Ionic-Self Assembly (ISA) as a route towards (highly ordered,liquid crystalline) nanomaterials with new architecture

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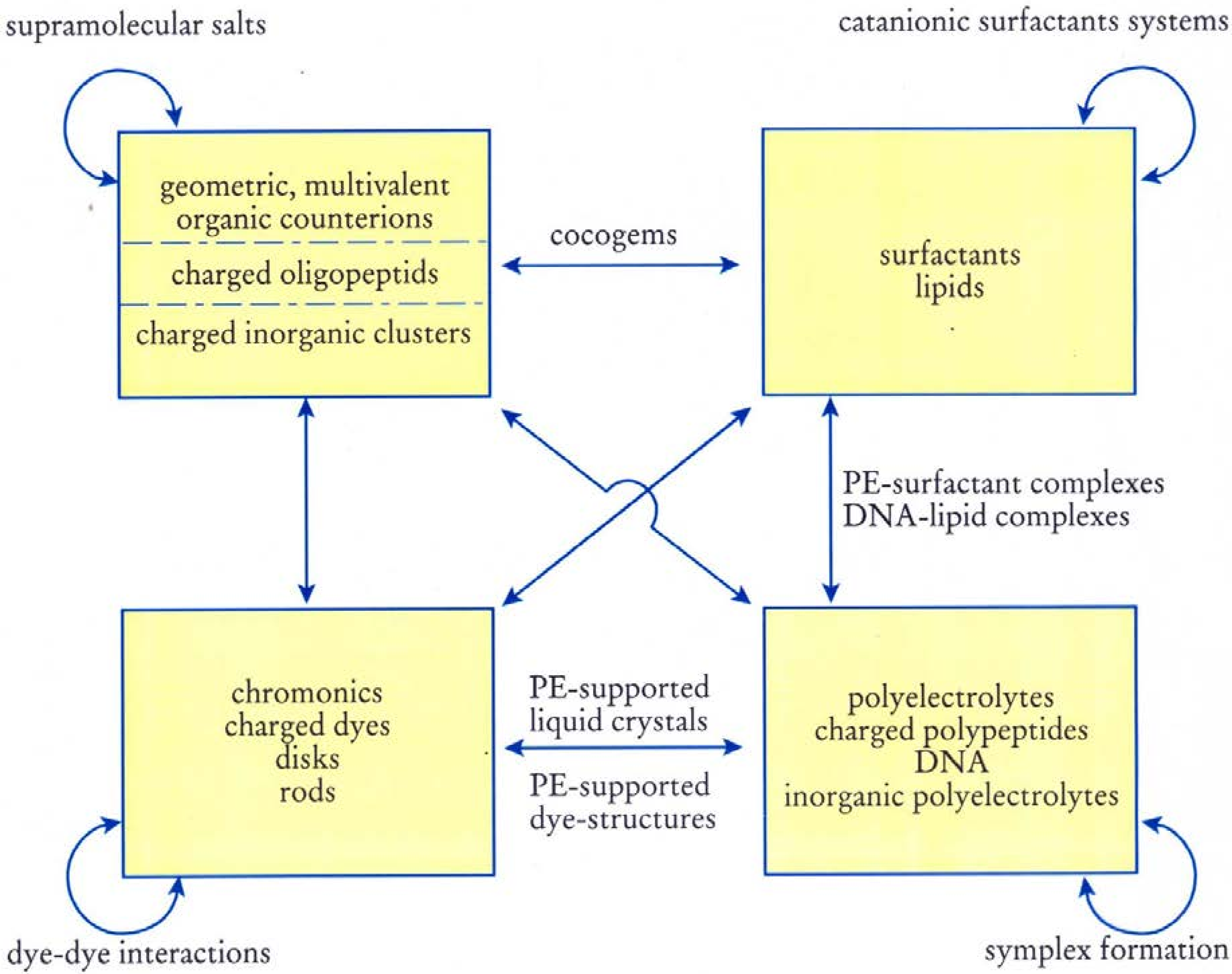

supramolecular salts
catanionic surfactants systems
geometric, multivalent organic counterions
charged oligopeptids
charged inorganic clusters
cocogems
surfactants
lipids
PE-surfactant complexes
DNA-lipid complexes
chromonics
charged dyes
disks
rods
PE-supported liquid crystals
PE-supported dye-structures
polyelectrolytes
charged polypeptides
DNA
inorganic polyelectrolytes
dye-dye interactions
symplex formation

