Structure and magnetic alignment of self-assembled rod-coil molecular aggregates

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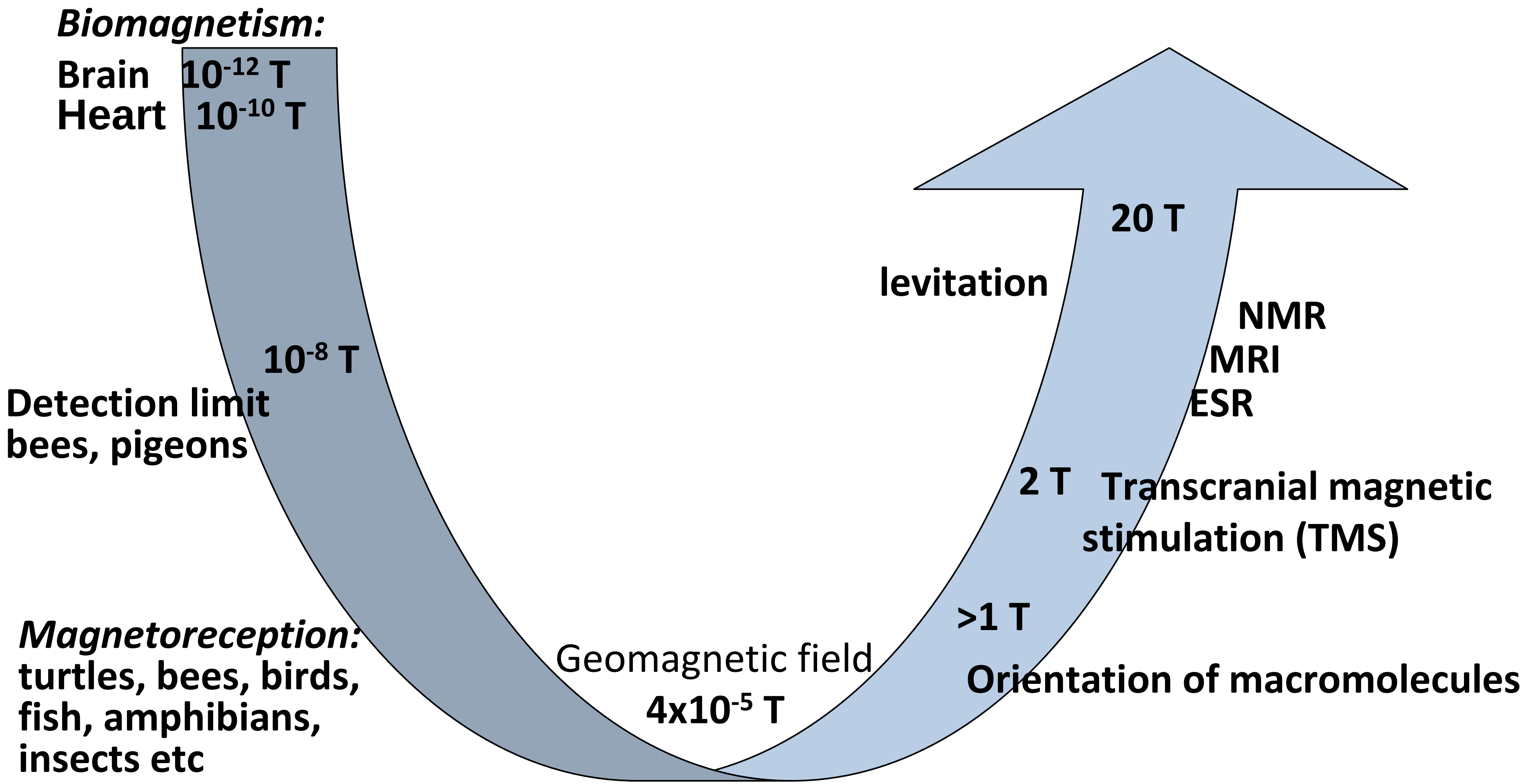
SYNEMAG - Grenoble October 17-19, 2012

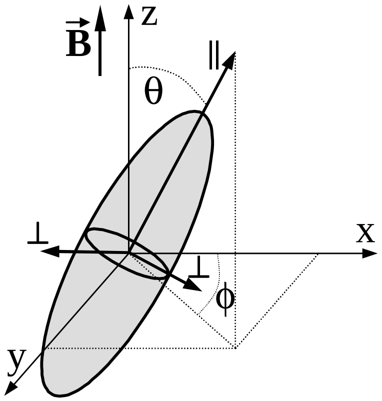
or

Soft matter manipulation via magnetic field



Magnetic Orientation

Anisotropic diamagnetic molecules in B:



$$\mathbf{m} = \frac{\chi V}{\mu_0} \cdot \mathbf{B}$$

$$\chi = \begin{pmatrix} \chi_{\perp} & \mathbf{0} & 0 \\ 0 & \chi_{\perp} & 0 \\ 0 & \mathbf{0} & \chi_{\parallel} \end{pmatrix}$$

$$\begin{cases} m_{\perp} = \dfrac{\chi_{\perp} V \cdot B}{\mu_0} & \Rightarrow \quad E = -\dfrac{\chi_{\perp} V}{2\mu_0} B^2 \\ m_{\parallel} = \dfrac{\chi_{\parallel} V \cdot B}{\mu_0} & \Rightarrow \quad E = -\dfrac{\chi_{\parallel} V}{2\mu_0} B^2 \end{cases}$$

$$\Delta E_{an} = -\frac{\left(\chi_{\parallel} - \chi_{\perp}\right) V}{2\mu_0} B^2 = -\frac{\Delta \chi V}{2\mu_0} B^2$$

The Physics of Liquid Crystals, P.G. de Gennes

Magnetic Field induced alignment

Requirement: $$\frac{\Delta\chi}{2\mu_0}B^2 \geq k_B T$$

Textbook example: Benzene molecule

$\Delta\chi$ = -750 x 10^{-12} m^3/mol

ΔE_{an} = 10^{-5} $k_B T$ (20 T, 300 K)

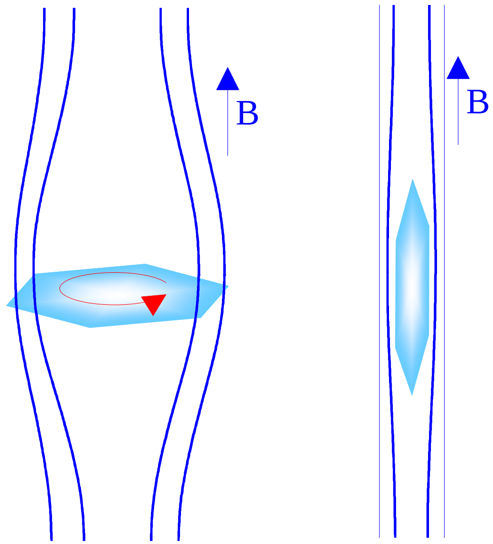
⇓

Too small for single molecule alignment

⇓

Liquid crystals, macromolecules, polymers, molecular aggregates

($N|\Delta\chi|H^2 > k_B T$)



G. Maret and K. Dransfeld (1985)

Orientation of Non-Magnetic Materials in a Magnetic Field

- **Most molecules have a diamagnetic anisotropy, $\Delta\chi$**
- **For non-interacting molecules:**

$$|\Delta\chi|H^2 << k_B T$$

Orienting energy << thermal energy
Weak orientation

has uses in the study of solutions:

- flexibility of polymers
- onset of cooperativity (liquid crystals)
- solution properties (ionic solutions)

- **When N molecules behave in unison their $\Delta\chi$s can addition giving a combined anisotropy:**

$$N|\Delta\chi|H^2 > k_B T$$

Orienting energy > thermal energy
High orientation

M > 10^{10} Daltons (H=10 T)

Can dramatically transform:

- information
- properties

High orientation requires cooperativity: large, ordered assemblies such as crystals, liquid crystals and semi-rigid polymers

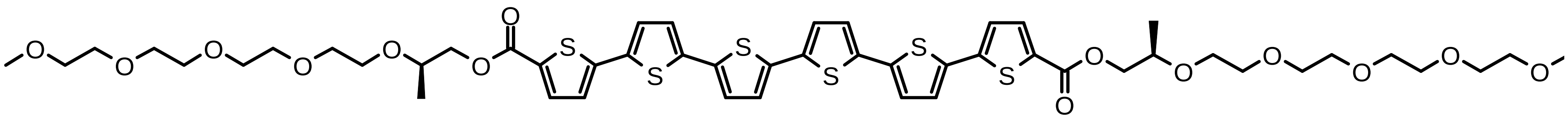
Several materials can be aligned

Liquid crystals	de Gennes, The physics of liquid crystals
Polymers	Kimura, Polymer Journal (‘03) , …
LC Polymers	Anwer, Polymer (‘91, ‘93), Benicewicz, Macromol. (‘98), Boamfa, PRL (‘03), …
Phospholipids	Tenforde, J. Th. Bio. (’88), Ozeki, J. Phys. Chem. (’00), …
Nucleic acids	Maret, Phys. Rev. Lett. (’75), …
Bacteriophages	Torbet, J. Mol. Biol. (’79); Banner, Nature (’81), …
Fibrin	Torbet, Nature (’81); …
Collagen	Torbet, Biochem. J. (’84); Tranquillo, J. Cell Sci. (’93), …
Tubulin	Bras, Biophys. J. (’98); …
Carbon nanotubes	Smith, APL (’00), Hone, APL (’00), Choi, JAP (’03), Garmestani, Adv. Mat. (‘03)
Protein Crystals	Wakayama, J. Cryst. Growth (‘01), …
Dye aggregates	Shklyarevskiy, J. Chem. Phys. (‘02), …

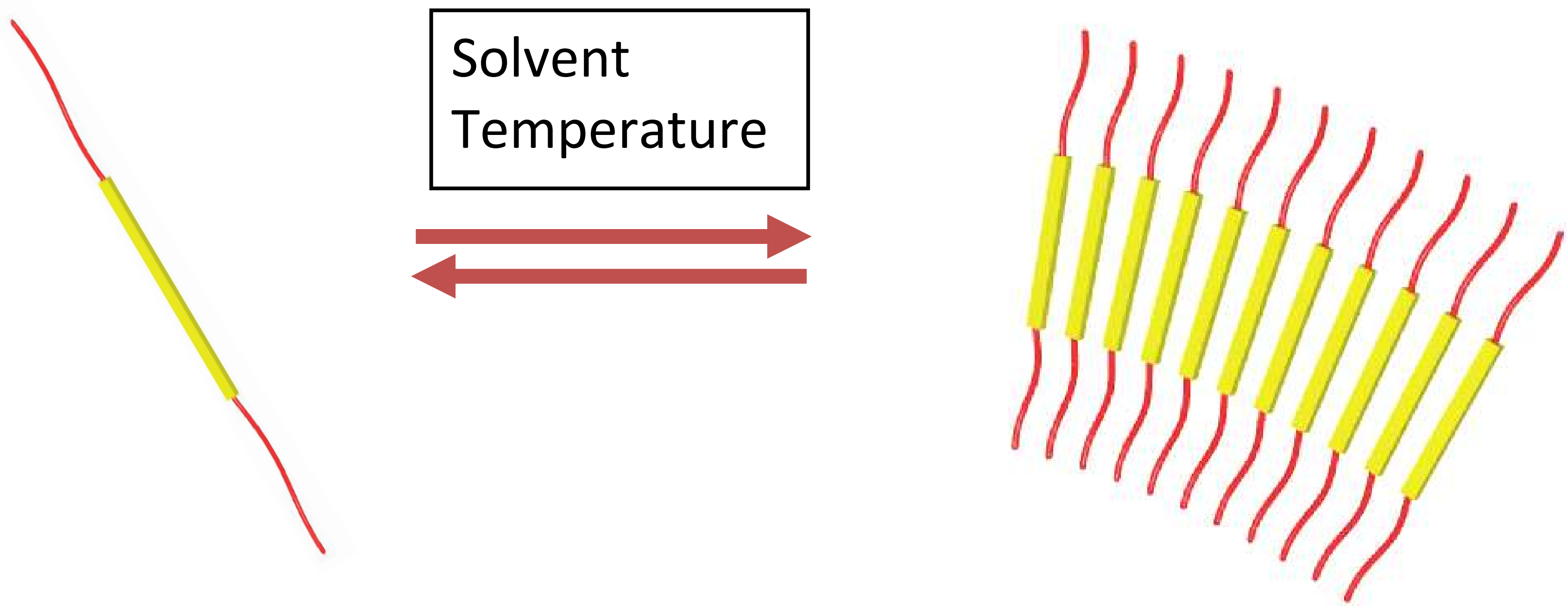
Review: G. Maret and K. Dransfeld (1985)

Sexithiophene (6T) aggregates

Self-Assembly of thiophenes



Coil – Rod – Coil molecule



Chemical Structure → **Supramolecular Organization** → **Macroscopic function:**
-energy transfer
-electron transfer

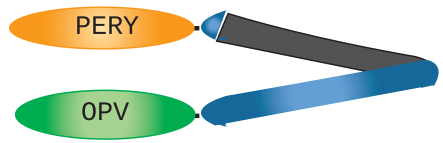
Cooling Rate (Thiophenes)

Purity

Shape

External Force (B-field)

Position (Foldamers)

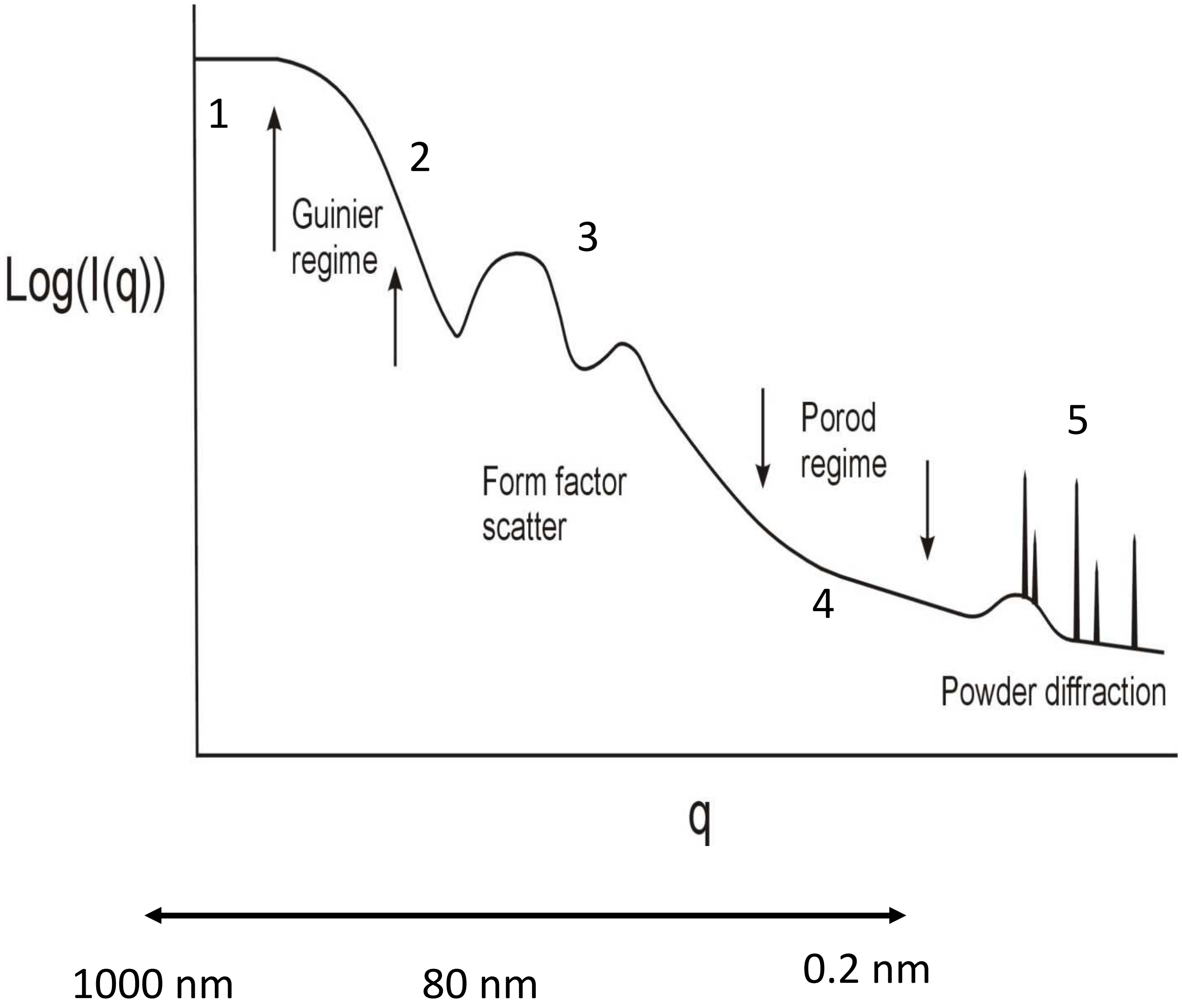


Length (Chainstopper)

