Preferred Order and Solidification of Polymeric Semiconductors

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The talk will cover two main topics:

1. ***"Self-Organisation within Thin Layers of Polymeric Semiconductors"***

2. ***"Crystalline Ordering at the Interface of Polymer Solutions"***

From "Polen2006"

Trondheim Oct. 20th 2006

“Self-Organisation within Thin Layers of Polymeric Semiconductors”

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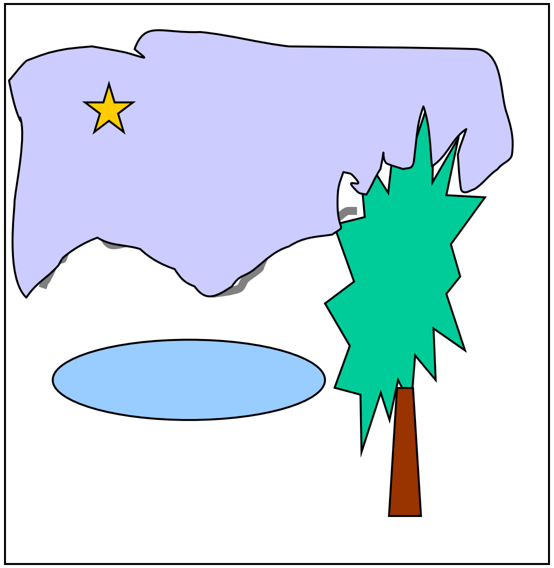
Hans-Jørg Fell[3]

Jostein Mårdalen[4]

Thin layer polymeric semiconductors, applications



Polymer electronics - transistors

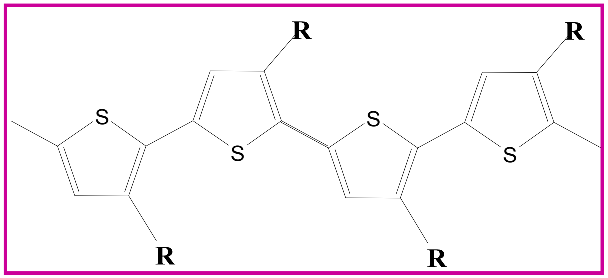
Polymeric memories

Polymeric lasers

Light-emitting diodes - and screens

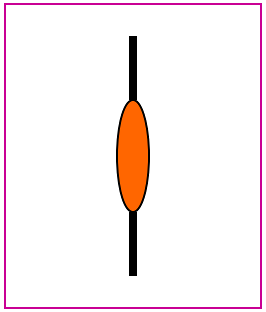
Examples

Polyacetylene	**PA**
Polypyrrols	**Ppy**
Poly(alkyl)thiophenes	**PAT**
Polyanilines	**Pani**
Polypyridines	**Ppyr**
Polyphenylenes	**PP**
Polyphenylene-vinylenes	**PPV**
etc.	



Chain

R = alkyl group;
hexyl, octyl, etc.



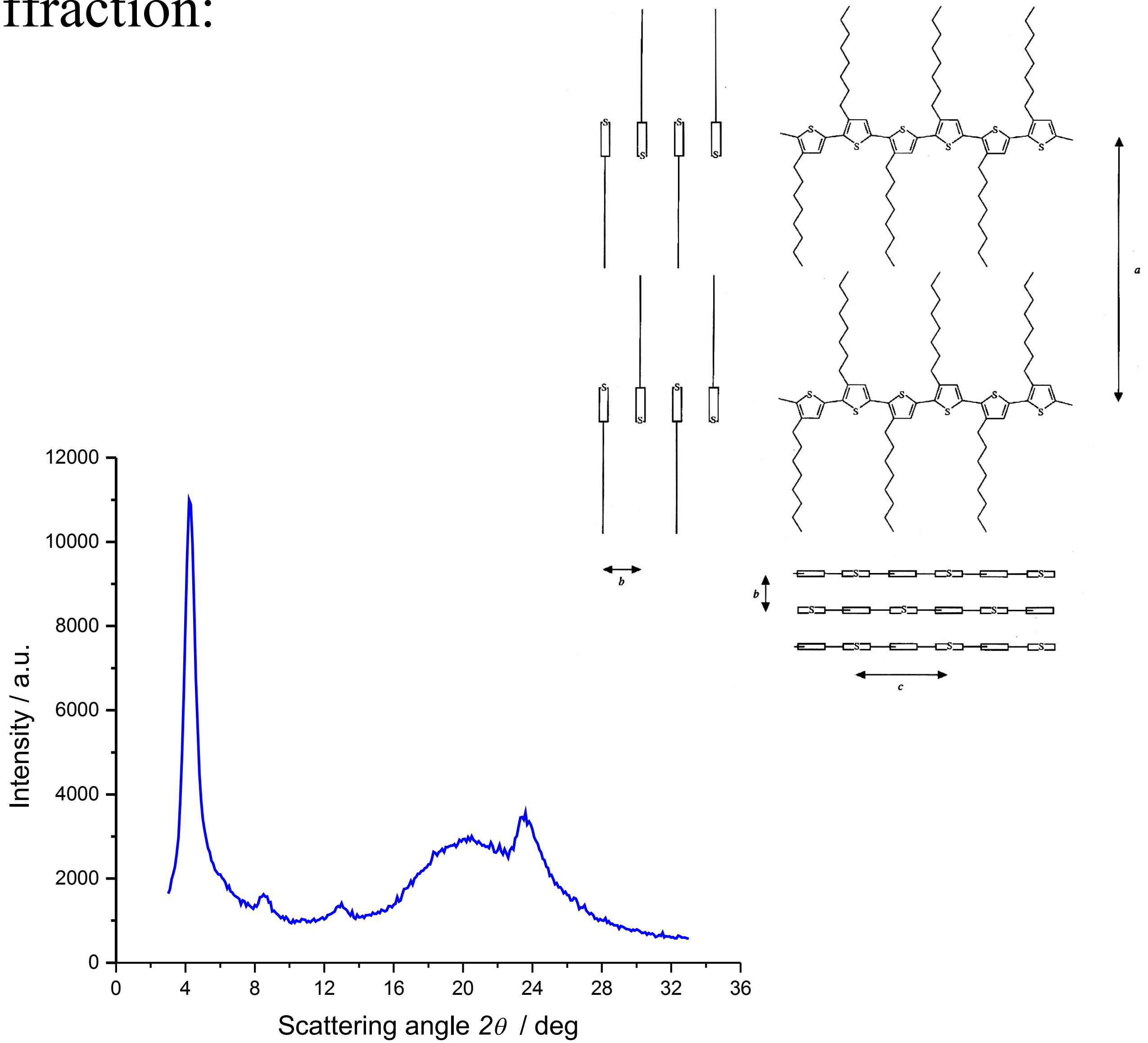
Along the chain

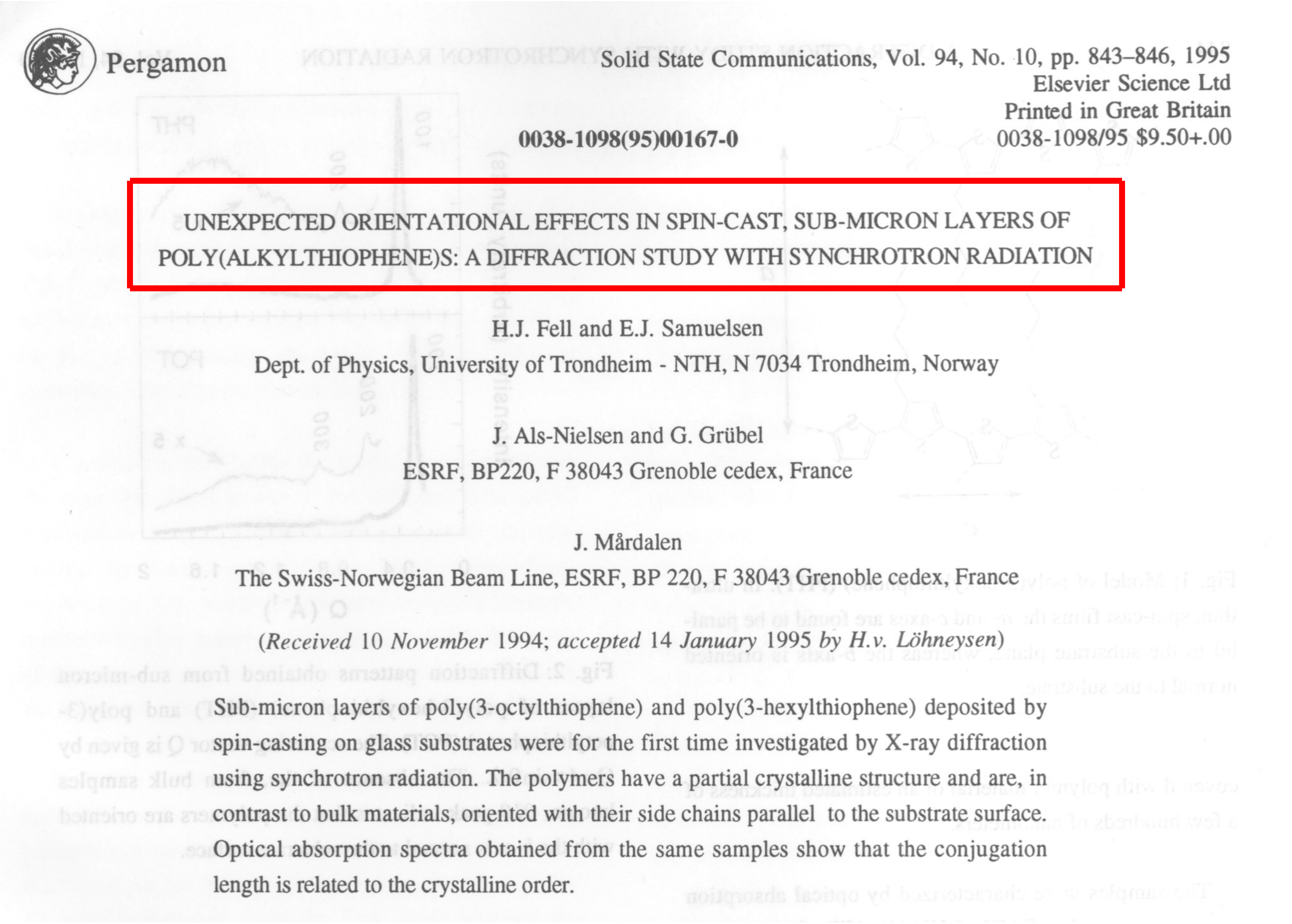
Discovery of strong tendency of preferred orientation: The first Norwegian project at the new synchrotron at ESRF, Grenoble, 1994

