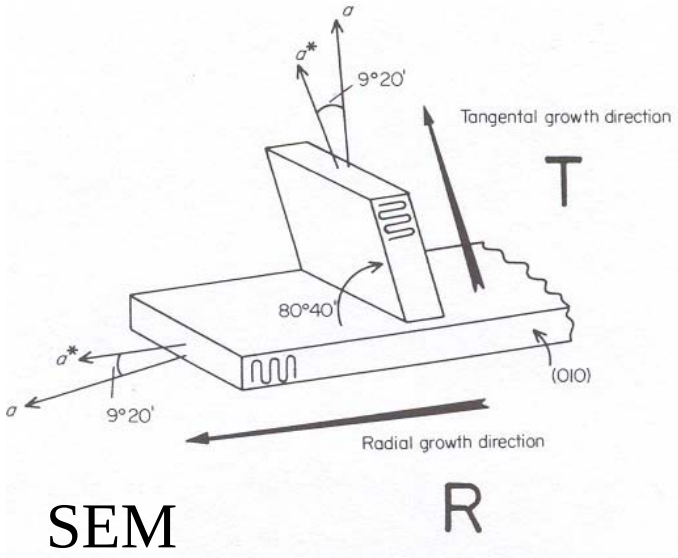




from Ellis *et al.*, *J Macromol Sci Phys* 2004, 43, 177

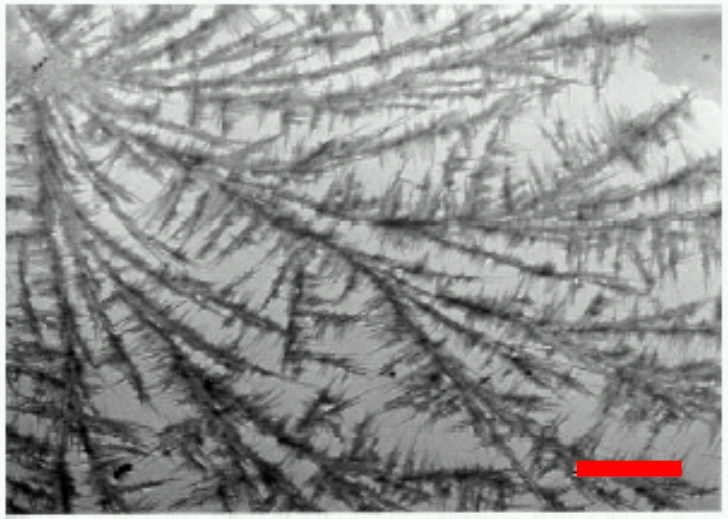
“Cross-hatching”

Lotz, Wittman, Lovinger,
Polymer 37, 4979 (1996)

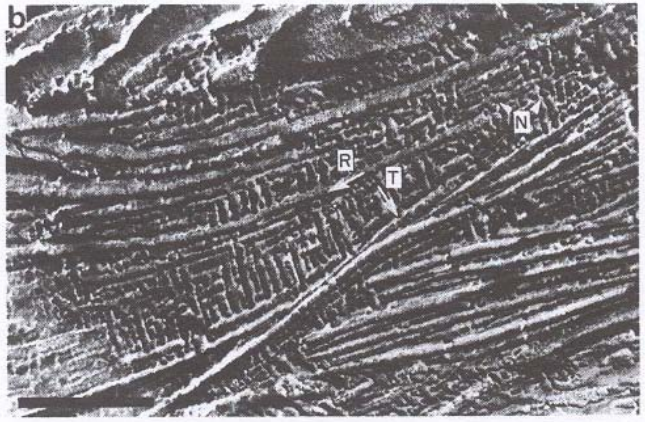


α–iPP

SEM
thin
film



SEM



Norton & Keller
Polymer, 26, 704 (1984)

Nedkov
e-Polymers, 41 (2002)

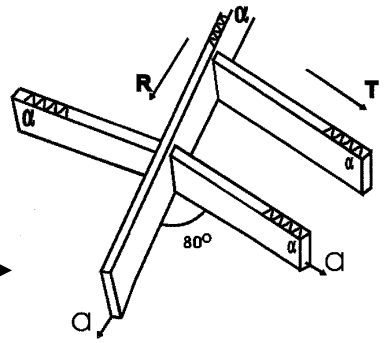
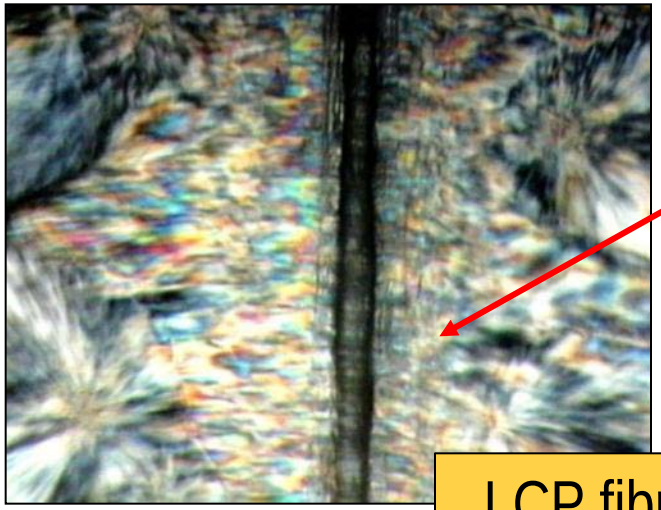


Fig. 9. Cross-hatching or branching. R – radially growing branches; T – tangentially growing branches

