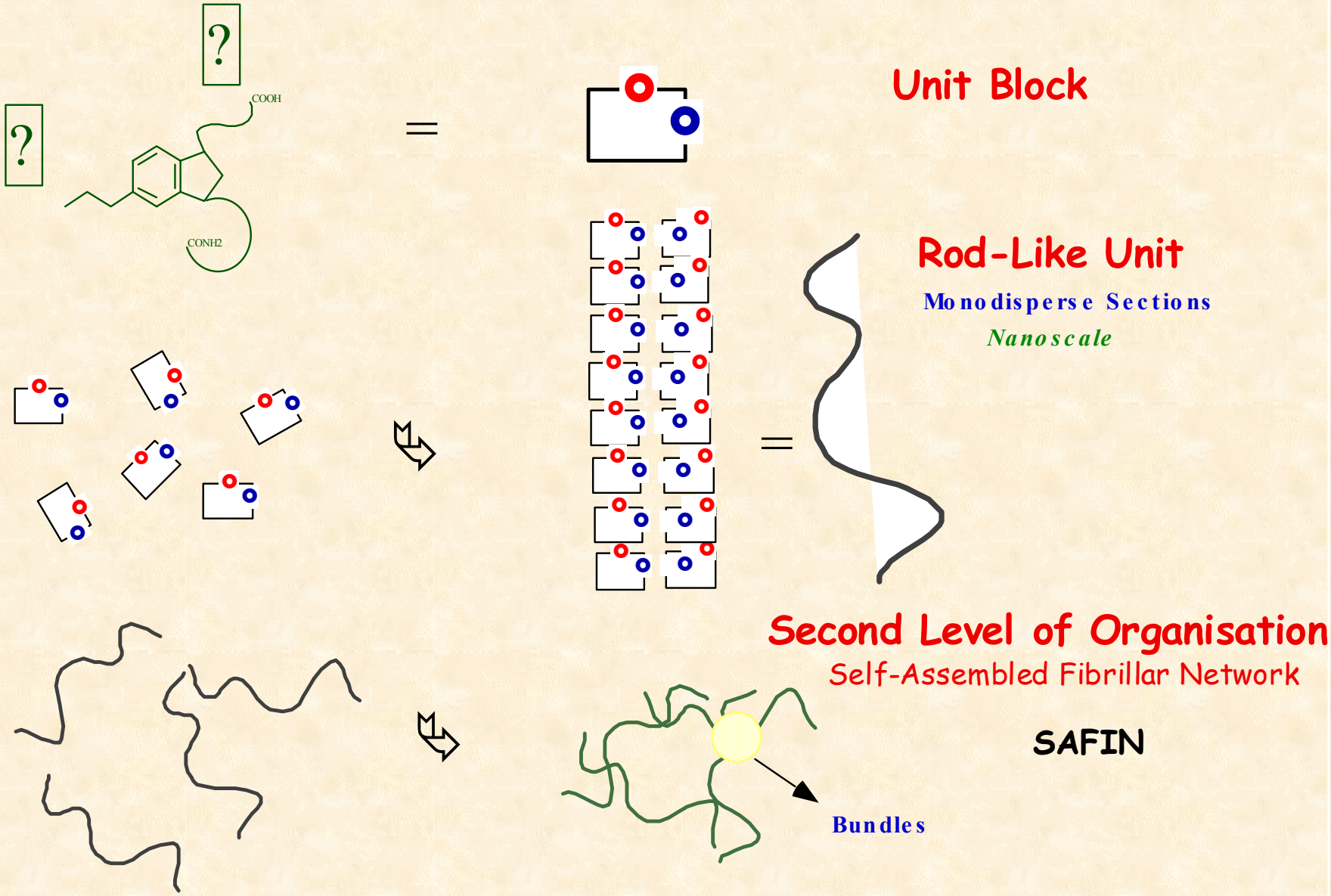
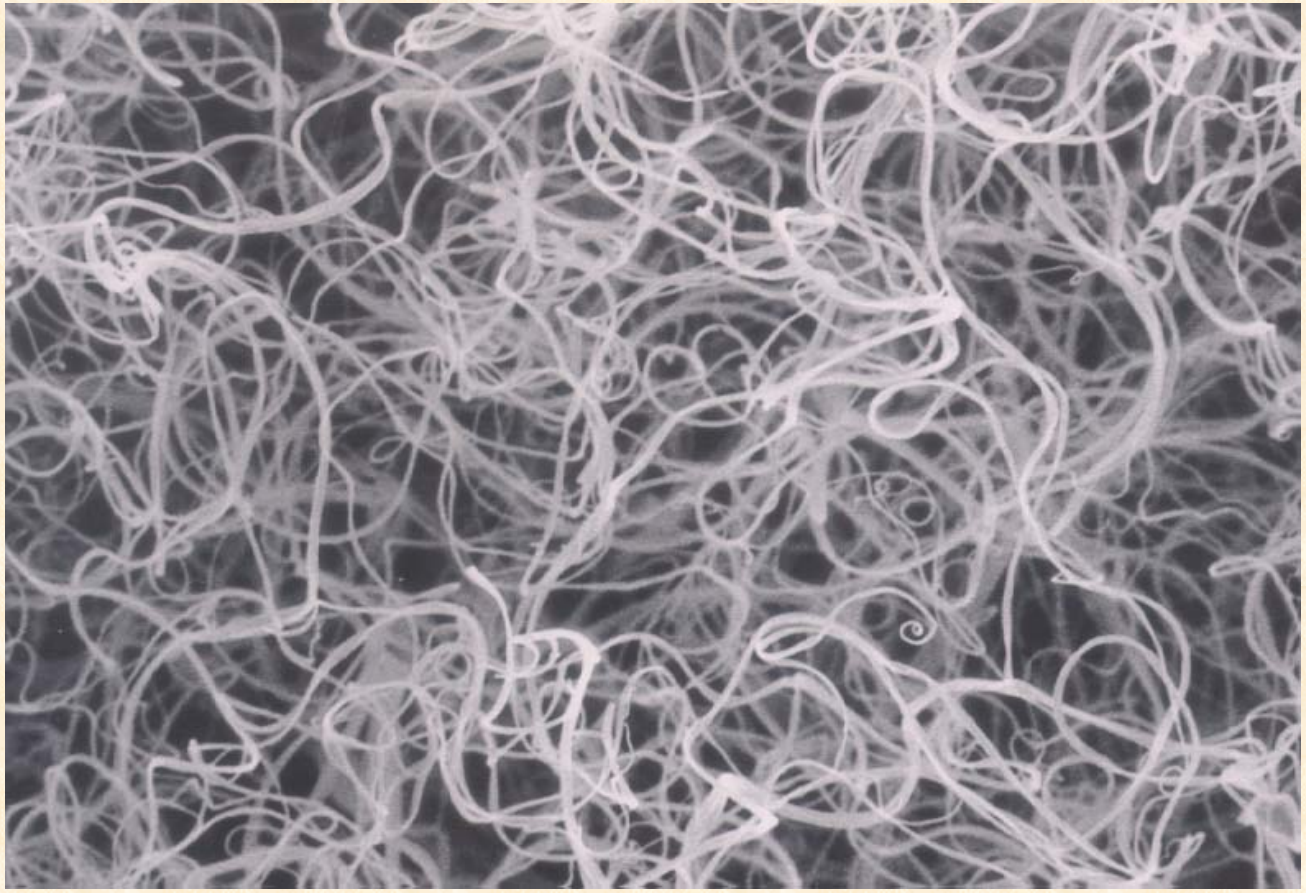


P. Terech & R.G. Weiss Chem. Rev. (1997)

Self-Assembled Fibrillar Networks (SAFINs)