Detailed exploration of conditions for preferred orientation: Various works 1996-2004

X-ray surface diffraction and reflectometry

Diffraction:





Pergamon

Solid State Communications, Vol. 94, No. 10, pp. 843–846, 1995
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0038-1098(95)00167-0

UNEXPECTED ORIENTATIONAL EFFECTS IN SPIN-CAST, SUB-MICRON LAYERS OF POLY(ALKYLTHIOPHENE)S: A DIFFRACTION STUDY WITH SYNCHROTRON RADIATION

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(*Received* 10 *November* 1994; *accepted* 14 *January* 1995 *by H.v. Löhneysen*)

Sub-micron layers of poly(3-octylthiophene) and poly(3-hexylthiophene) deposited by spin-casting on glass substrates were for the first time investigated by X-ray diffraction using synchrotron radiation. The polymers have a partial crystalline structure and are, in contrast to bulk materials, oriented with their side chains parallel to the substrate surface. Optical absorption spectra obtained from the same samples show that the conjugation length is related to the crystalline order.

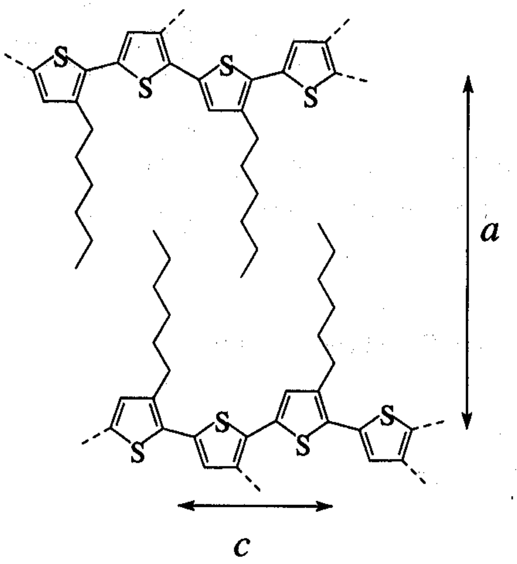


Fig. 1: Model of poly(3-hexylthiophene) (PHT). In ultrathin, spin-cast films the *a*- and *c*-axes are found to be parallel to the substrate plane, whereas the *b*-axis is oriented normal to the substrate.

covered with polymer material of an estimated thickness of a few hundreds of nanometers.

The samples were characterized by optical absorption spectroscopy with a CARY 5 UV-Vis-NIR photospectrometer.

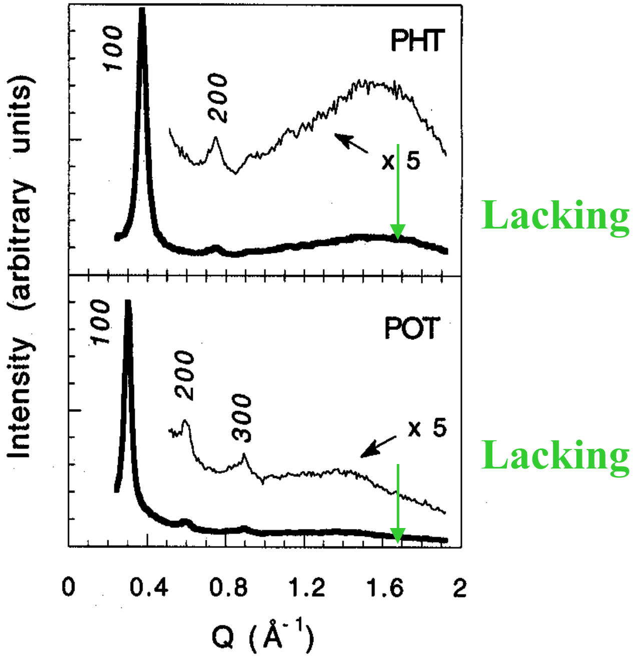
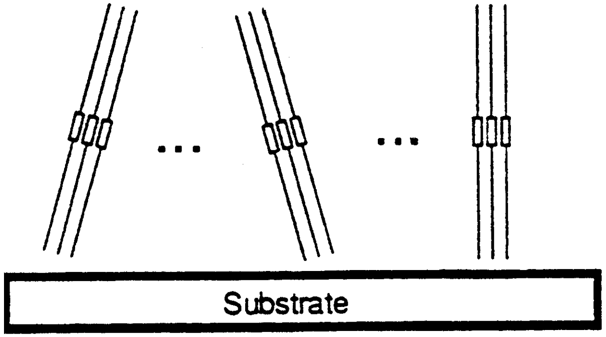


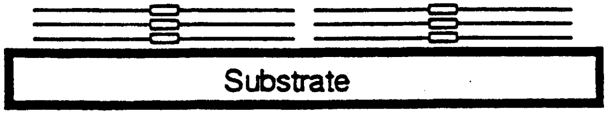
Fig. 2: Diffraction patterns obtained from sub-micron layers of poly(3-hexylthiophene) (PHT) and poly(3-octylthiophene) (POT). The scattering vector Q is given by $Q=4\pi\sin\theta/\lambda$. The absence of the, from bulk samples known, *010*-peak indicates that the polymers are oriented with the *b*-axis normal to the substrate surface.

A scintillation detector, elevated about 0.5° above the (horizontal) incident beam plane and equipped with a collimator slit was used to collect the diffracted X-ray by

Preferred orientation of the polymers:



As observed after slow evaporation



As observed after spin-coating

Fell *et al (1995);* **Aasmundtveit** *et al (1999)*

Macromolecules **2000,** *33,* 3120−3127

Structural Anisotropy of Poly(alkylthiophene) Films

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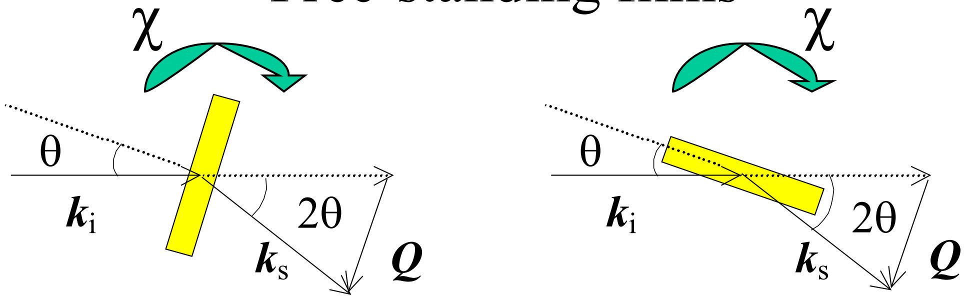
Received September 27, 1999; Revised Manuscript Received January 3, 2000

ABSTRACT: The structural anisotropy of various poly(alkylthiophene) films have been studied by X-ray diffraction, using both conventional methods and synchrotron radiation at grazing incidence. Solution-cast films orient with the side chains preferably normal to the film surface, whereas spin-cast films of nonstereoregular material orient with both the main and the side chains in the film plane. For thick (10−50 μm) solution-cast films, the degree of orientation depends strongly on the solvent used for casting, and on the stereoregularity of the polymer, films of stereoregular materials being more oriented than those of nonregular materials. The most oriented nonregular films are those cast from mixtures of chloroform and tetrahydrofuran. Thin (50−500 nm) solution-cast films are more oriented than the thicker ones, and the effects of different stereoregularity or different casting solvents are small. For spin-cast films, the degree of orientation is independent of substrate and solvent. Spin-cast films of stereoregular material have two different phases: One with the side chains normal to the substrate, and another where they are parallel to the substrate. The diffraction peaks of spin-cast poly(octylthiophene) narrow considerably upon heating.