Controlling Chemical Self-Assembly

Prof. Bert Meier Group – TU/e

SAXS/WAXS



1 limit q → 0
molecular weights

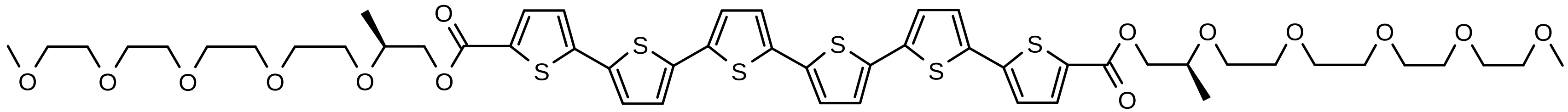
2 Guinier range
particle size

3 particle shape
large scale structures

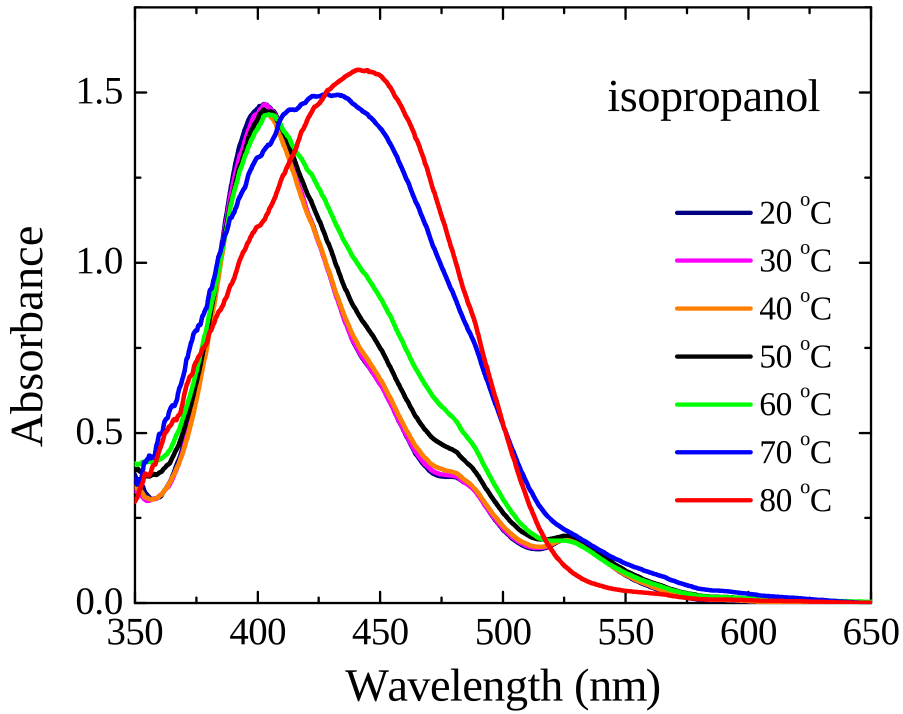
4 Porod range
particle surface

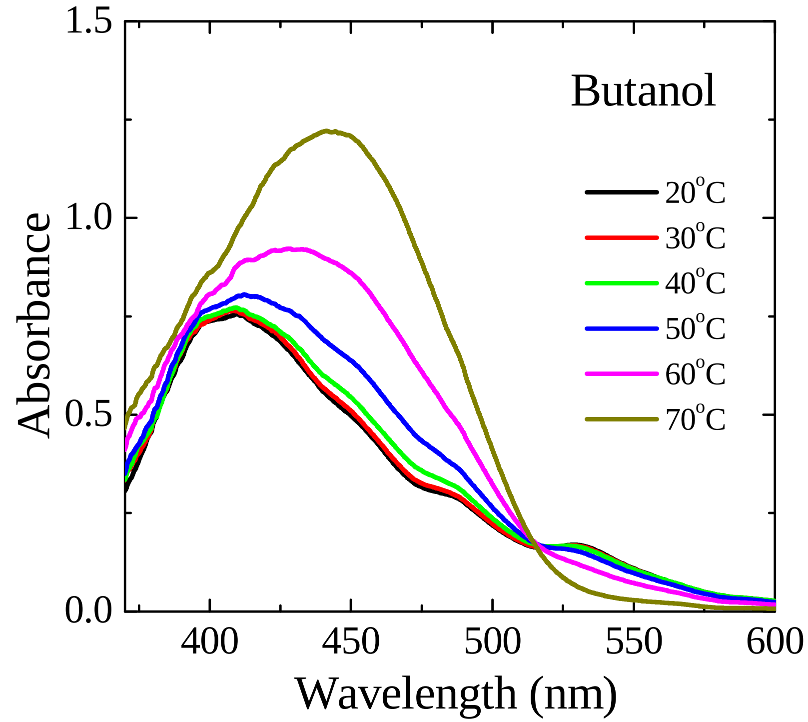
5 Intermolecular/atomic
ordering

Sexithiophene (6T) aggregates



6T

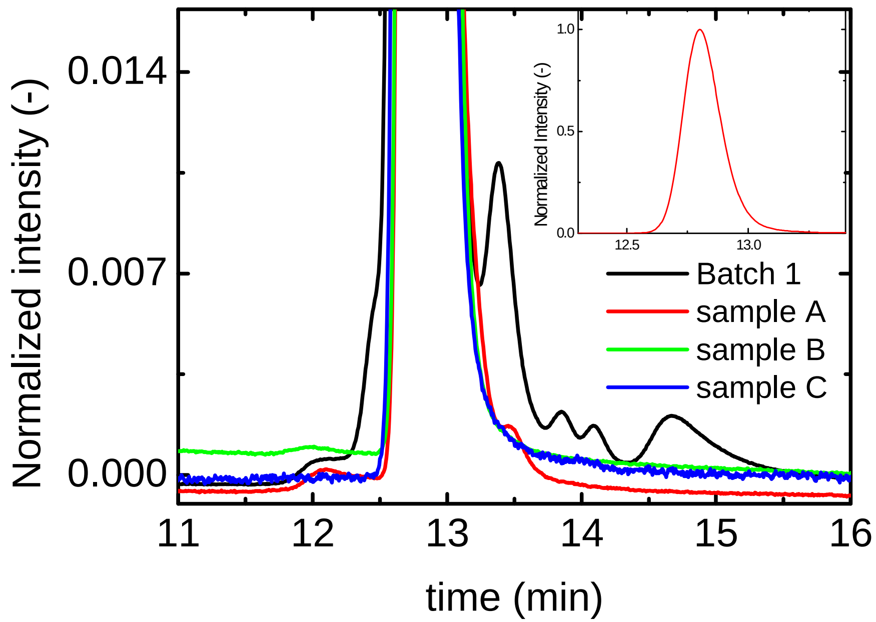


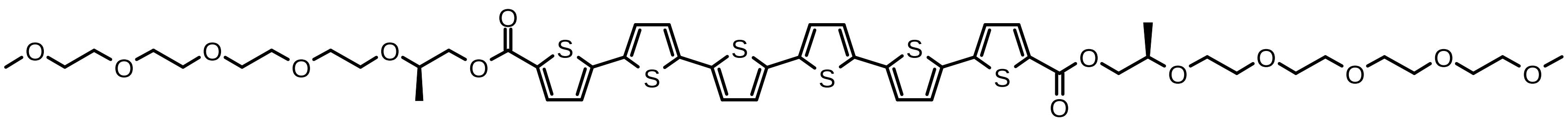


Schenning et al., J. Am. Chem. Soc. 124, 1269 (2002)

Purity of T6-βR

GPC



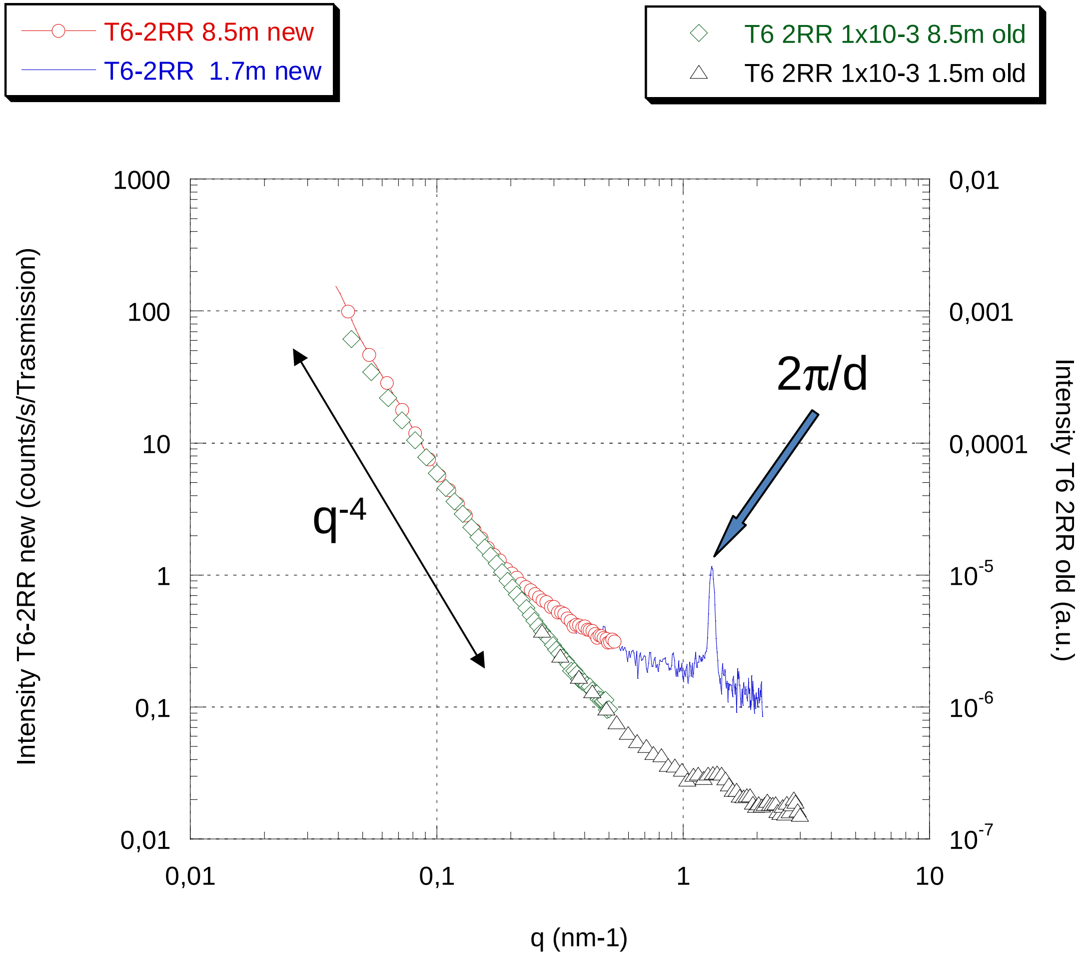


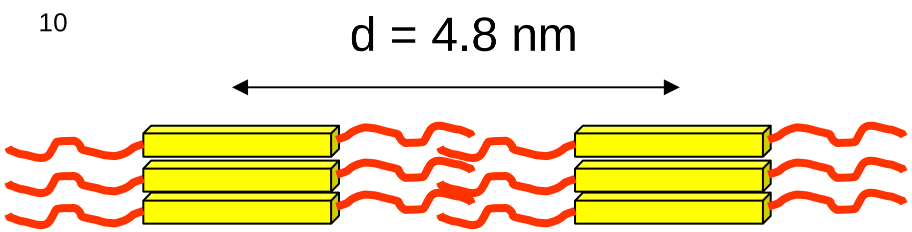
T6-βR

Sample A: 99.6 %
Sample B: 99.9 %
Sample C: 99.9+ %

Janus Leenders

X-ray Scattering on isotropic samples

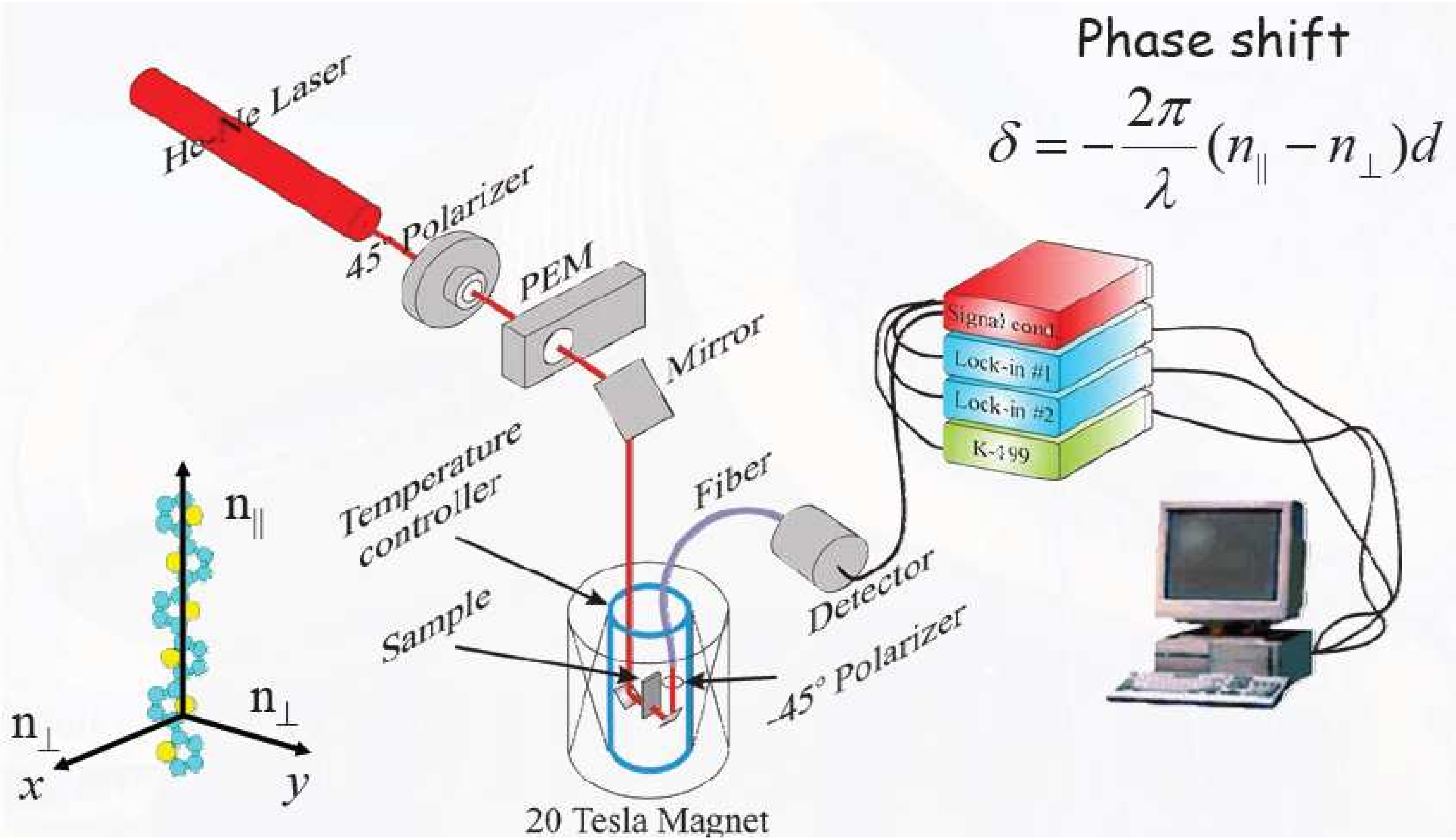




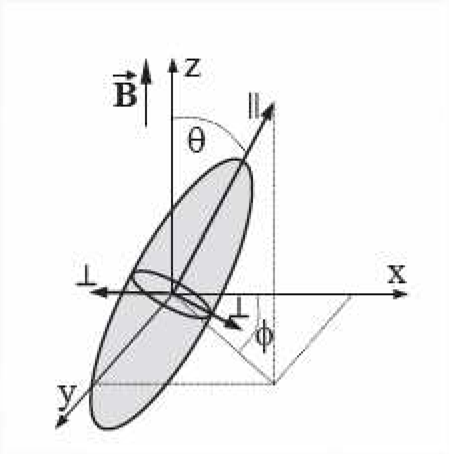
Sharp peak at 4.8 nm related to internal structure