Molecular Gels

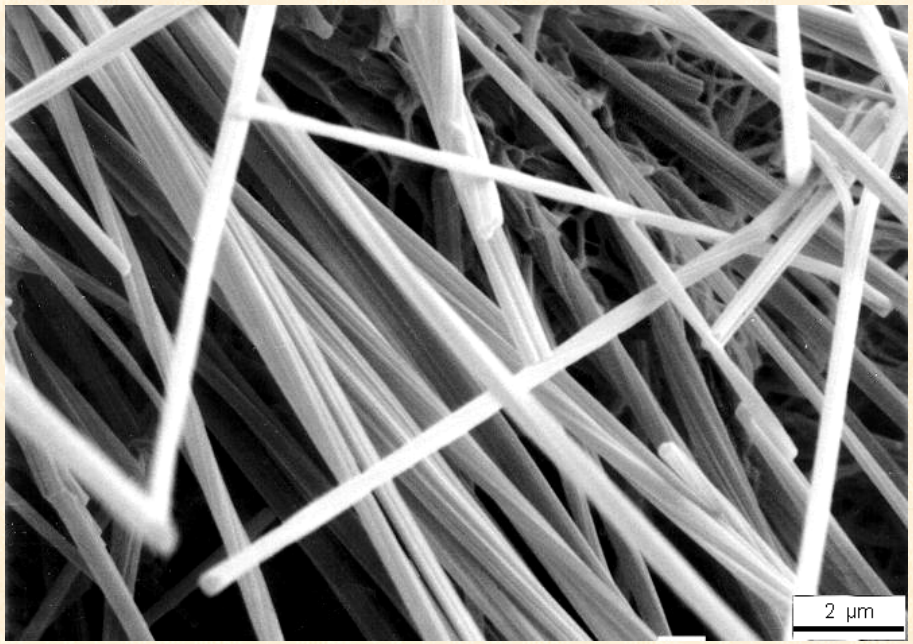


Diameter = 52 nm

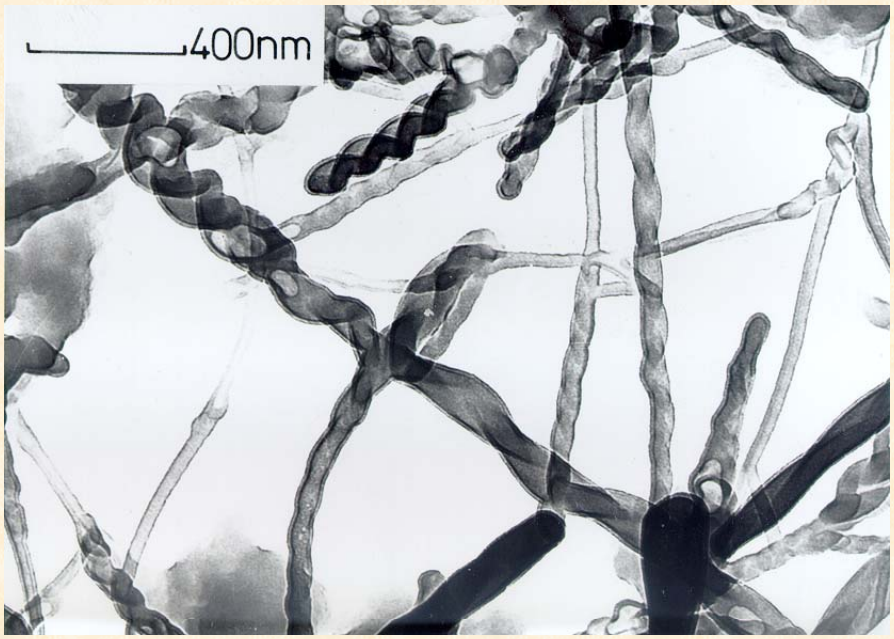
In Water

Molecular Gels

Rods & Fibers

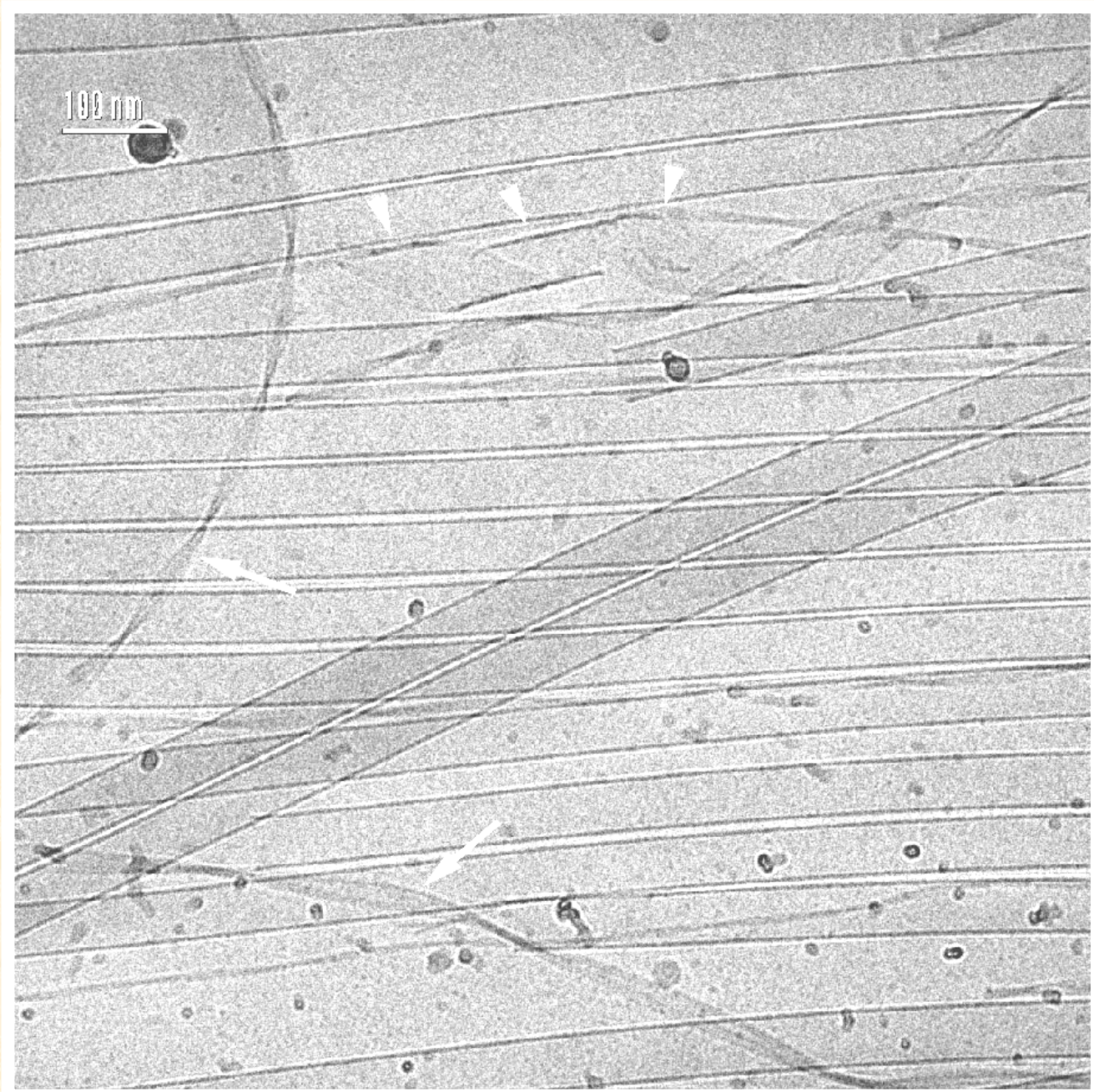


Helices



In Organic Liquids

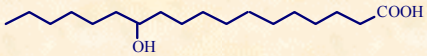
Bile Salt 0.1%
In Water



D_e = 52 nm

D_i = 49 nm

P. Terech & Y. Talmon
Adv. Mat (2002)



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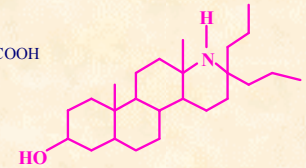

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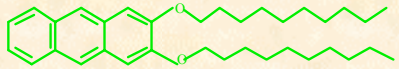

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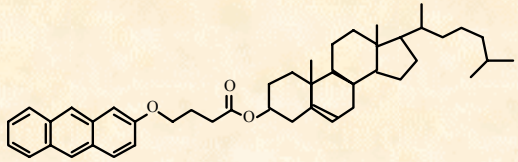

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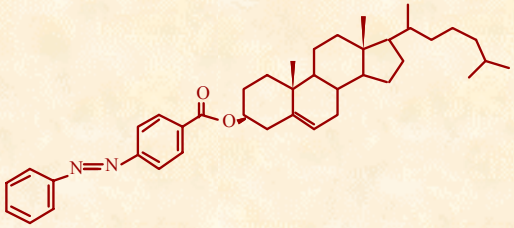

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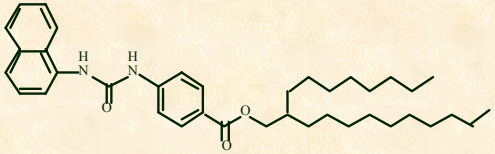

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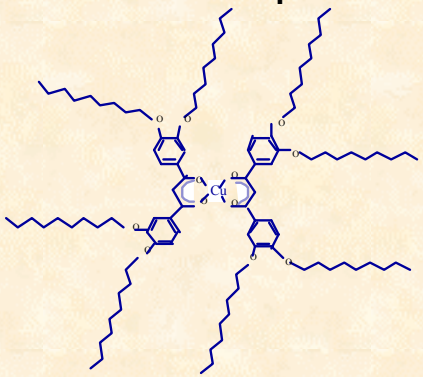

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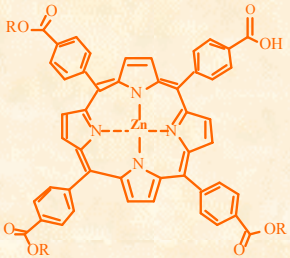

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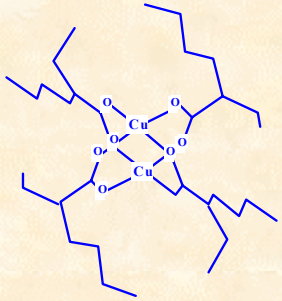

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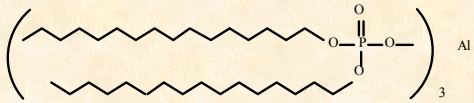

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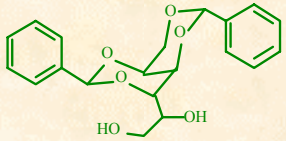

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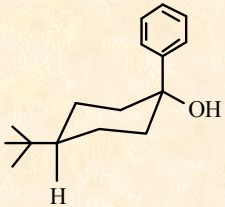

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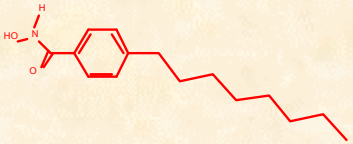

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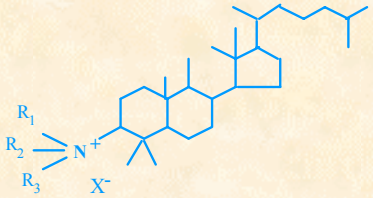