Observation of anisotropy by diffraction

Free-standing films



Transmission

Reflection

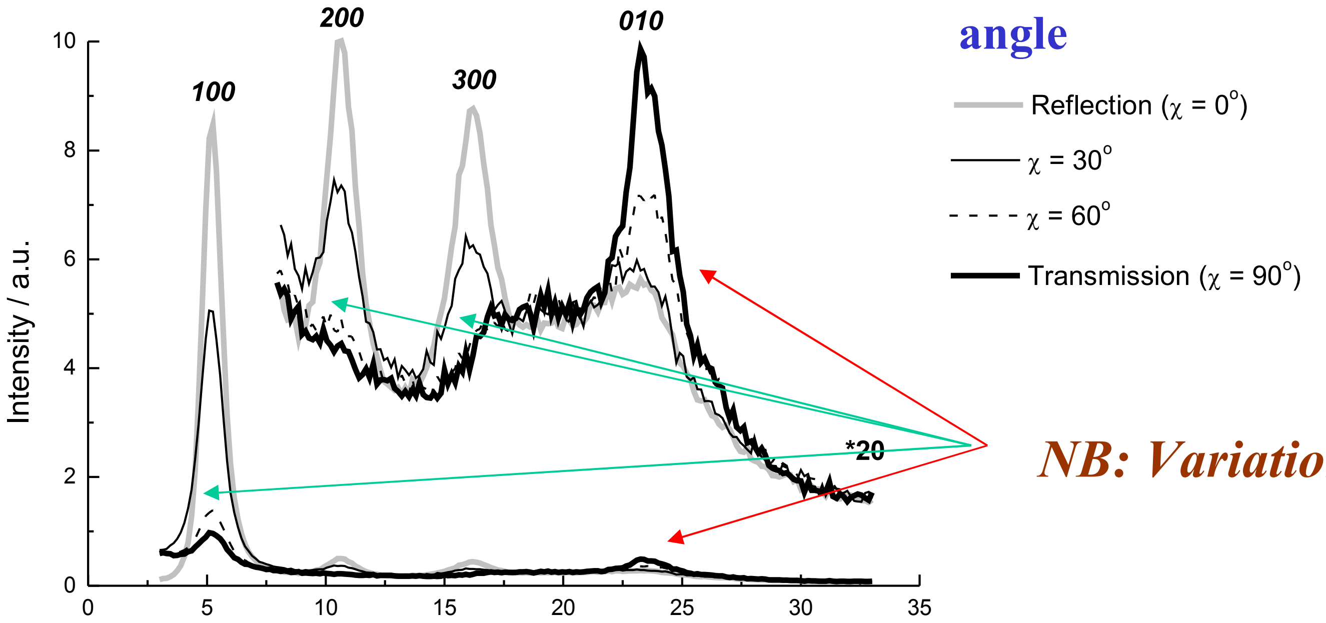
Sample turn angle:

$\chi = 90^o$

$\chi = 0^o$

Anisotropy of *POT* film, 20 microns thick, from chloroform-THF mixture

Rotation angle

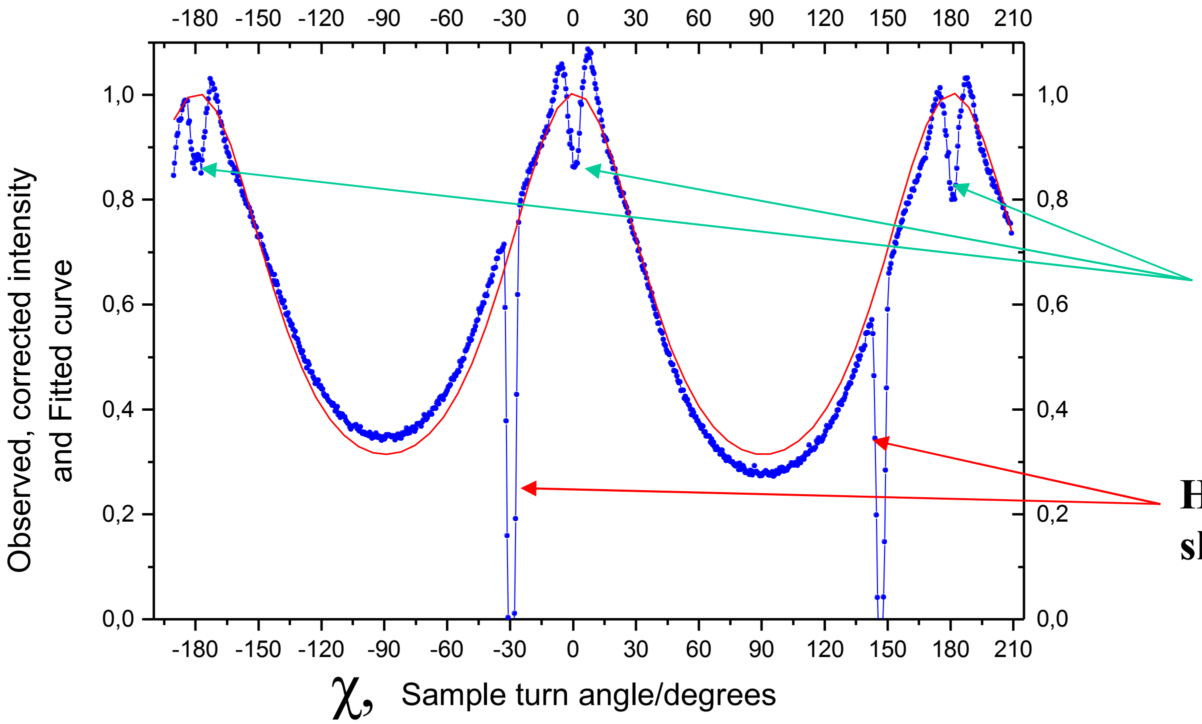


NB: Variations!

Scattering angle, degrees

From *Aasmundtveit et. al.* (2000)

Observed and fitted intensity *versus* turn angle for POT



Sample shadow

Holder shadow

***100*-reflection from strip of POT, showing the strong anisotropy**

(corrected for volume variation) Breiby and Samuelsen 2003

$$I = I_0 \Sigma_i \exp(-a_i \sin^{2i}\chi)$$

Determination of order parameters:

Observable intensity: $I = I_0 P(\chi)$, where the distribution function is

$P(\chi) = \Sigma_i \exp(-a_i \sin^{2i}\chi)$.

Herman order parameter: $S = <\frac{1}{2}(3\cos^2 \chi - 1)>$, giving
$S = 2/15\ a_1 + 4/315\ a_1^2 - 8/4725\ a_1^3 + \ldots$

For polyoctylthiophene films from various solvents S ranged from 0.06 (thiophene and toluene) to 0.23 and 0.46 (tetrahydrofuran THF/dichloromethane; THF/chloroform)

A weak correlation was found between *S* and the boiling points, but not with the Hildebrand solubility parameter (*δ*) of the solvents.

Results for poly-alkylthiophenes:

Stero-irregular ('atactic') polymers:

Cast from solutions: molecular plane ***normal*** to the substrate

Cast by spin-coating: molecular plane ***parallel*** with the substrate

Stero-regular polymers:

Cast from solutions: molecular plane ***normal*** to the substrate

Cast by spin-coating: molecular plane both ***parallel*** with and ***normal*** to the substrate

The normal orientation gives rise to a higher electron mobility

Review article

2004

Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases, 2003: 51-78
ISBN: 81-7736-083-3 Editor: Shu Hotta

2 Self-organisation within thin layers of polymeric semiconductors

Emil J. Samuelsen[1], Knut E. Aasmundtveit[2] and Dag W. Breiby[1]
[1]Division of Physics, Norwegian University of Science and Technology, (NTNU), N-7491 Trondheim, Norway; [2]Alcatel Space Norway, N-3191 Horten, Norway

Abstract

The review gives a systematic presentation of self-organisation observed in various polymeric semiconducting materials when prepared as thin films by solution casting, spin-coating and as ultra-thin layers on water surface or as Langmuir-Blodgett films. Examples are materials like substituted poly-thiophenes, poly-anilines, poly-phenylene-vinylenes, poly-pyridine, with emphasis on poly-thiophenes, which constitute the group of materials best documented. A general tendency is found that the polymer main chains take an orientation parallel with the film surface, in most cases with the molecular plane about normal to the surface, although important exceptions are also described. A short review is given of methods to study preferred orientation, with emphasis on diffraction. Ways of imposing preferred ordering are also shortly surveyed.