In-situ birefringence setup

HFML
Science in High Magnetic Fields



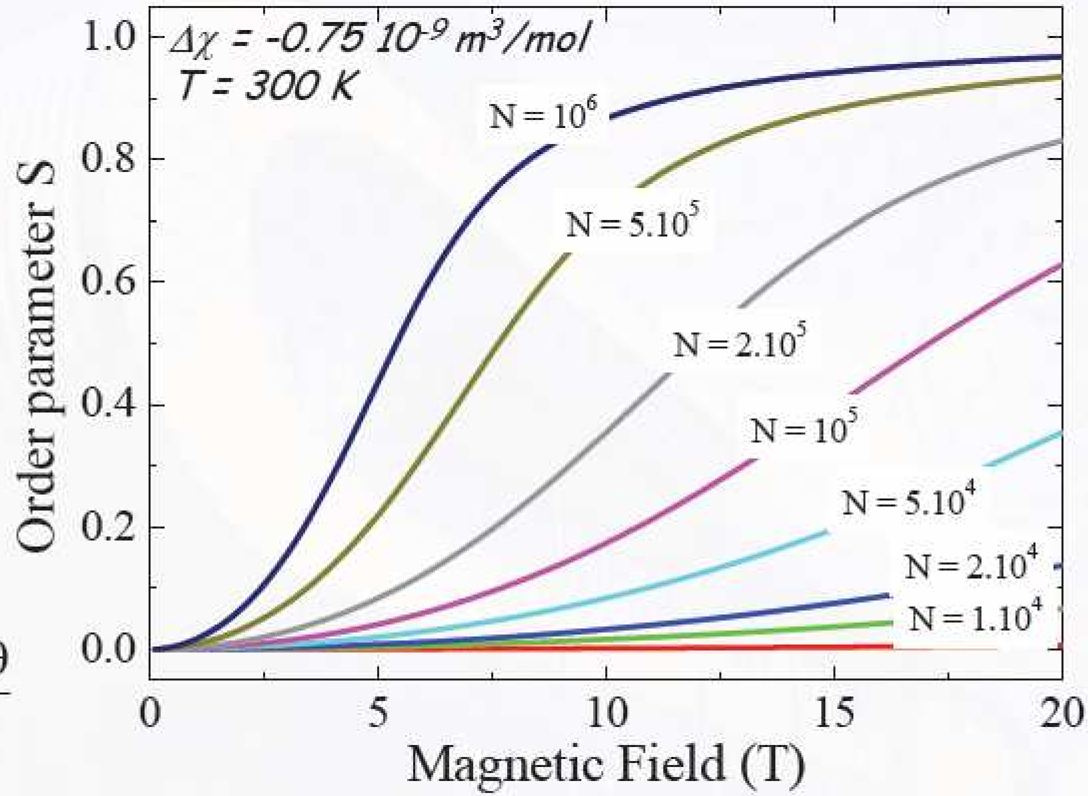
Birefringence – degree of alignment and size dependence



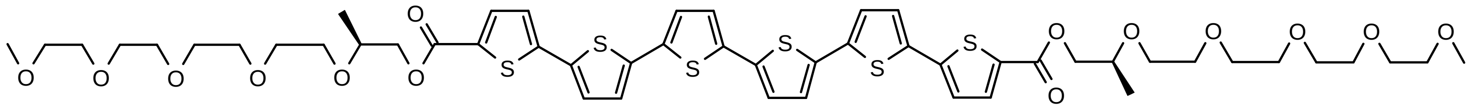
$$S = \frac{3 \cdot \langle \cos^2\theta \rangle - 1}{2}$$

$$\langle \cos^2\theta \rangle = \frac{\int \cos^2\theta \cdot f(\theta) \cdot \sin\theta \cdot d\theta}{\int f(\theta) \cdot \sin\theta \cdot d\theta}$$

$$f(\theta) \sim \exp\left[\frac{N \cdot \Delta\chi \cdot B^2 \cdot \cos^2\theta}{2\mu_0 \, k_B \cdot T} \right]$$

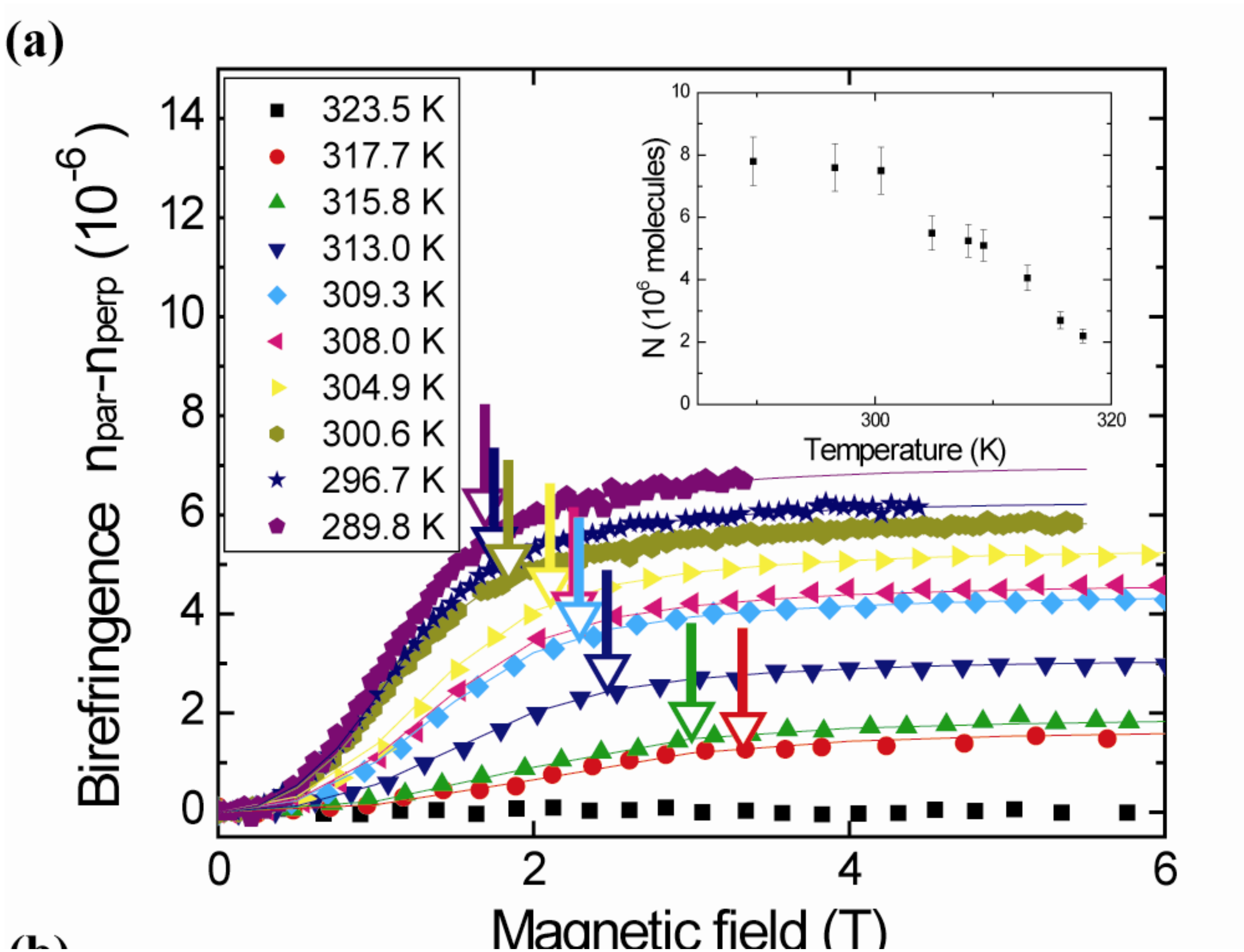


T6/Butanol

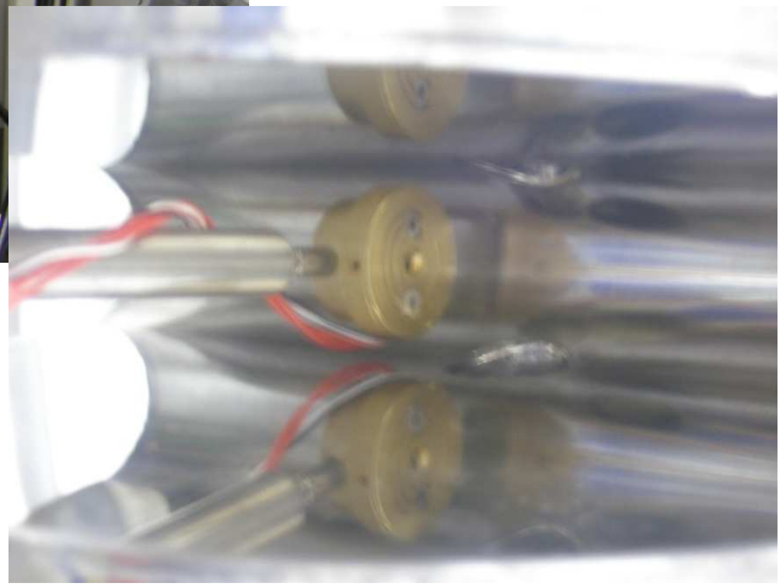


6T

$\Delta\chi$ = -300 10^{-6} m^3/mol

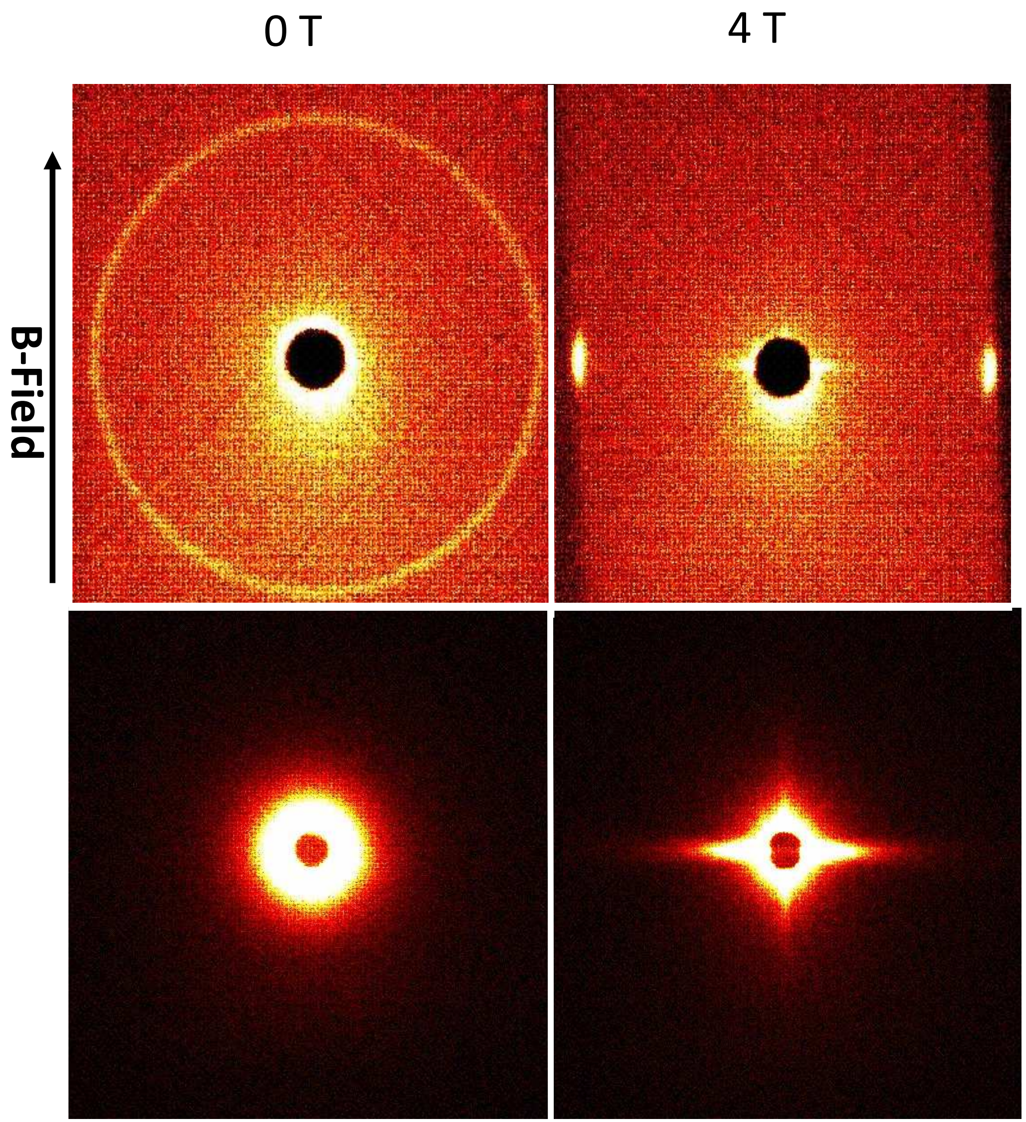


4 Tesla Helmholtz coils on Xmas beam line



BM28@ESRF

T6/butanol aggregates in magnetic field (B ⊥ X-rays)