Polyanion-Polycation complexes

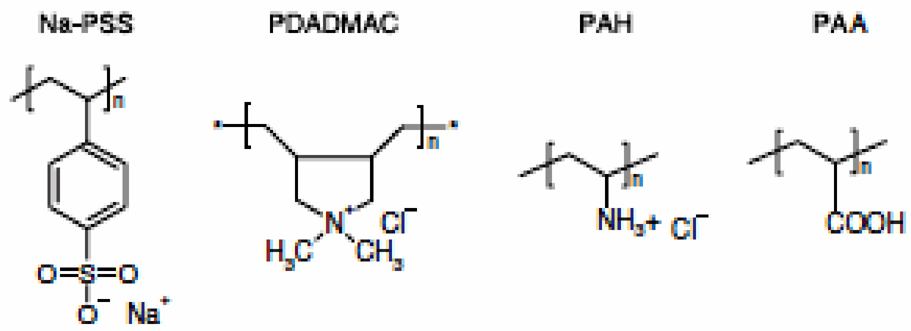


Figure 1. Polyelectrolytes employed for the self-assembly of multilayers.

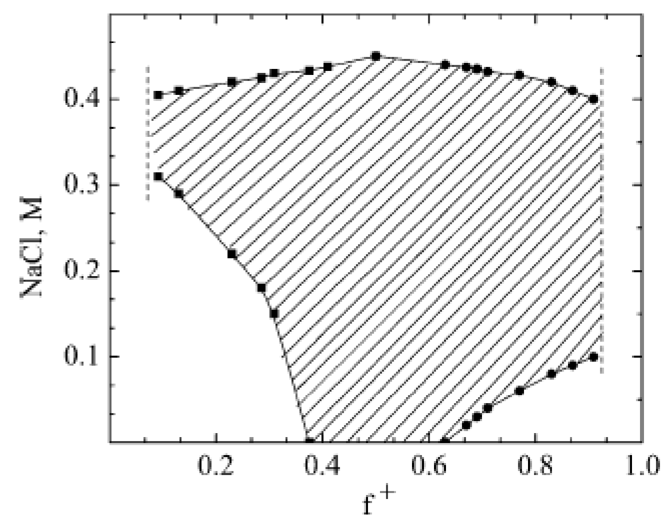


Figure 3. Phase diagram for QPVP/PMAA/NaCl mixtures in aqueous solution at pH 8.4 supported by 0.01 M phosphate buffer. Concentrations of polymers were 0.001 M, and degrees of polymerization of QPVP and PMAA were 900 and 1700, respectively.

precipitates from water,

easy synthesis

Strong and weak electrolytes behave differently

Classical in food and drug industry: ccoacervation

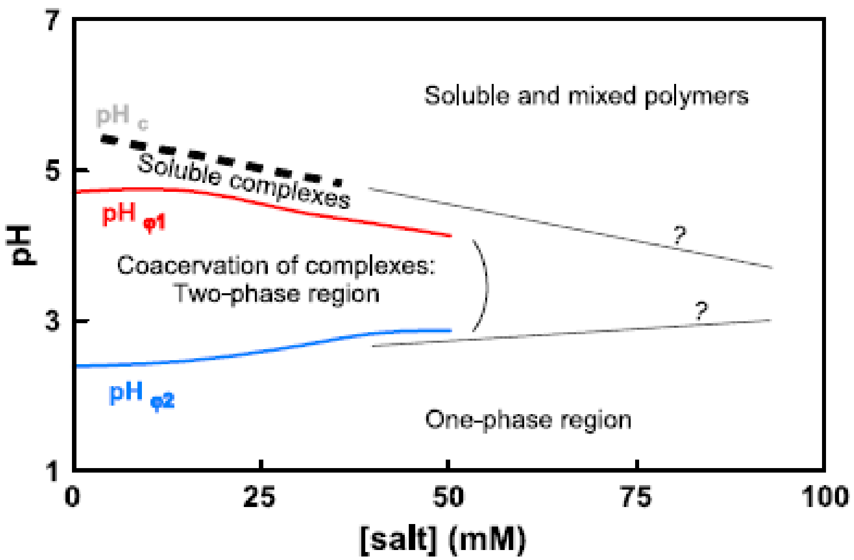


Fig. 1. Cartoon of two self-assembled complexes of gum arabic (white ribbon) and β-lactoglobulin (dark spheres). The complex as a whole is considered as a new colloidal entity. The picture is approximately to scale, a protein is 4 nm in diameter and the gum arabic has a diameter of approximately 50 nm.