Examples:

Poly-alkyl-thiophenes PAT

Poly-anilines PANI

Poly-phenylenes PPh

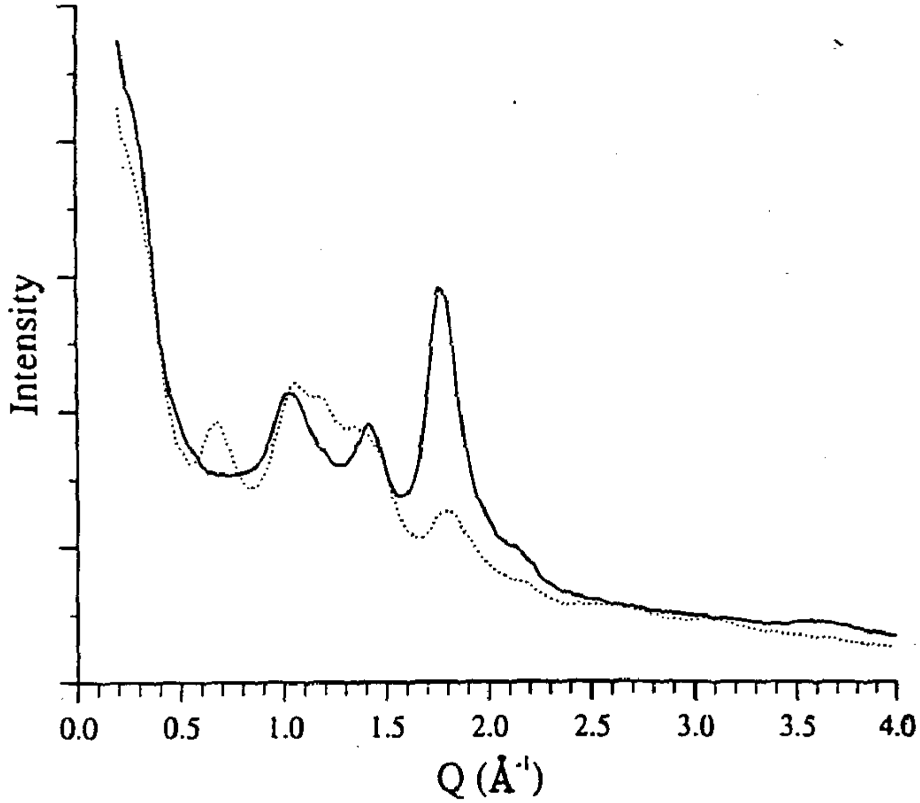
Poly-phenyl-vinylines PPV

Polypyridine Ppy

etc.

Also: **Langmuir films** (films floating on water)

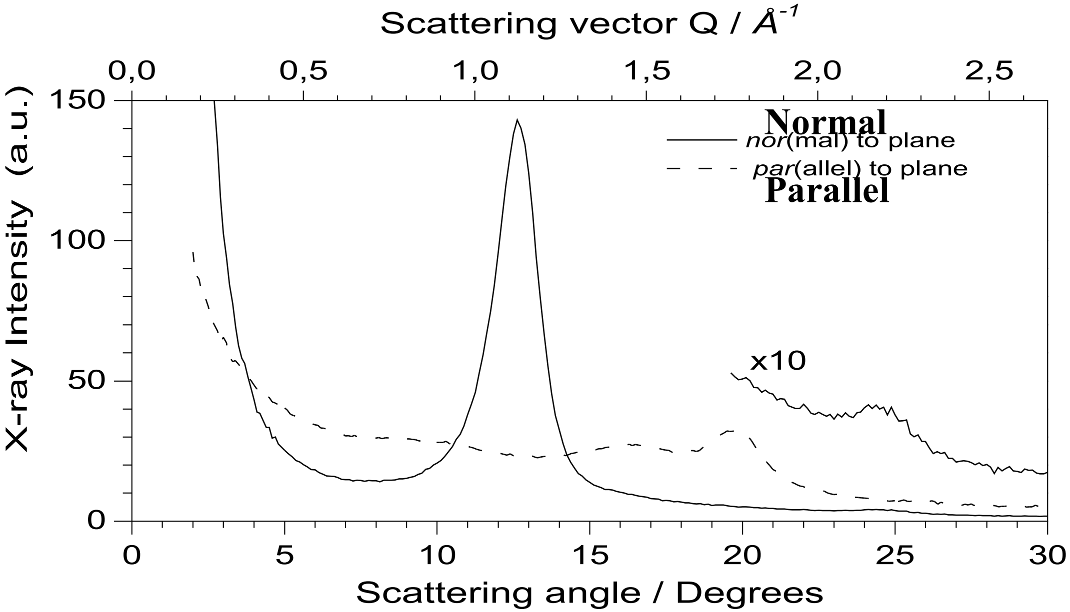
Anisotropy in PANI-CSA

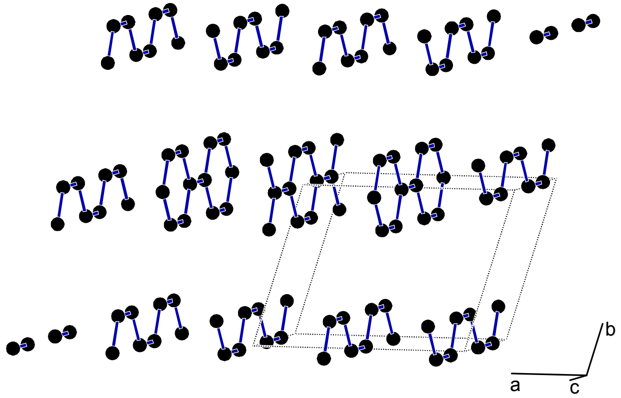


PANI-CSA. Full line: Equatorial (in-plane) scan. Dotted line: Meridional (out-of-plane) scan

Minto et al 1997

Anisotropy of polypyridine ($C_5N\,H_3$)





Samuelsen et al 2001

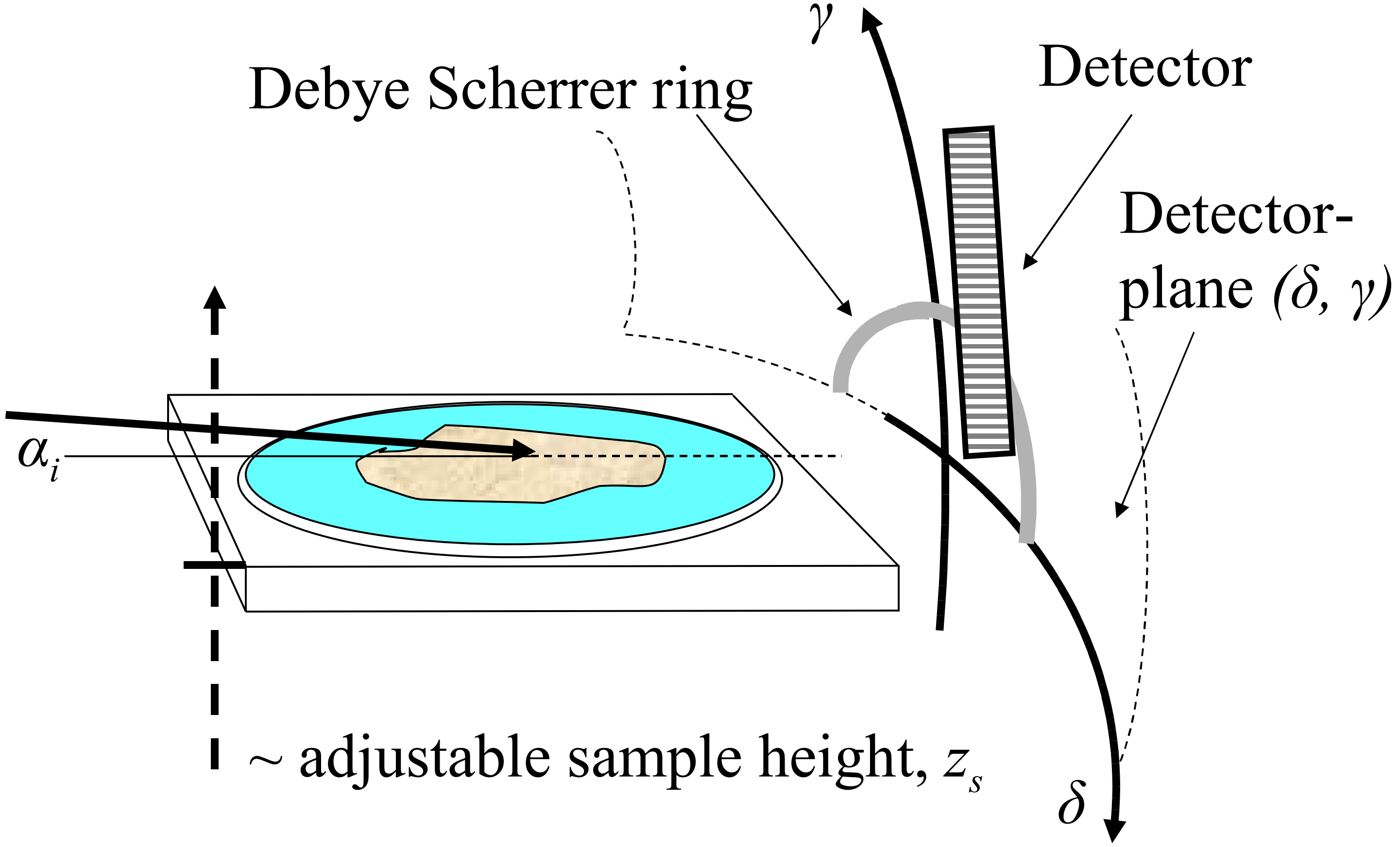
Langmuir film:

POT film floating on water

Diffraction and **reflectometry**

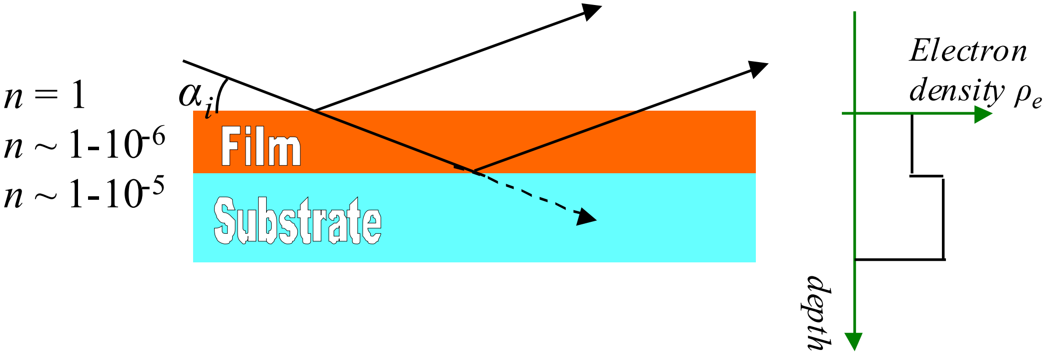
Breiby et al 2004

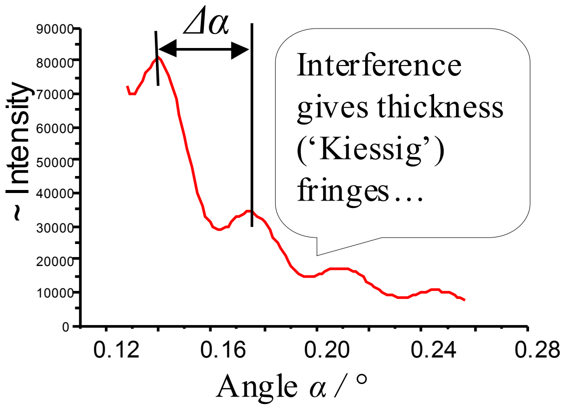
Studies of floating layer on water:



Study of floating layers on water:

Tool: Reflectometry





Interference gives thickness ('Kiessig') fringes…

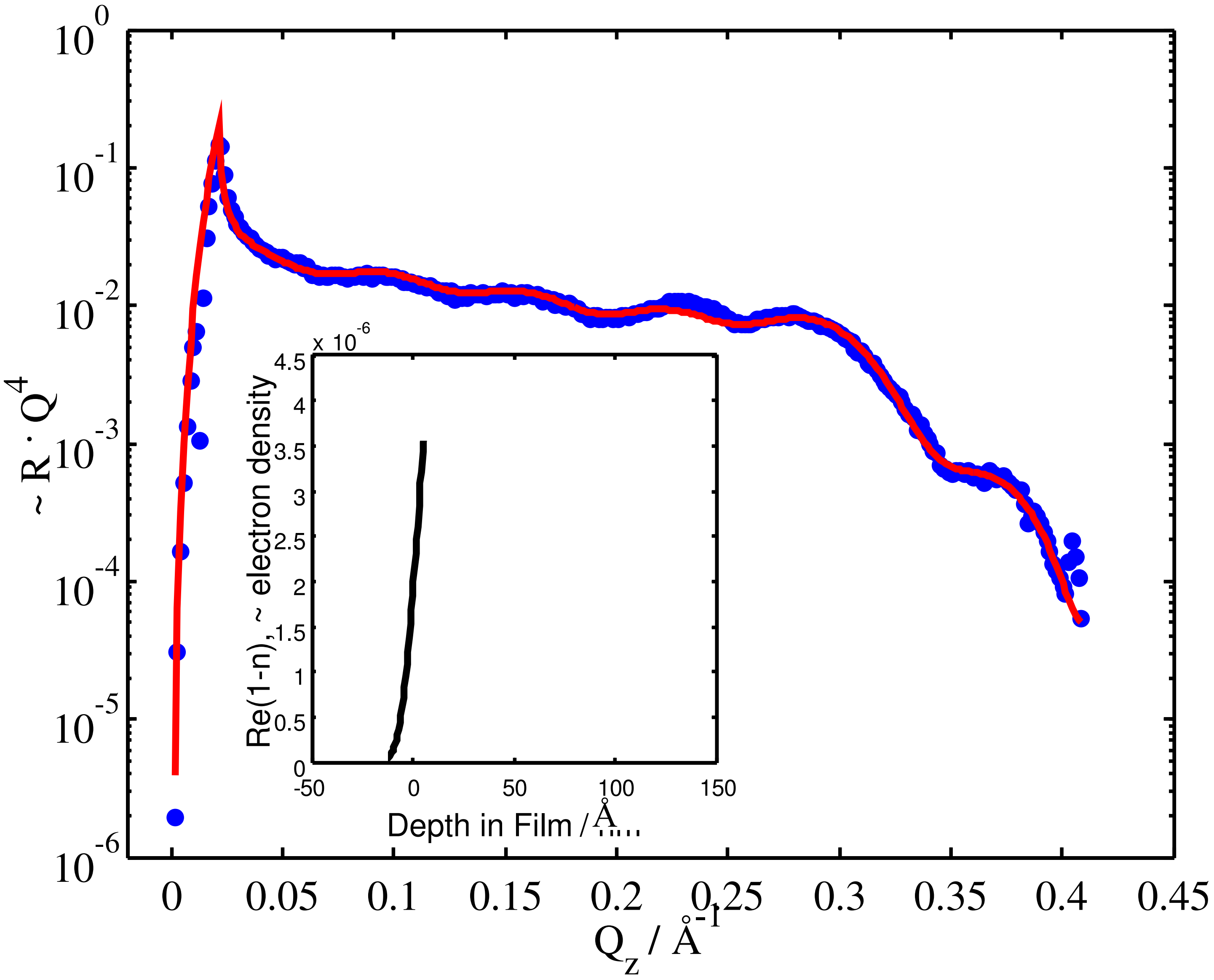
NB!! The angles are exaggerated!

Specular reflection: $\alpha = \alpha_{in} = \alpha_{out}$

Angular range $\alpha \sim 0$ - 4°

$$d = \frac{2\pi}{\Delta Q} = \frac{\lambda}{2\sin\Delta\alpha}$$

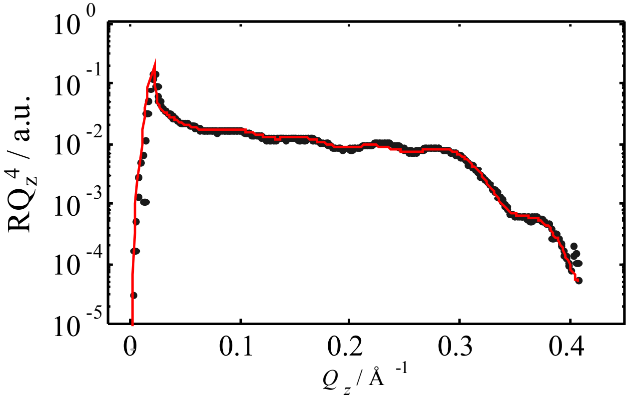
Reflectivity vs. Scattering angle + model:



Reflectometry results

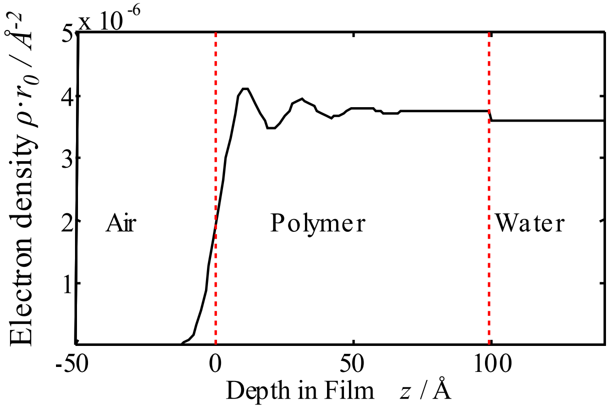
Experimental data

& Fitted curve:



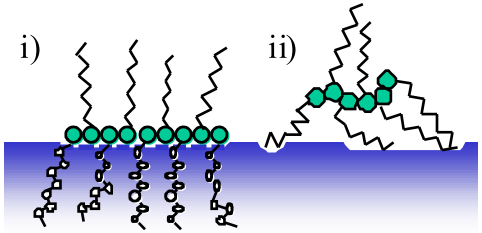
Obtained model for the

electron density *$\rho(z)$*:

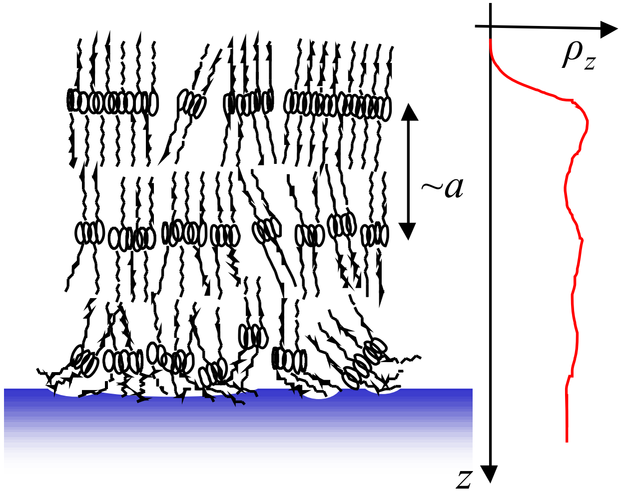


Interpretation

Amphiphilic molecules that self-organize!



Single-molecular layers
(studied by others)



- multiple molecular layers
- intrinsic tendency of orientation
- disorder due to hydrophobicity of the side chains

Preferred orientation appears to be a rather general phenomenon;Applies to very many semiconducting polymer

Self-organisation takes place, under the influence of a uni-axial ”field” by the substrate or other interfaces

Clustering through sidewise ”π-electron” attraction betwwen the molecules. Flakes or mats (large clusters) settle on the substrate as the solvent disappears => pref. Orientation.