14

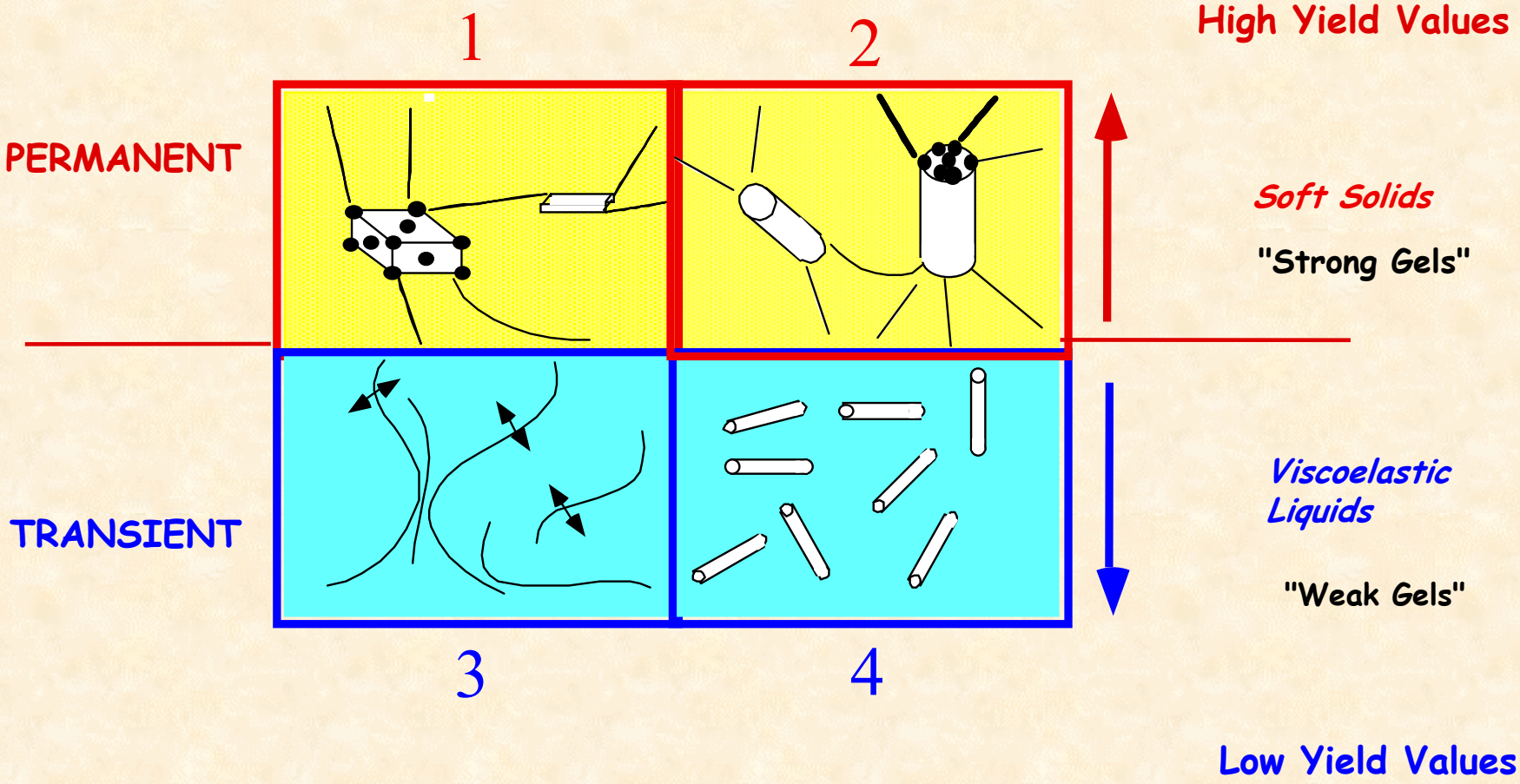
LOW-MASS THERMOREVERSIBLE GELS

QUESTIONS & OBJECTIVES

* WHY A SMALL MOLECULE CAN BE A GELATOR ?
  * STRUCTURAL CORRELATIONS (different states of gelator K, LC,gels → mechanisms)
* RELATIONSHIPS BETWEEN STRUCTURES AND VISCOELASTICITY ?
  * AT REST
  * UNDER EXTERNAL STIMULI
    - *SHEAR*
    - *pH*
    - *CAPPING CO-SURFACTANTS, .etc.*

MOLECULAR NETWORKS

JUNCTION ZONES



FORM-FACTOR of a CYLINDER

Cylindrical coordinates r = (r, α,z)

$$F(q) = \int_0^r \int_{-\pi}^{\pi} \int_{-L/2}^{L/2} \rho e^{i\, q.r}\, r dr d\alpha dz$$

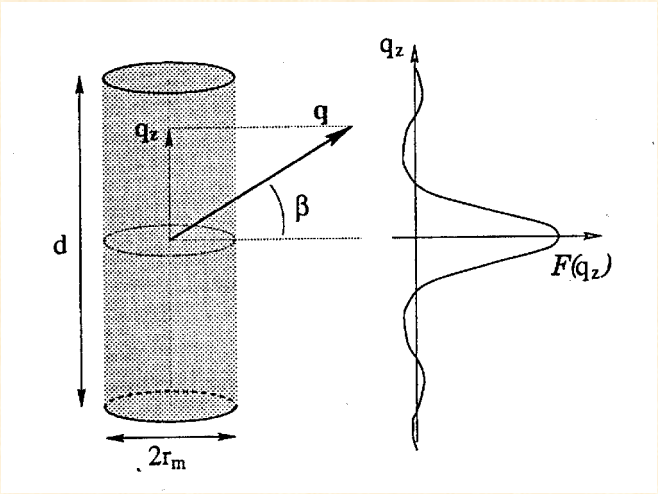
Length L radius r

$$F(q) = 2\pi L\rho\, \mathrm{sinc}(qL \sin\beta/2) \int_0^r r J_0(qr\cos\beta)\, dr$$

For qr cos β <<1

$$F(q) = \pi r^2 L \rho\, \mathrm{sinc}((qL \sin\beta)/2)$$

~~non-zero contributions in the plane of reciprocal space ⊥ to the rod axis
= **reciprocal disk**

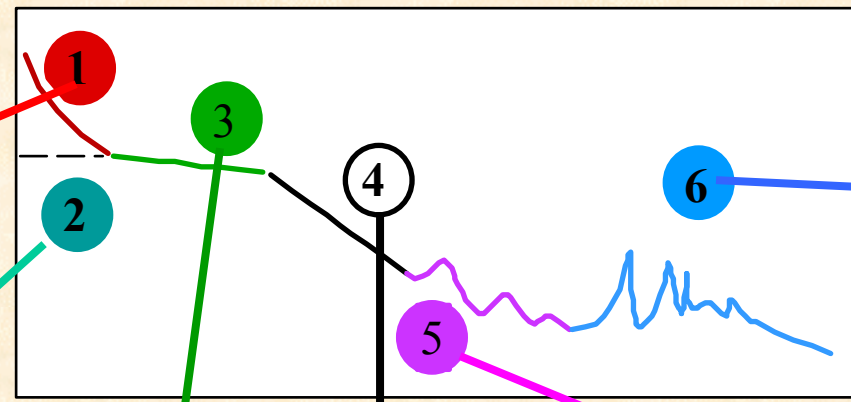


$$I(Q) = \pi L \underline{\rho}^2/Q\ [r^2 J_1(Qr)/Qr]^2$$

C. Fradin, thesis 1999

Small Angle Scattering for Self-Assembled Fibrillar Networks

Scattering Curve



Low-Q bump

Large scale heterogeneities*

Extrapolation at Q -> 0

Mass per unit length

Asymptotic decay $Q^{-\alpha}$

Morphology

$I = \phi(\pi r \Delta\rho)^2/Q \exp(-Q^2r^2/4)$

Gaussian decay

Geometrical Cross-sectional parameters

Bragg peaks

Internal Structure of the Fibers

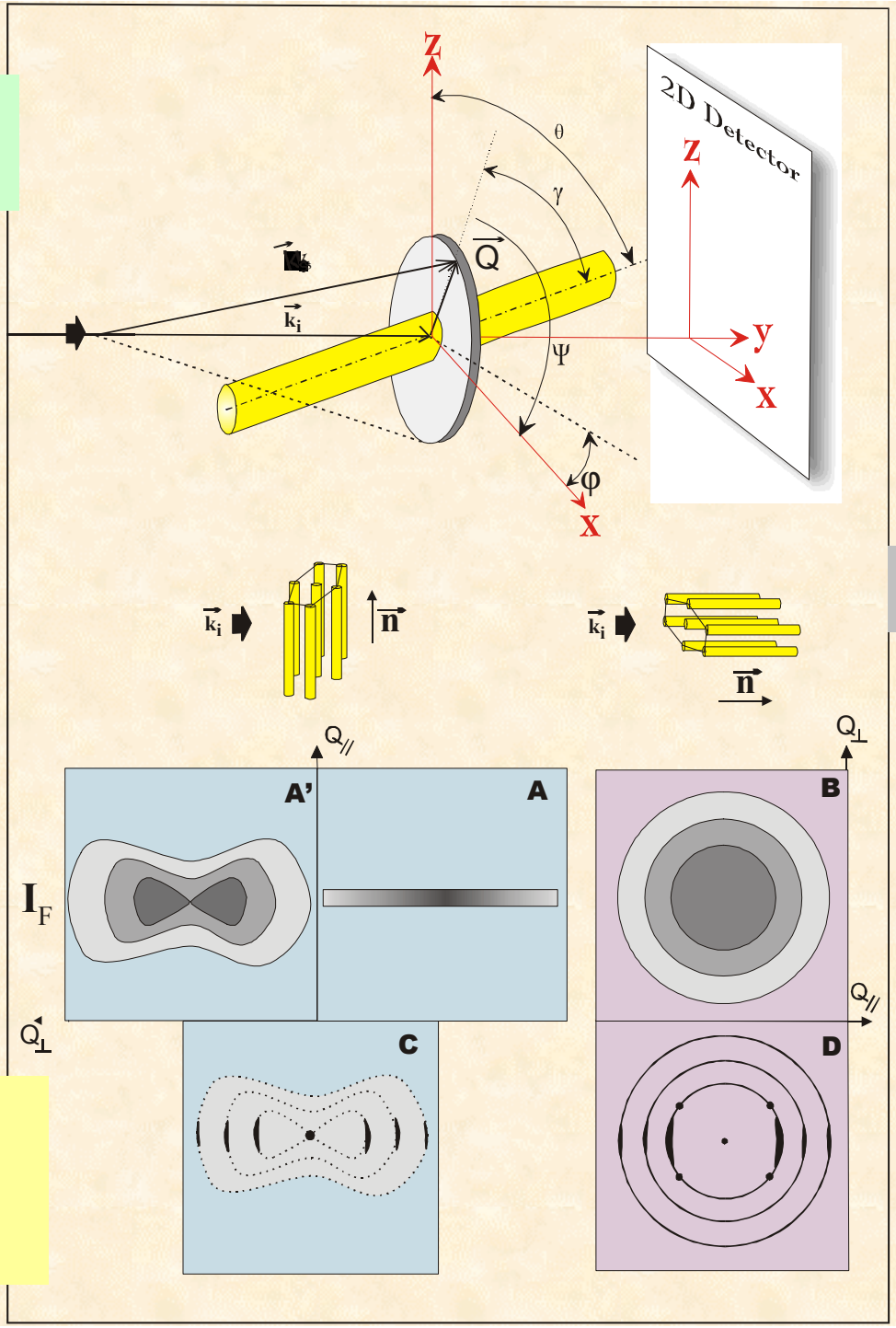
Form-factor oscillations

Dispersity & Heterogeneity

* Or Interfacial scattering # Structure Factor #Two-Phase system (Debye-Büeche) # Flexibility

