Application of WAXD to polymer science -a user perspective-

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DSM Material Science Center

Chemistry and Technology

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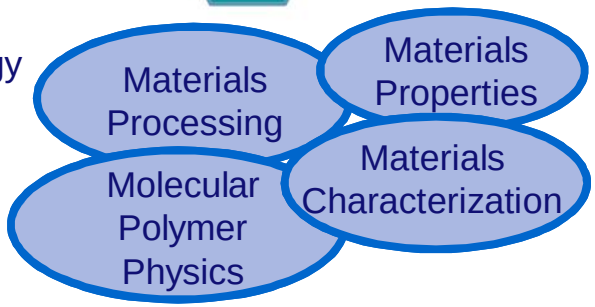
Applications



Outlook

1 Role of XRD (WAXD) in polymer science
2 Basic principles

3 Static measurements
- Crystal structures
- Polymorphism and inclusion of co-monomers in lattice
- Orientation and spatial heterogeneities

4 Dynamic measurements
- Cooling
- Flow
- Stress

5 Ageing of glassy polymers

- Collection of slides from different eras (colors, fonts,..)
- The red thread is: showing the potential of WAXD through examples (rather than a physics story)
- Thanks to lots of co-workers

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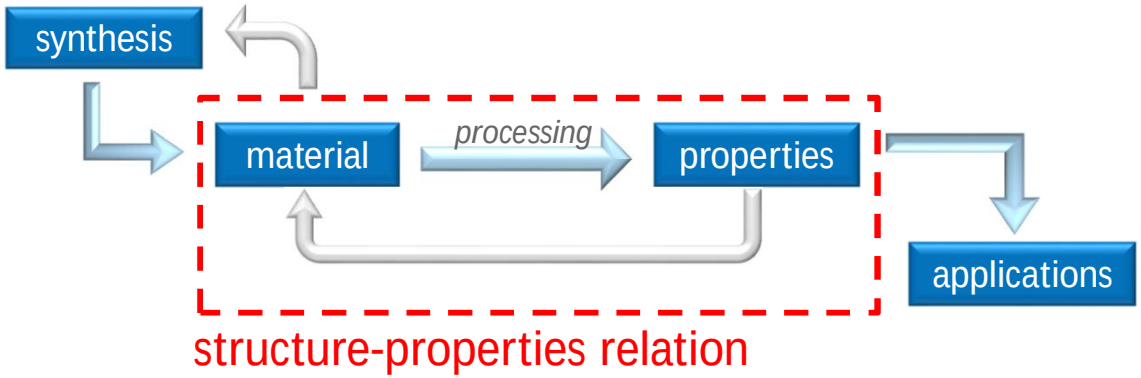
XRD (WAXD): a tool to study physics of materials



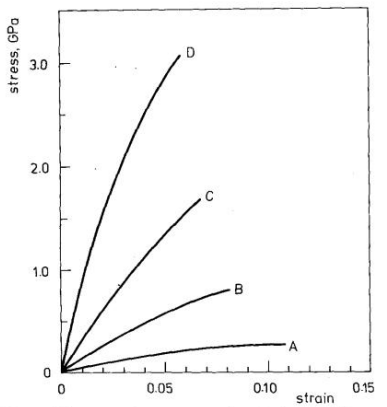
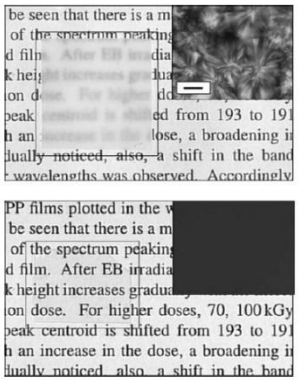


Figure 5 Stress–strain curves of solution-spun/drawn polyethylene fibres. Draw ratios: A 2.8; B 8.4; C 15.7; D 31.7.



Smith, P. & Lemstra, P.J. J Mater Sci (1980) 15: 505

Q. Zia, R. Androsch, H.J. Radusch, J. Appl. Polym. Sci. 2010, 117, 1013

Contribution of XRD:
generate mechanistic understanding of the structure-performance relation in (semi)crystalline materials by bridging observation at multiple length scales during deformation, heating/cooling, aging, … in combination with other analytical techniques

- highlight opportunities/limitations
- provide input for new chemistries
- connect properties to chemistry
- provide input for modelling

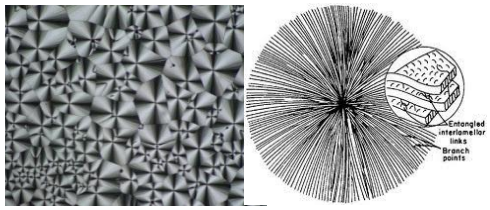
Useful to read:
Ward, I. M., Structure and properties of oriented polymers. Chapman and Hall: London, 1997.

Structure-properties relation to the max: Dyneema®

Dyneema fibers combine light weight with high strength/modulus, abrasion resistance, durability, low creep, cut resistance

Length scales in semi-crystalline polymers

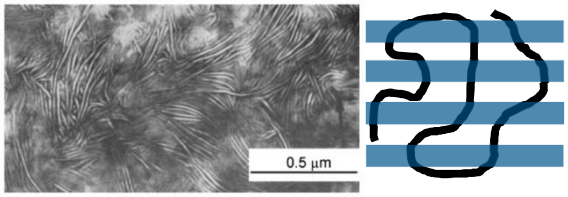
macro scale
spherulites



10-100 µm

Optical properties

meso scale
lamellae



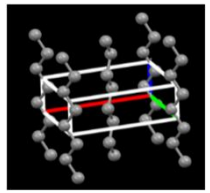
10-100 nm

Mechanical properties
Thermal properties
Barrier properties
Chemical resistance
…

morphology
- crystallinity
- crystal size and orientation
- lattice defects and polymorphism
- tie-molecules

SAXS

micro scale
unit cells



1-10 Å

Mechanical properties
Thermal properties
Dielectric properties
…

structure
- type of lattice
- orientation
- lattice defects
- polymorphism

WAXD

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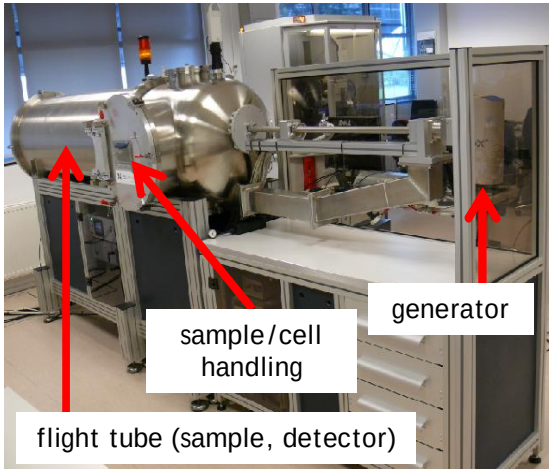
X-ray sources

Lab sources



Bright

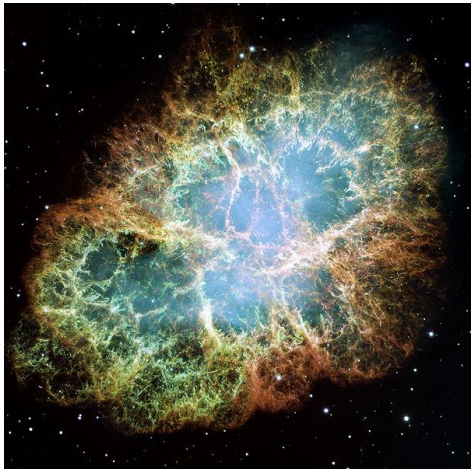
More suitable for static measurements

Synchrotrons

Brighter

More suitable for (fast) dynamic measurements and local analyses

Crab Nebula



Brightest

...open challenge...

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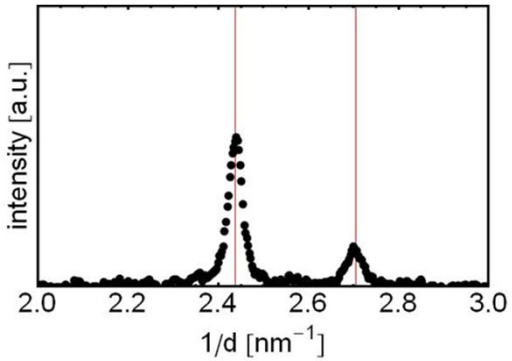
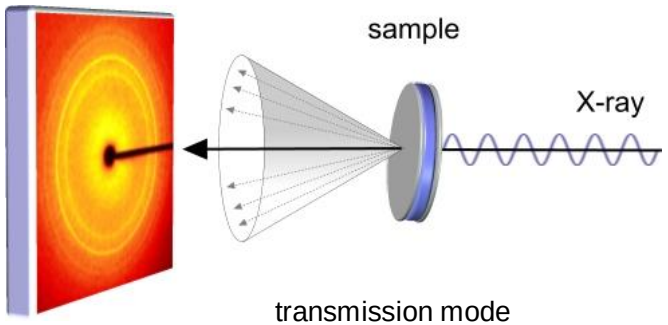
Pros and cons of XRD (WAXD)



data reduction



transmission mode

Pros
- instrument-independent data
- non-destructive
- no sample preparation
- time resolved (>30 frames/s)
- space resolved (beam spot size limiting, 50nm)
- statistically sound information
- combination with other techniques possible

Cons
- model dependent interpretation → needs input from other analyses
- only crystals
- projections
- beam damage

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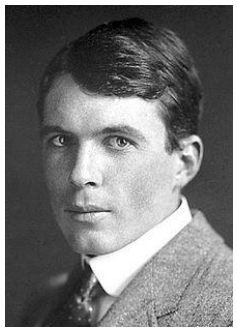
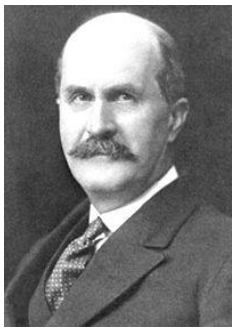
Interpretation of WAXD: Bragg's law

example of X-ray wave interference



W.L. Bragg
1890-1971



W.H. Bragg
1862-1942

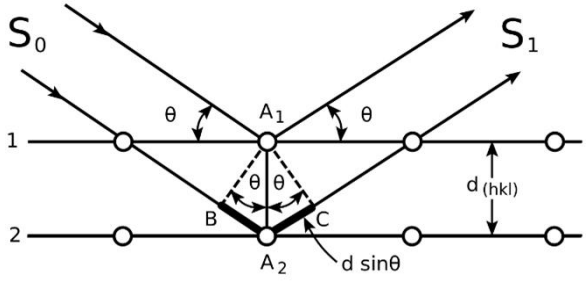
Nobel Prize in Physics (1915)

There is a peak!

when a sample is irradiated with X-rays:
waves are scattered in phase (*constructive interference*) when the path length difference is an integer number of wavelengths

path length difference = n·wavelength

$$2 \cdot d \sin\theta = n \cdot \lambda$$



$$2 \cdot d \sin\theta = n \cdot \lambda \quad \Leftrightarrow \quad \frac{1}{d} = \frac{2 \cdot sin\theta}{\lambda}$$

$$s = \frac{1}{d} = \frac{q}{2\pi}$$

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Interpretation of WAXD: Bragg's law

length scales in SAXS and WAXD

$$2 \cdot d \sin\theta = n \cdot \lambda$$

typical length scales: $d = \frac{\lambda}{2\sin\theta}$

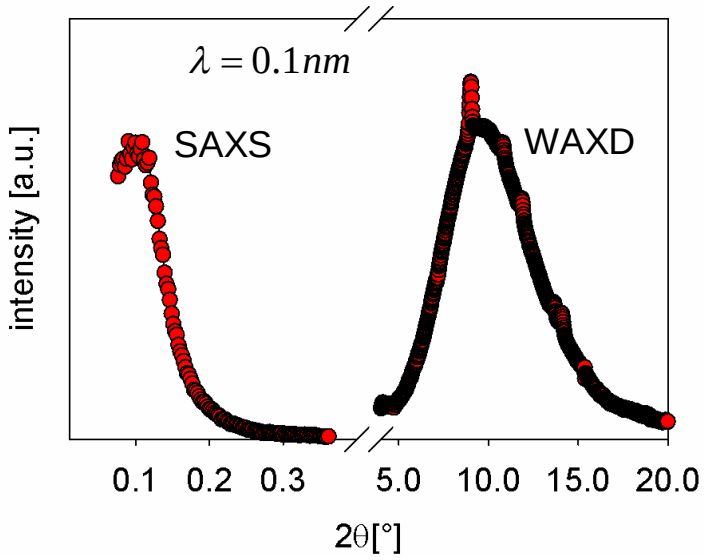
- small angles (SAXS) → large d
- wide angles (WAXD) → small d