S-to-D ~ 1.5m

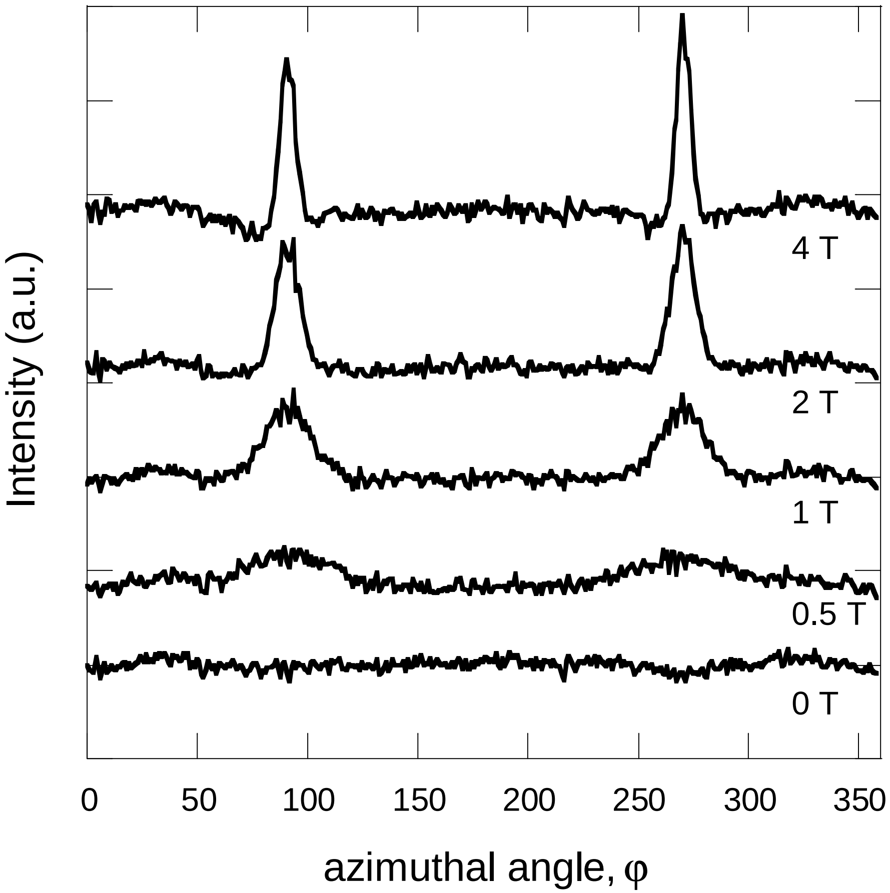
- diffraction ring transforms into diffracted “spots” (arks)
- molecules “highly” oriented perpendicular to the field

S-to-D ~ 8m

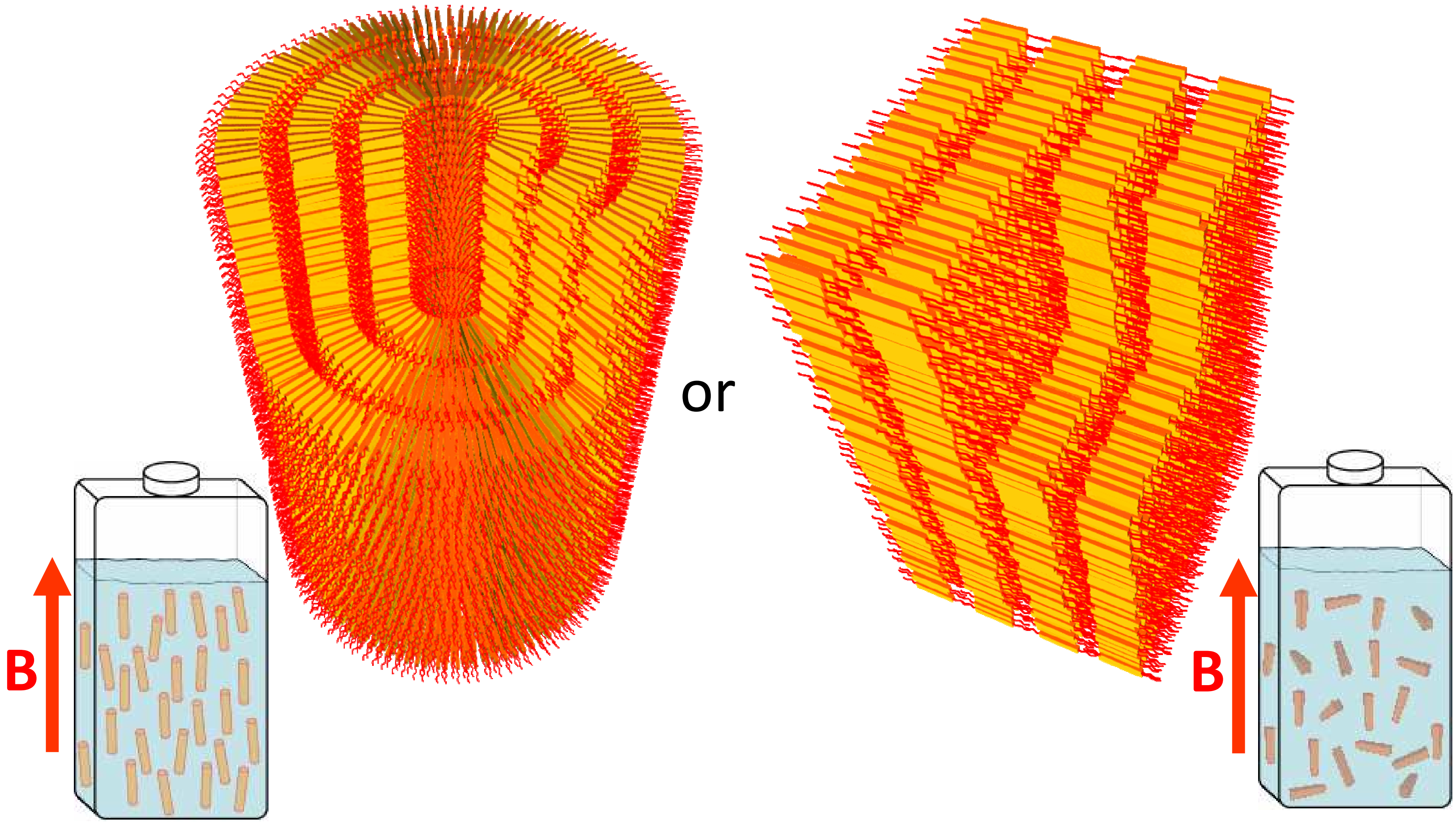
- strong anisotropy mainly in the horizontal scattering direction (perpendicular to the field)
- Aspect ratio from Porod ~ 7

J. Gielen, M. Wolffs, G. Portale, O. Henze, W. J. Feast, W. Bras, P. C. M. Christianen, A. P. H. J. Schenning, E. W. Meijer and J. C. Maan – Langmuir (2010)

T6/butanol aggregates in magnetic field (B ⊥ X-rays)



T6/Butanol

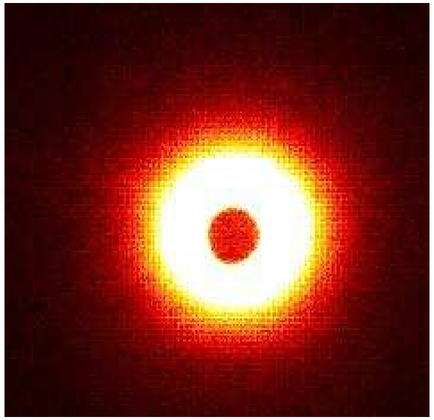


Langmuir 25, 1272 (2009)

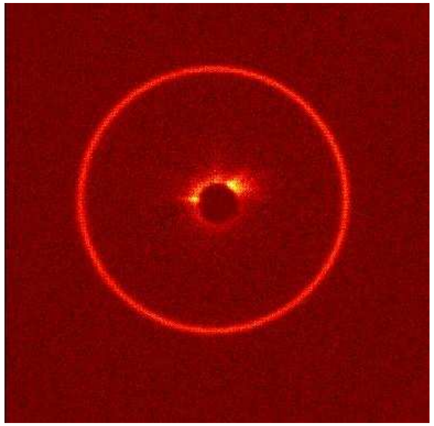
T6 aggregates in magnetic field (B ‖ X-rays)

2T

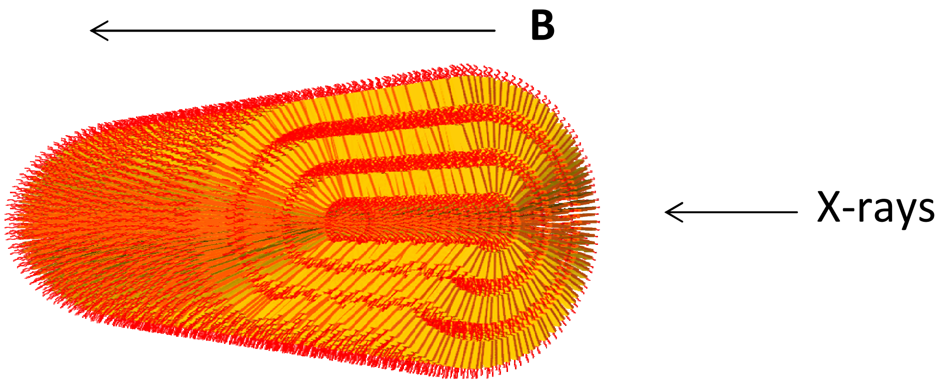
B ‖ X-rays



8 m

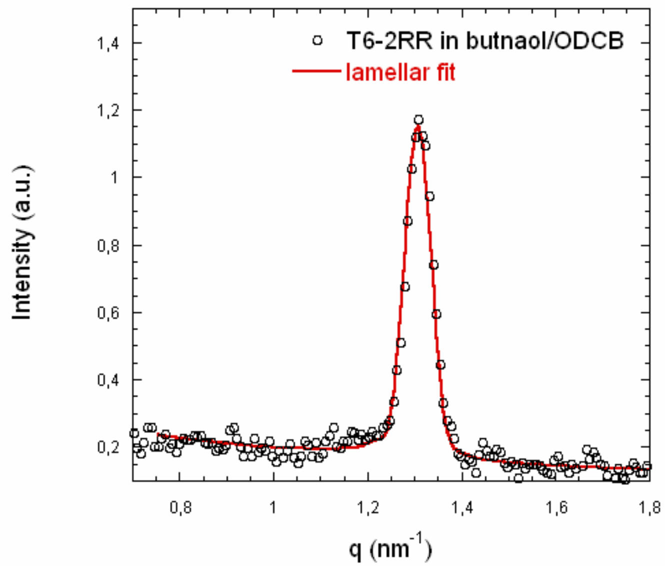


1.5 m



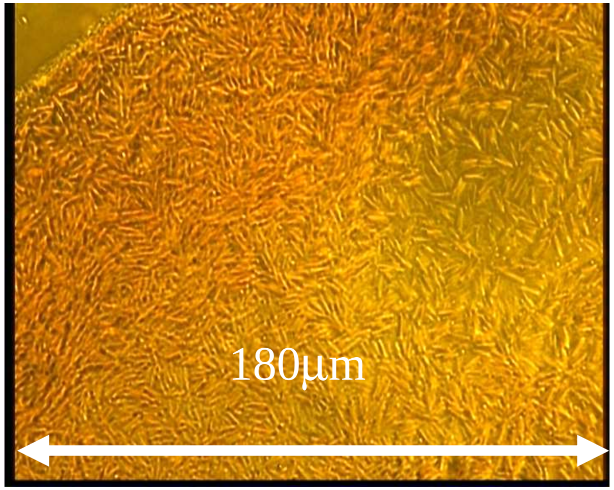
Debye-Scherrer:

Λ = 72.4 nm → 15 T6 layers

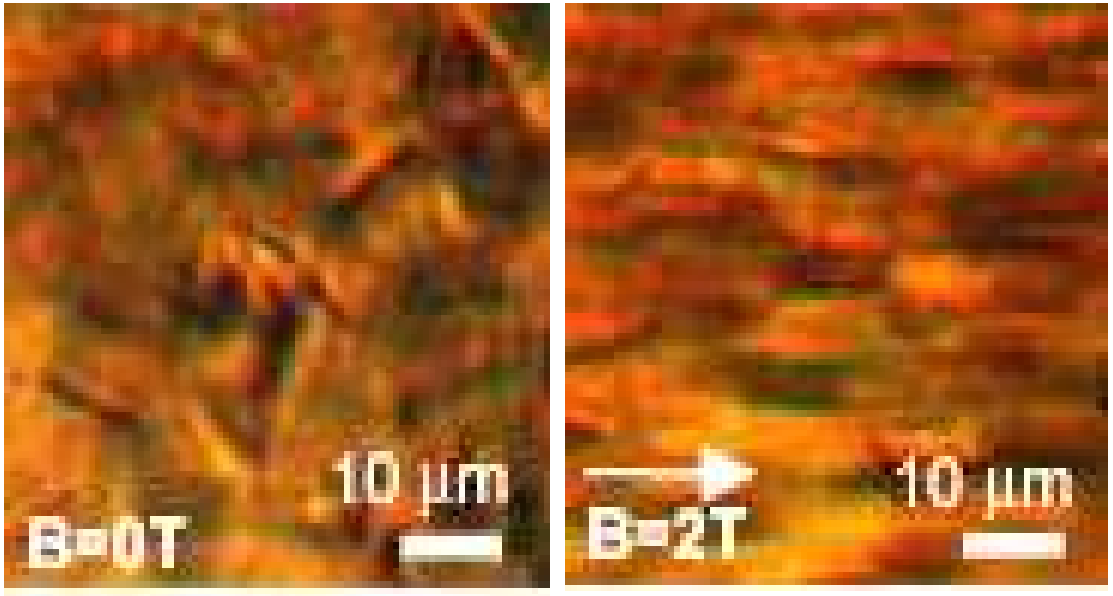


15.3 lamellar layers
(l_1 = 3.2nm, l_2 = 1.6nm)

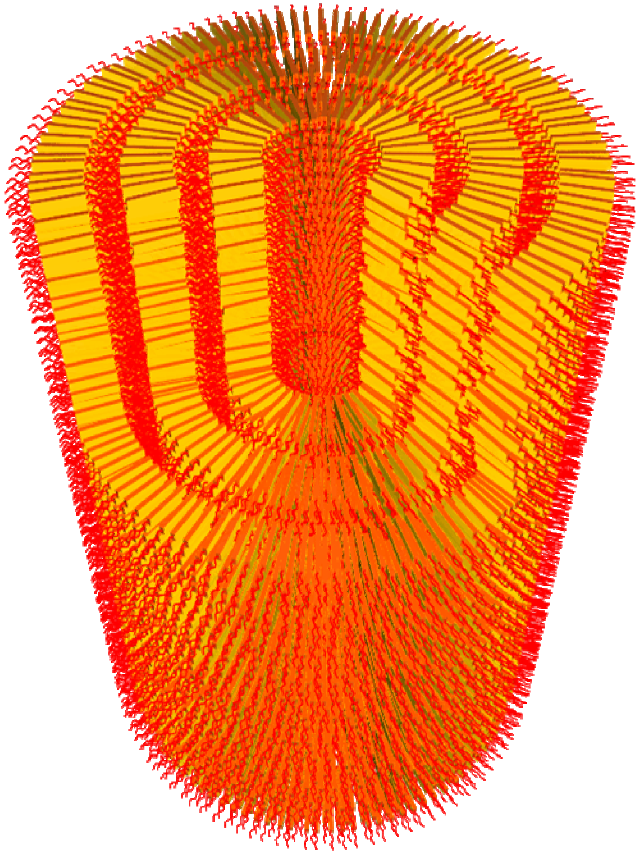
Optical confirmation (sample aged for 3 months)