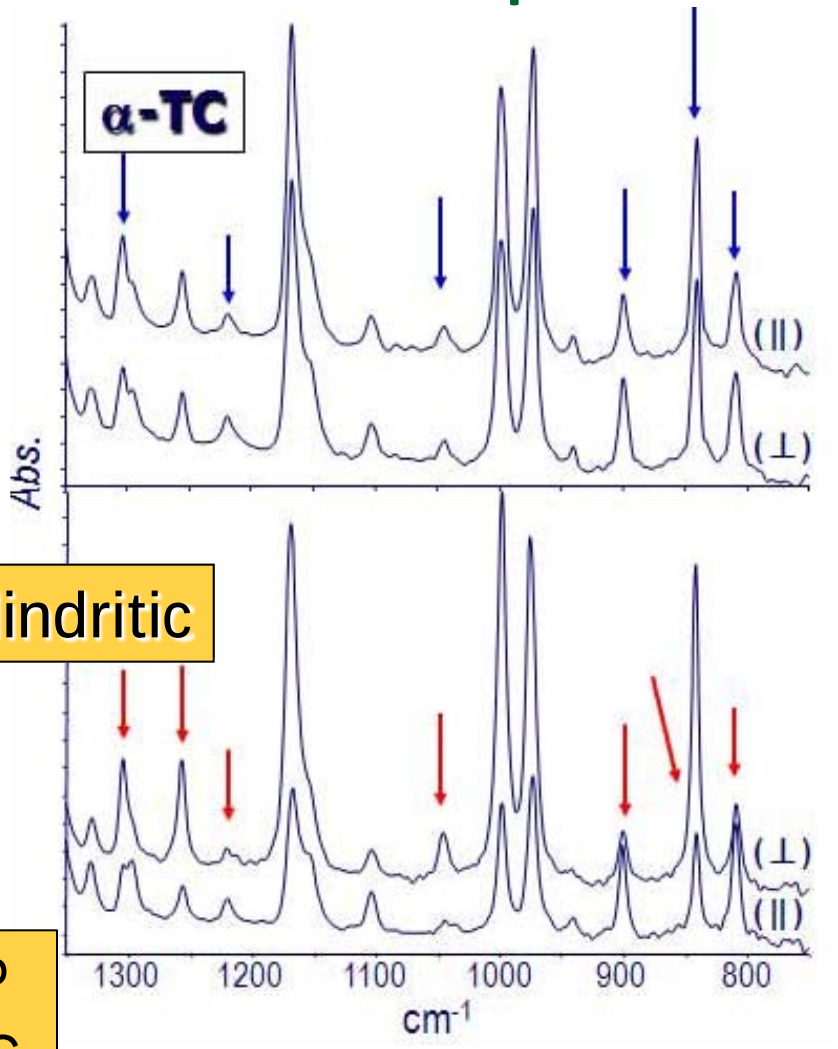
Interphase in iPP/ LCP-fibre composites

- Sheared by fibre-pulling
- Formation of β-polymorph
- Large differences in dichroic ratios
- ALLOWS US TO DIFFERENTIATE