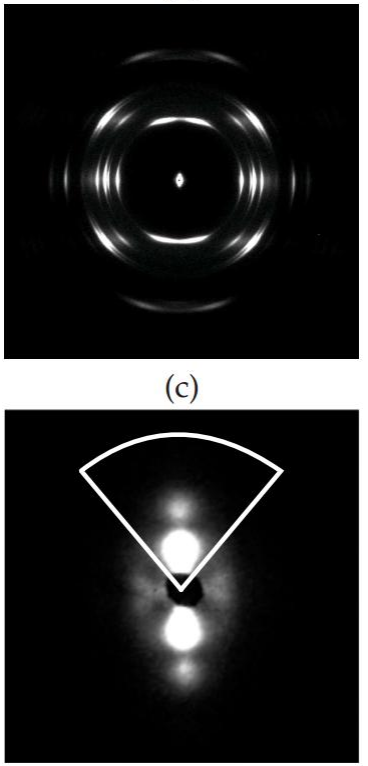
SAXS

$$d = \frac{0.1nm}{2\sin(0.1/2)} \cong 60\,nm$$

WAXD

$$d = \frac{0.1nm}{2\sin(9/2)} \cong 0.60\,nm$$





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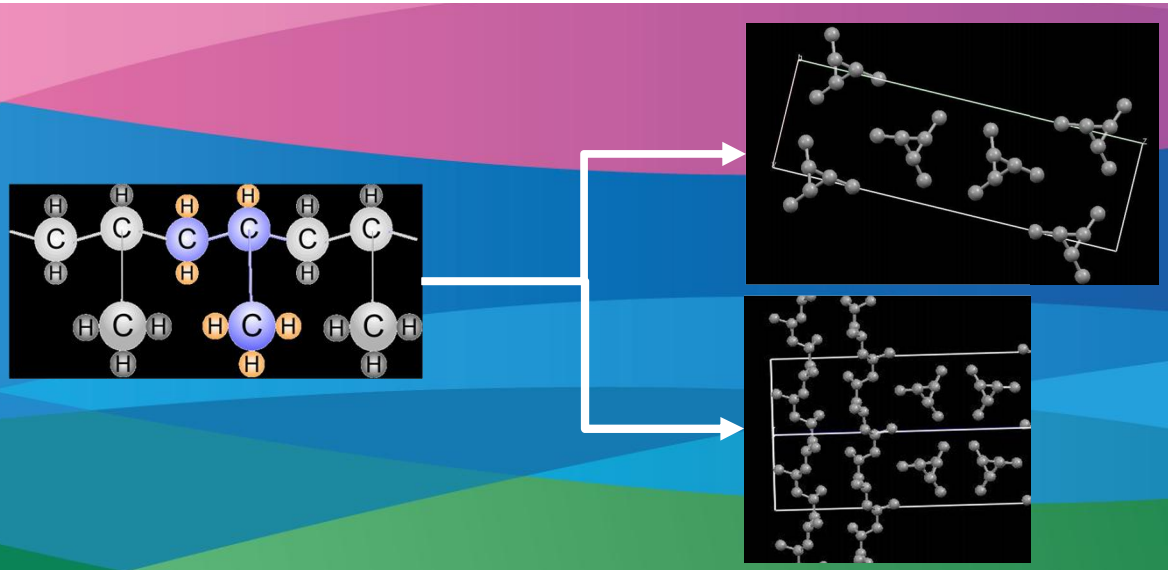
Molecules and lattices: polymorphism and inclusion of comonomers

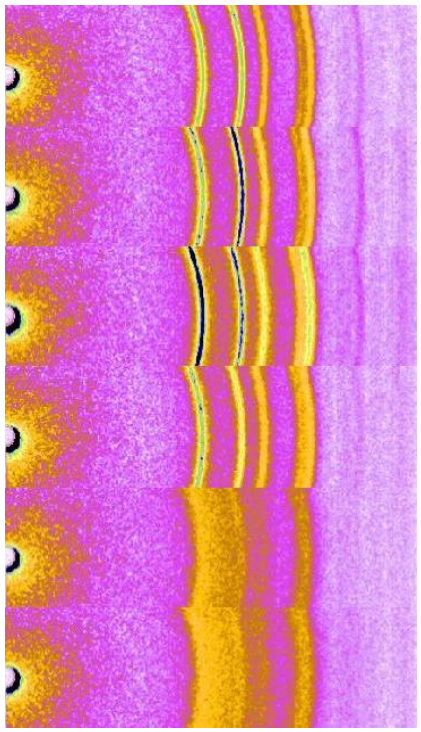
Polymorphism: ability of a molecule to crystallize in different structures



Processing induced polymorphism

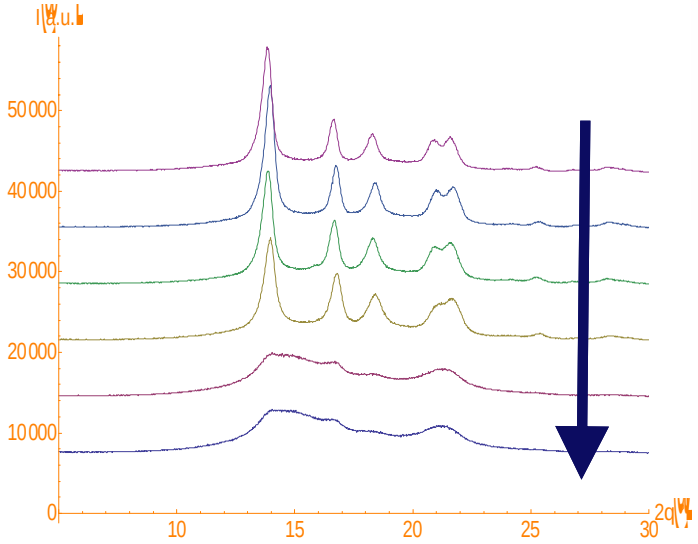
iPP homopolymer

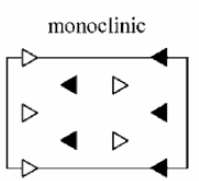
10°C/s

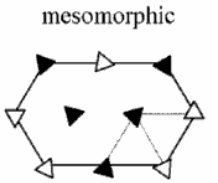


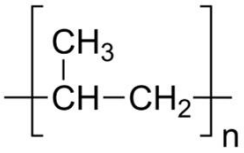
500°C/s

quenched thin films
(200 microns)







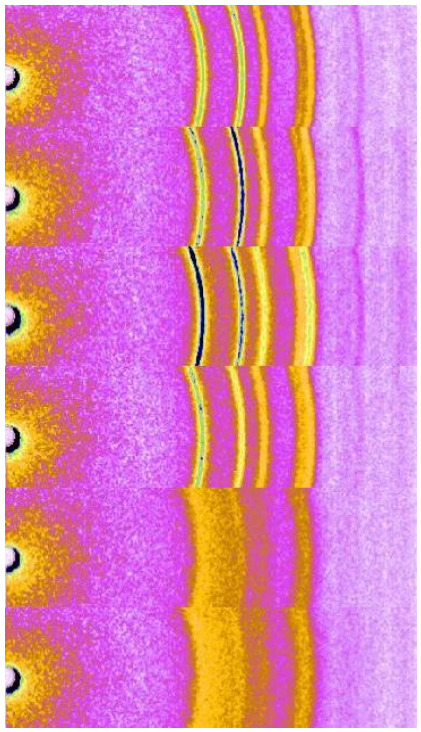


- Change in the Bragg peaks indicate occurrence of polymorphism (same molecule → different lattice);
- Process-induced polymorphism is common to several polymers:
  - Cooling rate, stress and pressure can play a role

Processing induced polymorphism

iPP homopolymer

10°C/s



500°C/s

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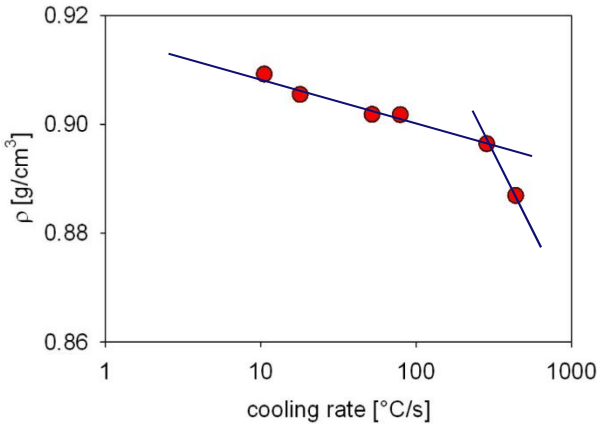
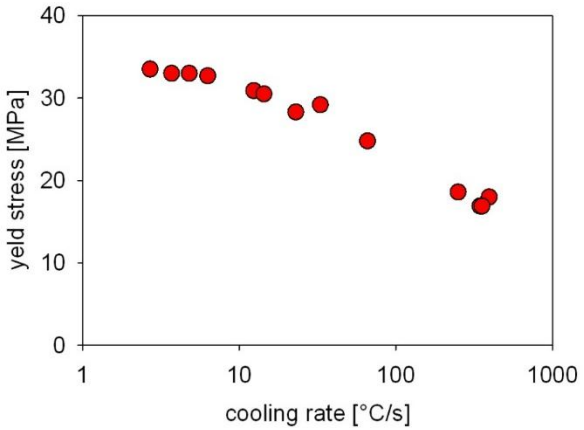
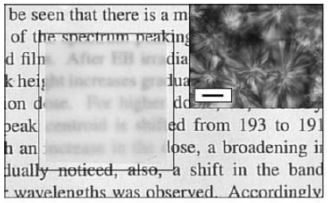
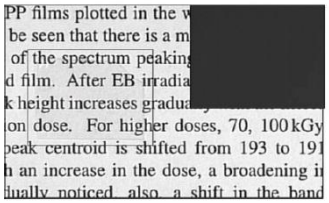








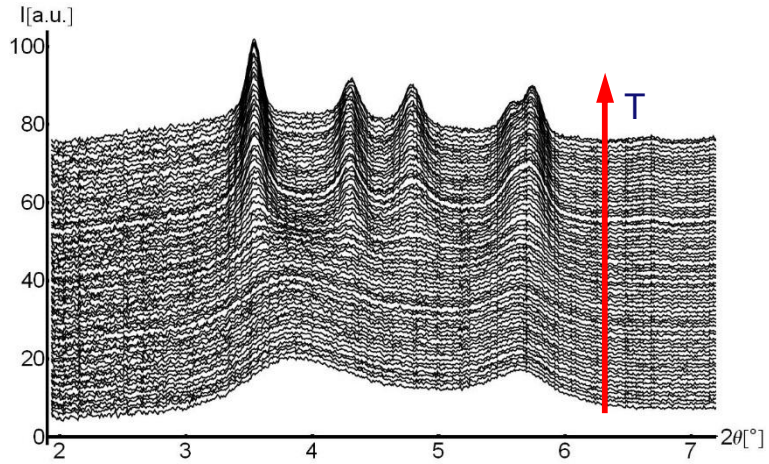
Quenched iPP samples exhibit:

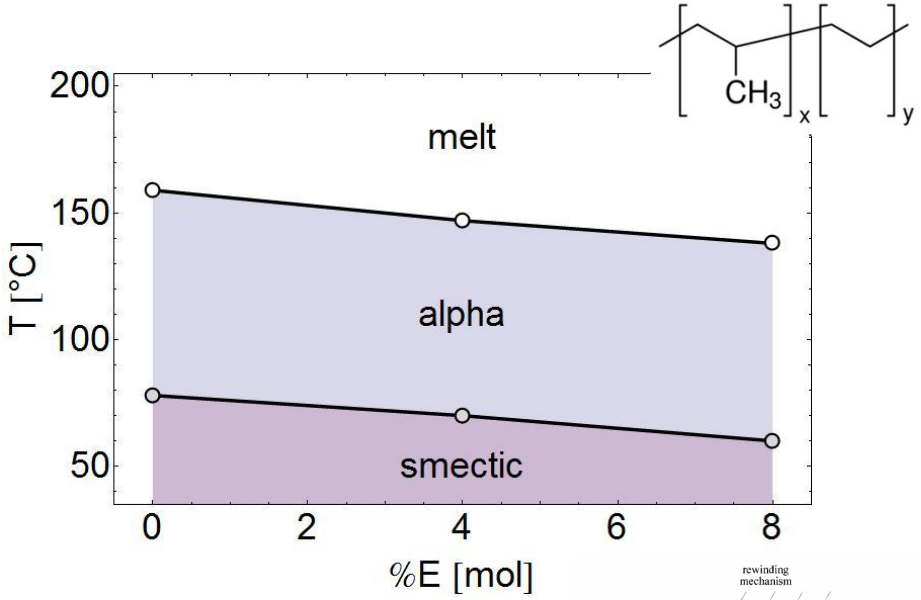
- Lower density;
- Lower yield stress;
- Higher transparency;

Q. Zia, R. Androsch, H.J. Radusch, J. Appl. Polym. Sci. 2010, 117, 1013

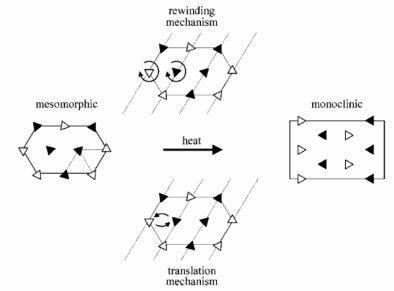
Thermal properties of quenched iPP

It was shown that presence of Ethylene co-units facilitate the formation of the mesomorphic phase of iPP.