$$I_{DB} = 8\pi\phi_{nodes}(1-\phi_{nodes})\Delta\rho^2 d^3/(1+d^2Q^2)^2$$

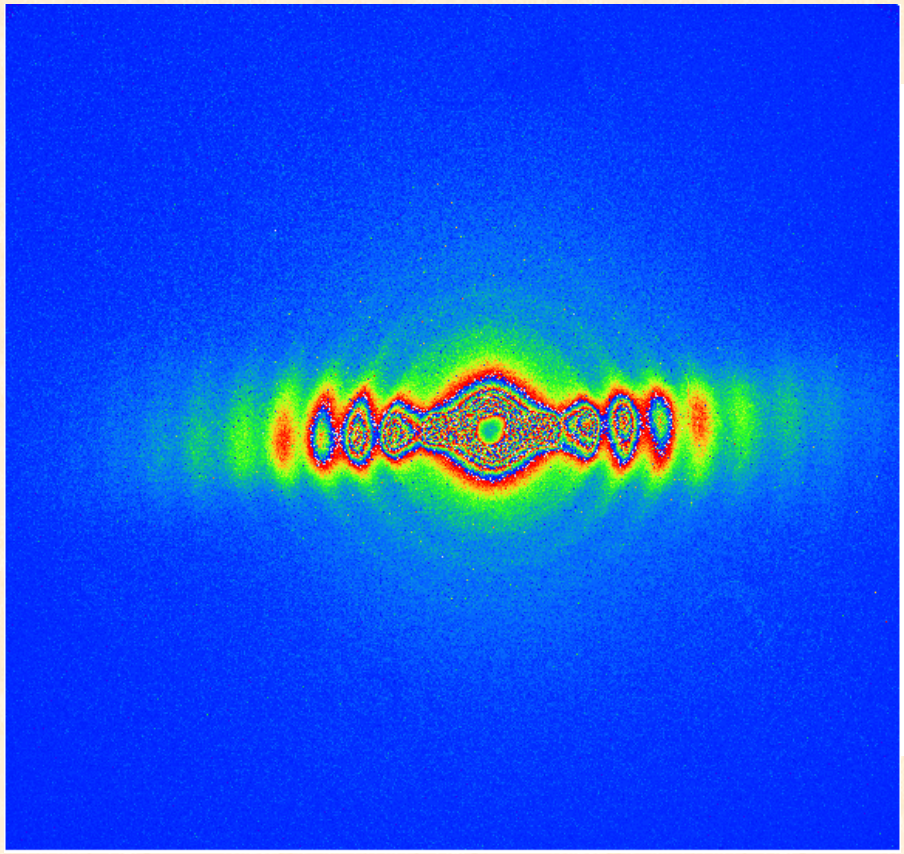
Scattering of Oriented Rod-like Systems

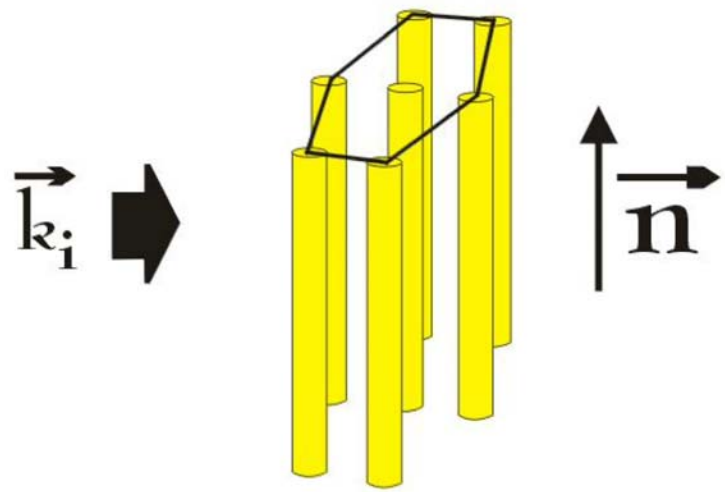


$$F(Q,\gamma) = 2\rho V \times \sin(QL/2\cos\gamma)/(QL/2\cos\gamma) \times J_1(Qr\sin\gamma)/(Qr\sin\gamma)$$