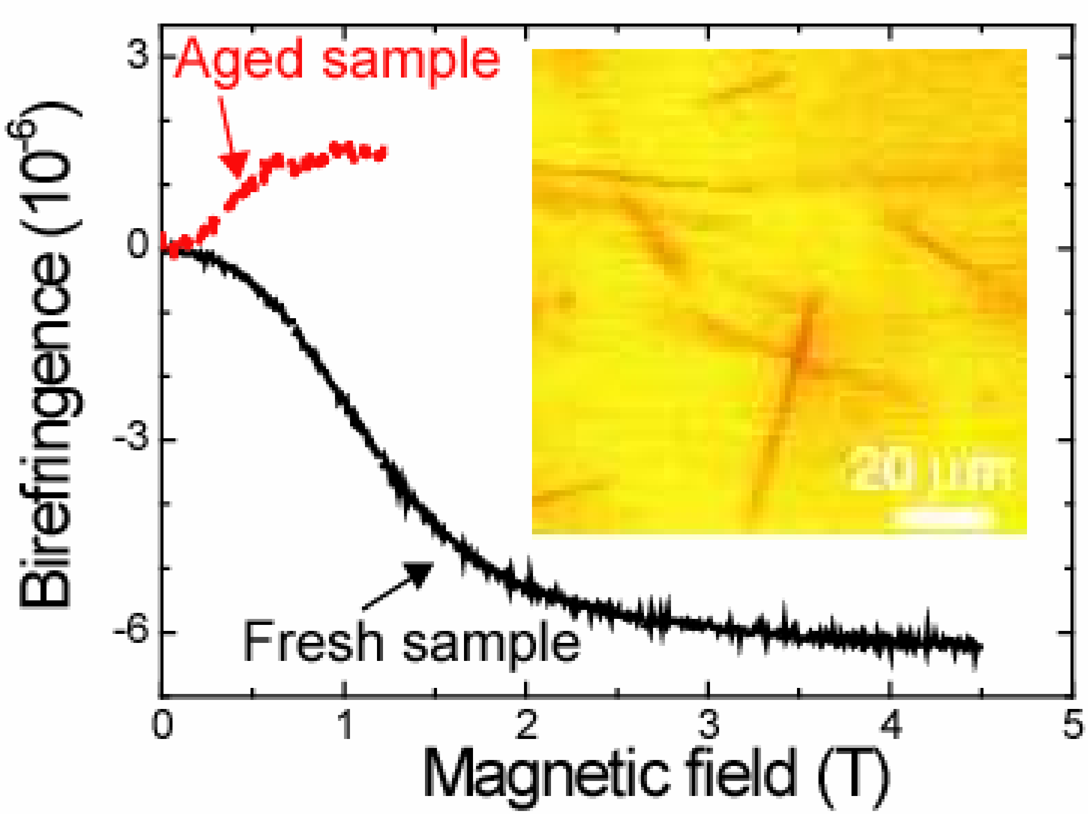


In-situ confocal microscopy



Cylindrical aggregates

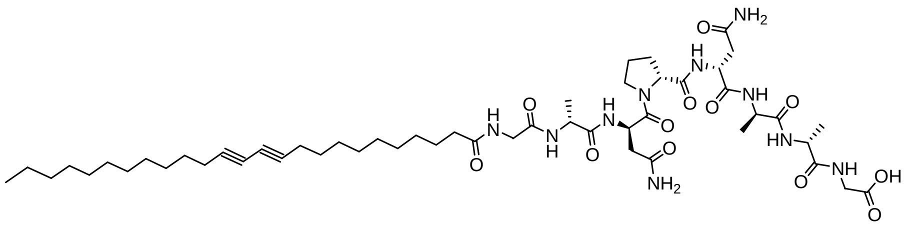




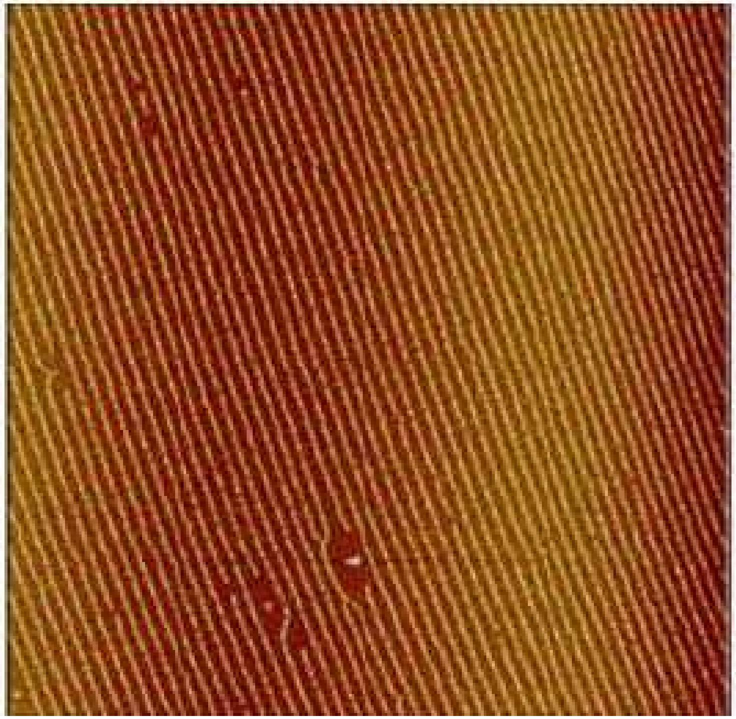
Langmuir 25, 1272 (2009)

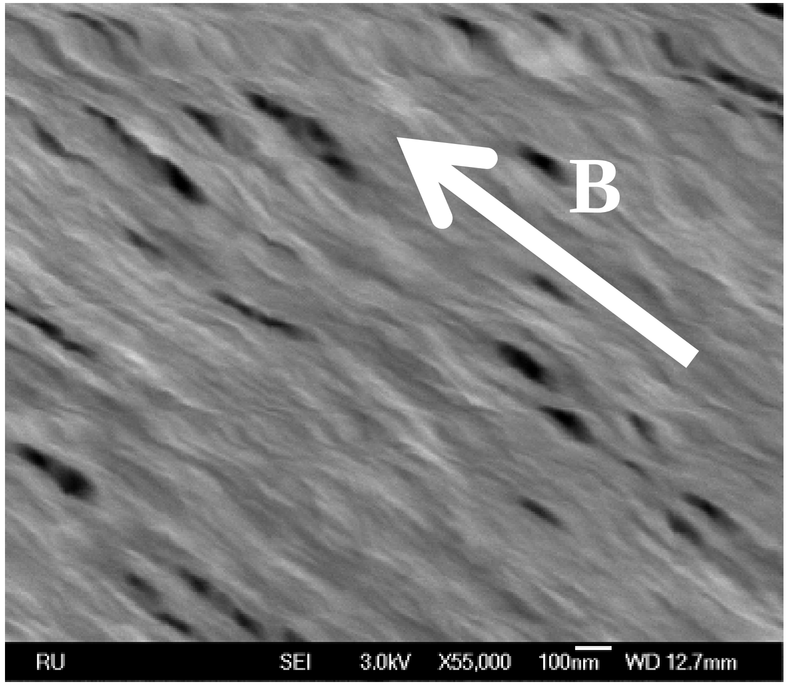
DUBBLE

Peptide nanofibers



Porphyrin nanofibers





HFML
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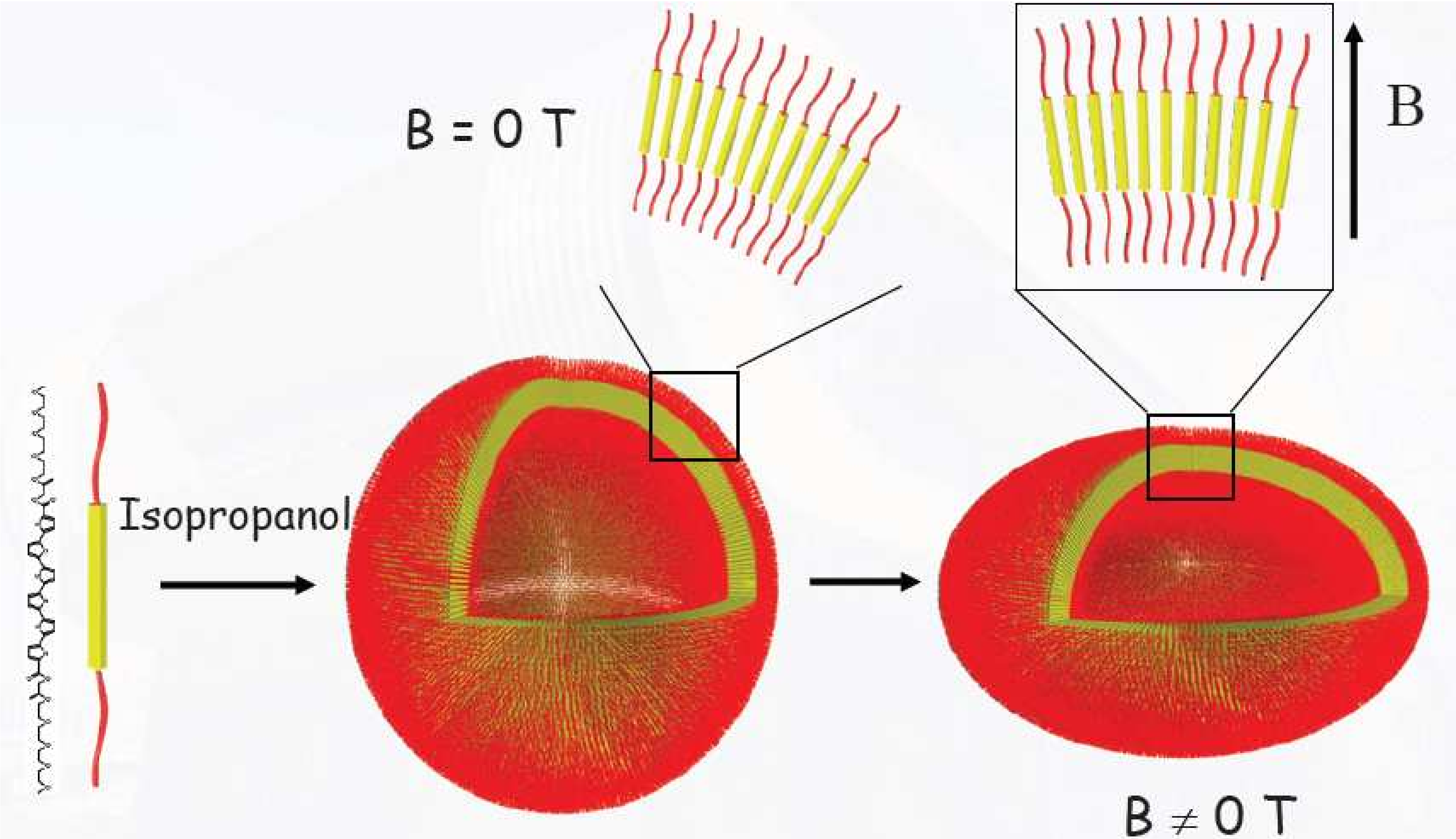
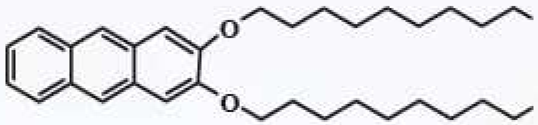
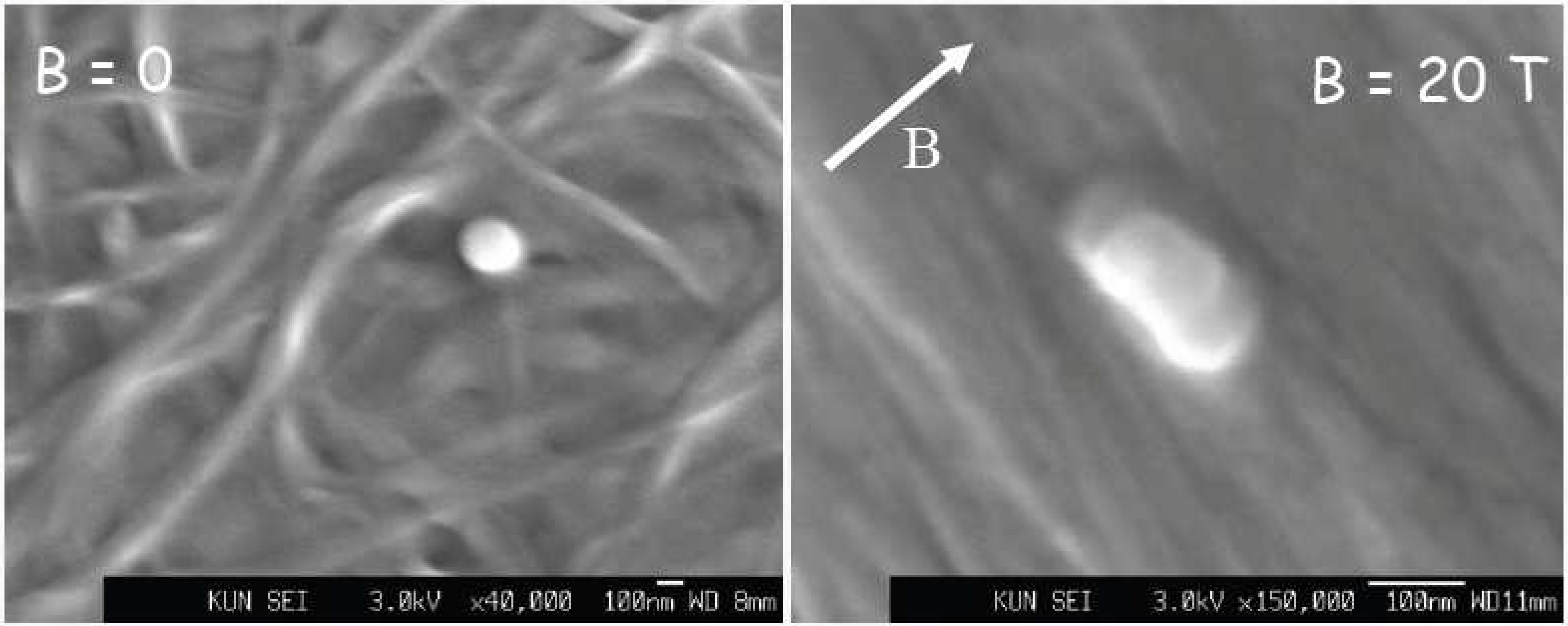
Magnetic deformation of T6 nanocapsules