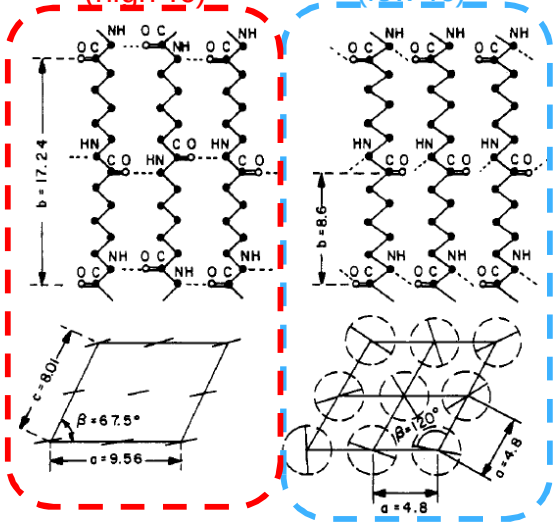
- Smectic transforms into monoclinic α upon heating;
- The mesomorphic phase of co-polymers is less thermally stable (transforms into the monoclinic α at lower T);

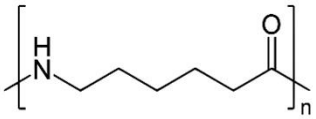


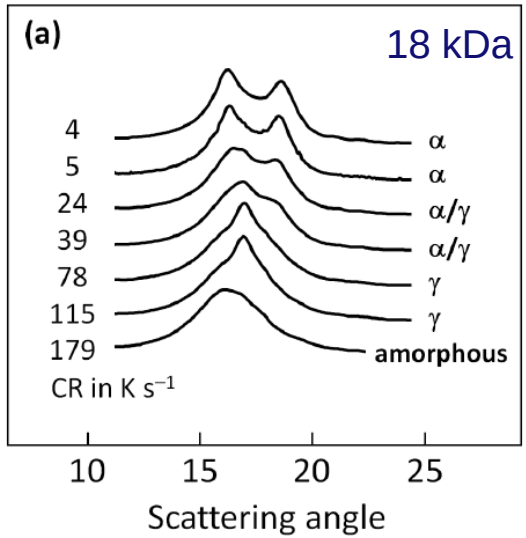
Polymorphism in PA6: effect of molecular weight

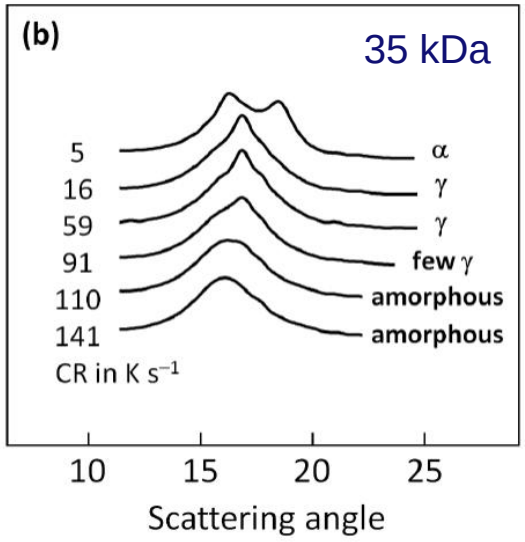
α form
monoclinic
(high Tc)

γ form
pseudo-hexagonal
(low Tc)









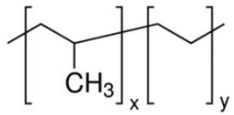
- γ PA6 crystals can be stretched easier than α PA6 crystals → advantage in film casting;
- Higher Mw makes γ appear at lower cooling rates;

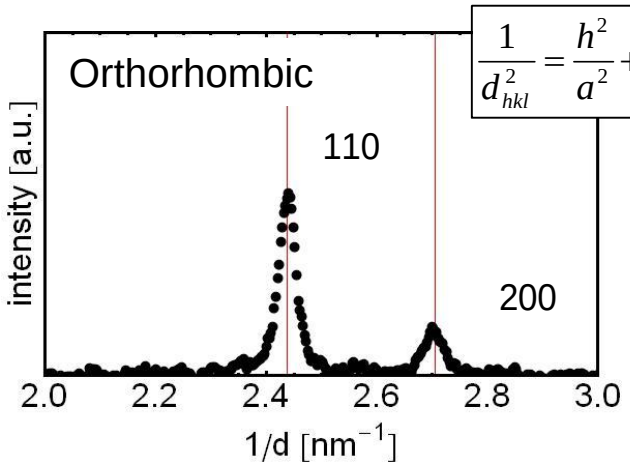
D. Cavallo et al. *Colloid and Polymer Science* 2011, 289 (9), 1073

Inclusion of co-monomers in the lattice

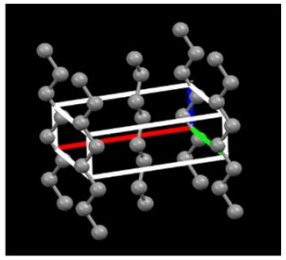
Classic crystallization theories, based on thermodynamics, assume that co-monomers are rejected from the crystalline lattice

Polyethylene with small amount of propene co-units





$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$



a=0.74 nm
b=0.49 nm
c=0.25 nm

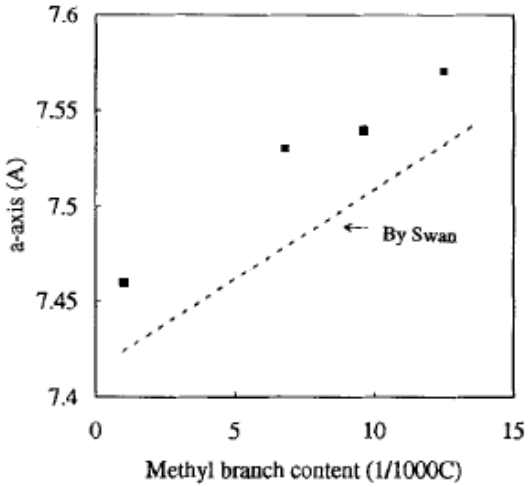


Figure 11. Influence of CH_3 branch content on the a-axis size of UHSPE fibers with data line by Swan.[11]

- Correlation between methyl branch content and a cell parameter indicates co-crystallization of the co-monomer;
- Kinetics beats thermodynamics; ☺
- Change of *a* and not of *b* indicates how the co-monomer "adapts" to the lattice;

Otha et al., J. Pol. Sci. B, Pol. Phys. 1994, 32, 261

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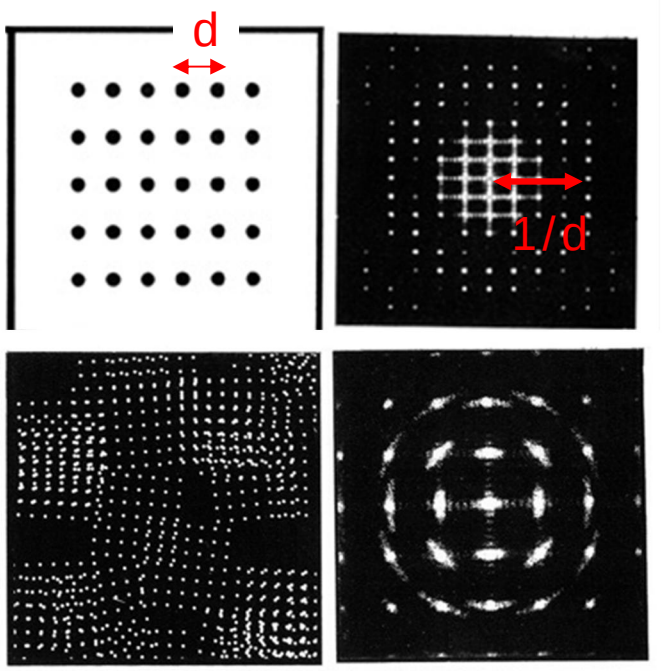
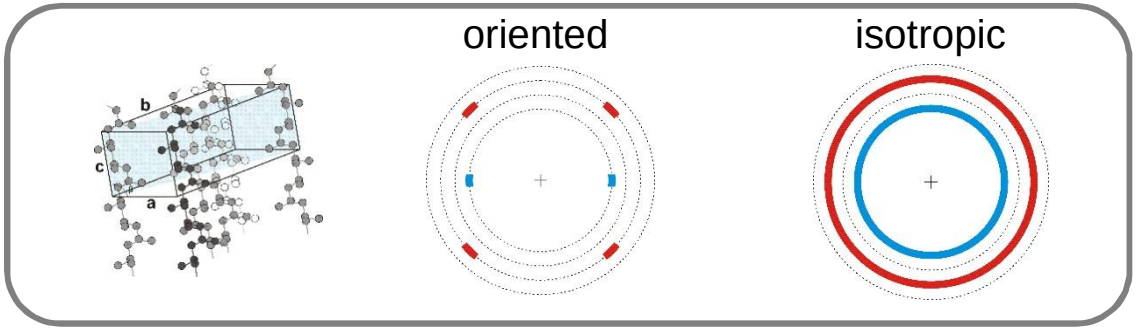
Orientation and spatial heterogeneities

Orientation of Bragg peaks



- Mathematically speaking, the diffraction pattern of a lattice is its Fourier Transform (d→1/d);
- The FT of a lattice is another lattice, reciprocal of the original;

- When crystals are misaligned around a preferred direction, the diffraction peaks tend to become arcs (in the azimuthal direction);
- Taken to the limit, if crystals have no preferential orientation, this would result in circular diffraction peaks (isotropic system);



http://www.xtal.iqfr.csic.es/Cristalografia/parte_05_3-en.html

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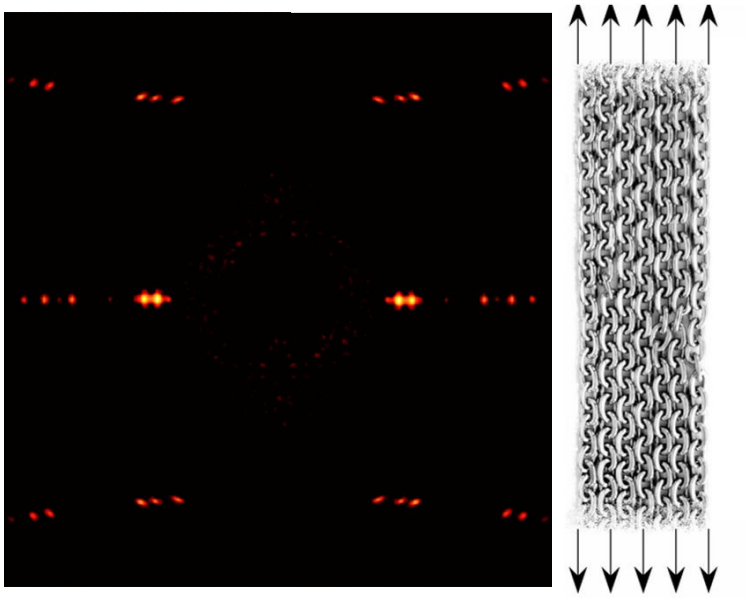
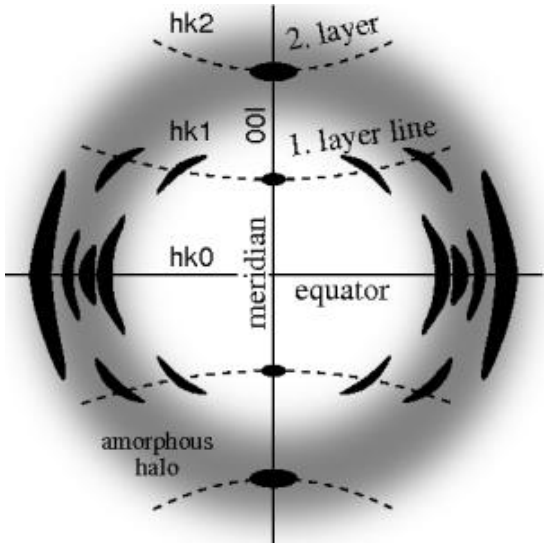
Orientation of Bragg peaks

fibers

experiment



theory



- High orientation;
- Fiber symmetry;
- Roughly homogenous;