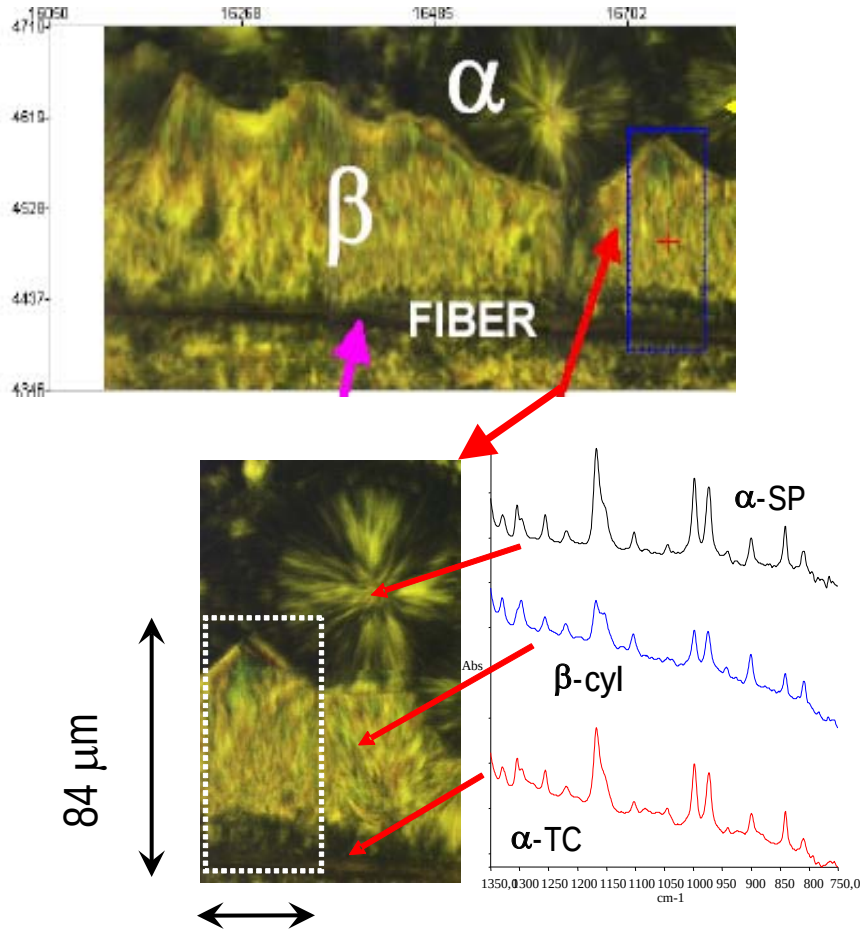
β-cylindritic

LCP fibre in iPP
$T_c = T_{pull} = 133^oC$

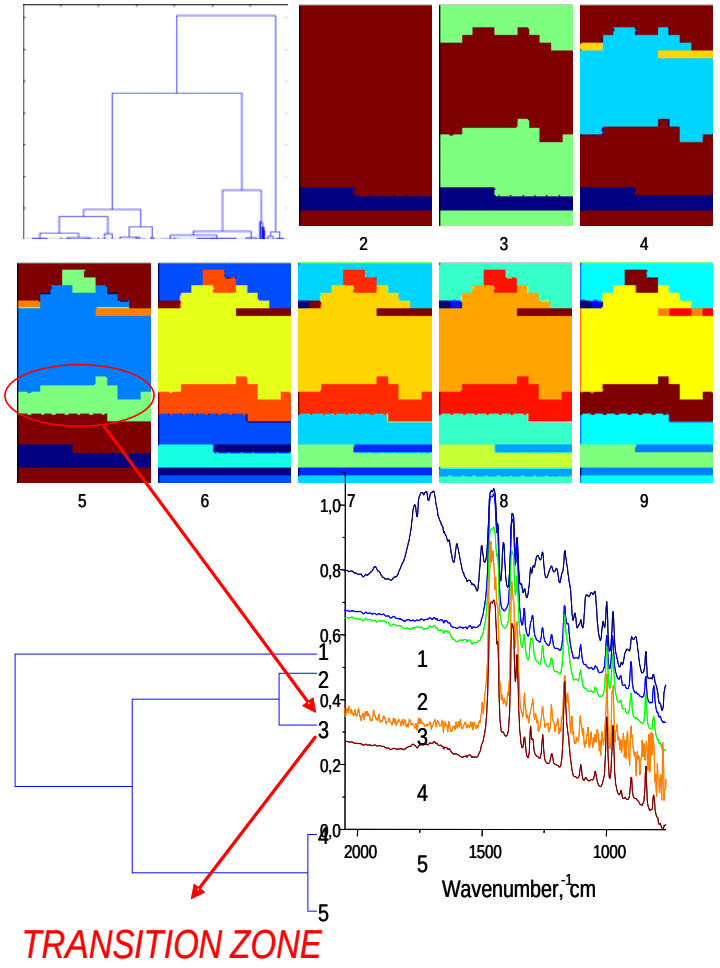


from Ellis *et al.*, *J Macromol Sci Phys* 2004, 43, 177

Interphase in iPP/ LCP-fibre composites



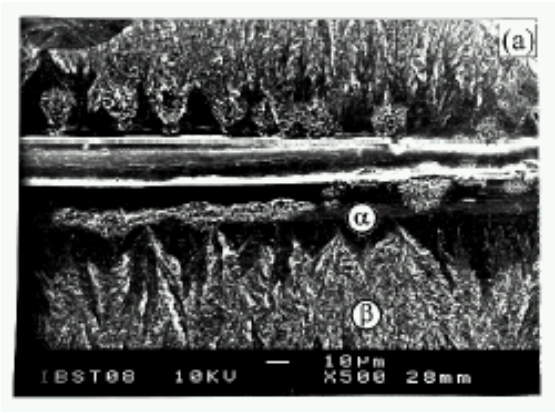
Hierarchical Cluster Analysis



from Torre *et al.*, *Macromolecules* 2006, 39, 5564

Shear: Complex interphase morphology

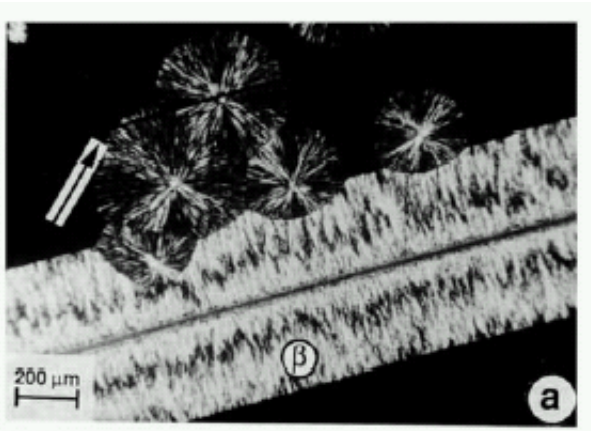
Kevlar 49 fibre in iPP
$T_c = T_{pull} = 133^oC$

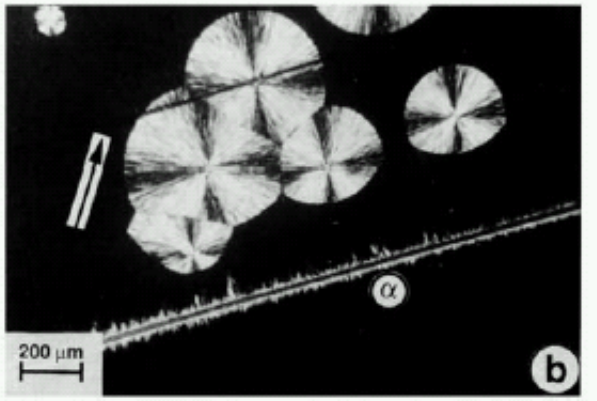


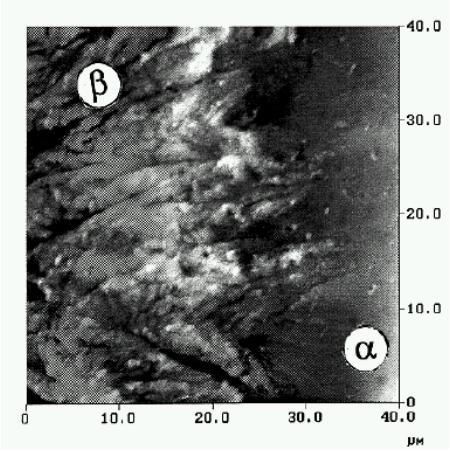
SEM micrograph

Karger-Kocsis *et al.*,
Polymer Bulletin 41, 493 (1998)

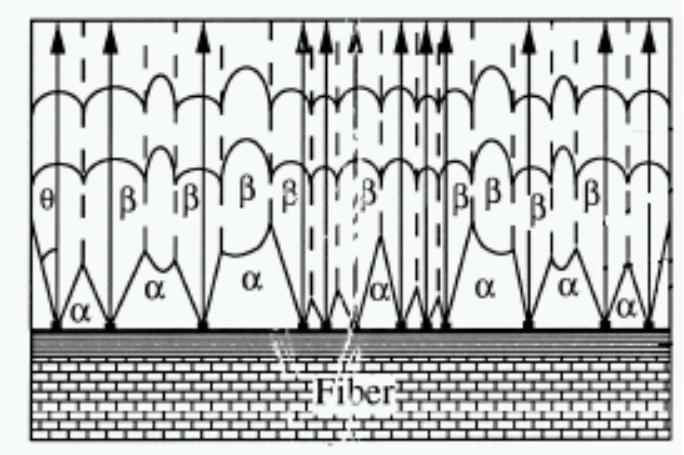
Thermooptical microscopy







Tapping AFM



Model

Varga & Karger-Kocsis et al.,
J. Polym. Sci. B. Polym. Phys. 34, 657 (1996)