Conclusion:

Deposited polymers normally show a preferred orientation on substrates

2

”Crystalline Ordering at the Interface of Polymer Solutions”

Emil J. Samuelsen[1], Dag W. Breiby[1] and Oleg Konovalov[2]

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[2] Experimental Division, European Synchrotron Radiation Facility, F-38043 Grenoble, France

Polymeric semiconductors, like substituted polythiophenes, are known to exhibit self-organisation into preferred crystalline orientation when deposited onto substrates. A deep understanding of the formation of crystalline order is of pivotal importance for the successful exploitation of these semi-crystalline materials within molecular electronics and optronics.

Employing *in situ* grazing incidence synchrotron x-ray diffraction we have found that the formation of solid phase often takes place within a *skin* on top of the polymer solution. The actual solidification process depends on the polymer concentration and the rate of blowing (of inert gas) above the solution surface. In fact, by controlling these two parameters the drying process may be tuned between two regimes; “edge-drying” and “skin formation”. The crystalline anisotropy in the resulting dry film depends on the choice of solvent.

Polymer solutions while drying:

Self-organisation at liquid-vapour interface?

or

Solidification onto the substrate?

Polymeric semiconductors for application are deposited as nanometer-thin layers on substrates or flat electrodes

Examples PPV, PAT, PEDOT a. o.

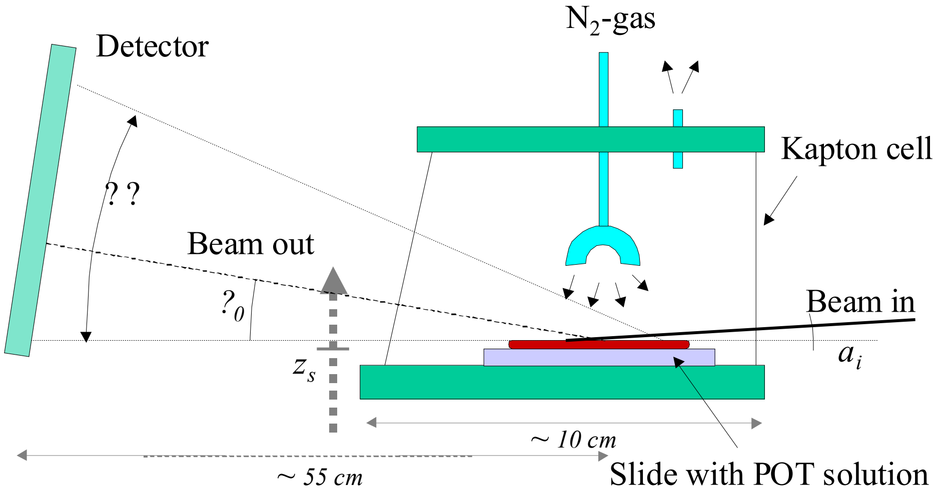
Thinfilm luminiscent screens

Thinfilm memories

Thinfilm polymer electronics

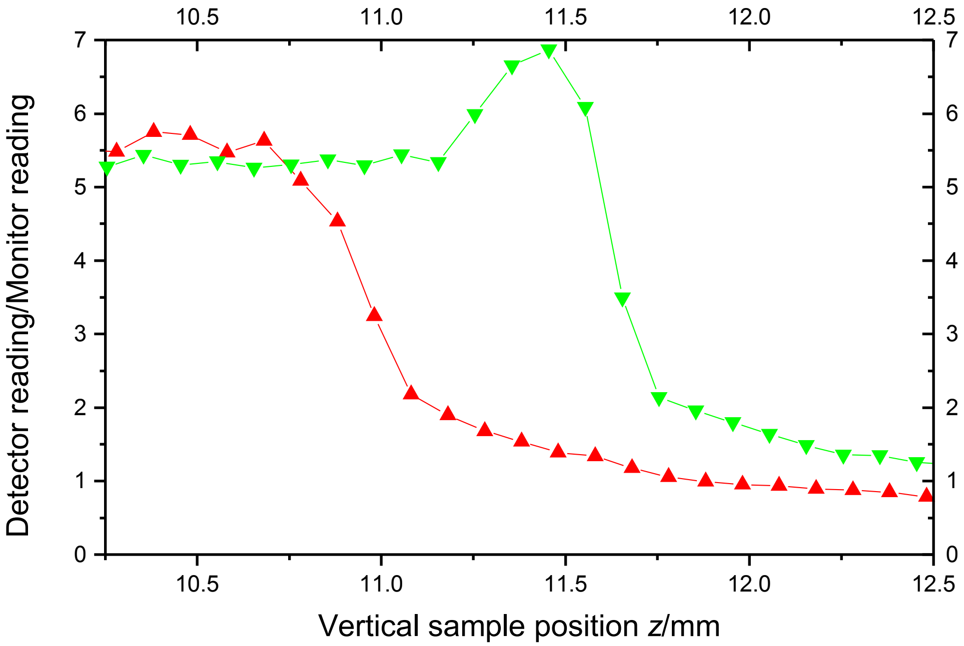
Drying conditions:

- **Concentrated solutions of poly(octylthiophene) POT in**
- ***tetrahydrofuran* THF or *chloroform* CLF on a glass substrate, kept in a closed compartment**
- **Compartment may be ventilated by dry *N_2- gas* to control evaporation rate**
- **Surface state monitored by *grazing incidence x-ray diffraction* using synchrotron radiation at the *ESRF***



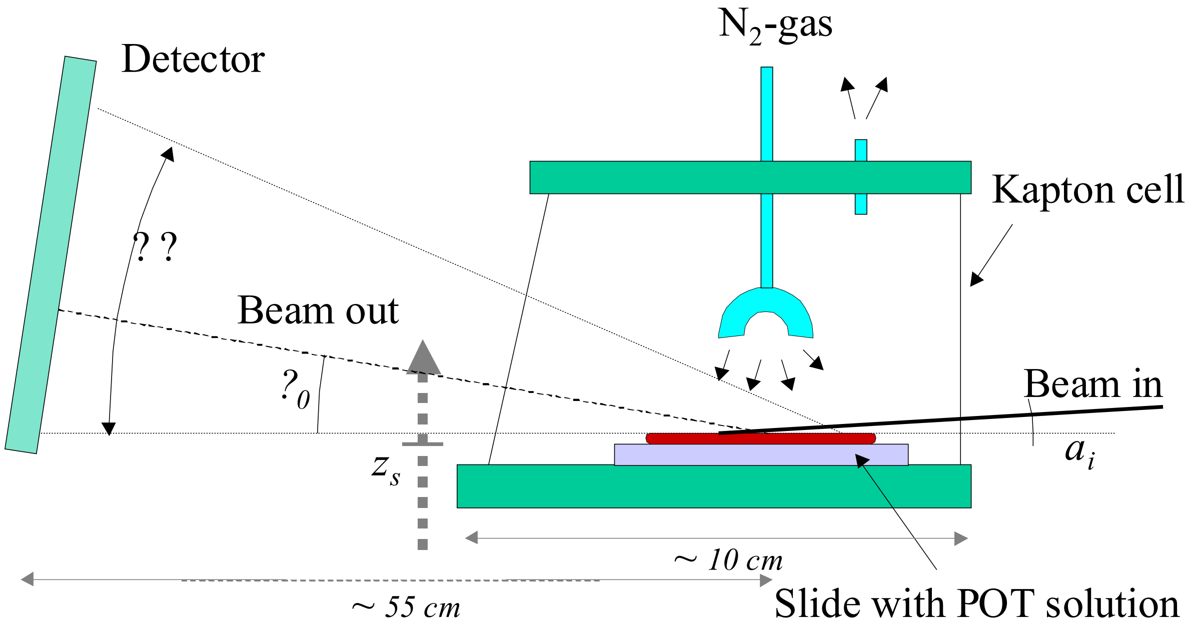
Height ajustment by recording reflected intensity *versus* vertical cell position *z*