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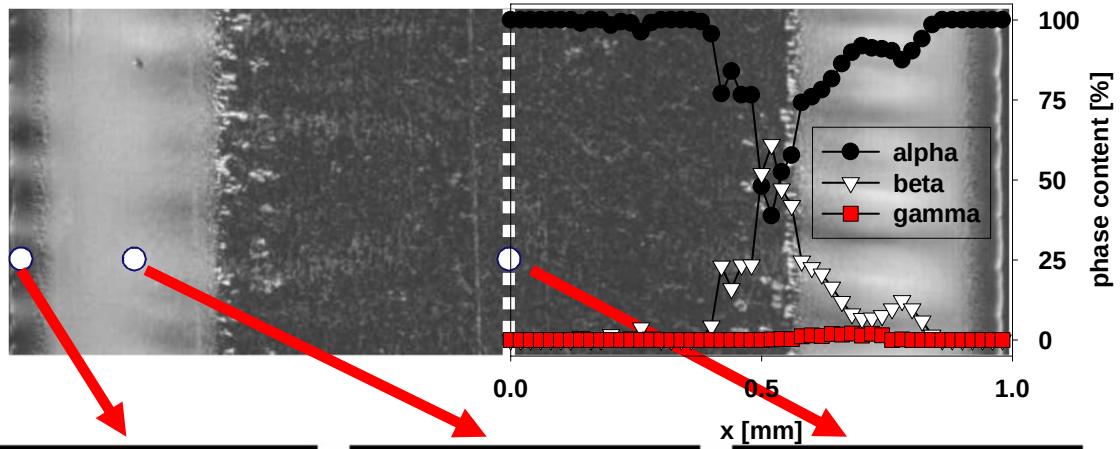
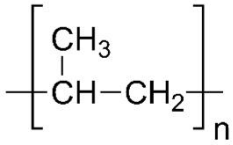
Orientation of Bragg peaks

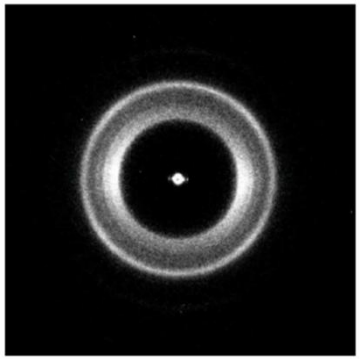
Injection molding

Local analysis with spatial resolution down to 100nm



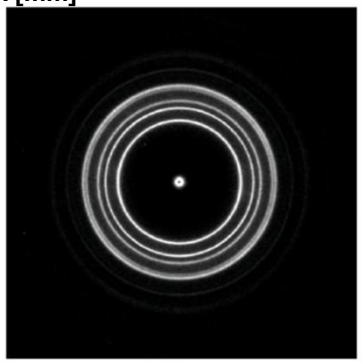


MD Vertical



Smectic

Oriented monoclinic α



Isotropic γ iPP

JW Housmans, PhD Thesis, TU/e (2008)

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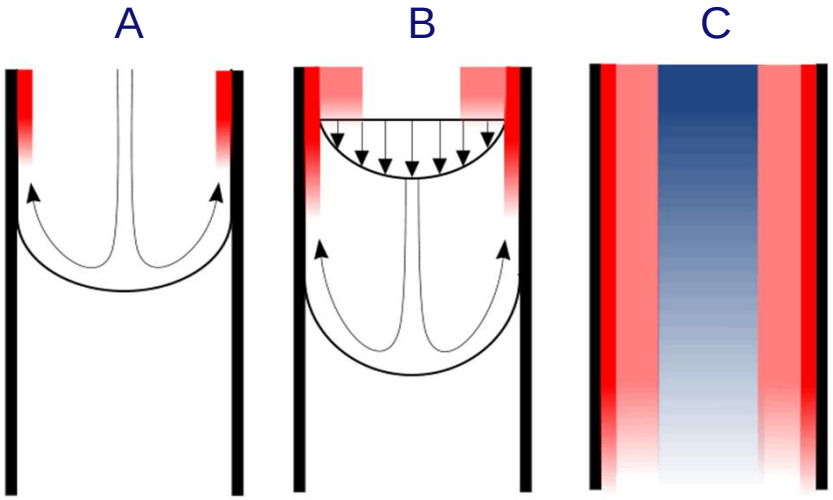
Orientation of Bragg peaks

Injection molding



skin layer

rapid cooling
(~100 °C/s)

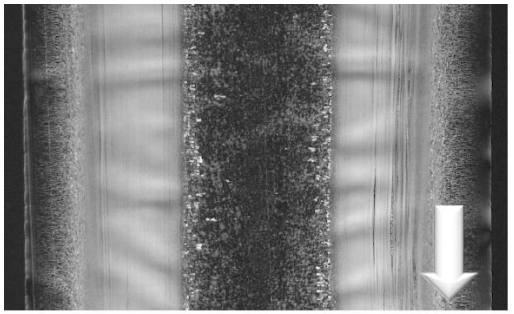
shear layer

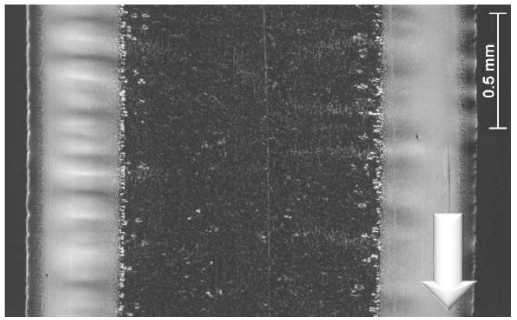
flow induced
crystallization
(~1000 s^{-1})

core layer

pressure induced
crystallization
(~1000 bar)

typical cross section of semi-crystalline products





- Analysis of the structure allows to identify the dominating driving force for the crystallization process during filling of the mold;

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Dynamic experiments: crystallization as function of cooling rate

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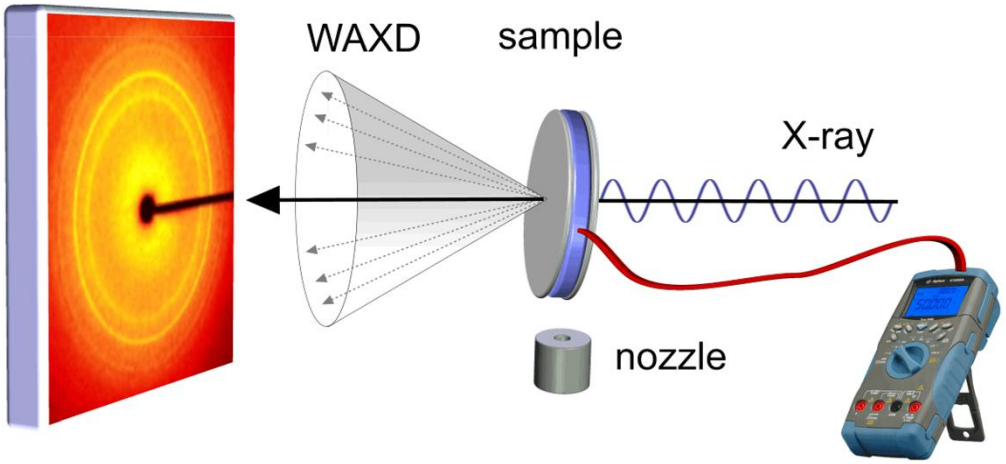
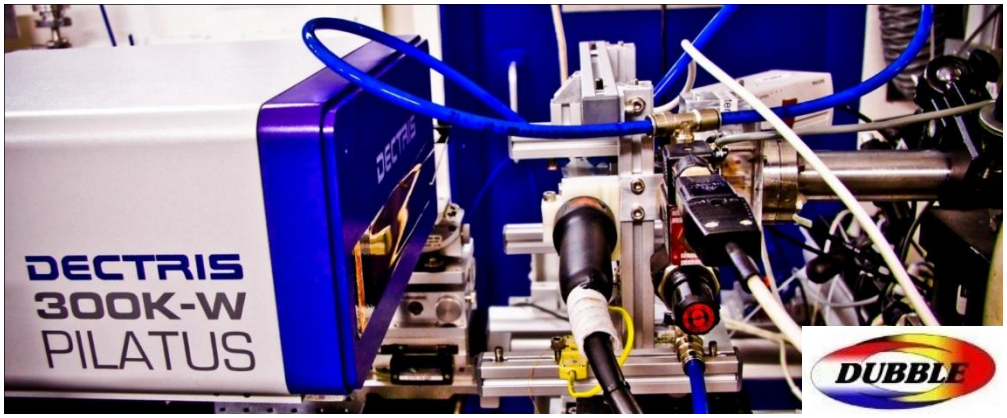
time-resolved WAXD, 20 images/s





DUBBLE

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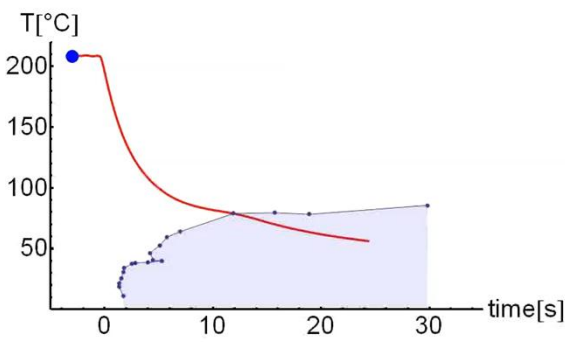
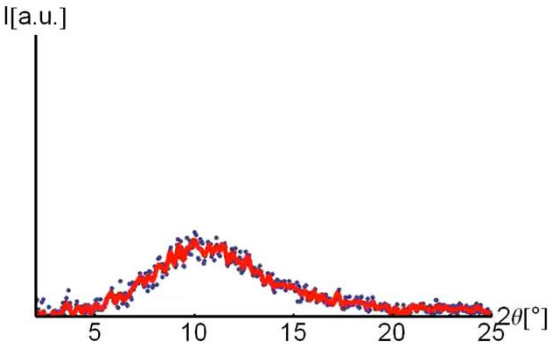
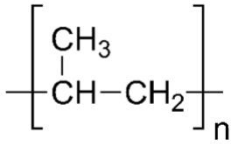
real-time structure formation