Steroid Nanotubes in Water

$Q_{//}$





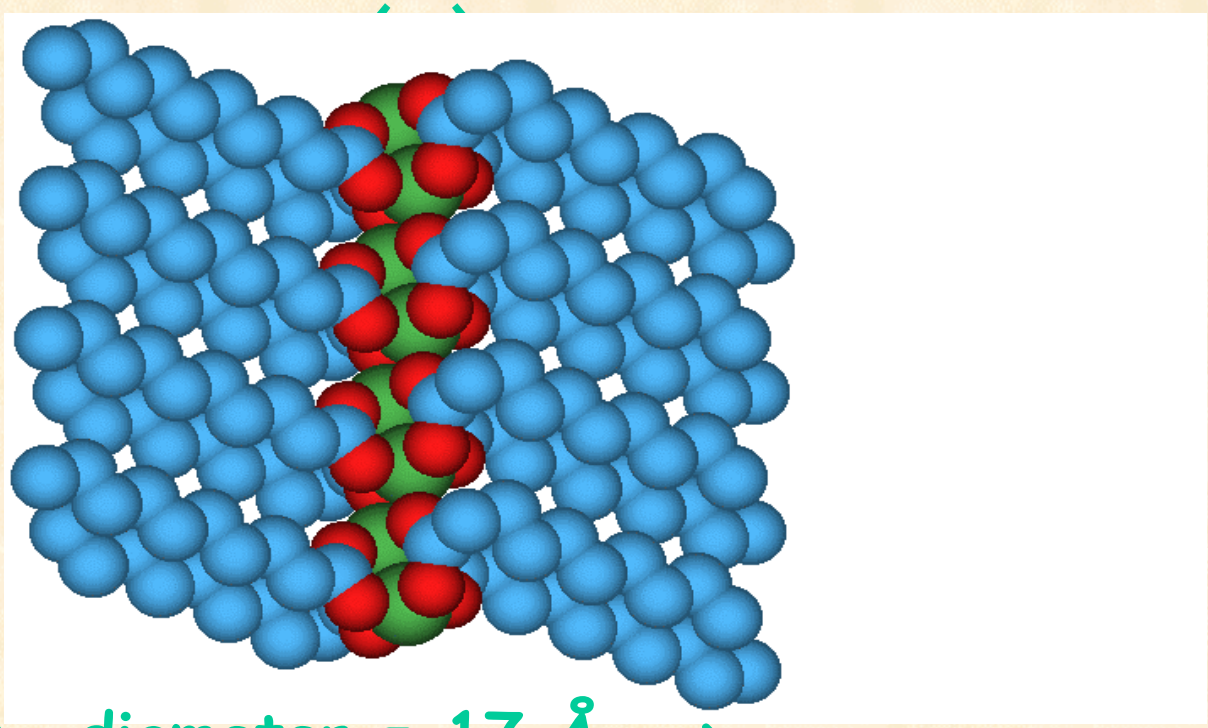
Organometallic Molecular Wires

bicopper tetracarboxylates

Cu_2L_{10}

polar core

↑
rod axis
↓



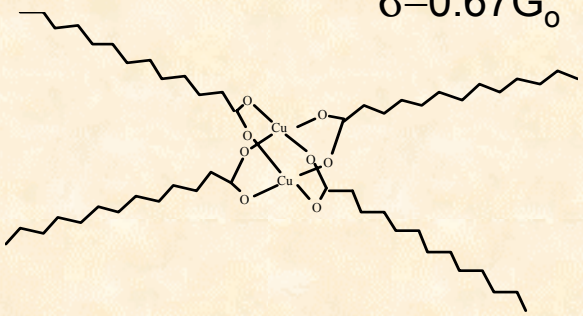
<- diameter = 17 Å ->

P. Terech et al. J. Phys. Chem. 2001 & Langmuir (1999)

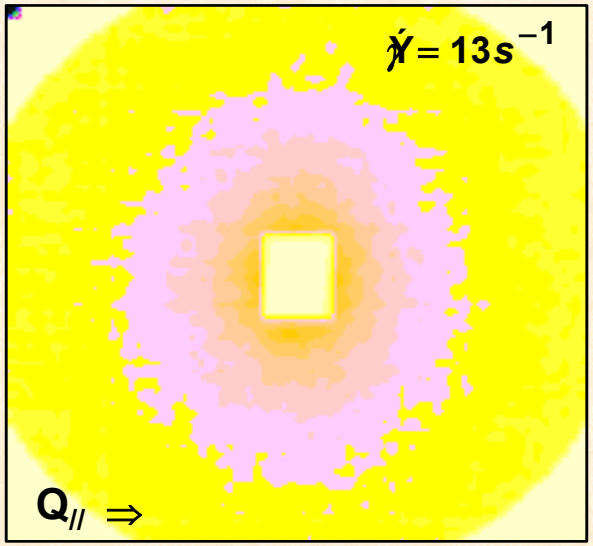
Different fibers under shear

Giant breakable worm-like micelles

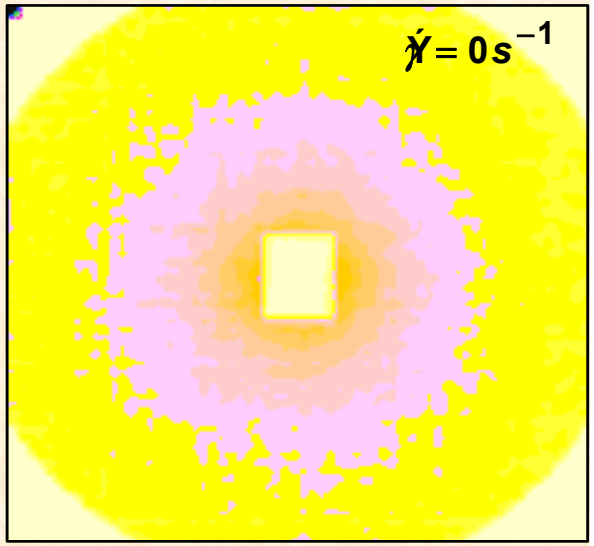
$\sigma = 0.67 G_o$



Isotropic at rest

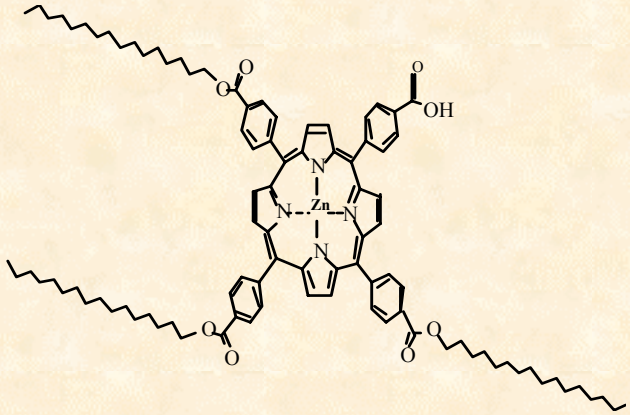


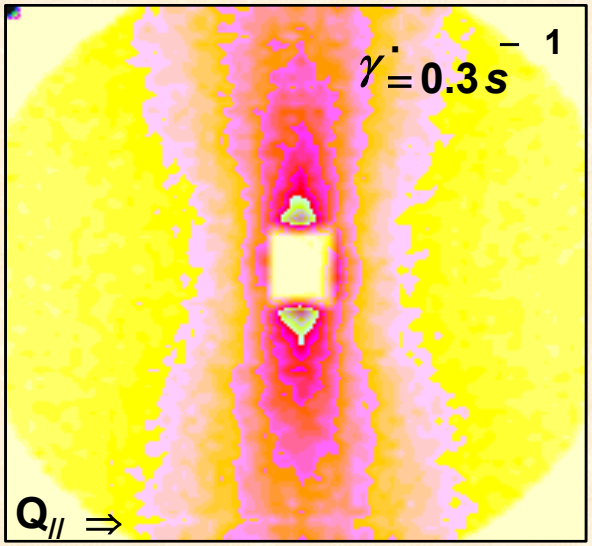
Under shear

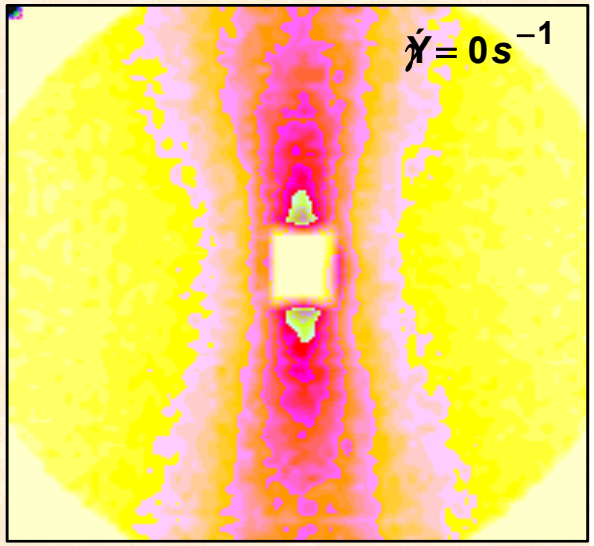


Relaxation

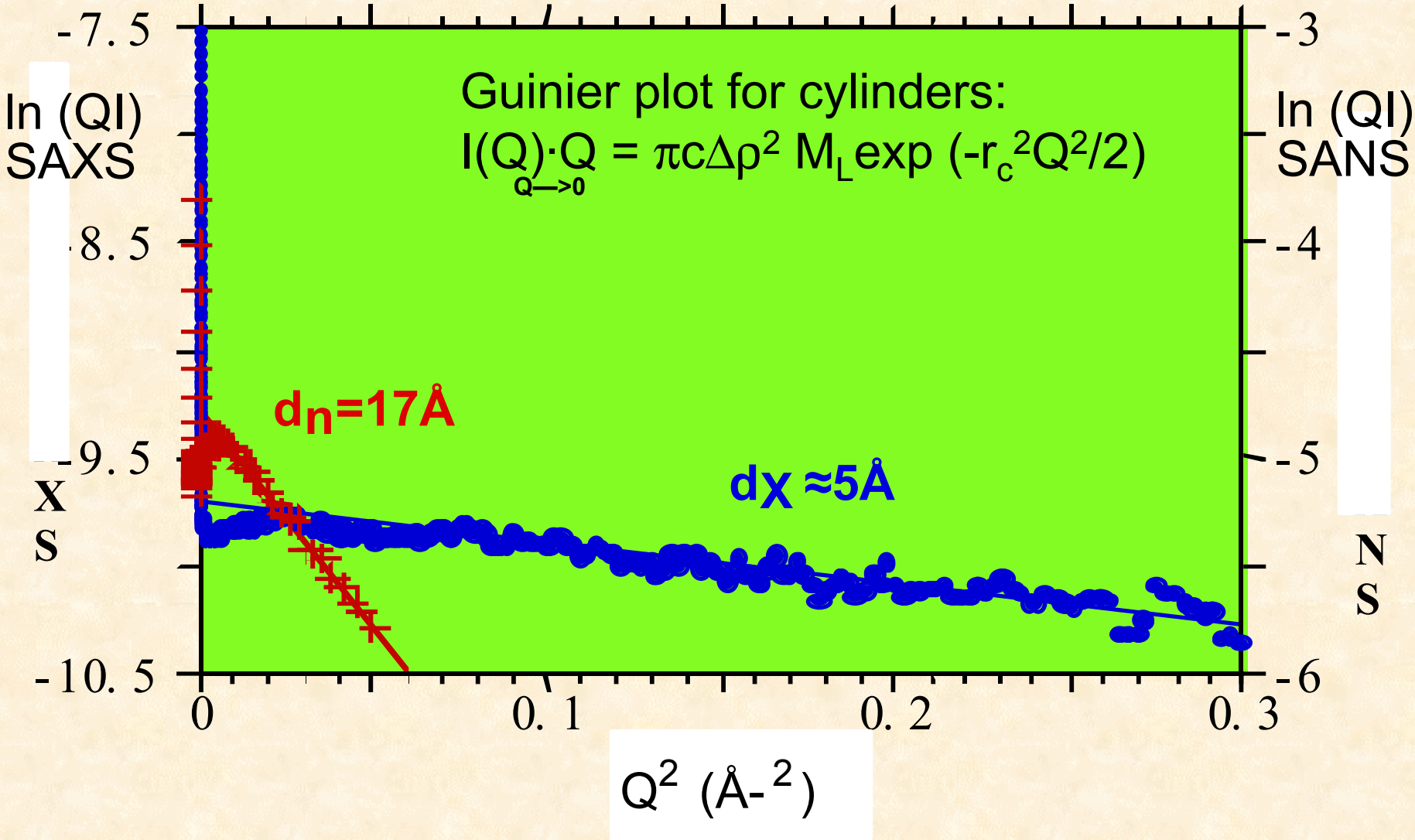
Rigid rods





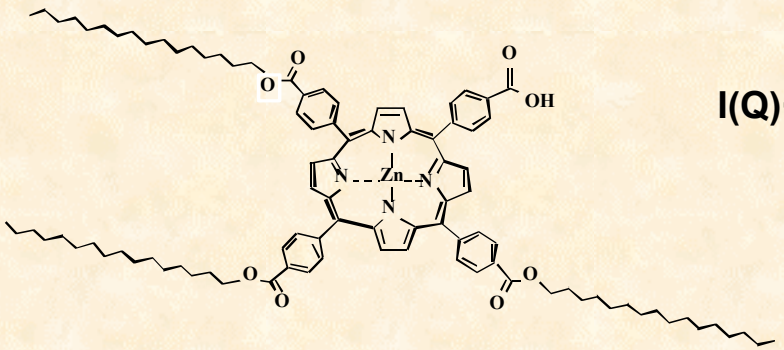


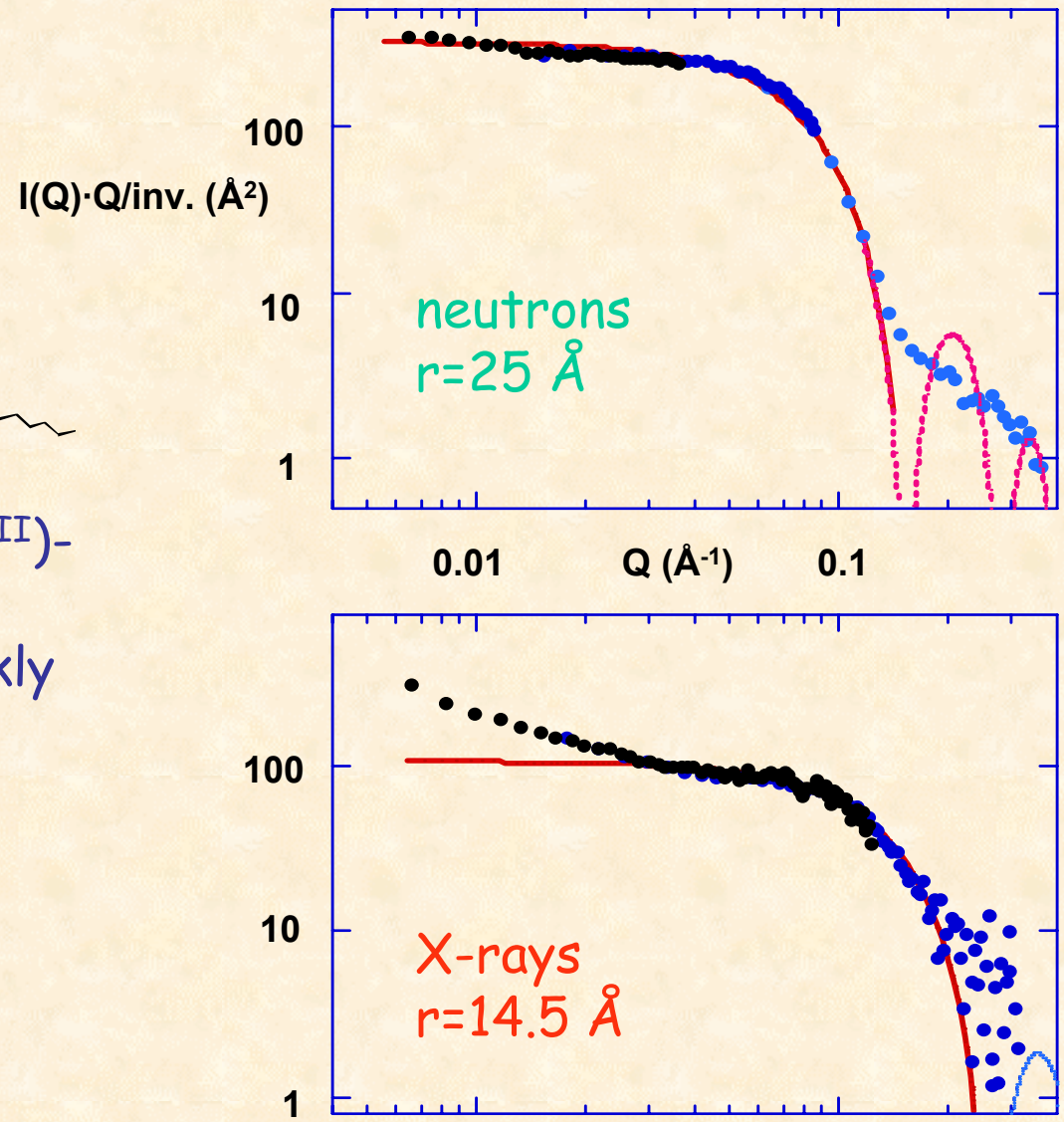
Organometallic Molecular Wires



P. Terech et al. J. Phys. Chem. (2001) & Langmuir (1999)

Metallo porphyrin as seen by n and X



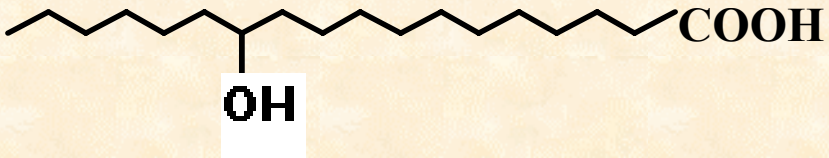


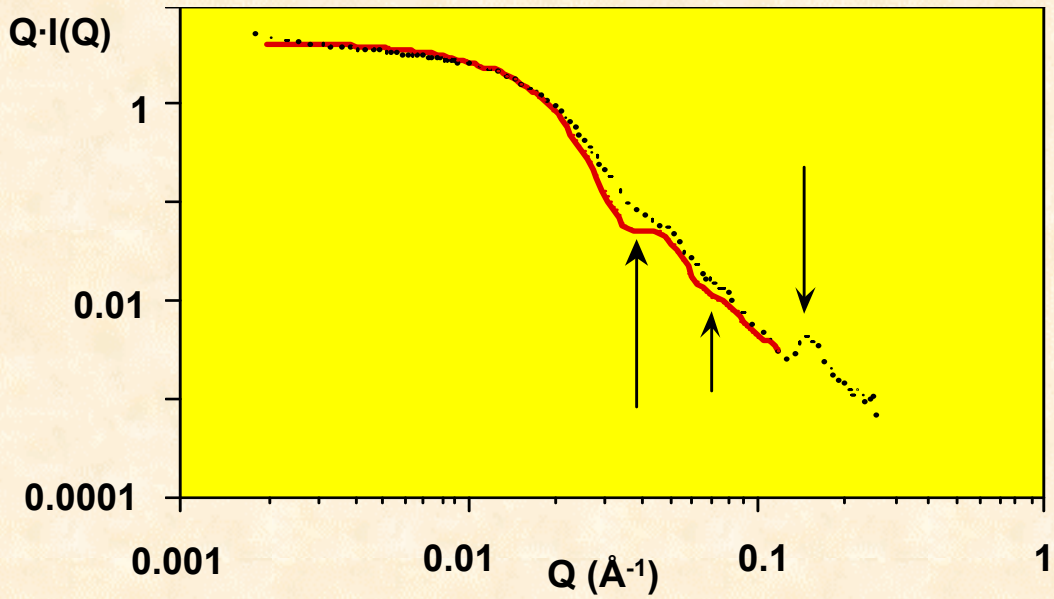