Complimentary: Synchrotron microfocus XRD

@ ID13 beamline ESRF

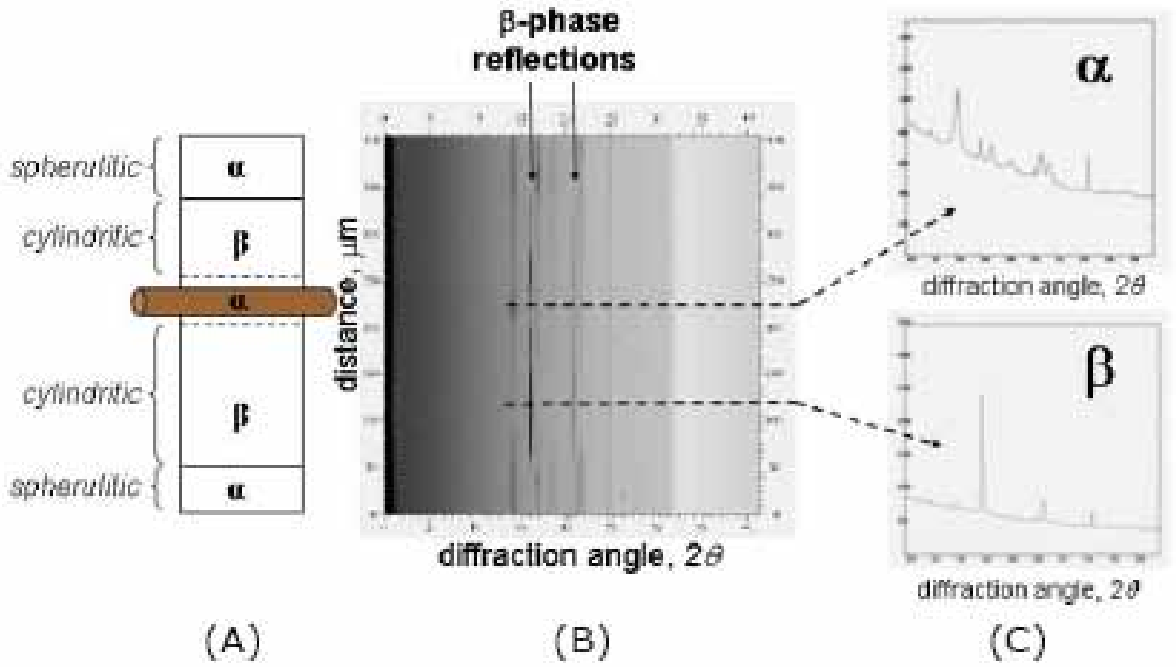
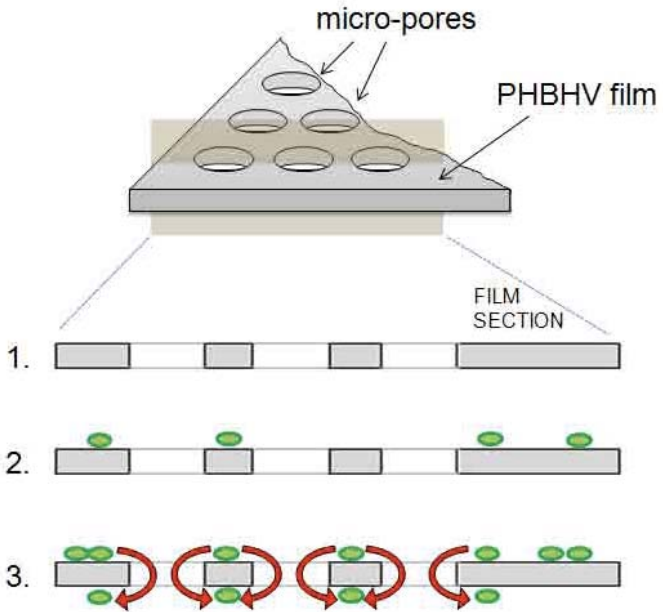


Figure 2. *Synchrotron x-ray microdiffraction. (A) Schematic of sampled region showing original position of LCP fiber, (B) integrated intensities of x-ray patterns obtained from a 400 μm line-scan, and (C) diffraction patterns from positions marked.*

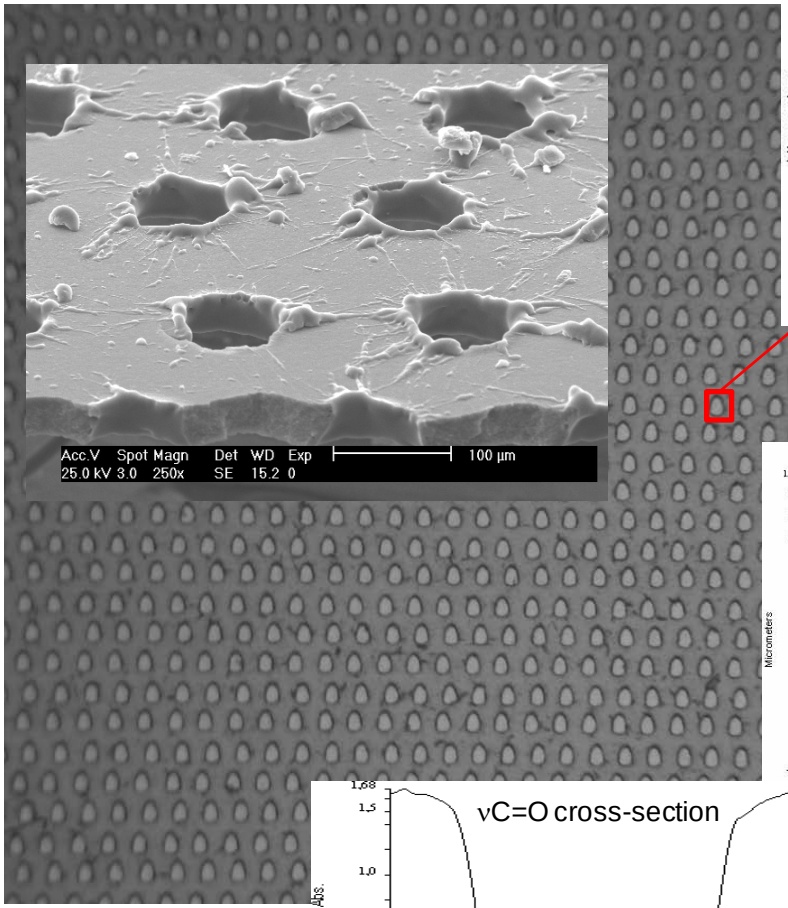
From Torre *et al.*, *Macromolecules* 2006, 39, 5564