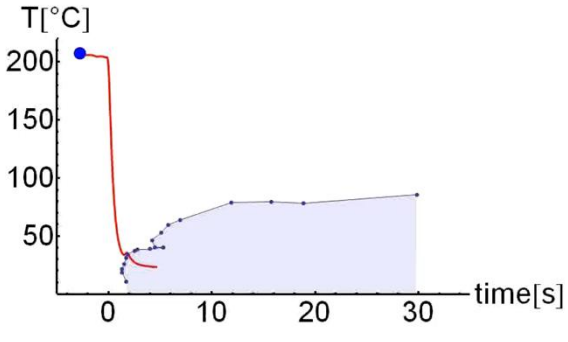
T= 208.0 °C – t= –3.03 s

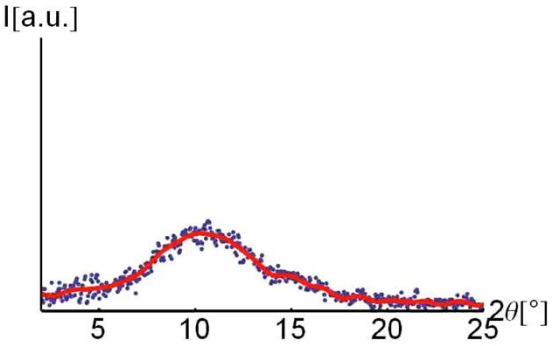






T= 207.0 °C – t= –2.78 s





cooling rate → crystallization temperature→ phase

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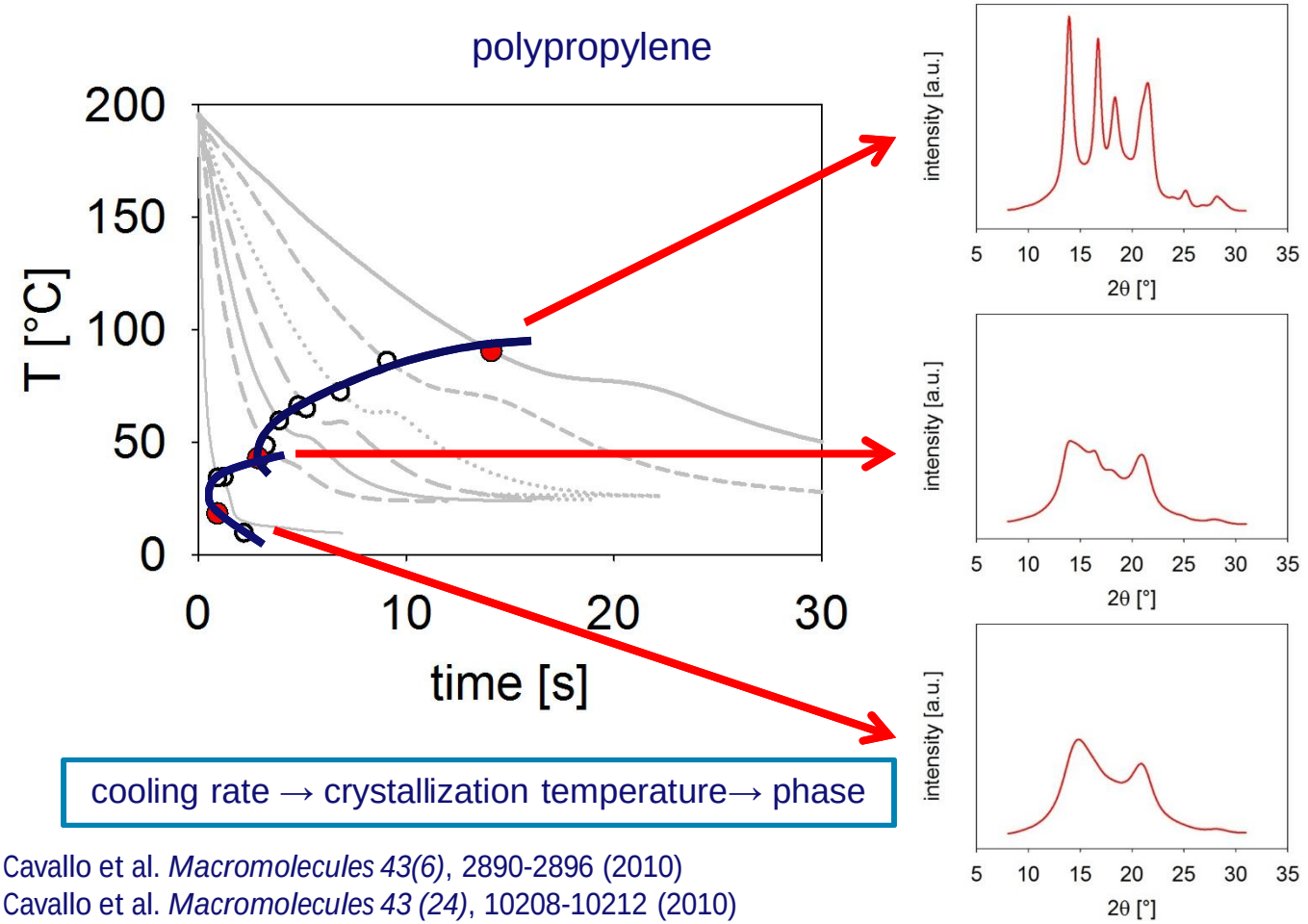
CCT and structure



cooling rate → crystallization temperature→ phase

D. Cavallo et al. *Macromolecules 43(6)*, 2890-2896 (2010)
D. Cavallo et al. *Macromolecules 43 (24)*, 10208-10212 (2010)

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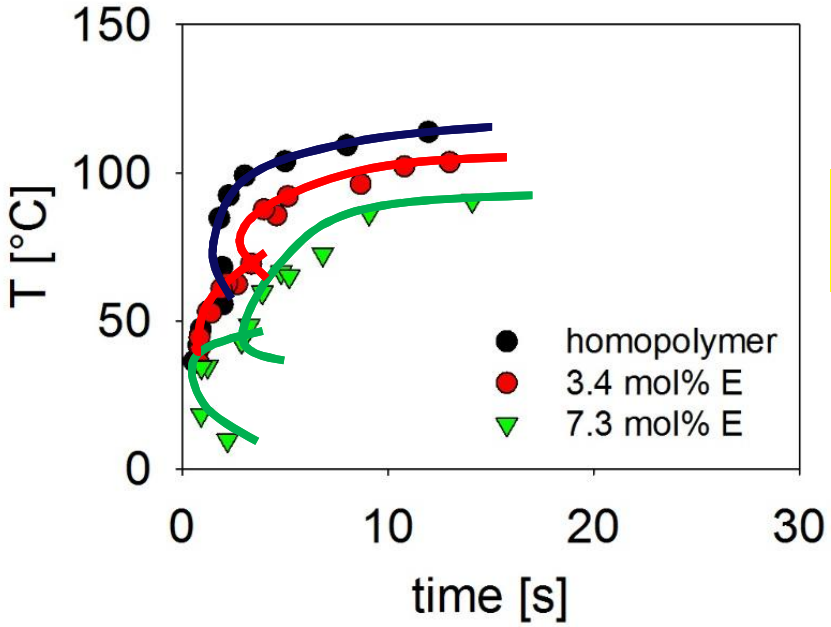
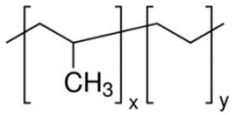
random P/E copolymers





- high T (slow cooling) → large effect of co-monomer
- low T (fast cooling) → small effect of co-monomer

cooling rate → crystallization temperature→ phase

D. Cavallo et al. *Macromolecules 43(6)*, 2890-2896 (2010)
D. Cavallo et al. *Macromolecules 43 (24)*, 10208-10212 (2010)

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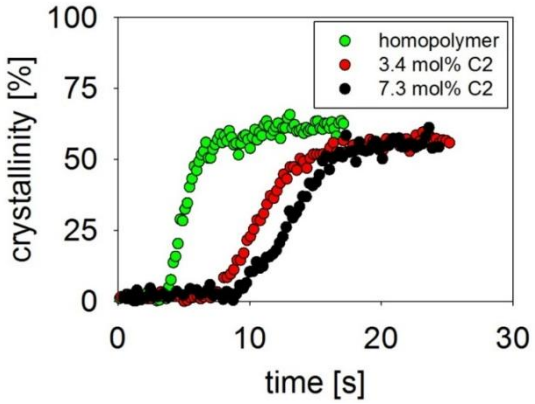
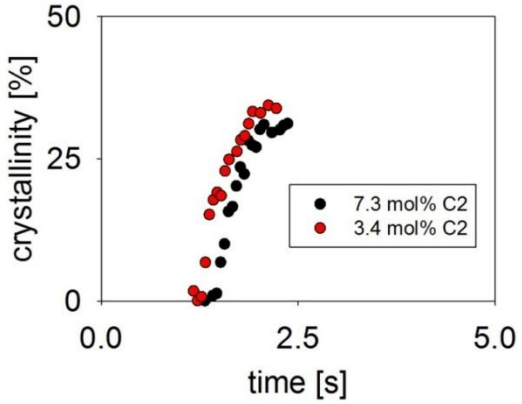
solidification kinetics and C_2 inclusion

slow cooling
~20 °C/s
α phase



strong composition dependence → C_2 rejected from the lattice

fast cooling
~150 °C/s
smectic phase



weak composition dependence → C_2 included in the lattice

D. Cavallo et al. *Macromolecules 43(6)*, 2890-2896 (2010)
D. Cavallo et al. *Macromolecules 43 (24)*, 10208-10212 (2010)

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Dynamic experiments: crystallization under hydrostatic pressure

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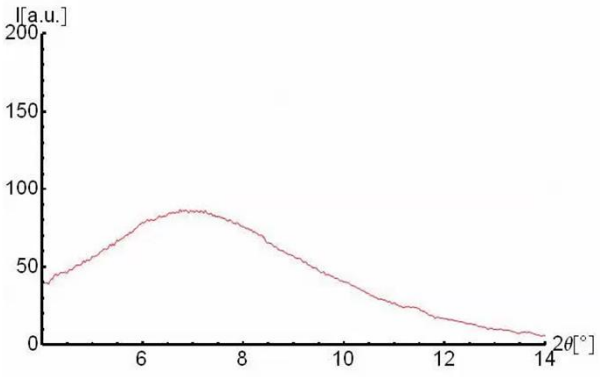
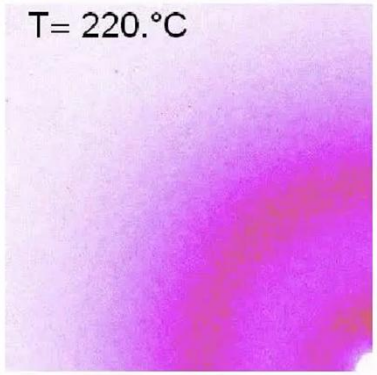
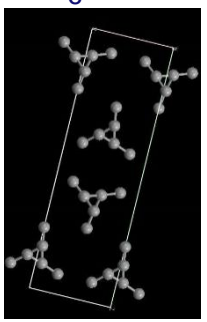
crystallization under pressure

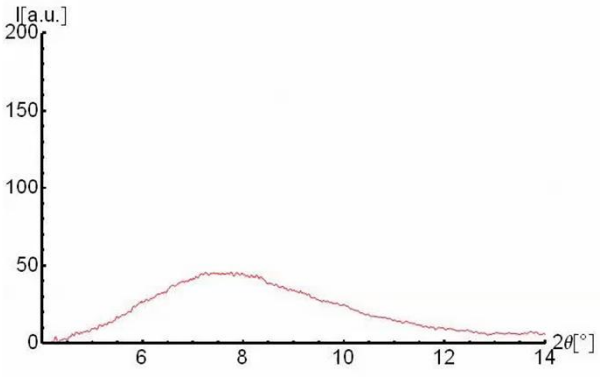
cooling at 10°C/min

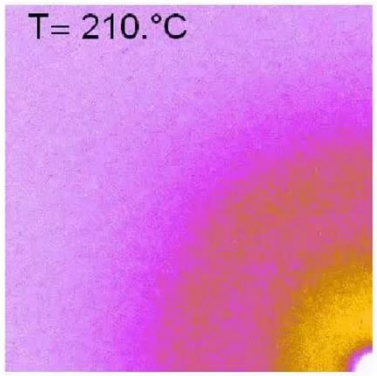




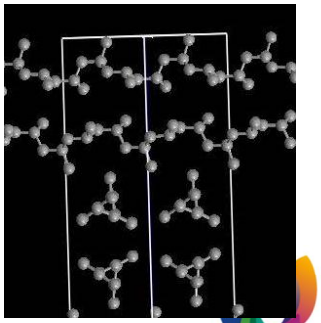
1 bar - T_c≈120°C







1000 bar - T_c ≈150°C



T±2.5°C

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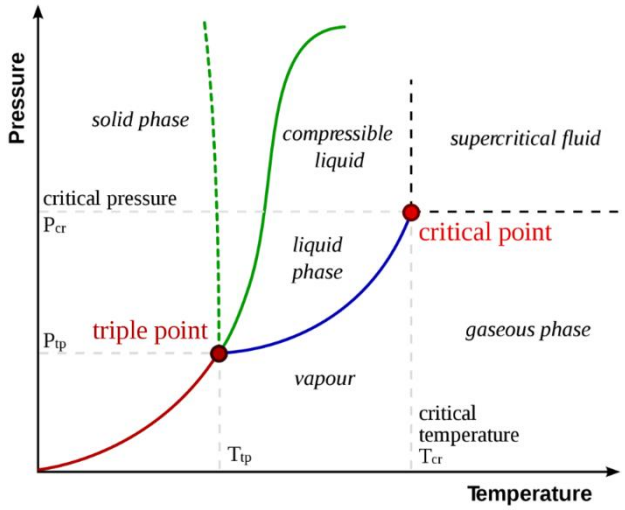
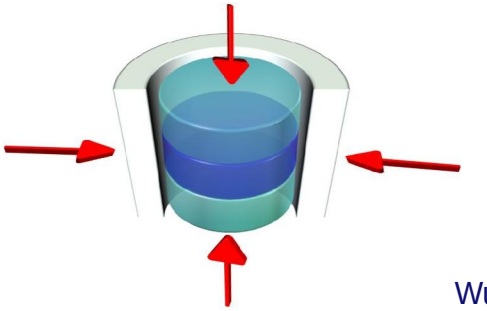
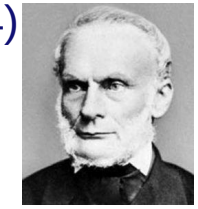
phase diagram for a single compound