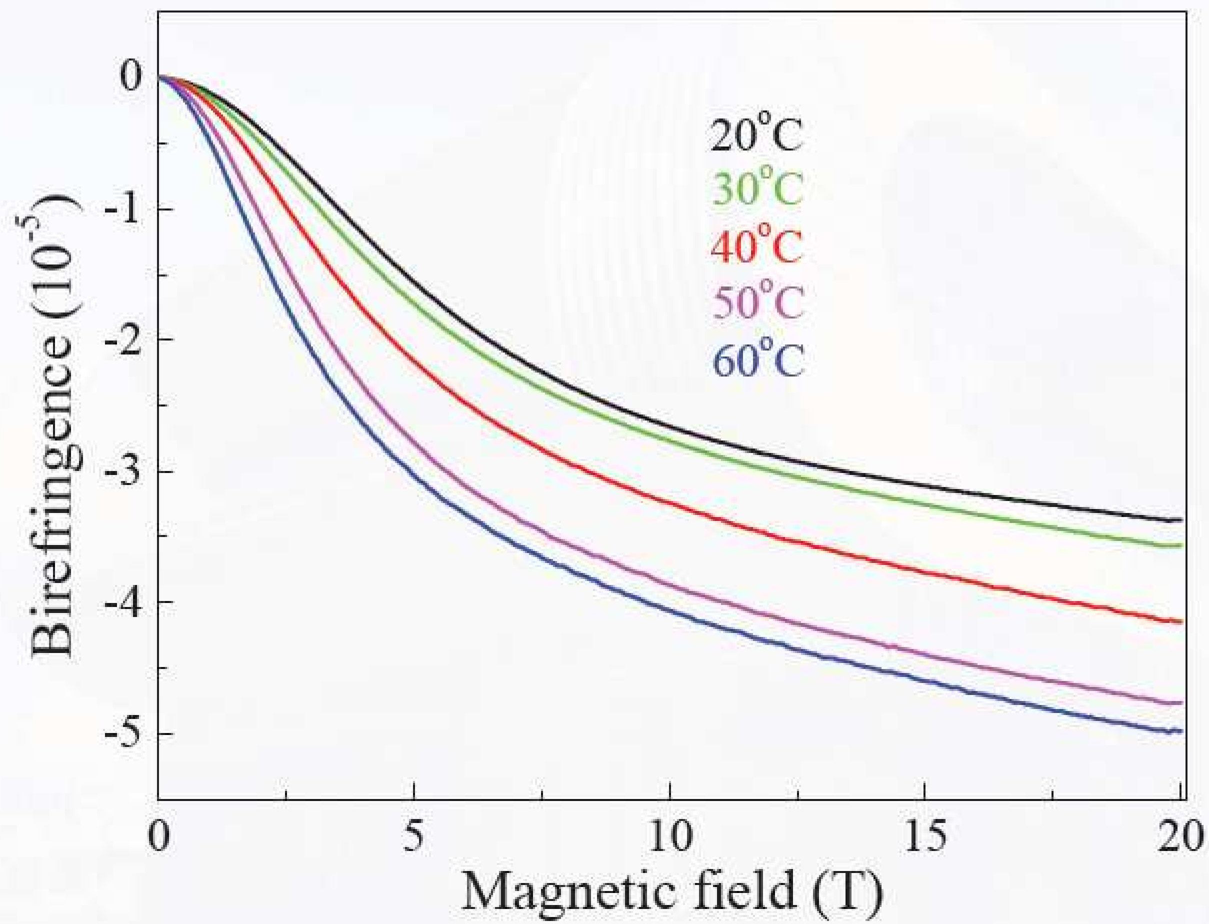




Gelators
- of alcohols
- forming fiber network

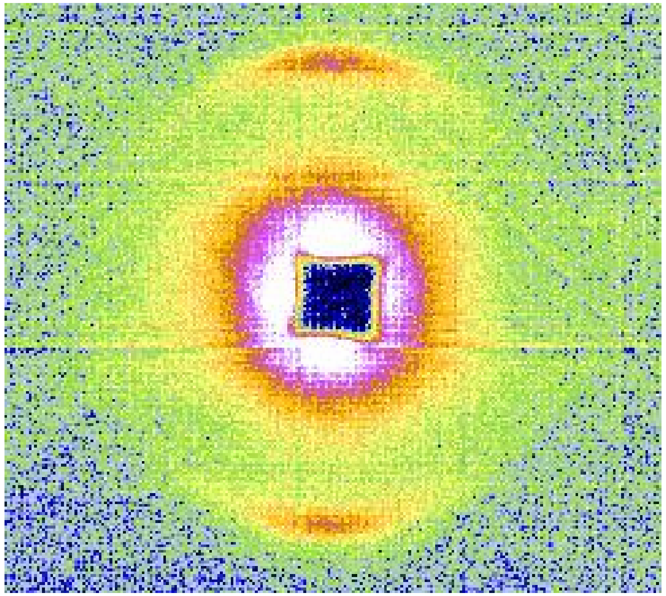
J-P. Desvergne et al., JACS 6, 416 (1991)



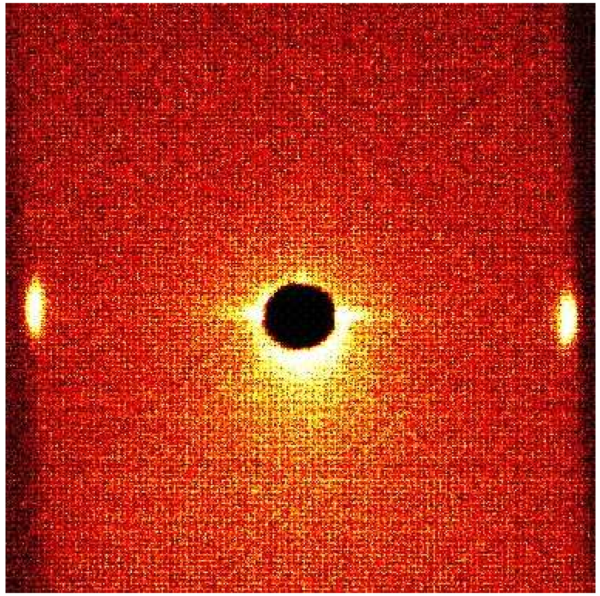


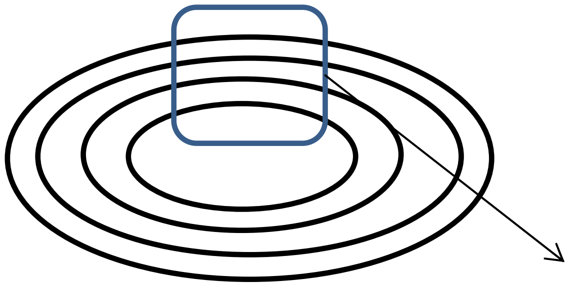
raw birefringence data Δn

Deformed T6/isopropanol vescicles



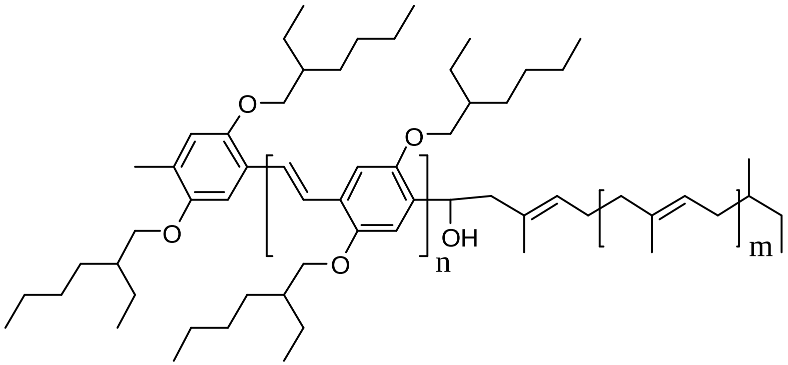
Aligned T6/Butanol cylinders





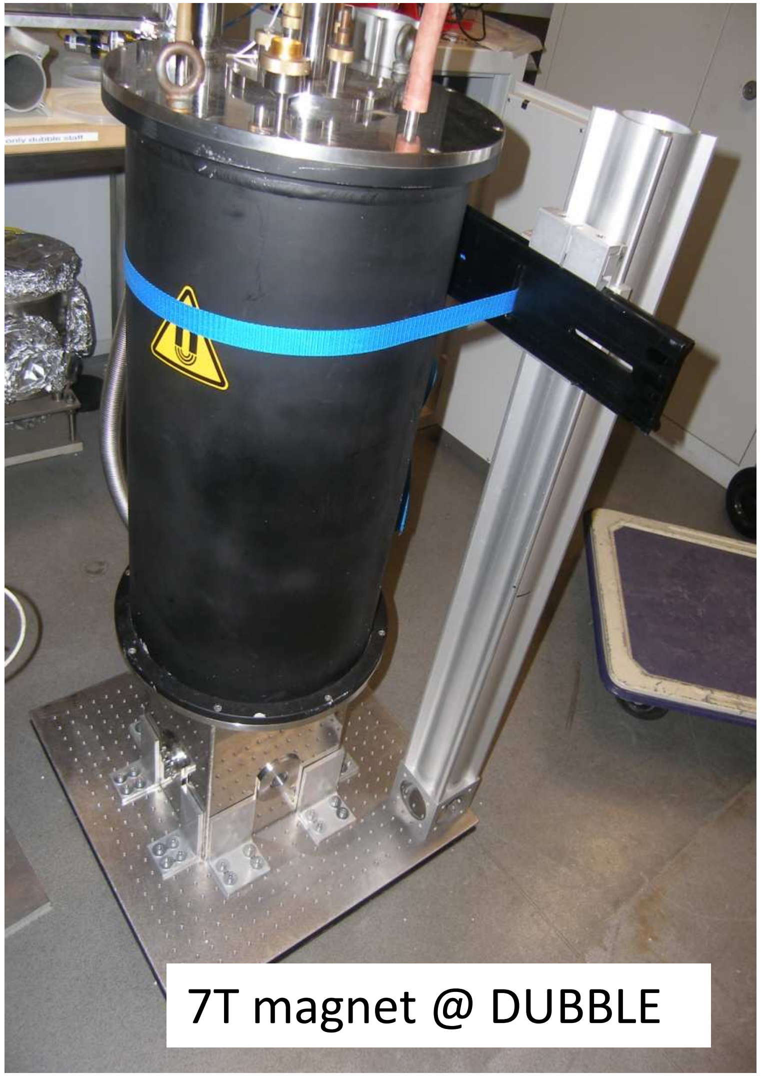
PPV-PI rod-coil block copolymer in 7T magnet

Poly(2,5-di(2'-ethylhexyloxy)-1,4-phenylene vinylene)-*b*-polyisoprene



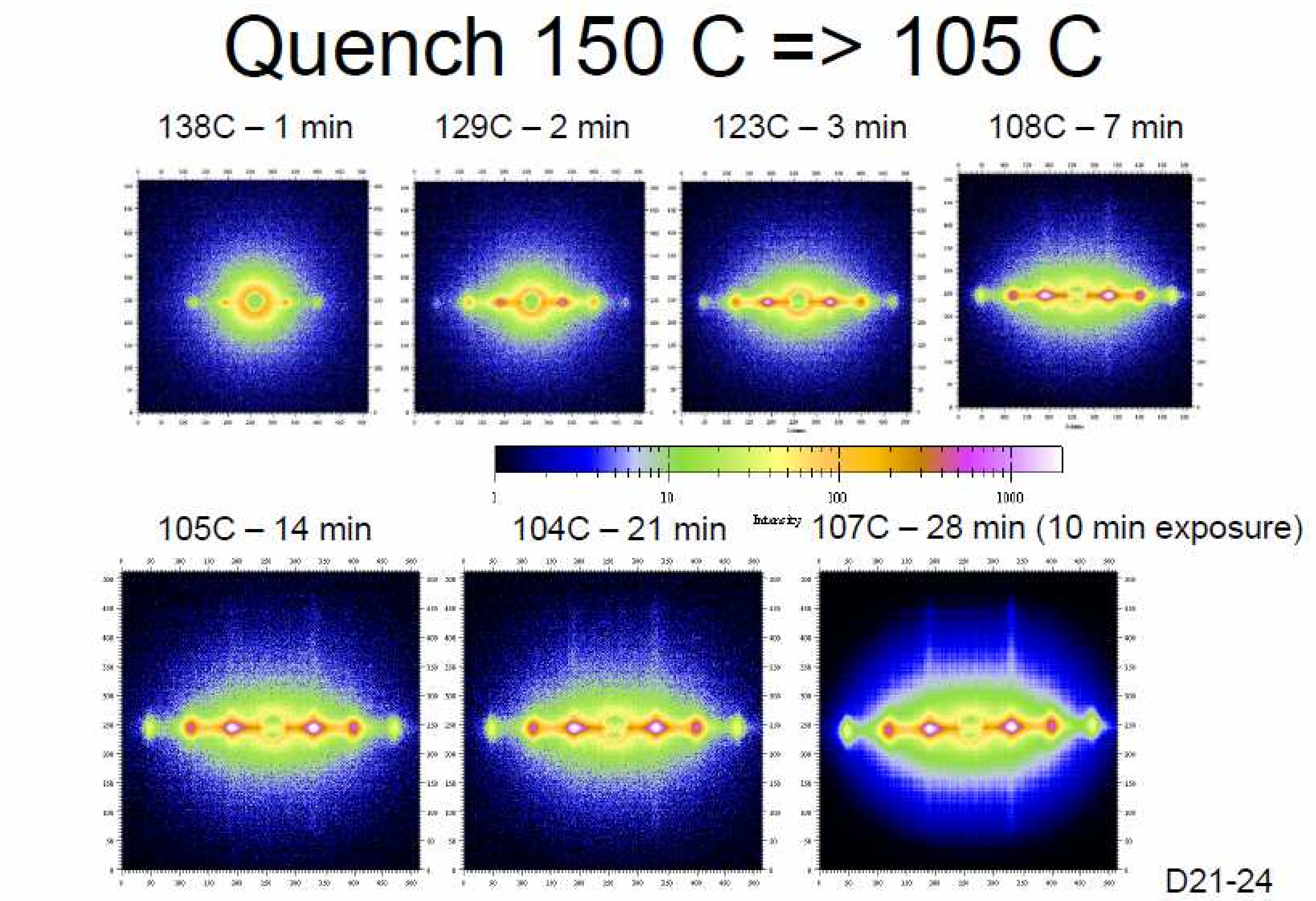
Rod - Coil

T_{ODS} = 115 °C
Smectic phase above 60 °C



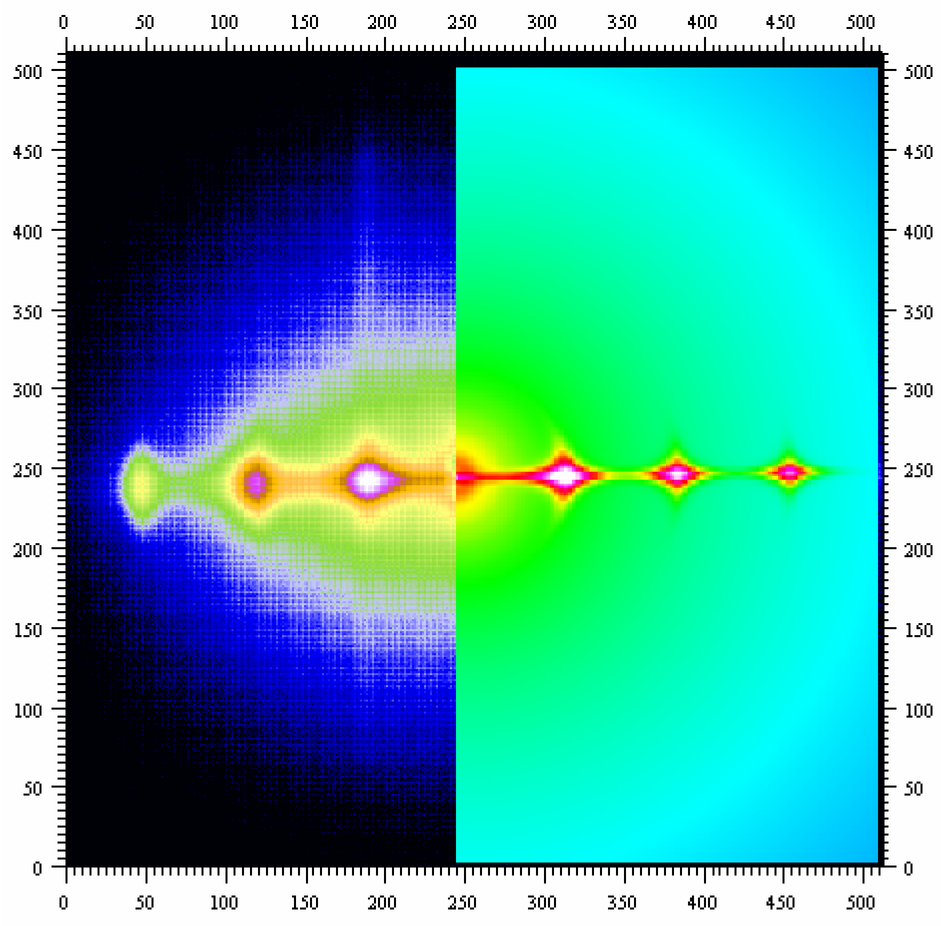
7T magnet @ DUBBLE

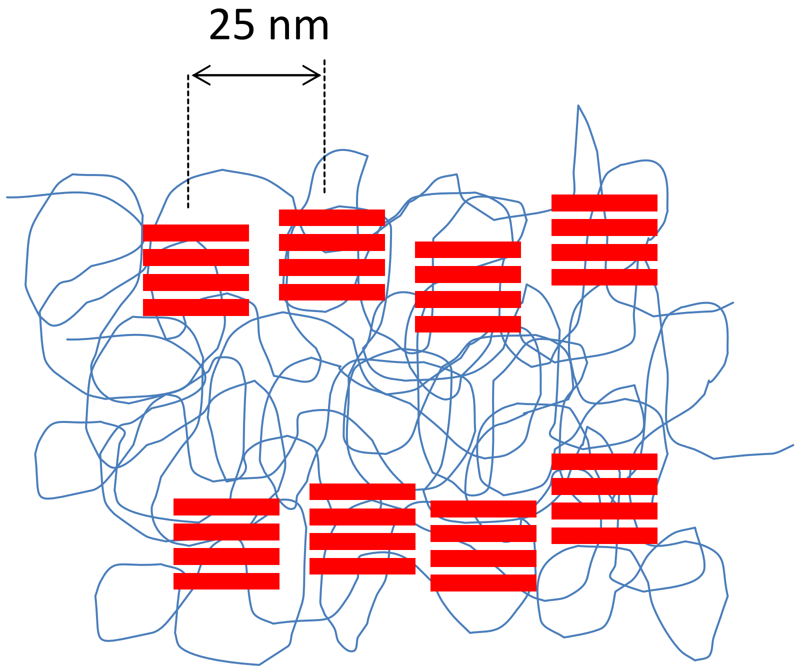
PPV-PI rod-coil block copolymer in 7T magnet