Optimal position at intensity inclination points



Red curve: At an early stage; solution **Green curve: Final stage; solid film**

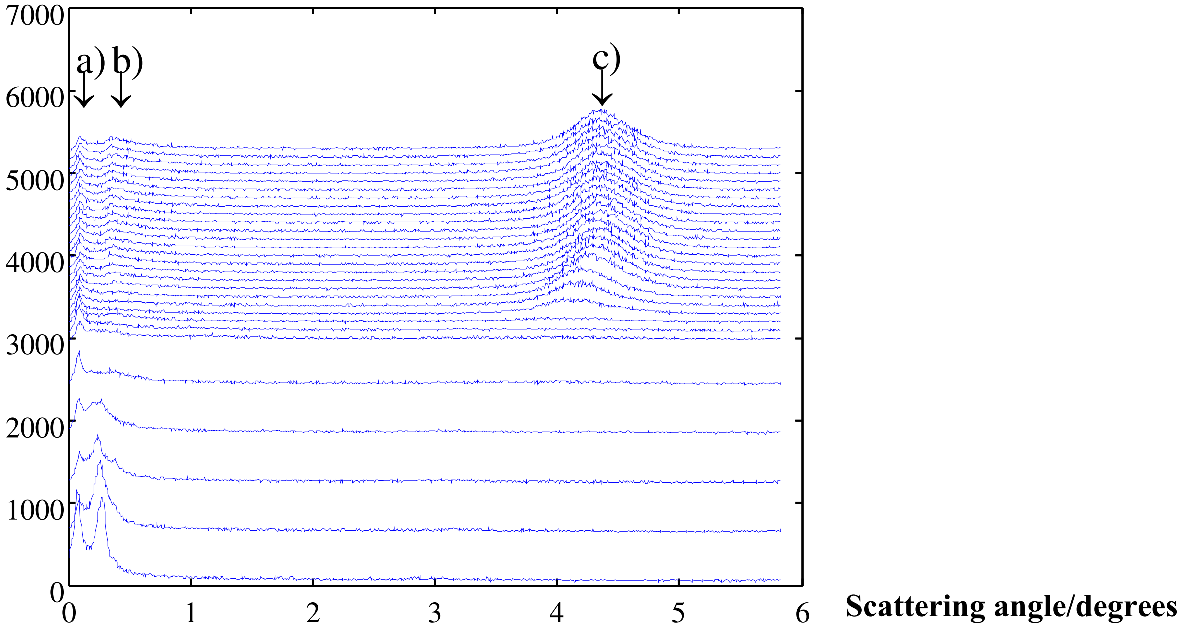
Cell for drying studies:



Beam incidence at 0.15°

The height (z_s) of the solution surface and possible diffraction signal (at 4.2°) from ordered polymer are monitored continously during the drying

Diffraction pattern *versus* time:



Diffractograms separated in time by about 3 minutes. The five curves following the first have been given offsets of 600, the others an offset of 50. 'a', 'b' and 'c' denote the air-scattered direct beam, the reflected beam and the *100* Bragg peak. The Bragg peak grows, and shifts to higher scattering angle γ (i.a. lattice contraction) as the solution dries.

Dependent on external conditions:

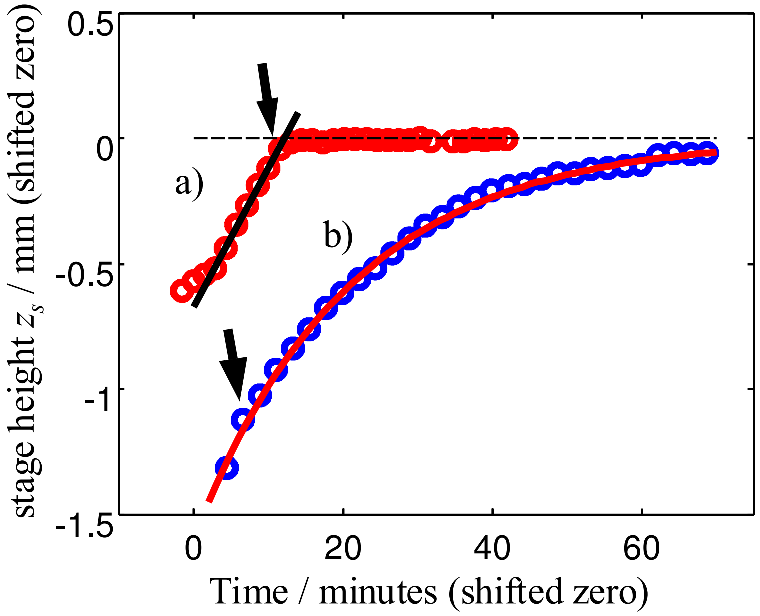
”Edge drying”

Low concentration
a)
Low ventilation

or

”Surface skin formation”

High concentration
b)
High ventilation



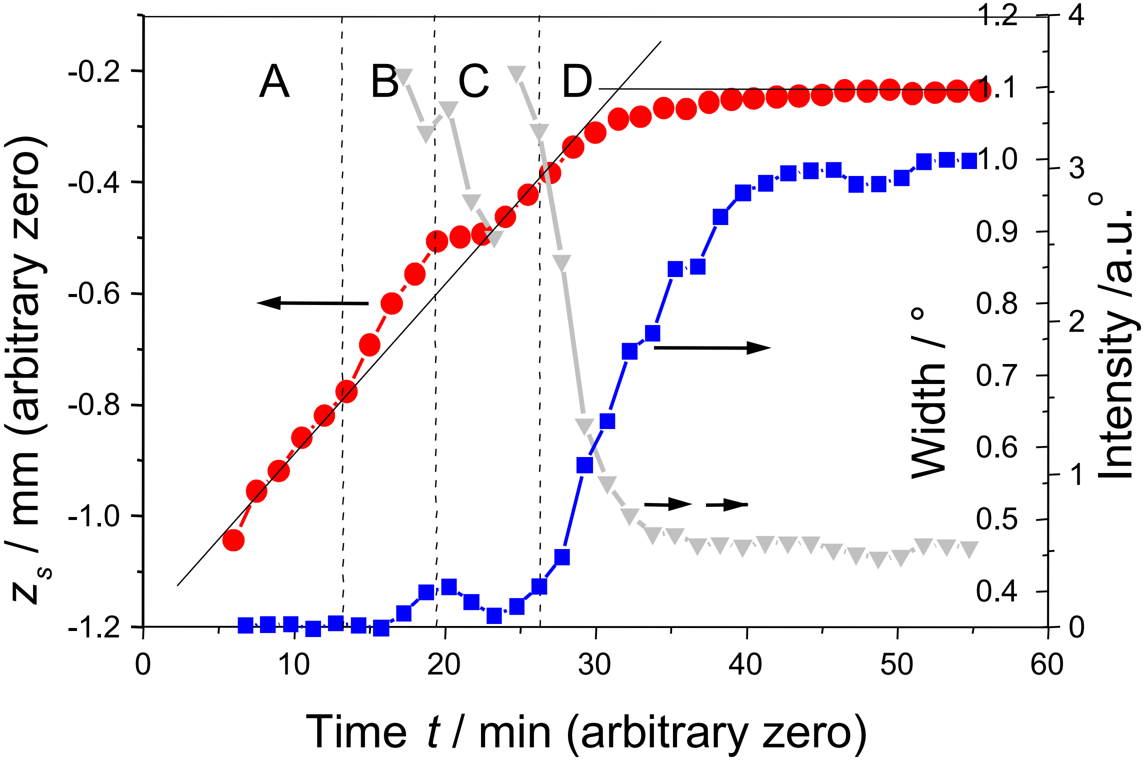
”Constant rate period”

or ”Falling rate period”

↓ appearance of Bragg peak

Skin formation:

Surface level, appearance of Bragg peak, peak width and intensity *versus* drying time

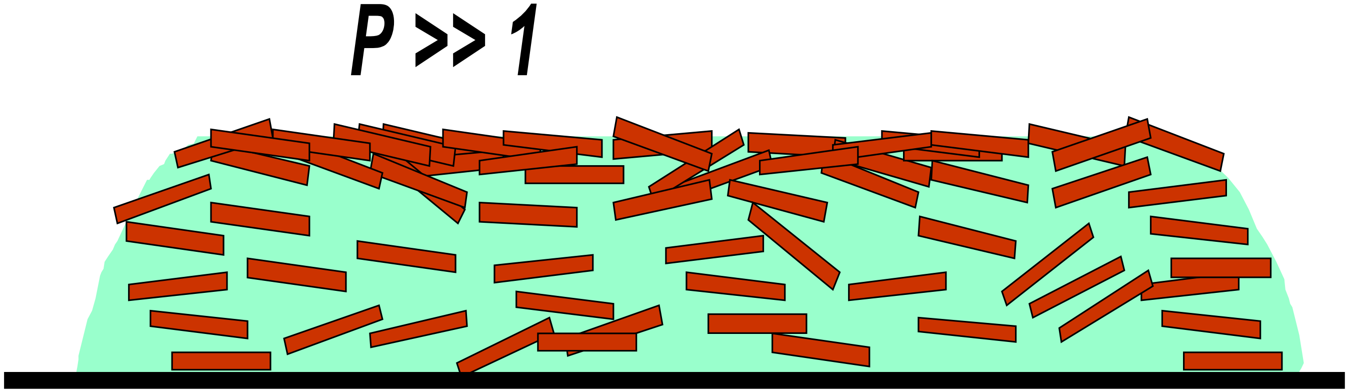


A: Constant ventilation B: Increased vent. C: Halt of vent. D: Resumed original ventilation

Skin formation:

High evaporation rate and/or low polymer diffusion rate (i.e. high *Pechlet number P*) promote skin formation (*P = Thickness * Evap.rate/Diff.rate*).