Tri-substituted metallo (Zn^{II})-porphyrin self-associates in cyclohexane and forms weakly viscoelastic solutions

P. Terech et al. Langmuir (1996)

HSA fatty acid organogel in d-benzene

Hydroxy stearic acid/C_6D_6 2.5 wt.%





$$I(Q) = \frac{2L}{Q}\int_0^{2\pi}\left[A\Delta\rho\frac{\sin Qa\cdot\cos\varphi}{Qa\cdot\cos\varphi}\cdot\frac{\sin Qb\cdot\sin\varphi}{Qb\cdot\sin\varphi}\right]d\varphi$$

$$I(Q,\varepsilon) = I_o\frac{1}{\varepsilon}\sqrt{\frac{\ln 2}{\pi}}\int\left[I(Q)\exp\left(\frac{\ln 2}{\varepsilon^2}\cdot(x-1)^2\right)\right]dx$$

Fit results:

k (anisometry) = b/a = 1

ε (dispersity) = 0.08

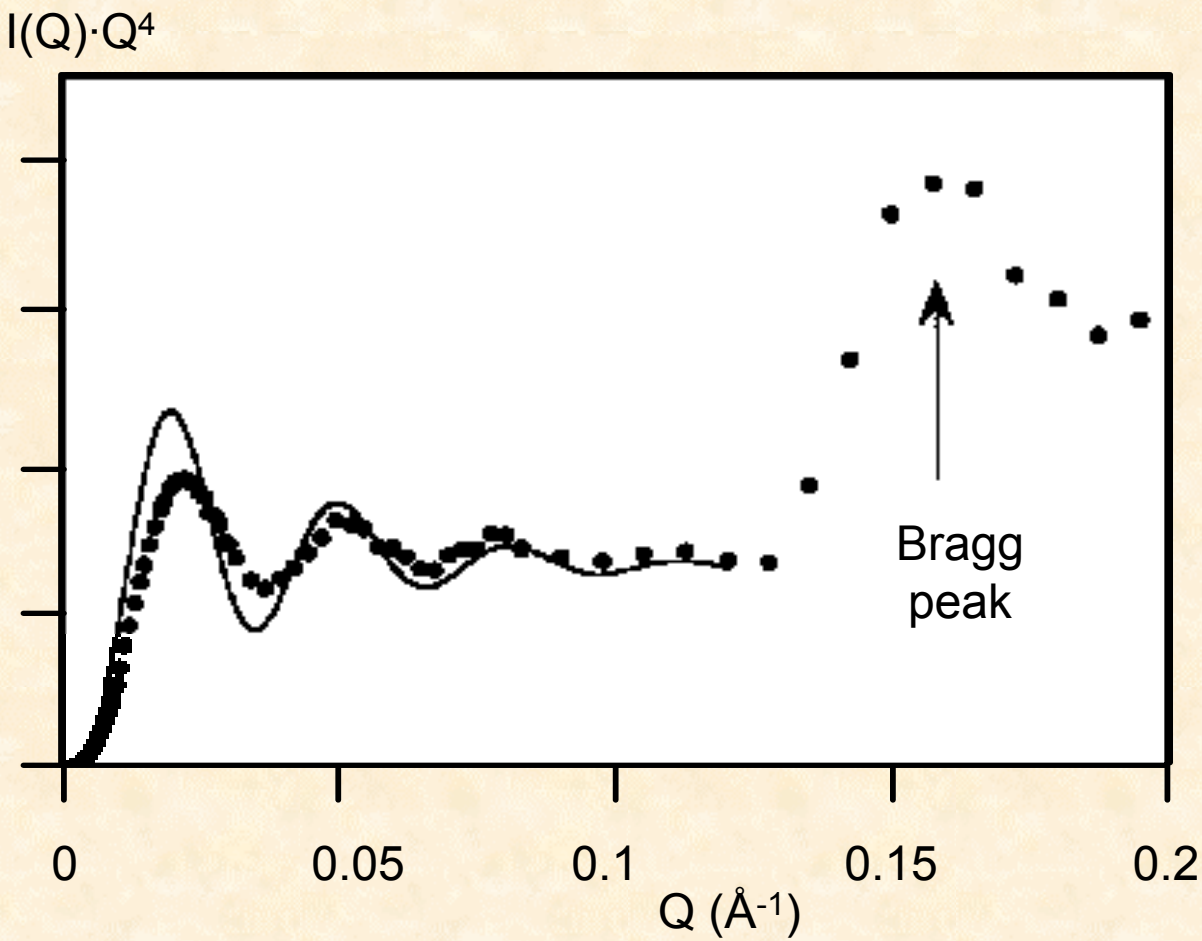
b (half width) = 103 Å

n_L (weight per length) = 40 mol $Å^{-1}$

P. Terech, V. Rodriguez, J.D. Barnes, G.B. McKenna (1994) Langmuir 10, 3006-18

HSA fatty acid organogel in d-benzene

HSA/C_6D_6 2.5 wt.%



Porod plot

$$I(Q)_{Q\to\infty} = -8\pi Q^{-4}\left[\frac{dP(r)}{dr}\right]_{r=0}$$

Scattering function

$$I(Q) = \frac{\pi}{Q} L_V \Delta\rho^2 (AB)^2 \int_0^{2\pi} g(A,B,\varepsilon)\, d\varphi$$