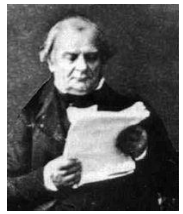
Clausius-Clapeyron (1834)



$$\frac{dp}{dT} = \frac{\Delta H}{T \cdot \Delta \upsilon}$$

ΔH enthalpy

$\Delta \upsilon$ specific volume



becomes handy in the form:

$$\frac{dT}{dp} = \frac{T \cdot \Delta \upsilon}{\Delta H} = \frac{T(p_2) - T(p_1)}{p_2 - p_1}$$

Wunderlich B, Journal of Polymer Science Part A, 2, 3697, 1964

He, Zoller - Journal of Polymer Science Part B Polymer Physics 32 6 1994

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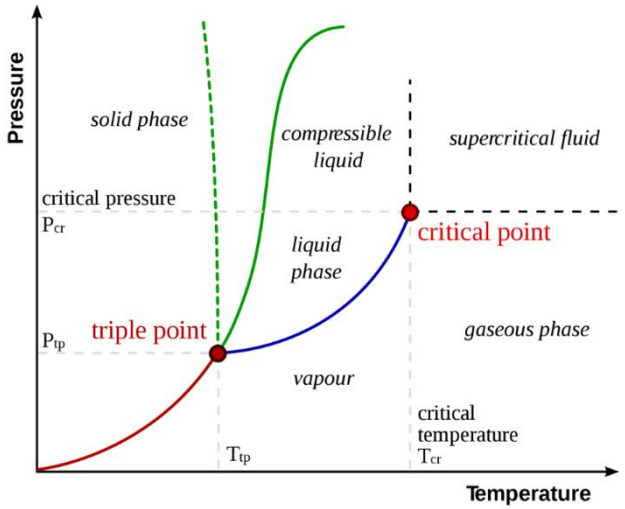
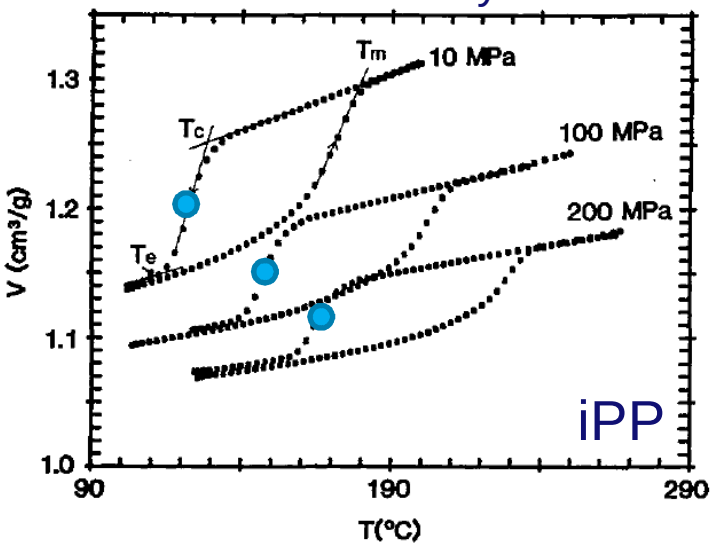
phase diagram for a single compound



dilatometry



He, Zoller - Journal of Polymer Science Part B Polymer Physics 32 6 1994

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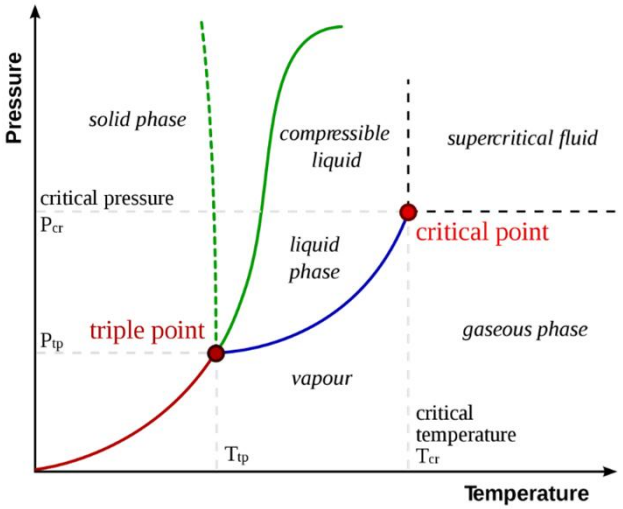
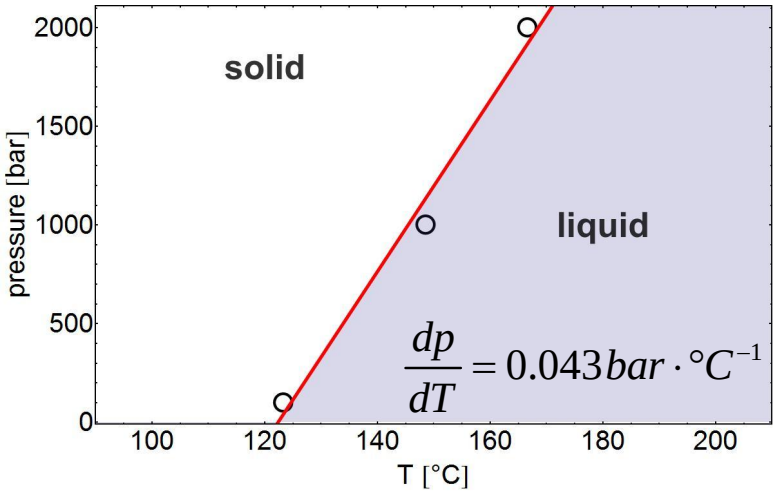
phase diagram for a single compound





for polyolefins: $\frac{dp}{dT} \cong 0.03 bar \cdot °C^{-1}$ ⇒ $\frac{\Delta T}{\Delta p} \cong 30\ °C \cdot K bar^{-1}$

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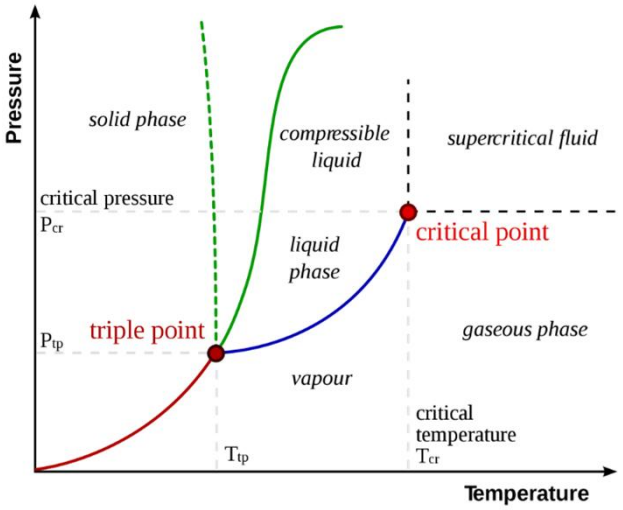
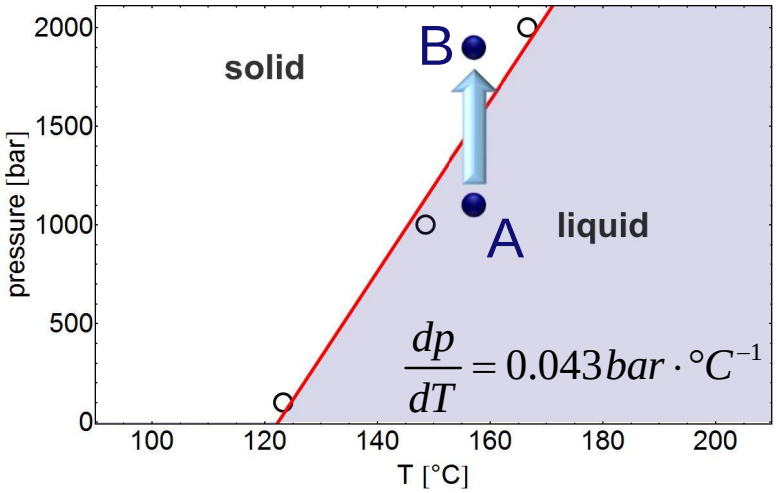
Wunderlich B, Journal of Polymer Science Part A, 2, 3697, 1964

phase diagram for a single compound





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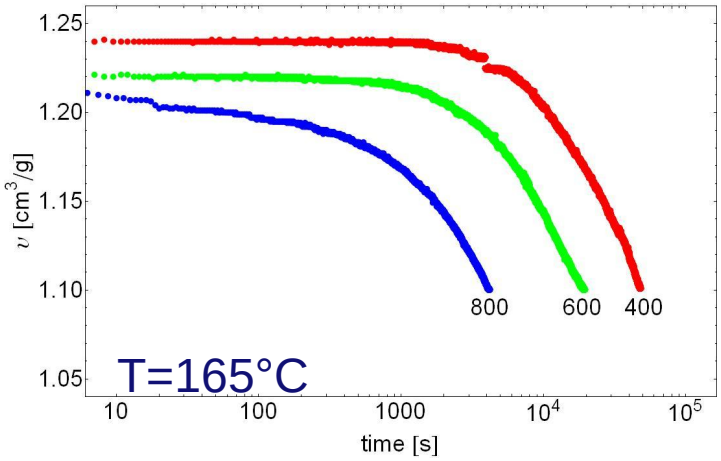
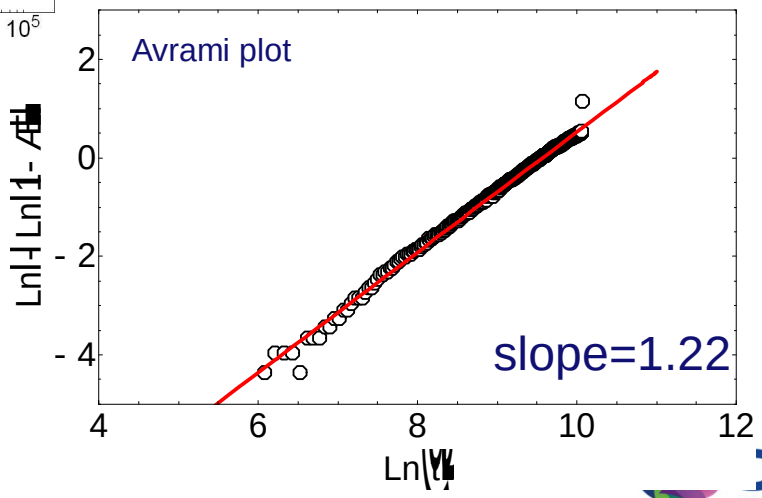
Wunderlich B, Journal of Polymer Science Part A, 2, 3697, 1964

isothermal and isobaric experiments



$$\phi = \frac{\upsilon - \upsilon_0}{\upsilon_\infty - \upsilon_0}$$

υ_∞ extrapolation of the volume of the solid



see also: He, Zoller - Journal of Polymer Science Part B Polymer Physics 32 6 1994

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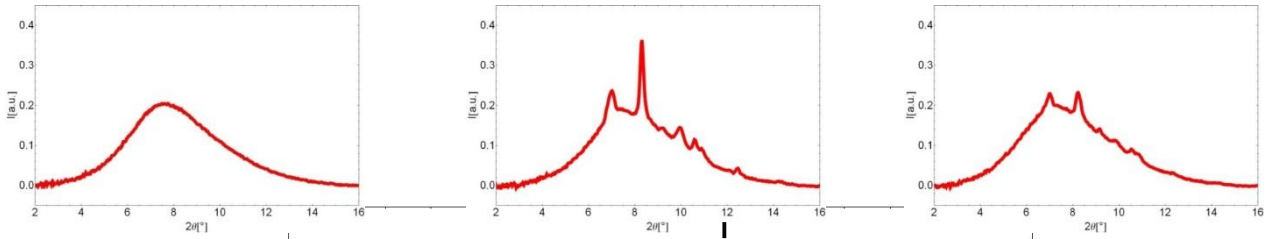
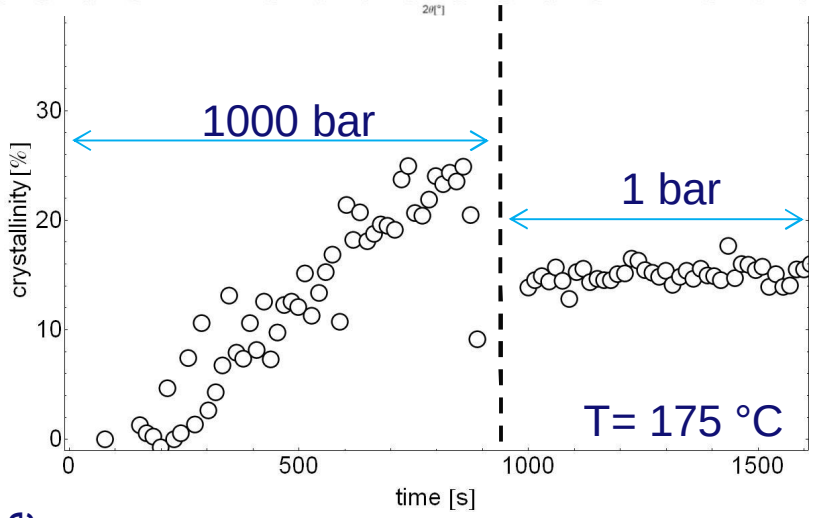
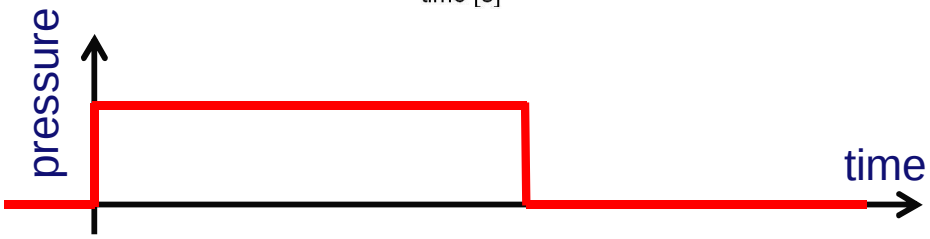
step pressure