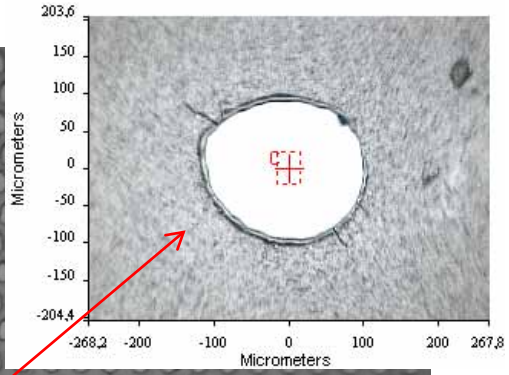
Biodegradable polymer substrates

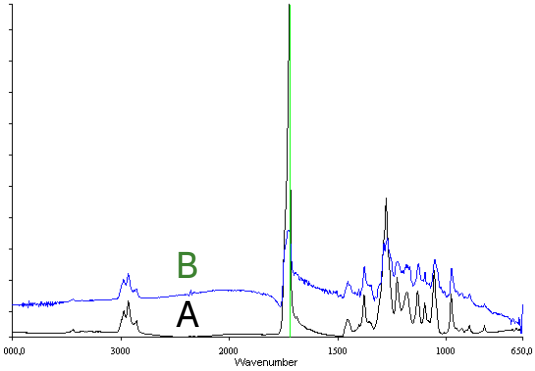
- Copolymers PHBHV (Hydroxybutyrate-hydroxyvalerate)
  - Supports for cell growth
    - eg. *Mesenchymal* stem cells, urethral cells, etc.
  - Tissue therapy (e.g. skin repair)
  - Diverse preparative strategies to promote cell adhesion and growth
    - Chemical modification
    - Plasma modification
    - Laser perforation
  - Design of localized heterogeneities
    - Polarity
    - Hydrophobic/hydrophilic interactions
    - Directional cell propagation