Gaussian distribution

g(A,B,ε)

Monodisperse Sections

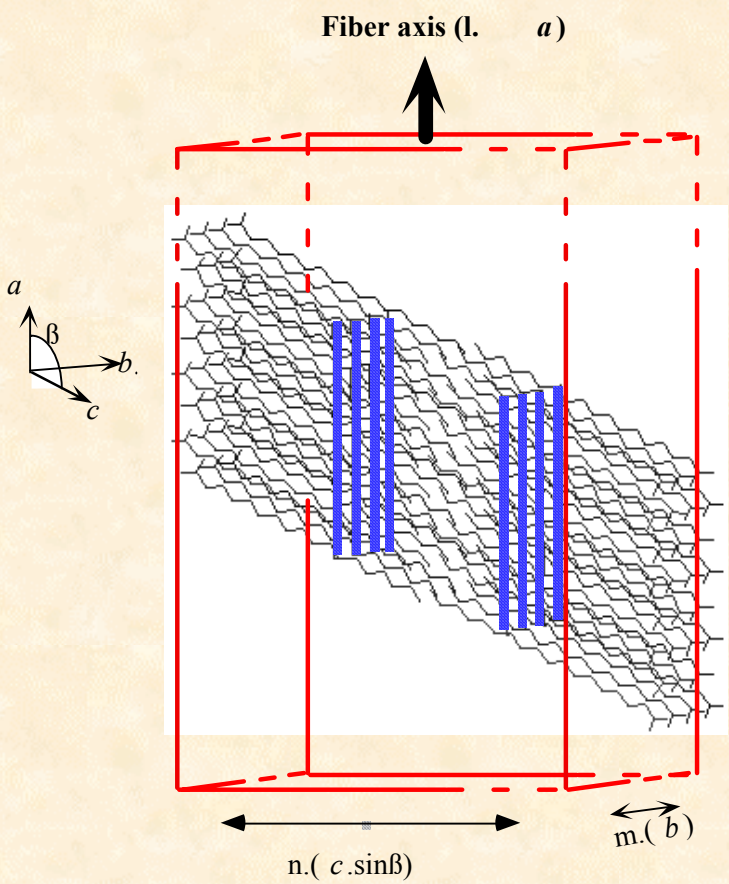
+

Internal Structure

P. Terech, V. Rodriguez, J.D. Barnes, G.B. McKenna (1994) Langmuir 10, 3006-18

12-Hydroxy Stearic Acid Self-Assembled Fibers in Toluene

X-ray powder diffraction ⇒

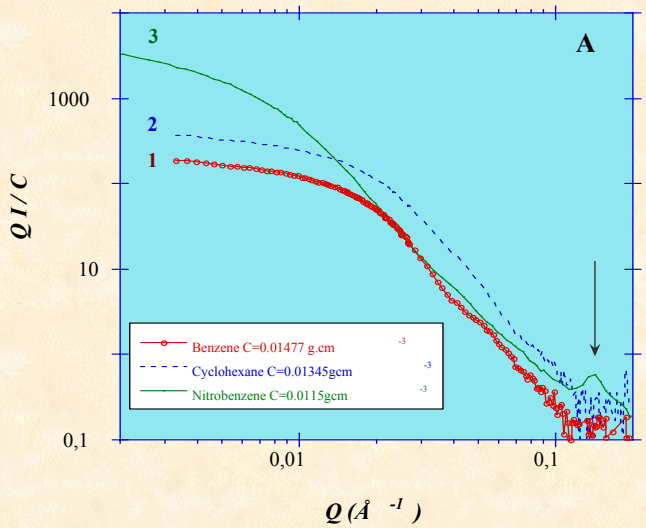


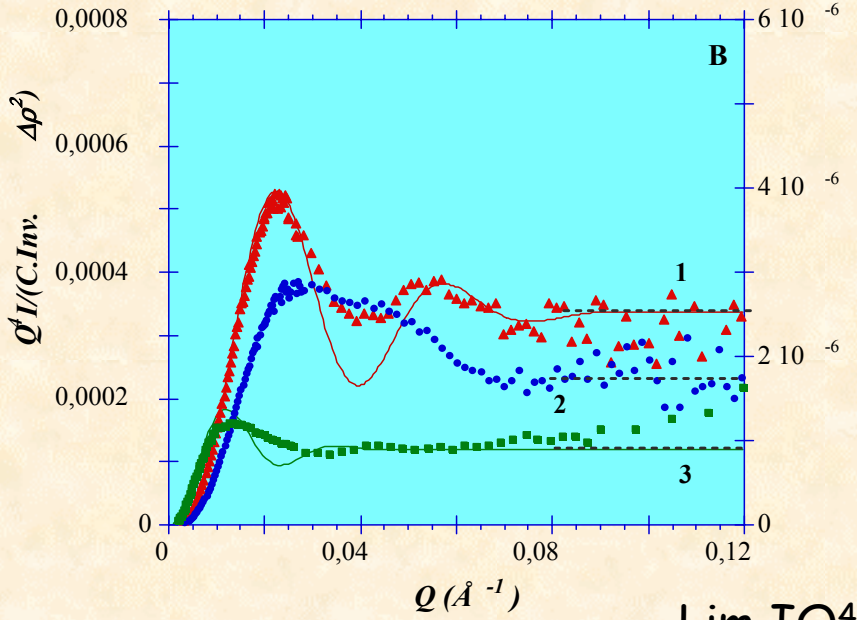
- OH-OH H-BOND SEQUENCES
- TILTED head-to-head BIMOLECULES
- RESIDUAL INTERFACIAL POLARIZATIONS
- CHIRAL EFFECTS: enantiomorphic super-chirality + limited "chiral bilayer effect"

MONOCLINIC SYMMETRY (DL-HSA : P21/a ; D-HSA : P21)

HSA fatty acid molecular organogel

$$QI = \pi L_V \Delta\rho^2 (AB)2 \int[\sin(QA\cos\varphi/2)/QA\cos\varphi/2) * \sin(QB\cos\varphi/2)/QB\cos\varphi/2)]^2 d\varphi$$





Lim IQ^4, Q -> ∞

Nitrobenzene >> Cyclohexane > Toluene

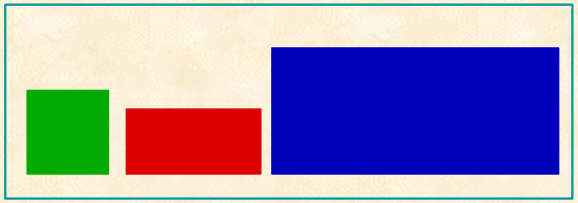
$$INV = \int Q^2 I(Q) dQ = 2\pi^2 \Delta\rho^2 V \lim IQ^4 = 2\pi\Delta\rho^2 S$$

$$\lim IQ^4/INV = S/\pi V = 2(A+B)/\pi AB$$

P. Terech et al., Langmuir (2001)

NANOSTRUCTURE-VISCOELASTICITY CORRELATION

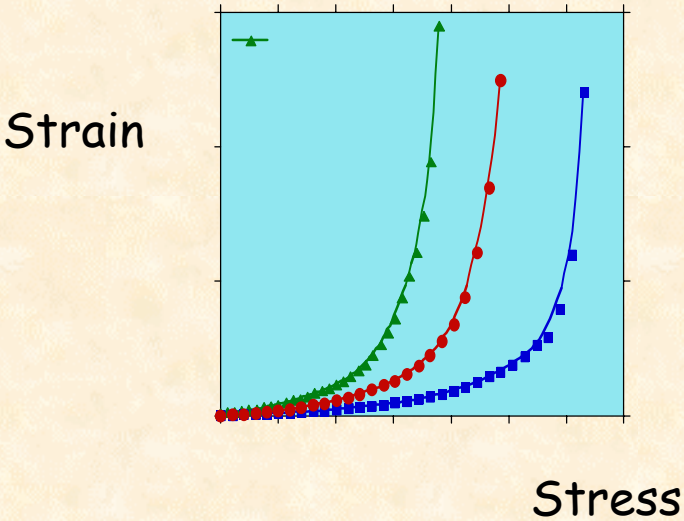
* Cross-sectional Morphology :

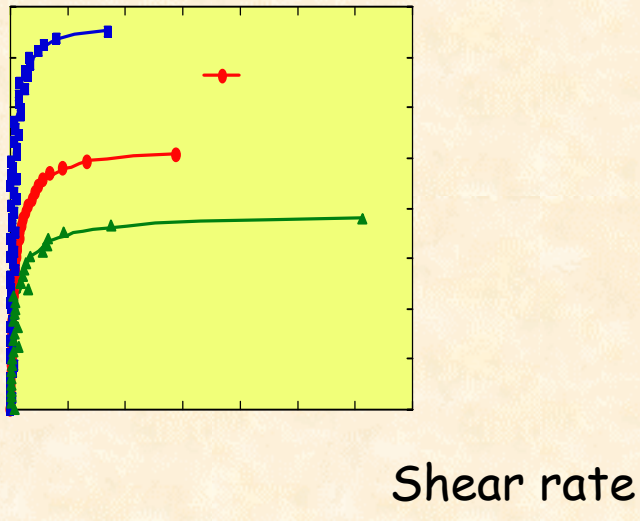


Sizes in toluene: 21.4 x 21.4 nm

Toluene Cyclohexane Nitrobenzene

* Yield Stress :