T±2.5°C



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Dynamic experiments: morphology changes during deformation

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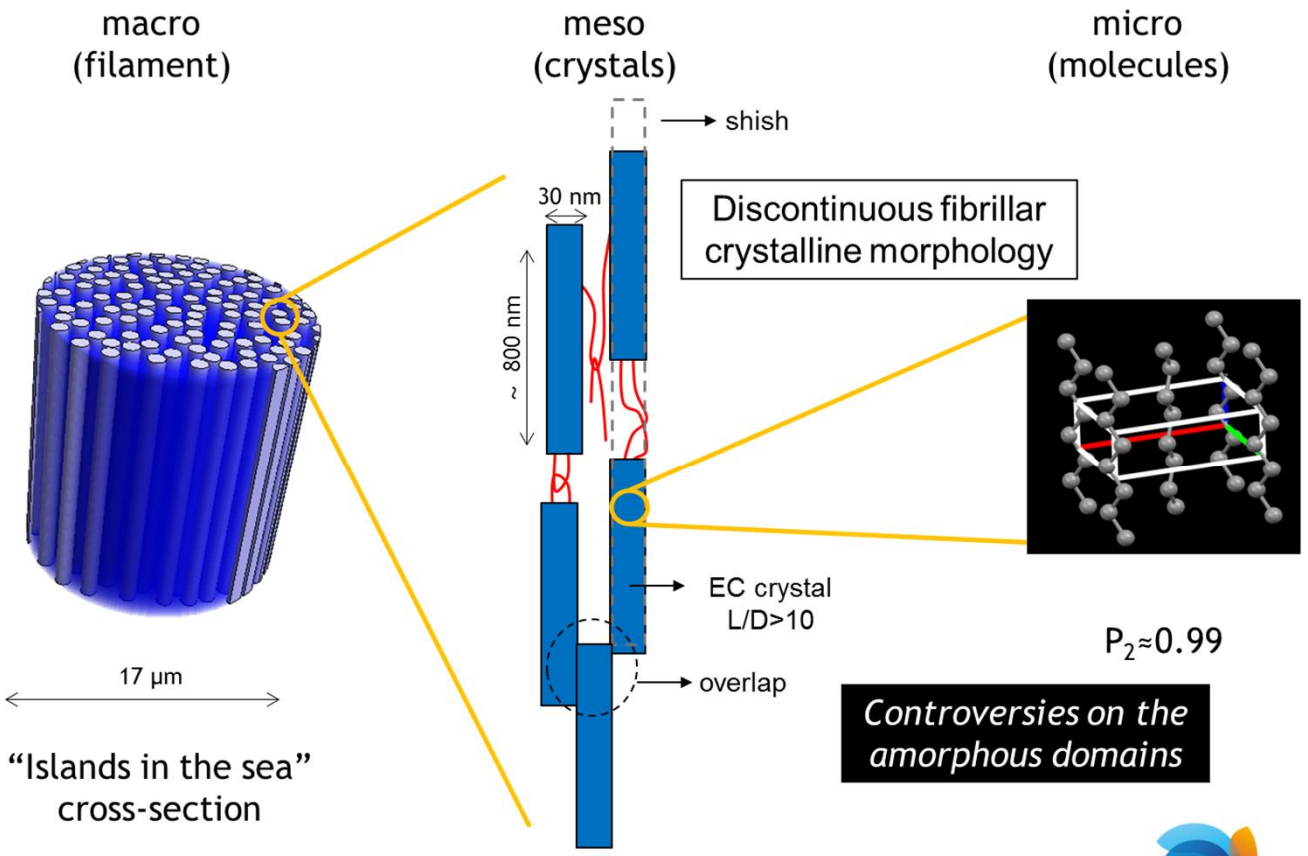
Multiscale structure of Dyneema® filaments



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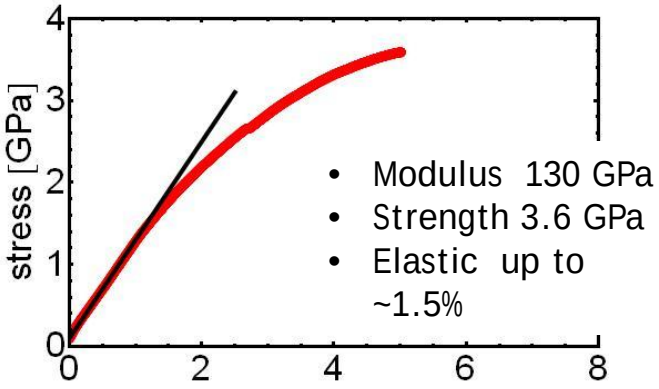
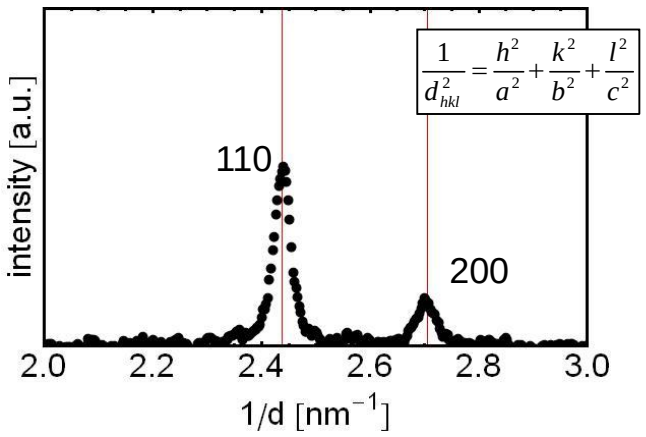
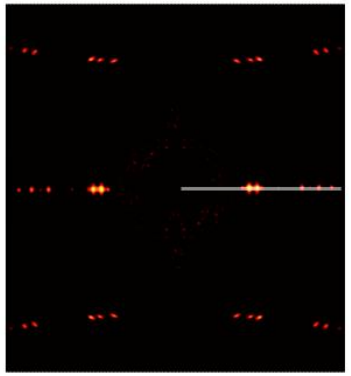
Micro-mechanics during tensile deformation

SK75, single filament
10^{-4} s^{-1}, room temperature

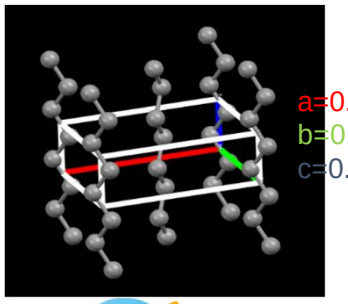




WAXD



orthorombic PE



a=0.74 nm
b=0.49 nm
c=0.25 nm

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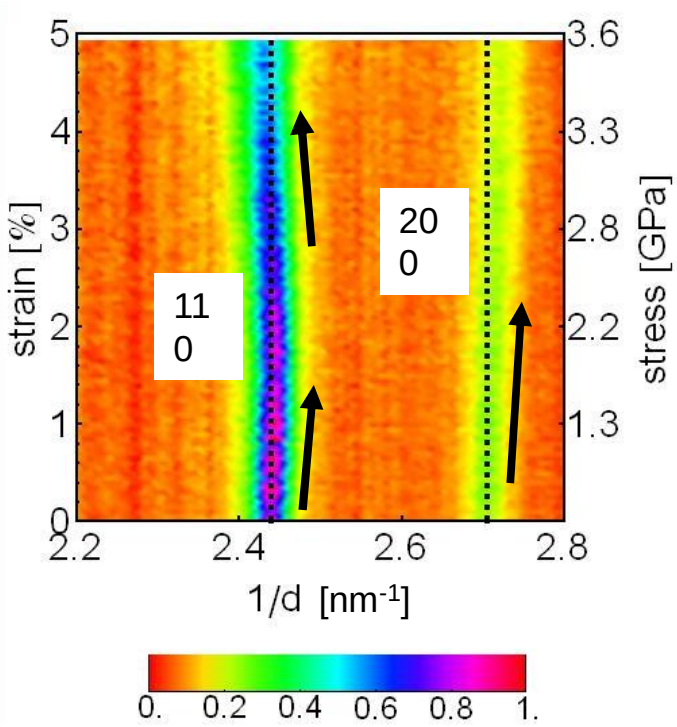
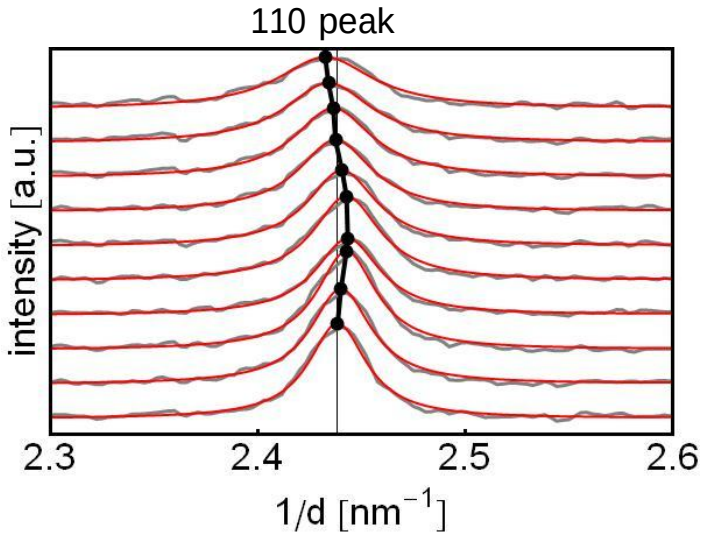
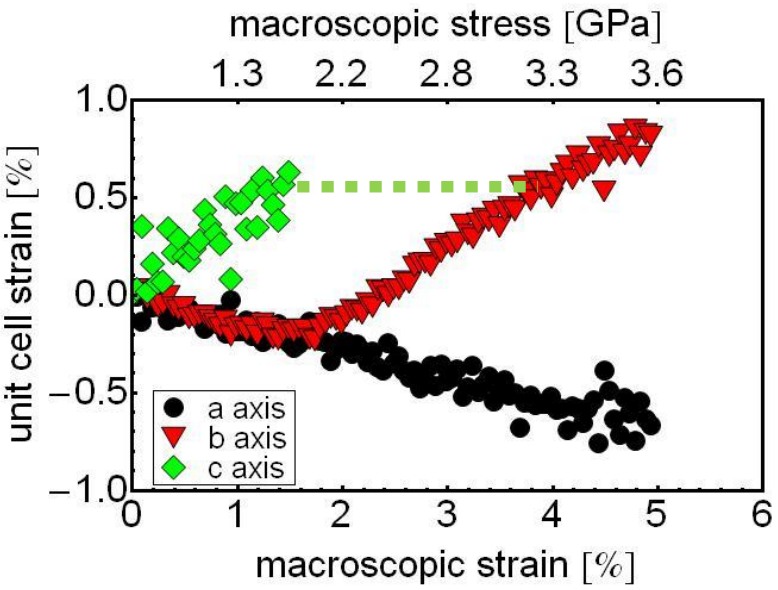
Micro-mechanics during tensile deformation

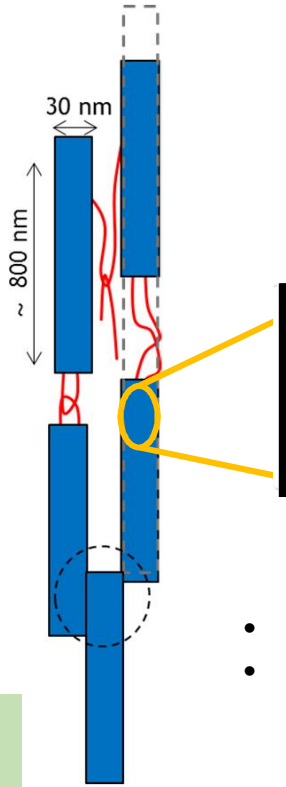


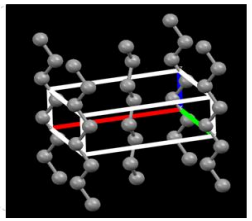


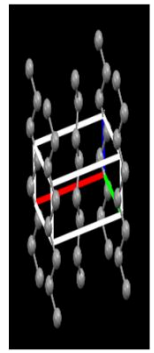
- 200 shifts to larger 1/d
- 110 shifts to:
  - larger 1/d until 1.5% (1.8GPa)
  - lower 1/d after 1.5%
- Peaks broaden but crystallinity remains nearly constant
- No phase transformations

Micro-mechanics of the unit cell









- a,b directly measured;
- c calculated
- Change at 1.5% strain;

$$\varepsilon_c = -\frac{1}{\nu_{ac}}\varepsilon_a$$

- Compression a- and b- axis
- Extension c-axis

Exactly what you would expect!