The skin acts as a barrier for the the evaporation, leading to an exponential time dependence of thickness

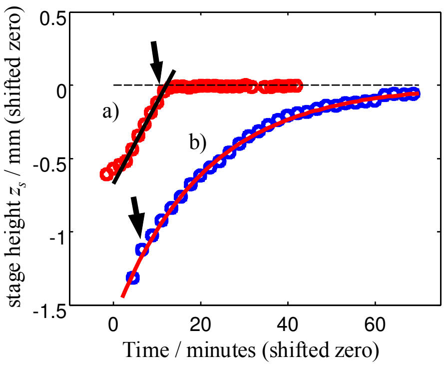


Edge evaporation:

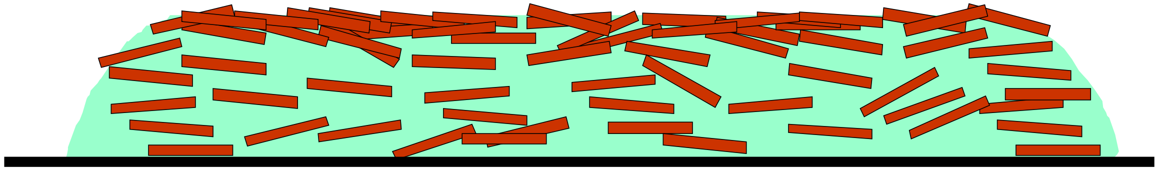
Low evaporation rate and/or high polymer diffusion rate (i.e. low *Pechlet number P*) promote edge evaporation

Visual observation of shrinking edges of the solution:

Skin and edge:

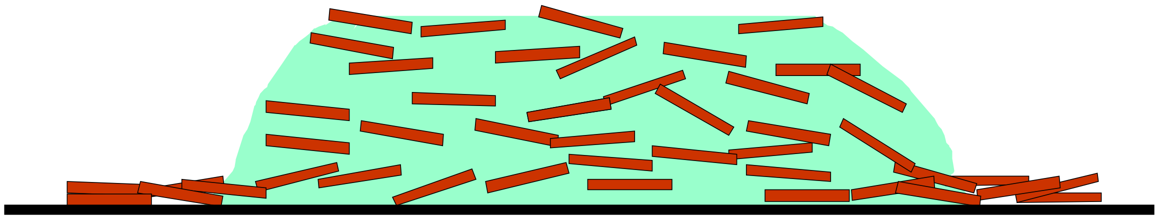


P >> 1



Skin

P << 1



Edge

Preferred orientation:

The dry films were investigated for preferred orientation

Preferential orientation with side-chains normal to surface, expressed by *Herman parameter S* ranging from 0.06 to 0.43 (S= 1 is full order, S= 0 is full disorder). Tendency of lower order in **”Skin growth”.**

Previous studies show that *sub-micrometer* solution cast films exhibit higher *S*-values

Conclusions and references:

Solidification of polymers from solution may be grouped into two categories, depending on evaporation rate and polymer diffusivity (i.e. concentration), expressed by *Pechelet number* *P* = (Thickness x Evaporation rate/Diffusion Coefficient):

1. *P*>> 1: ”Skin formation” on top of the solution, slowing down further evaporation

1. *P*<< 1: ”Edge drying”; solidification directly on to the substrate

References:

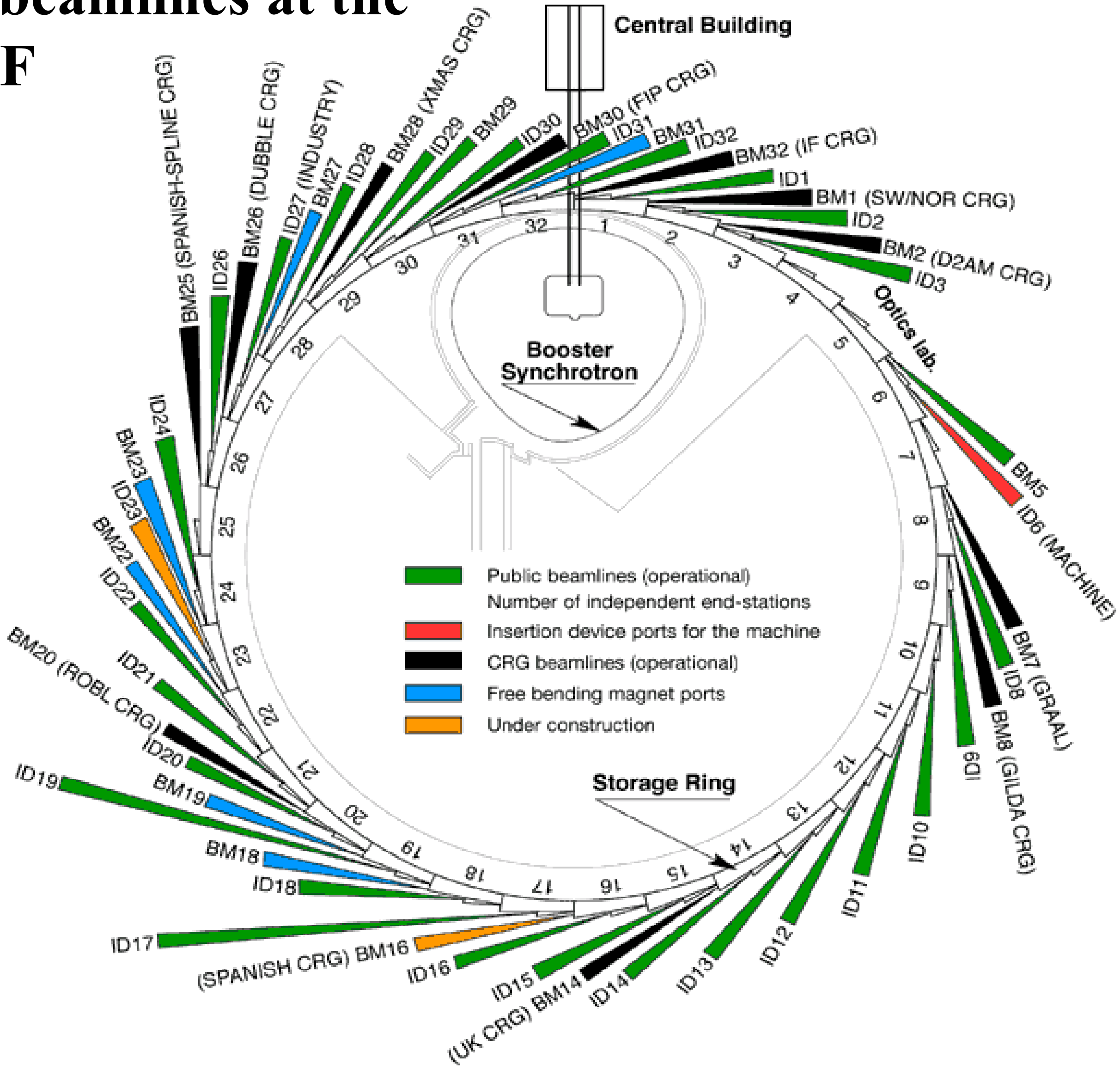
E. J. Samuelsen *et al. Synthetic Metals* 123 (2000) 165 (”Skin formation on POT”)

D. W. Breiby *et al. Synthetic Metals* 139 (2003) 361 (”Edge drying and skin formation on POT”)

J. M. Salamanca *et al. Langmuir* 17 (2001) 3202 (”Drying of latex emulsions”)

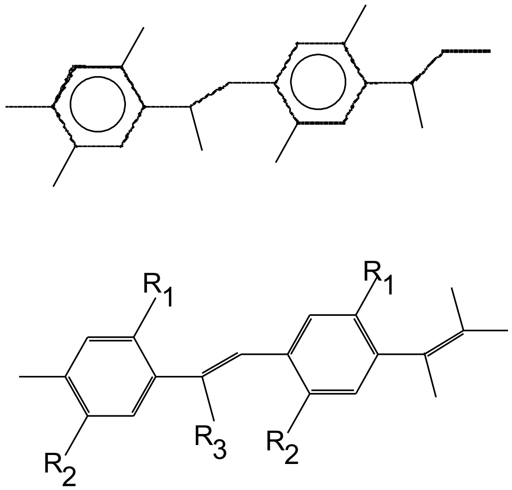
L’ESRF vu de l’ouest

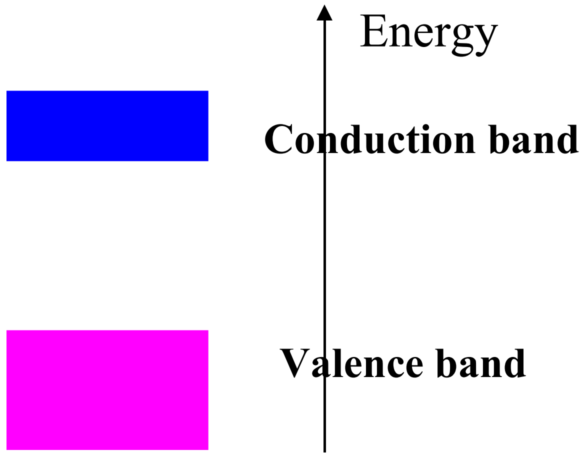
The beamlines at the ESRF



Examples

Poly-phenylene-vinylenes PPVs





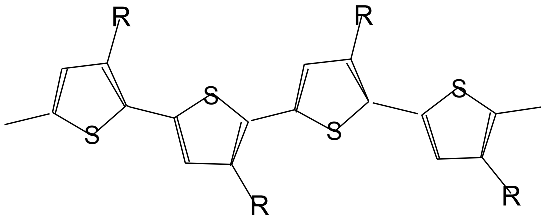
Energy

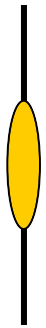
Conduction band

Valence band

The double bonds contain an extra (localized) electron. This electron becomes itinerant in the excited state (lower figure).

Poly-alkyl-thiopenes





(Sulpher-containing heterocycle; *R* = hexyl; octyl etc.)