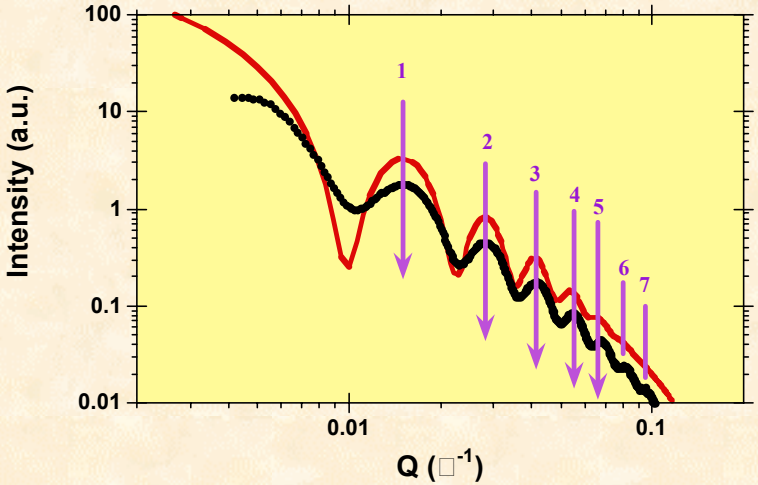




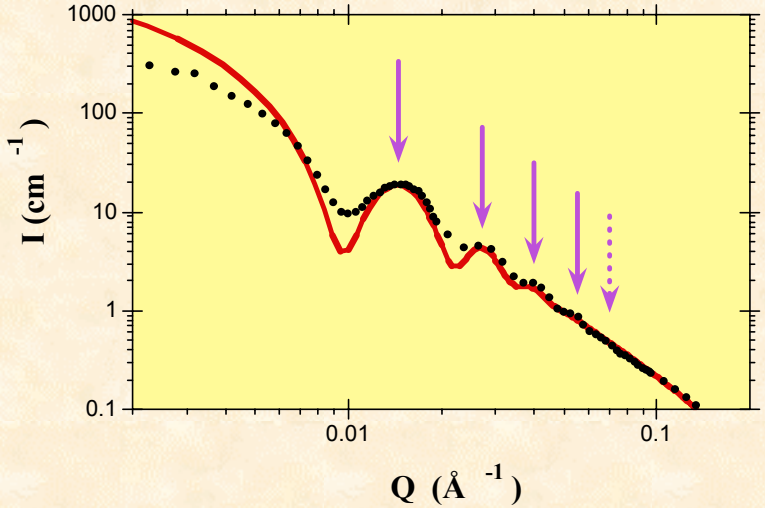
Sequence: Nitrobenzene > Dodecane > Toluene

STEROID NANOTUBES

SAS Characterization



Synchrotron source : ESRF, Grenoble



Neutron source : ILL, Grenoble

$$I_F^C(Q) \propto [(J_1(QD_e/2)/(QD_e/2)) - (D_i/D_e)^2 (J_1(QD_i/2)/(QD_i/2))]^2$$

Monodisperse cross-sections

D_e = 52 nm D_i = 49 nm

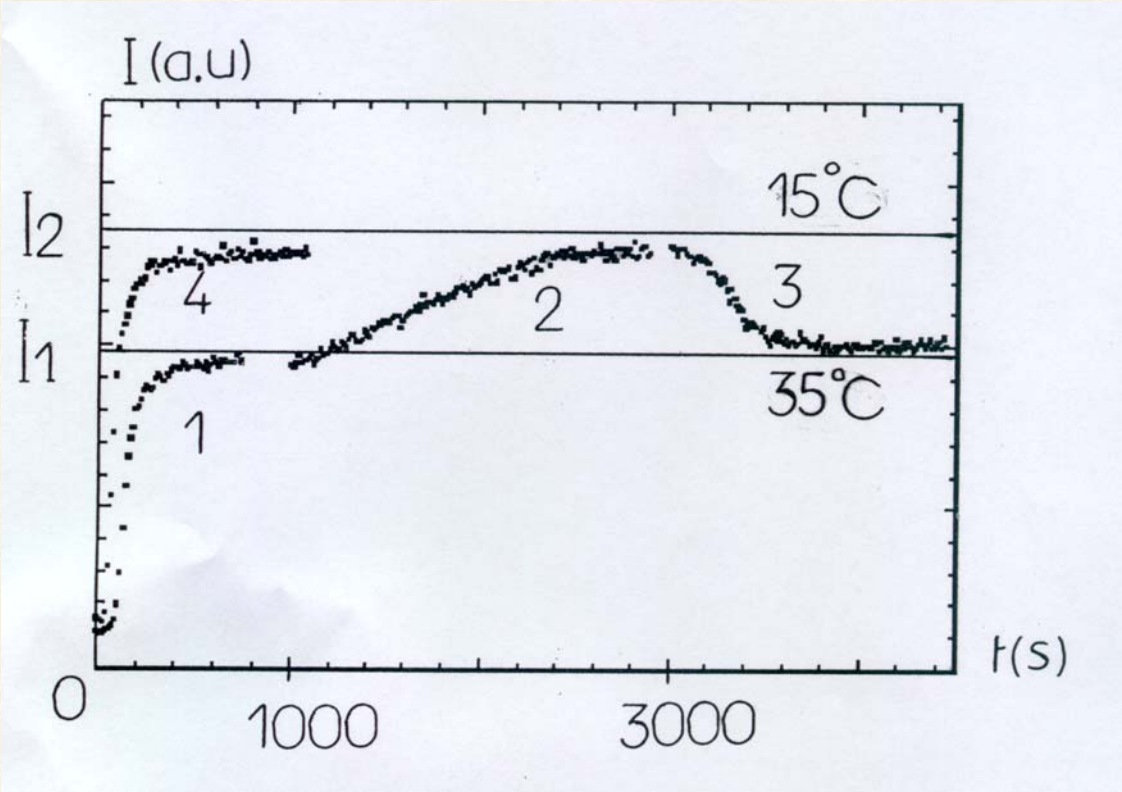
Single-Walled Nanotubes

P. Terech & Y. Talmon, Langmuir (2002)

Molecular gels

Thermoreversibility/Kinetics of the aggregation process

Androstanol derivative STNH/cyclohexane C= 0.059 g cm^{-3}

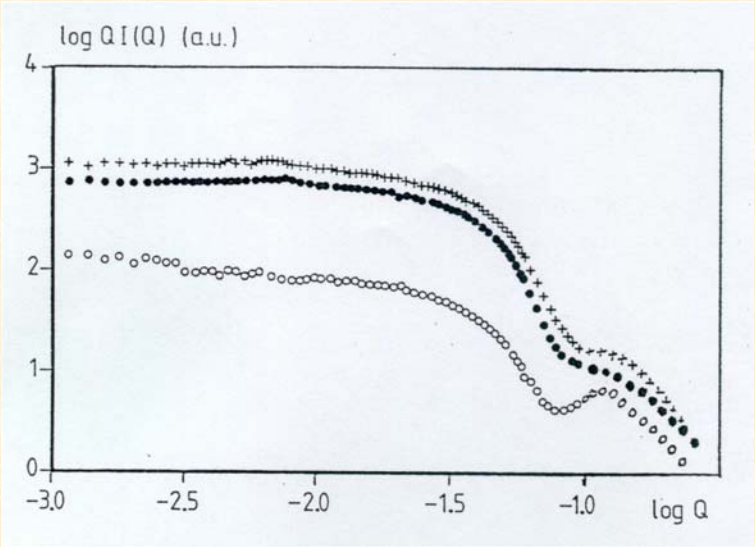


Integration of the total counts in a central window

$$\Delta Q = 0.008 - 0.2\ A^{-1}$$

P. Terech

Small Angle Neutron Scattering for Self-Assembled Fibrillar Networks



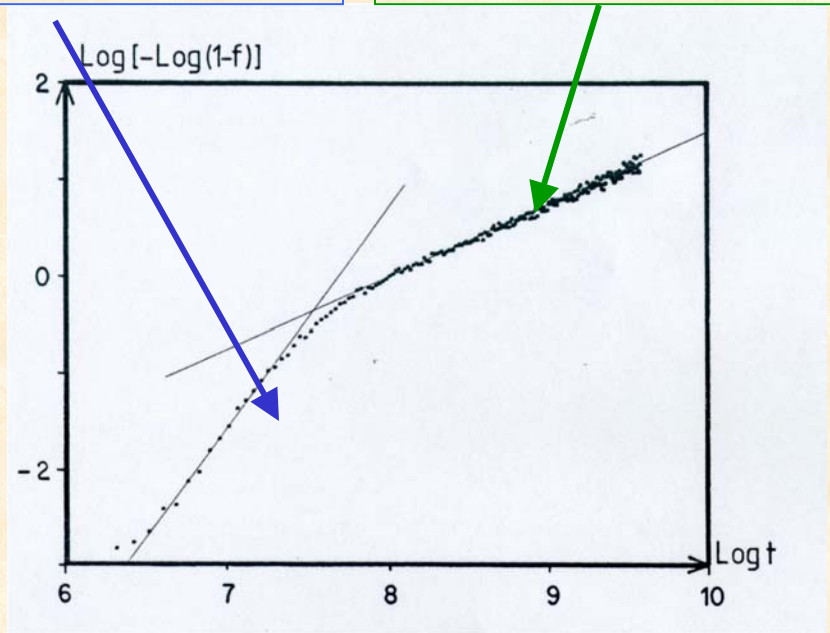
Kinetics

I= form-factor component during aggregation process

$$I(Q) = \pi C/Q\ \Delta b^2\ M_L\ [2\ J_1(Qr)/(Qr)]^2$$

Slope 2.3 (th.=2.0)

Slope 0.8 (th.=1.0)



Heterogeneous kinetic model

Avrami laws (*vs.* fractal model)

$t \to 0 \quad 1-f(t) \sim \exp(-Kt^{n+1})$

$t \gg 0 \quad 1-f(t) \sim \exp(-Kt^{n})$

n : dimensionality of the aggregate growth