Amornsakchai et al, *Macromolecules* 1997, 30(17), 5034
C. Xu and M. Matsuo, *Macromolecules*, vol. 32, no. 9, p. 3006–3016, 1999.

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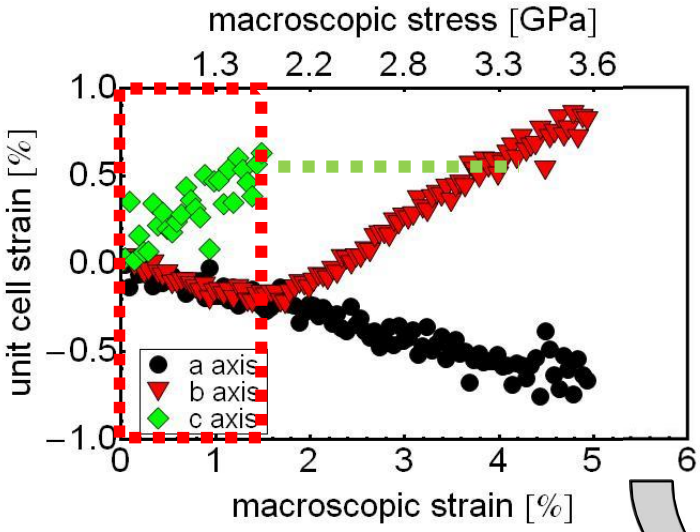
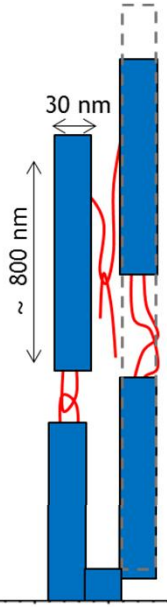
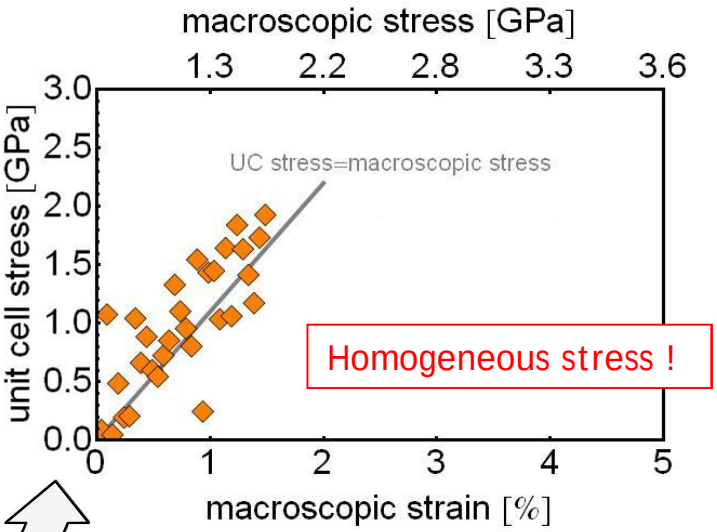
Stress transfer: how different from ideal?

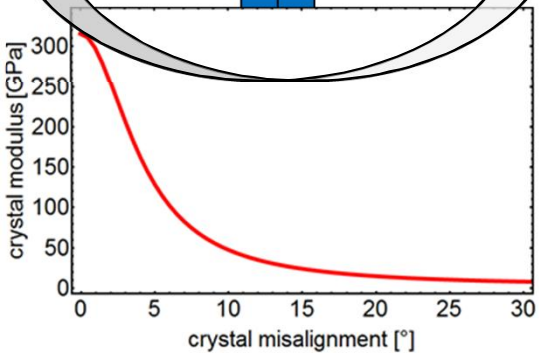






Homogeneous stress !

$$1/E(\theta) = s_{11}\cos^4\theta + s_{22}\sin^4\theta + (2s_{12} + s_{66})\sin^2\theta\cos^2\theta$$



Tashiro K. et al., *Macromolecules* 1978, 11 (5), 914

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Dynamic experiments: aging and rejuvenation of glassy polymers

Unfinished story

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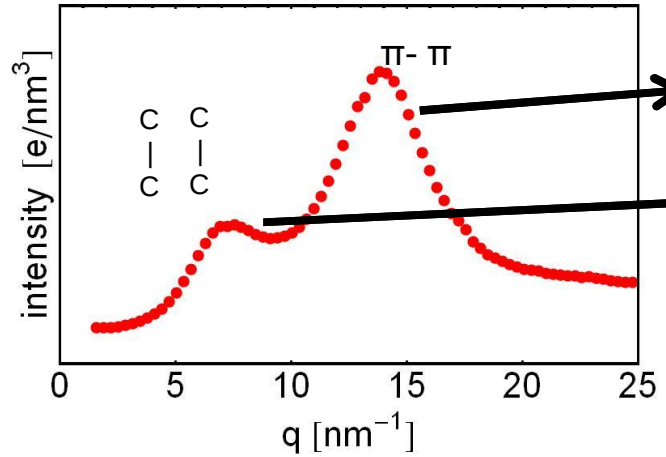
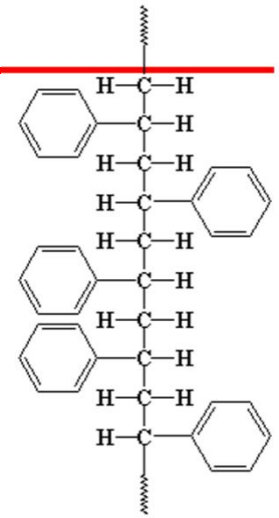
Ageing of glassy polystyrene



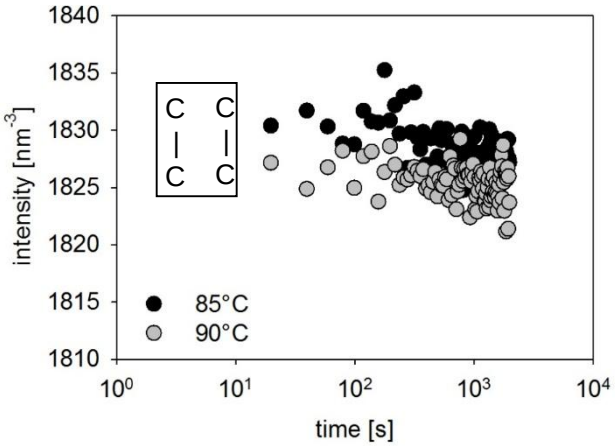
phenyls interaction

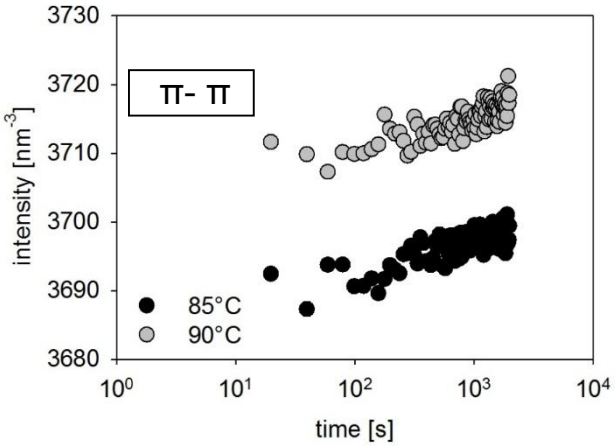
lateral packing of molecules

Mitchell, Windle, Polymer, 25, (1984)



Atactic



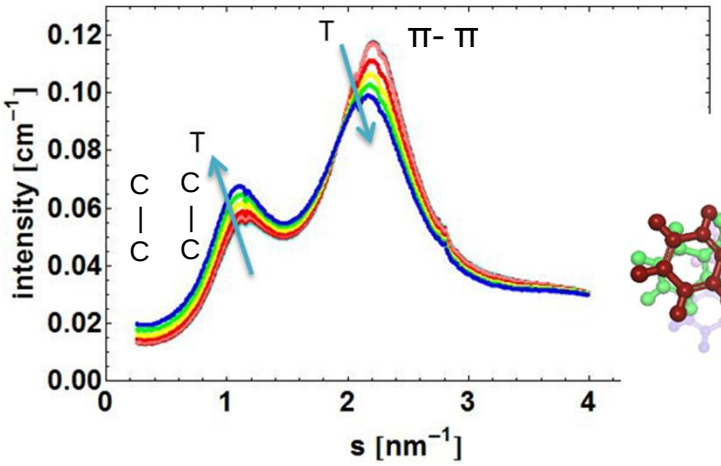


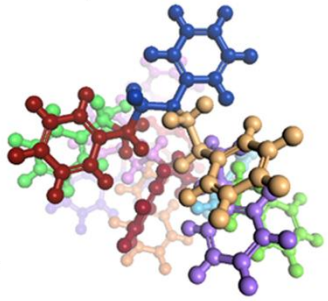
Physical ageing leads to:

- Weakening of interaction between backbones;
- Intensification of π- π interaction;

Molecular picture?

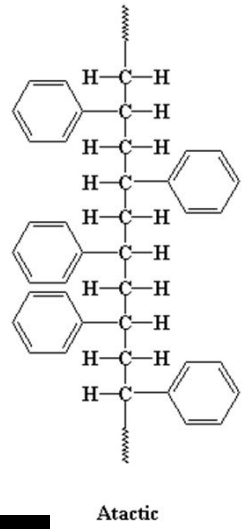
aPS: heating after quenching

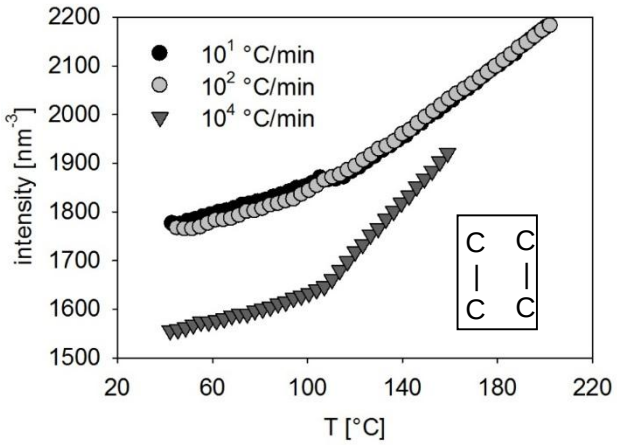


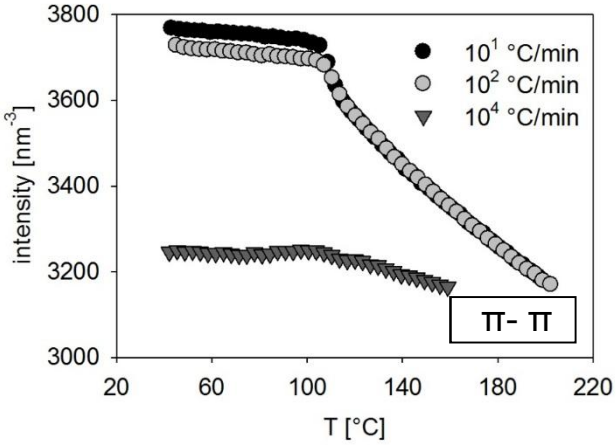


“dissolution” of static heterogeneities

- phenyl rings loose correlation
- backbones of the molecules are now free to align better







Insight in the mechanism of physical ageing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