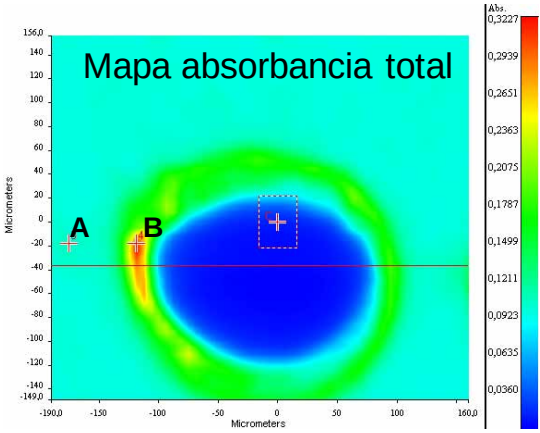


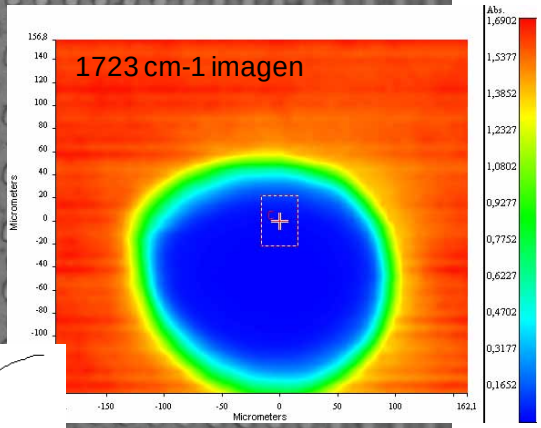
Laser microperforated PHBHV

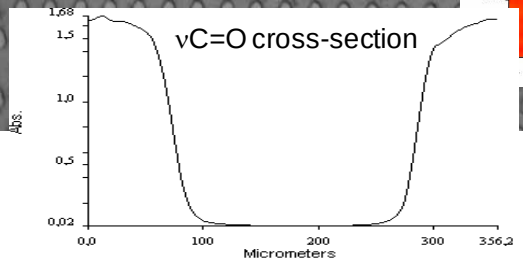


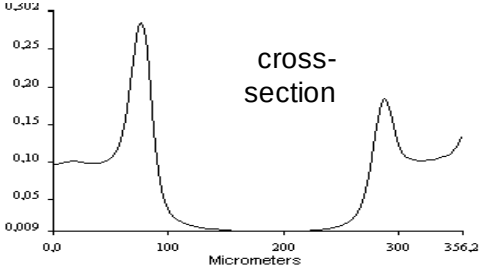






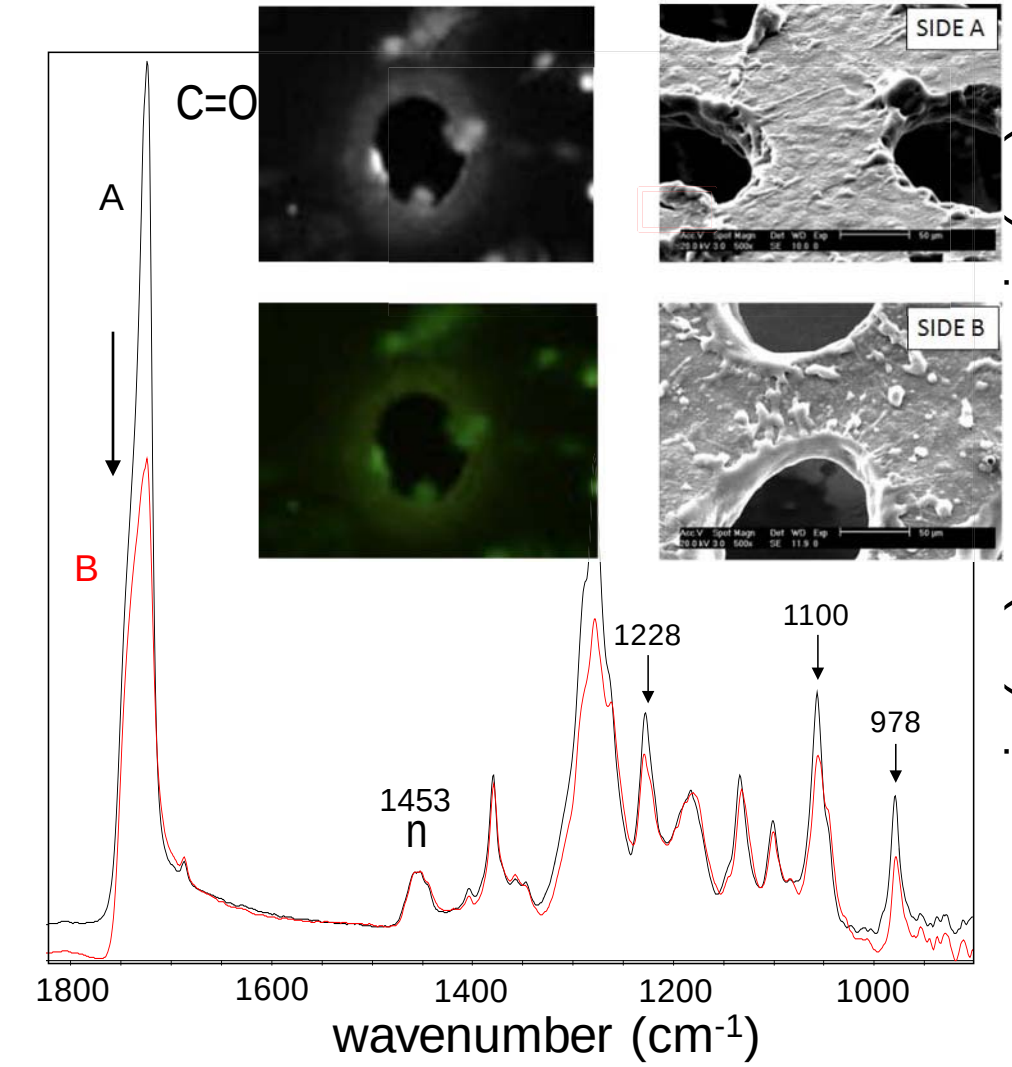


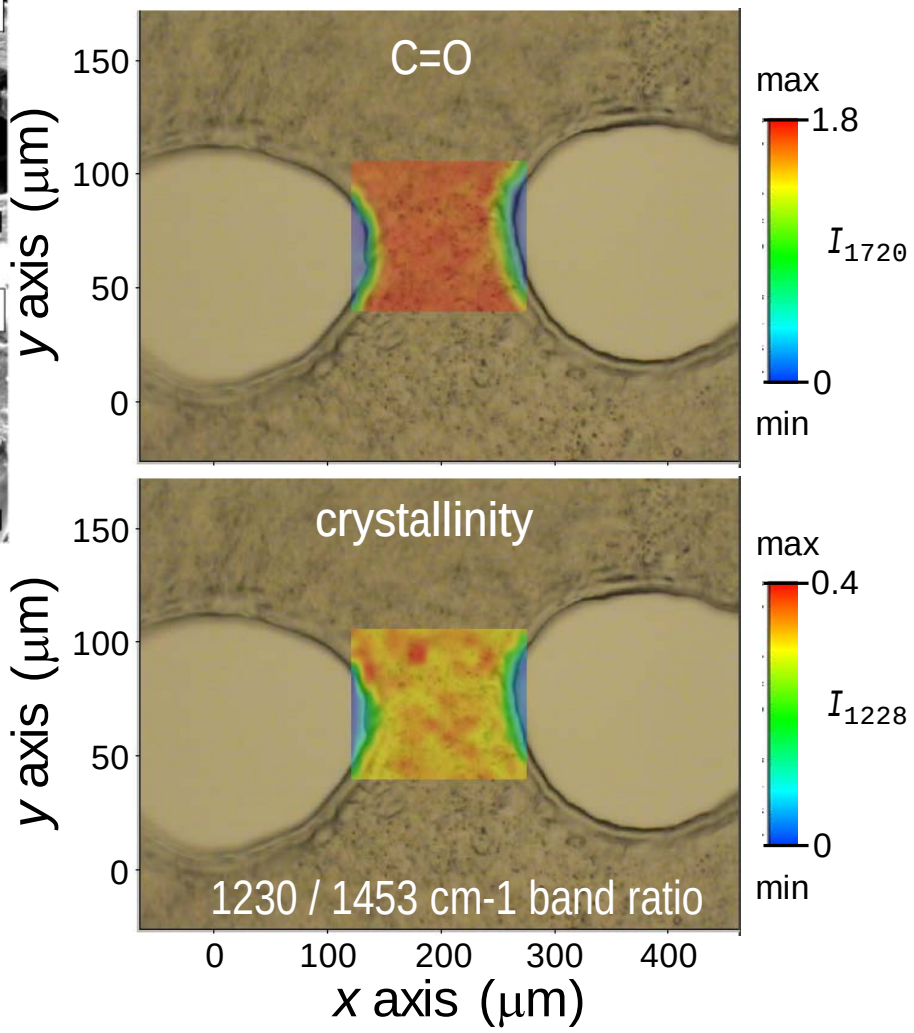




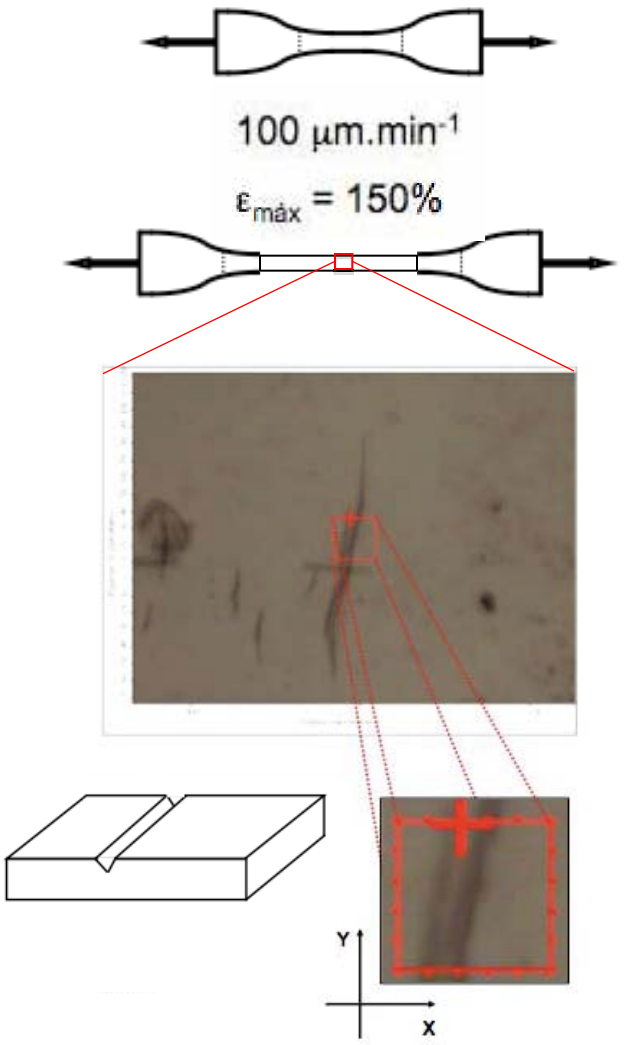
from Serrano *et al.*, *Biomateriales* 2007, 28, 650
and Ellis et al., *Anal. Bioanal. Chem.* 2011

Laser microperforated PHBHV



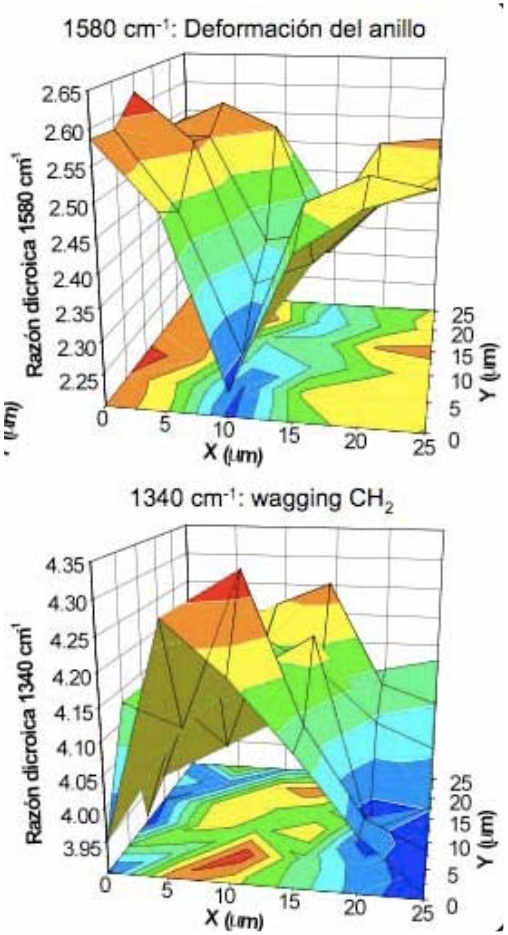