McCullock et al. Macromolecules (2011)

PPV-PI rod-coil block copolymer in 7T magnet

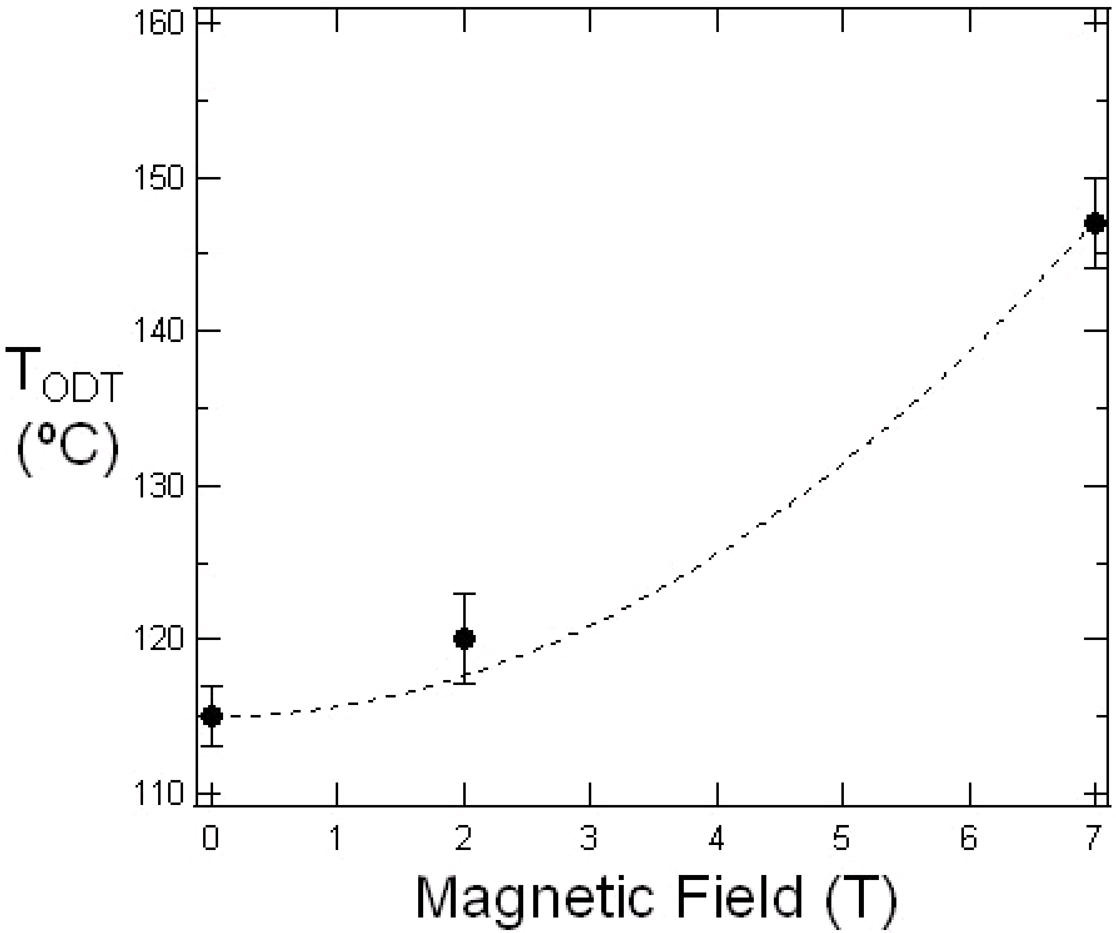




B = 7T

PPV-PI rod-coil block copolymer in 7T magnet

T_{ODT} influenced by magnetic field



Application of magnetic field stabilizes the smectic phase, extending its T-range of existence

Conclusions

• Manipulation of soft-matter coupled with SAXS/WAXS helps in understanding complex structures

• Could be used to control orientation in devices from advanced functional materials (π-cojugated structures)

• Pulsed (high) magnetic fields coupled with XFELs may help solving structure of single molecules (i.e. proteins, small aggregates etc.)

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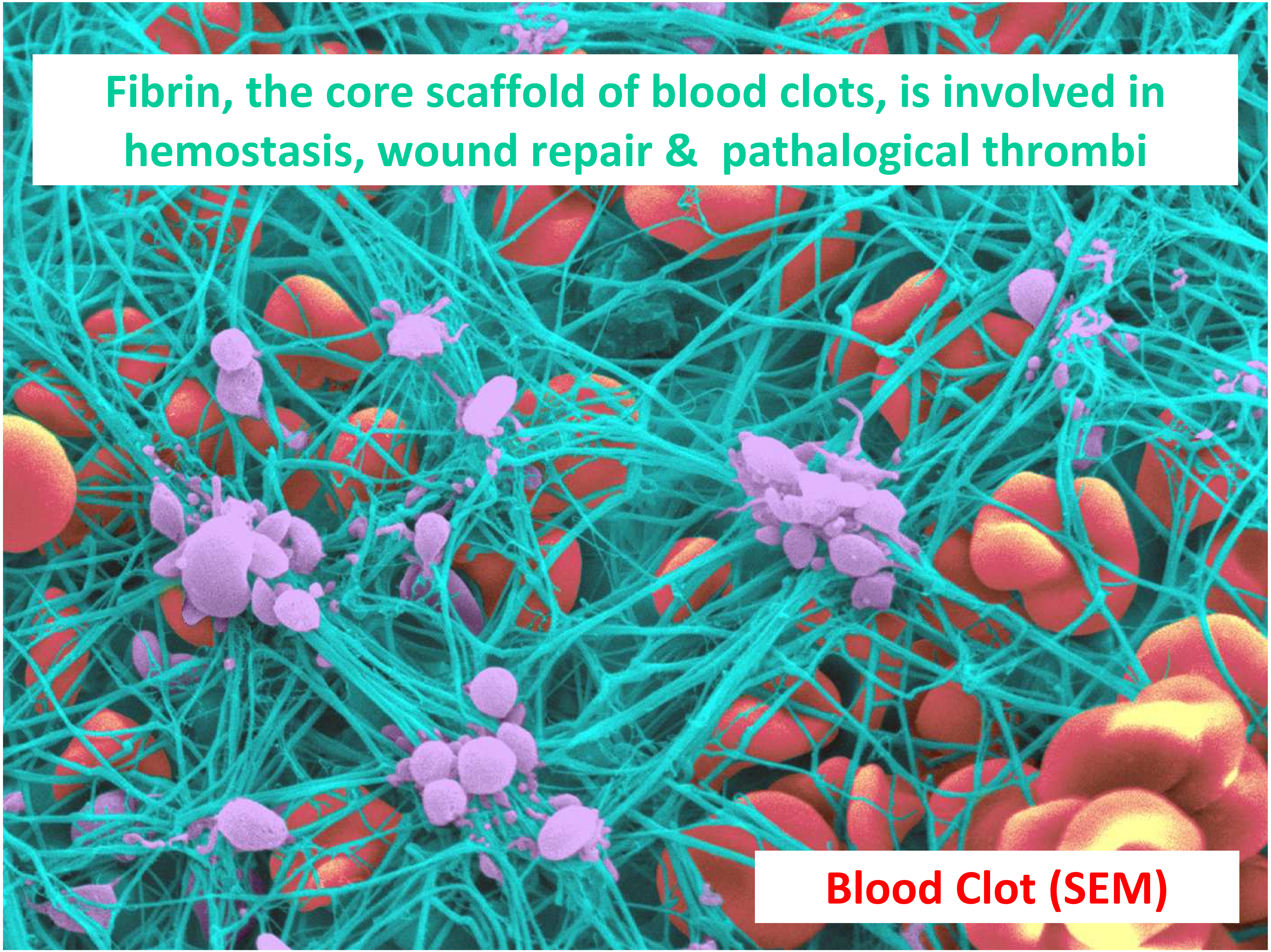
Bert Meijer
Albert Schenning
Martin Wolffs

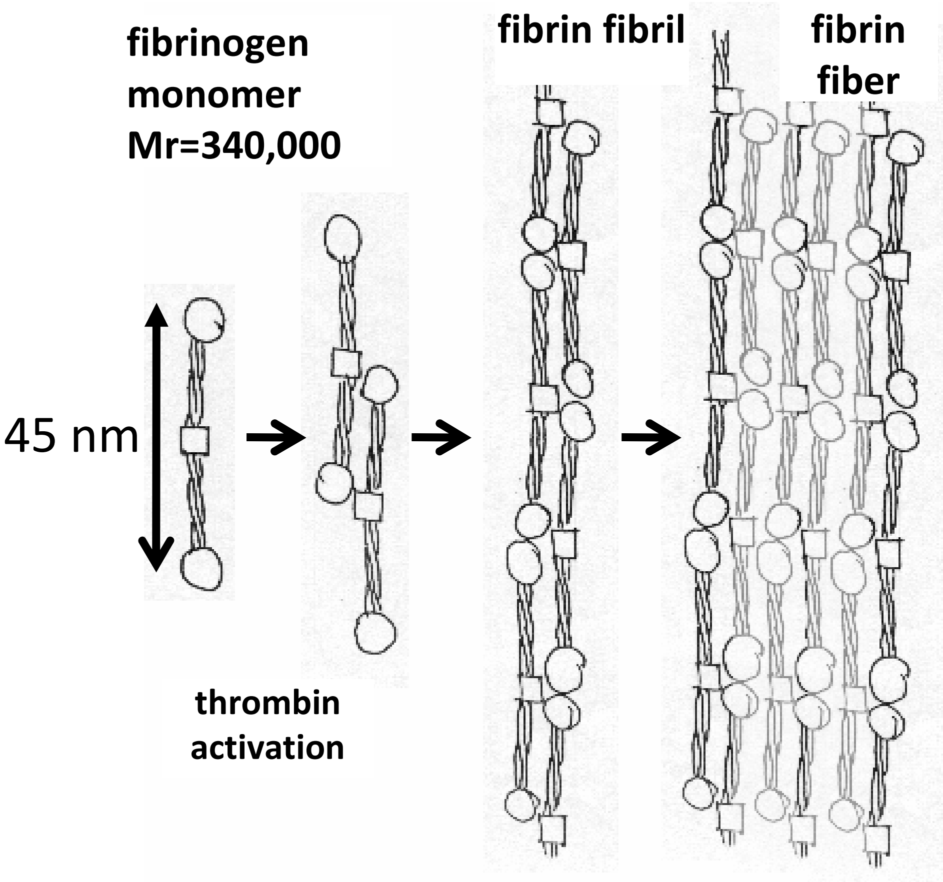
Fibrin, the core scaffold of blood clots, is involved in hemostasis, wound repair & pathalogical thrombi



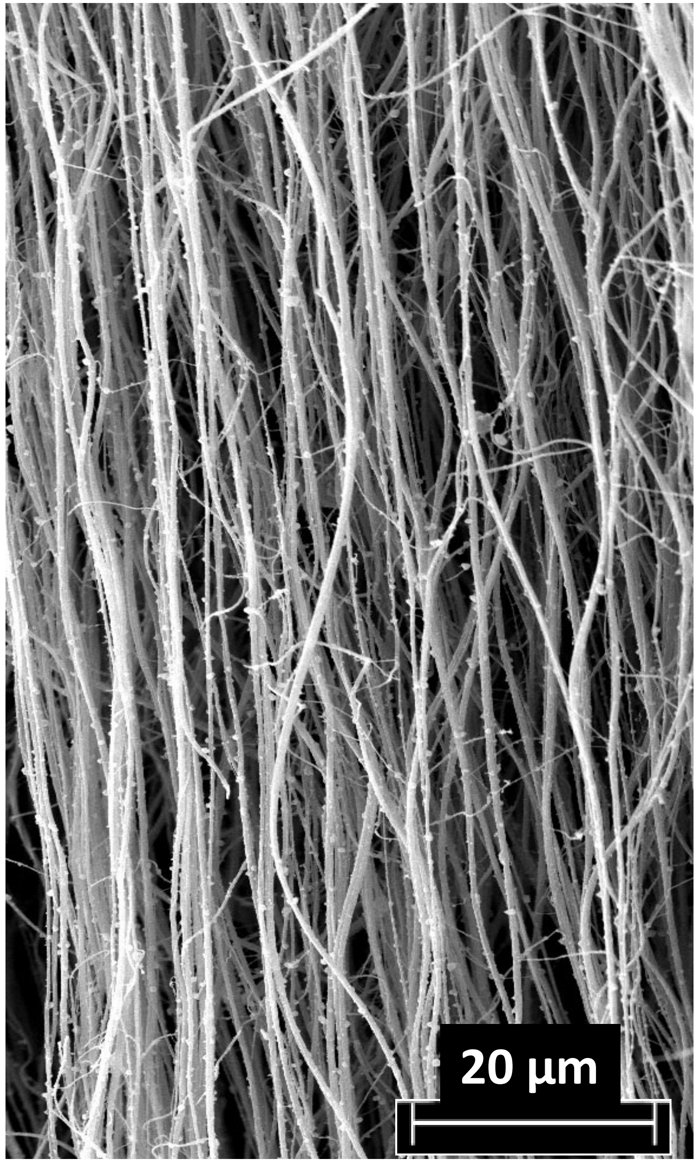
Blood Clot (SEM)