Craze initiation in drawn PET



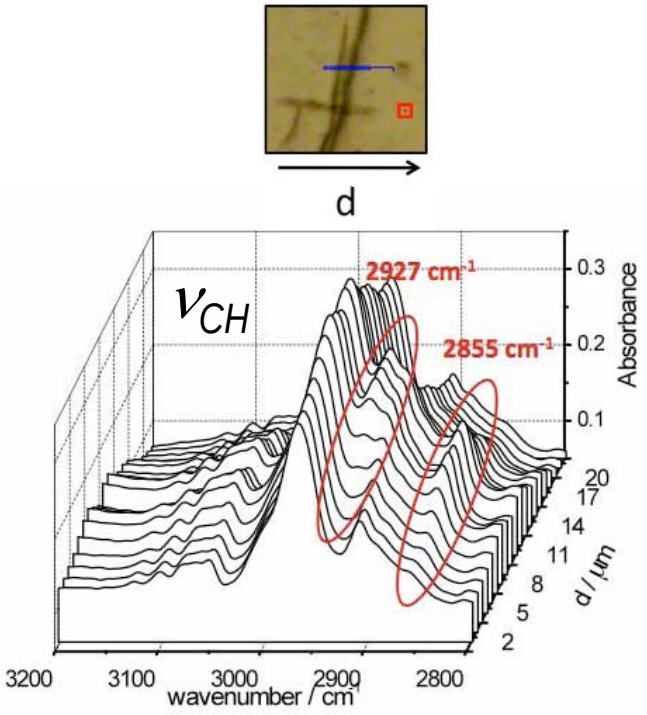
DICROISMO

$D = A_{||} / A_{\perp}$



STRUCTURAL FACTOR

$S = (A_{||}+2A_{\perp})/3$



Aperture: 4x4 μm²; step 1 μm; 256 scans
Natural polarisation of BMR

Future Developments (partial "wish list")

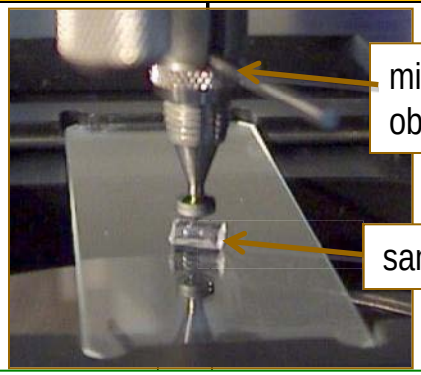
- Wider!
  - *Far-infrared and terahertz regions*
- Smaller!
  - *ATR imaging microspectroscopy*
  - *Near-field techniques*
- Faster!
  - *Coupling to bidimensional arrays*