thrombin

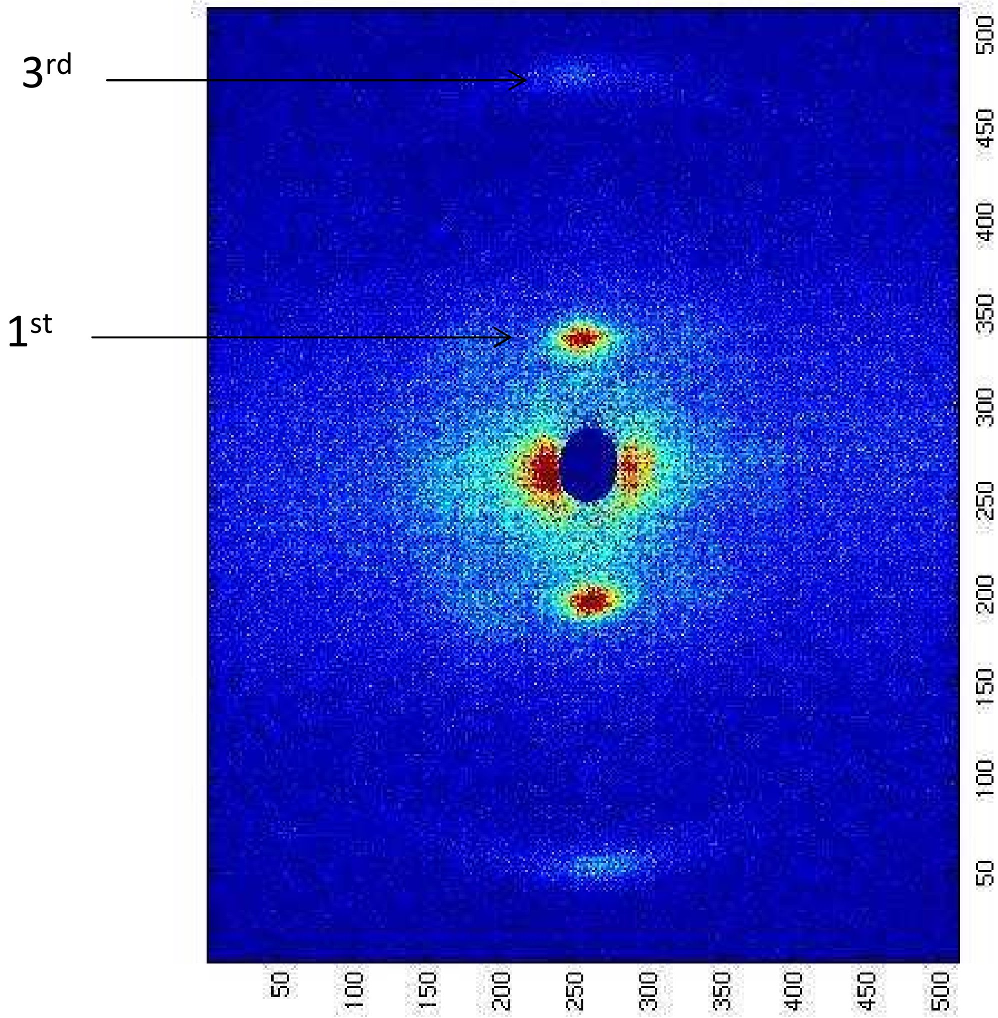
fibrinogen monomers → fibrin polymer



Human blood plasma clot assembled in 7 T

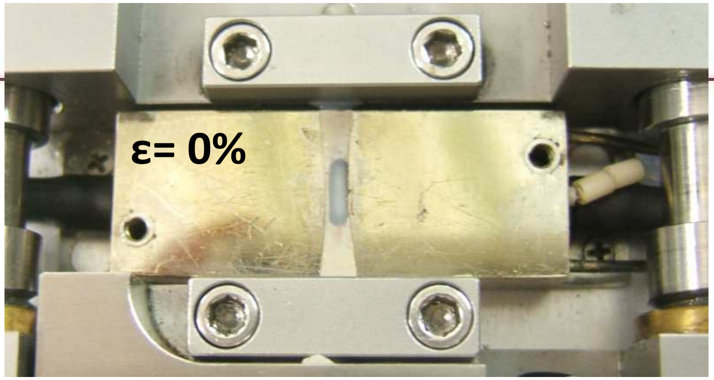


X-ray diffraction of Fibrin assembled in 12T magnet



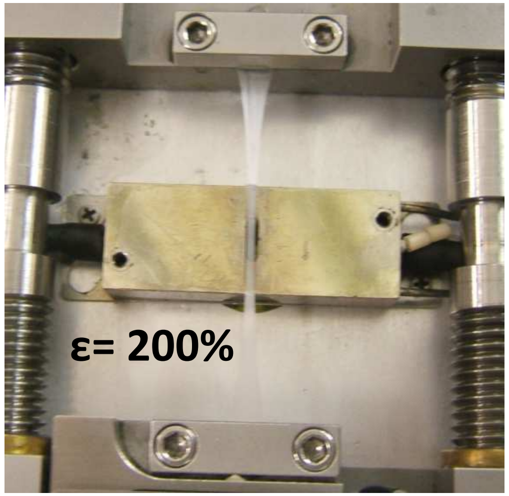
d = 22nm

Why magnetic orientation: The near perfectly aligned gels means that all fibers are simultaneously stretched to the same degree.



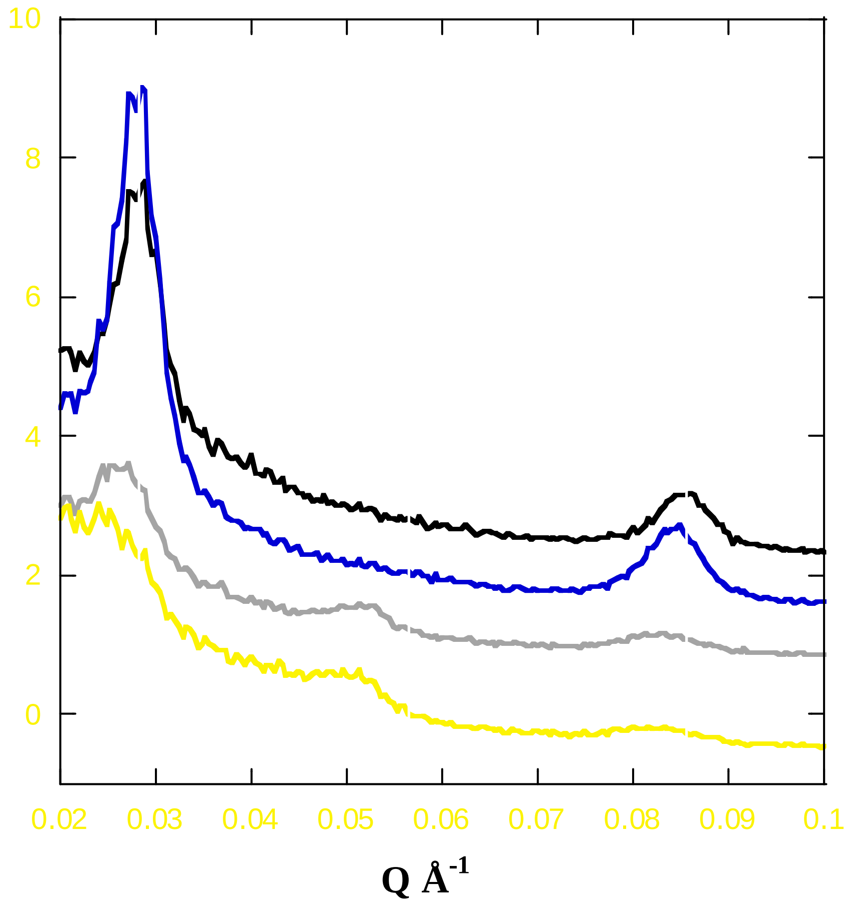
Human platelet free plasma clot assembled in 12 T

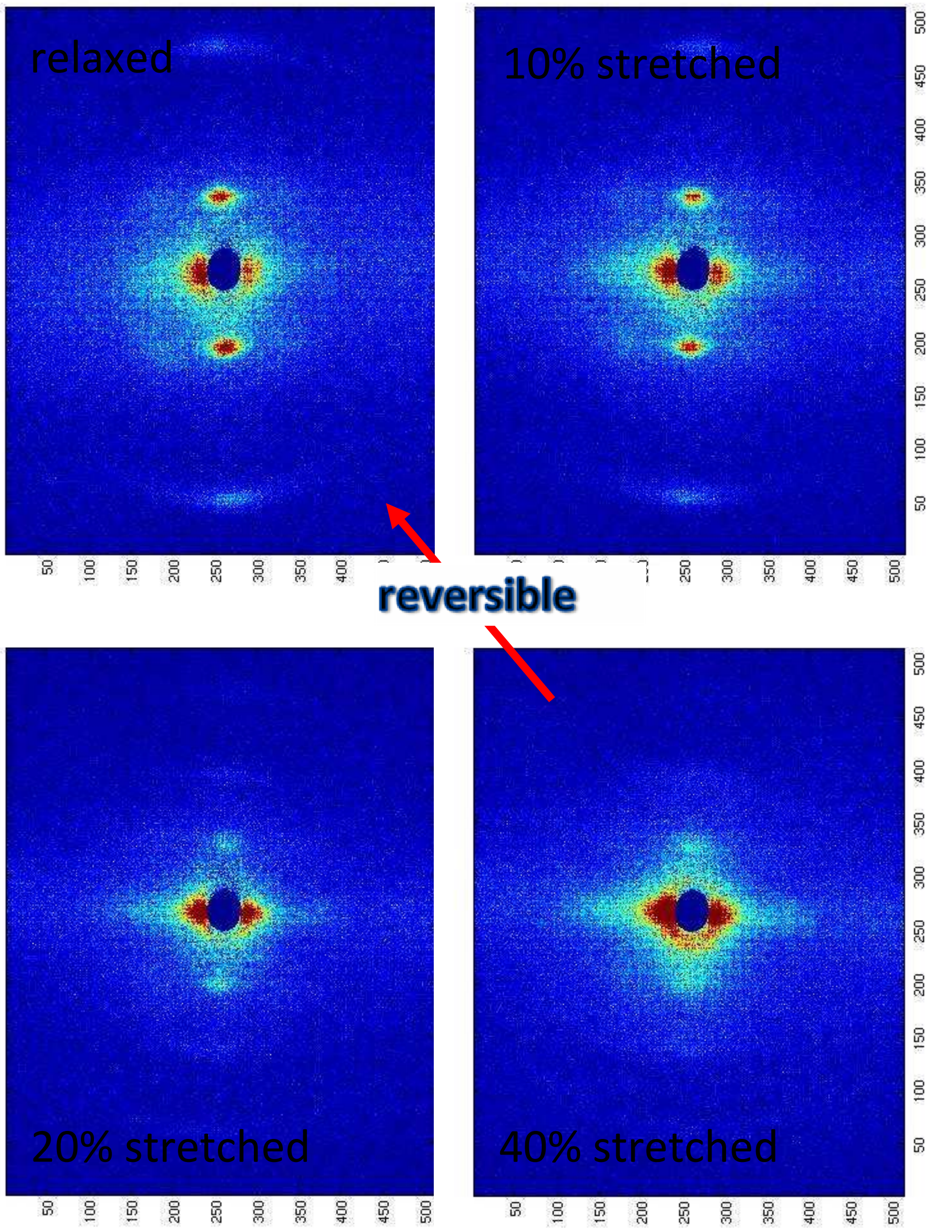
Why stretch: Fibrin is subjected to different degrees of tensile stress: in the short term, by platelet induced contraction during clot consolidation, and cell traction, during wound repair, &, in the long term, by the shear caused by blood flow round pathological thrombi.

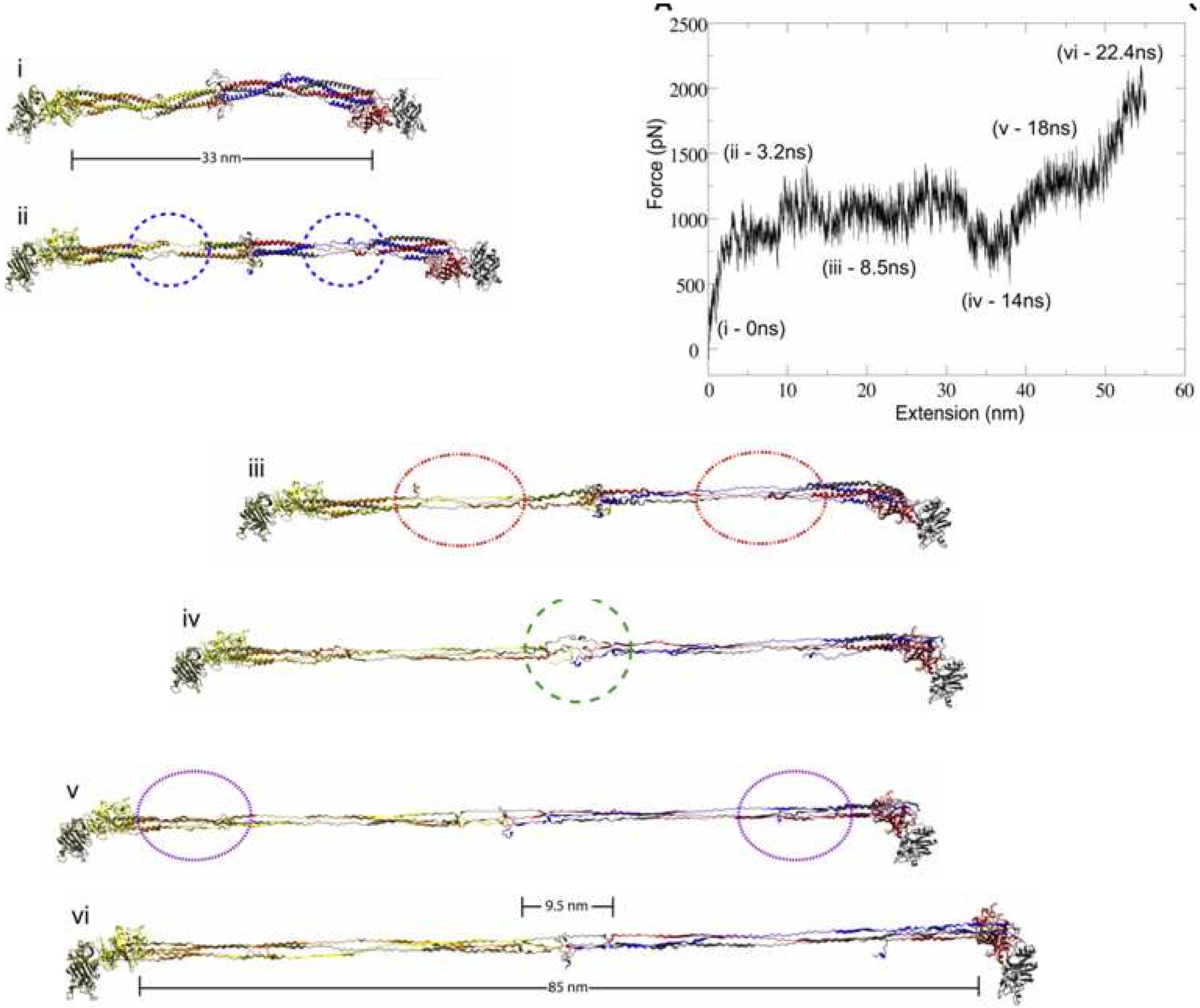


Stretching device in a water saturated atmosphere & X-rayed (BM26, DUBBLE)

Forced unfolding of fibrin






i
33 nm
ii
2500
2000
1500
1000
500
0
Force (pN)
0
10
20
30
40
50
60
Extension (nm)
(i - 0ns)
(ii - 3.2ns)
(iii - 8.5ns)
(iv - 14ns)
(v - 18ns)
(vi - 22.4ns)
iii
iv
v
vi
9.5 nm
85 nm

- The initial half-stagger axial repeat is only stretched by about 5% when it disappears at an extension, $\varepsilon \approx 40\%$.
- A new Bragg peak appears $\varepsilon \approx 20\%$ belonging to a different lattice, indicating the formation of a new ordered transition state which lingers beyond $\varepsilon = 40\%$.
- On relaxation clots stretched beyond 40% recover to their original length giving axial diffraction again but, surprisingly, the repeat is shorter than the initial value. The structure of stretched relaxed samples is different and the difference increases with the number of stretch-relaxation cycles and the maximum value of ε experienced. After stretching to ε=200% a Bragg spacing of only 18nm was recorded.