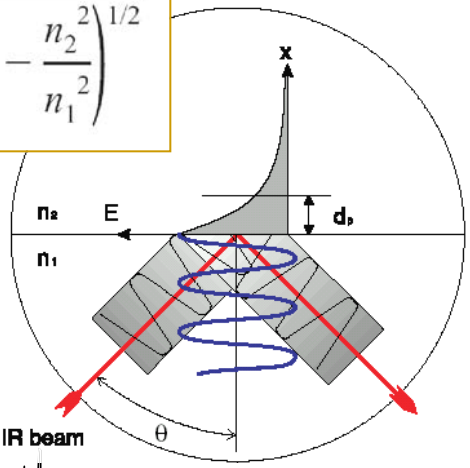
Smaller!

ATR IMAGING MICROSPECTROSCOPY

e.g. Germanium ATR crystal (n_1 = 4.0)
Polymer sample (n_2 = 1.5)

$$d_p = \frac{\lambda}{2\pi n_1 \left(\sin^2 \theta - \frac{n_2^2}{n_1^2} \right)^{1/2}}$$





BETTER THAN λ / 5

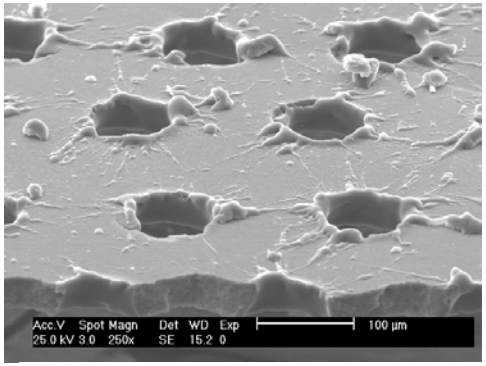
4000	3000	2000	1500	1000	650	cm^{-1}
λ 2.5	3.3	5.0	6.7	10	15	μm
λ/2 1.2	1.7	2.5	3.4	5	7.5	SR
λ/5 0.4	0.6	0.9	1.2	1.8	2.6	ATR

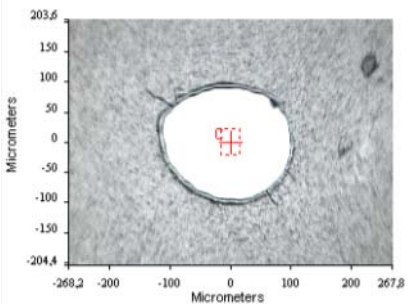
Laser microperforated PHBHV copolymer

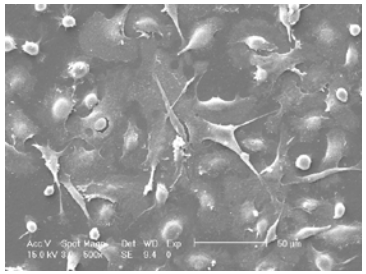
ATR IMAGING MICROSPECTROSCOPY

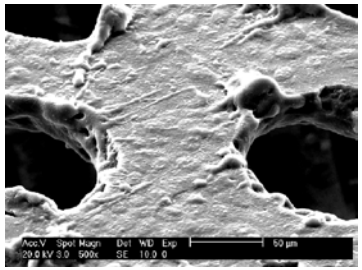
- Supports for cell growth
- Tissue therapy (repair)

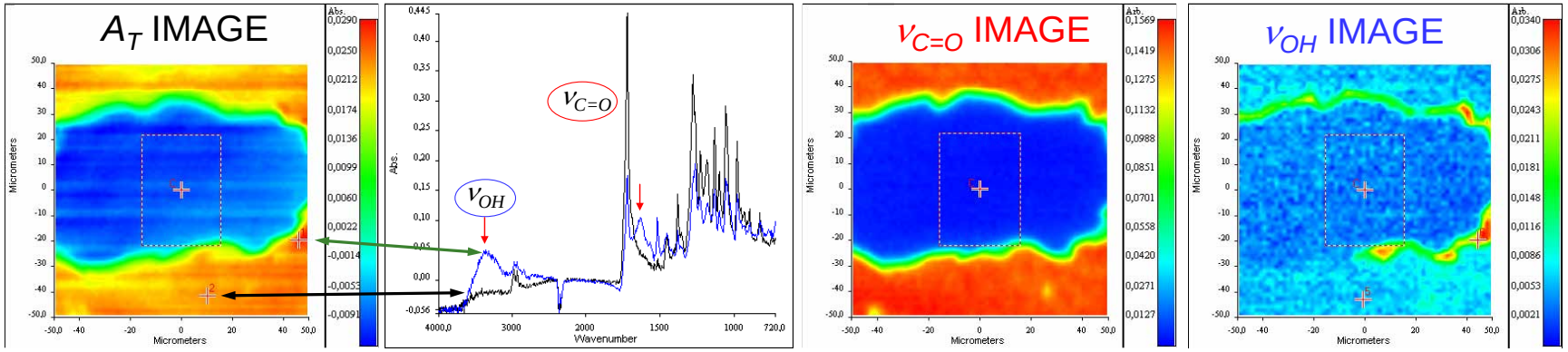
- Higher surface amorphicity
- Higher hydrophilicity observed
- Improved cell adhesion











Hydrophilicity ↑

Gary Ellis

"Synchrotron IR Microspectroscopy: A powerful tool for Polymer Science.

Conclusions

- SIRmS is a powerful and versatile chemical and structural imaging tool for polymer scientists
- Diffraction-limited spectroscopy available and sub-micron imaging to come…
- **If you haven't tried it yet…**

JUST DO IT!

Where to do it, …where we did it,

…. and where we hope to do it!

Agknowledgements

€€'s
EU
Spanish Govt
$$'s
U.S. Dept. Energy

- Paul DUMAS
  Synchrotron SOLEIL (Gif-sur-Yvette, Paris, France)
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Thankyou...

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