			flocculated particles)
Weak (carboxylated) PE/gelatin	Xanthan gum/gelatin	Lii et al. [71]	Coacervation
Weak (carboxylated) PE/gelatin	Gum arabic/gelatin	Peters et al. [72]	Coacervation
Weak (carboxylated) PE/gelatin	Sodium carboxymethyl guar gum/gelatin	Thimma and Tammishetti [62]	Coacervation
Weak (carboxylated) PE/globular protein	Low and high methylated pectin/β-lactoglobulin	Girard et al. [19**,33–36]	Coacervation ? (although referred to as electrostatic complexes)
Weak (carboxylated) PE/globular protein	High-methoxyl pectin/β-lactoglobulin	Kazmiersi et al. [73]	Precipitation for a modified pectin with higher charge density
Weak (carboxylated) PE/globular protein	Xanthan gum/whey protein	Laneuville et al. [74]	Coacervation ? (fibrous complexes)
Weak (carboxylated) PE/globular protein	Gum arabic/β-lactoglobulin	Sanchez et al. [75–77]	Coacervation
Weak (carboxylated) PE/globular protein	Gum arabic/β-lactoglobulin	Schmitt et al. [25,78–80]	Coacervation
Weak (carboxylated) PE/plant protein	Carboxy methyl cellulose/potato proteins	Vikelouda and Kiosseoglou [81]	Precipitation
Weak (carboxylated) PE/globular protein	Gum arabic/whey proteins	Weinbreck et al. [21,30**,31,37,47**,82]	Coacervation
Cationic polysaccharide/plant protein	Chitosan/faba bean legumin	Plashchina et al. [83]	Precipitation
Two polysaccharides (weak PE/chitosan)	Alginate/chitosan	Yan et al. [84,85]	Coacervation
Two polysaccharides (strong PE/chitosan)	Carrageenan/chitosan	Shumilina and Shchipunov [86]	Precipitation
Strong (sulfated) PE/gelatin	κ-carrageenan/gelatin	Antonov and Gonçalves [87]	Precipitation
Strong (sulfated) PE/globular protein	ι- or κ-carrageenan or dextran sulfate/bovine serum albumin	Galazka et al. [88]	Precipitation
Strong (sulfated) PE/globular protein	ι-carrageenan/poly(L-lysine)	Girod et al. [26]	Coacervation
Strong (sulfated) PE/globular protein	Dextran sulfate/sodium caseinate	Gurov et al. [89]	Precipitation

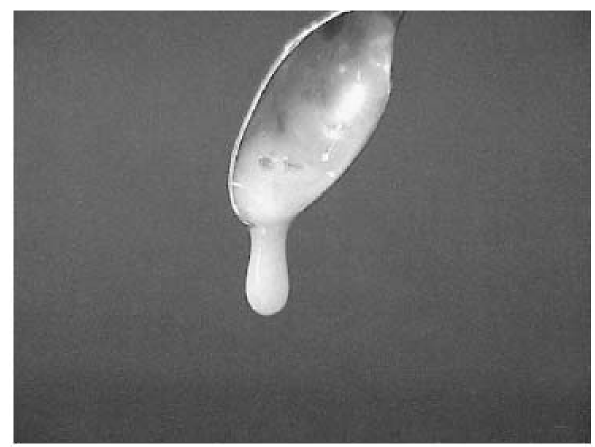
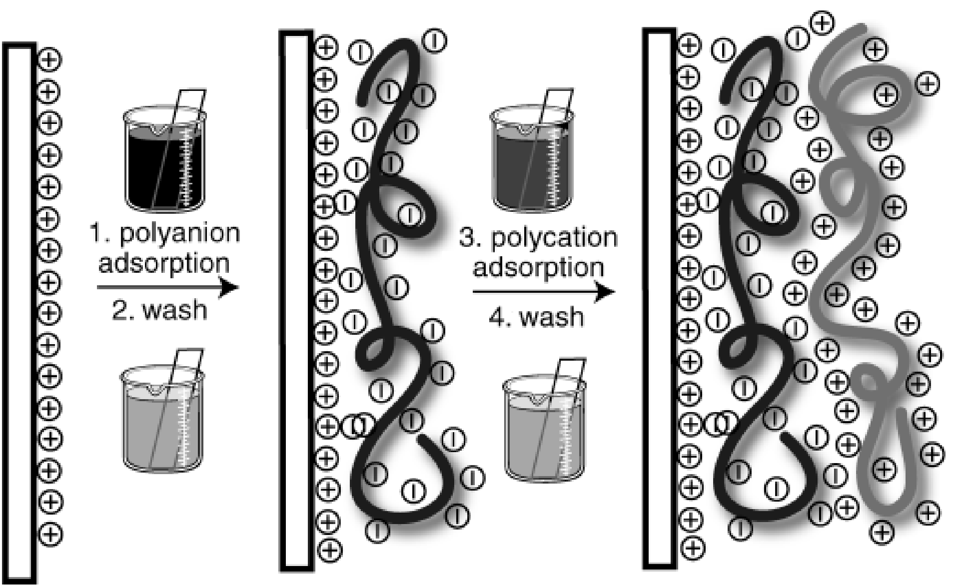
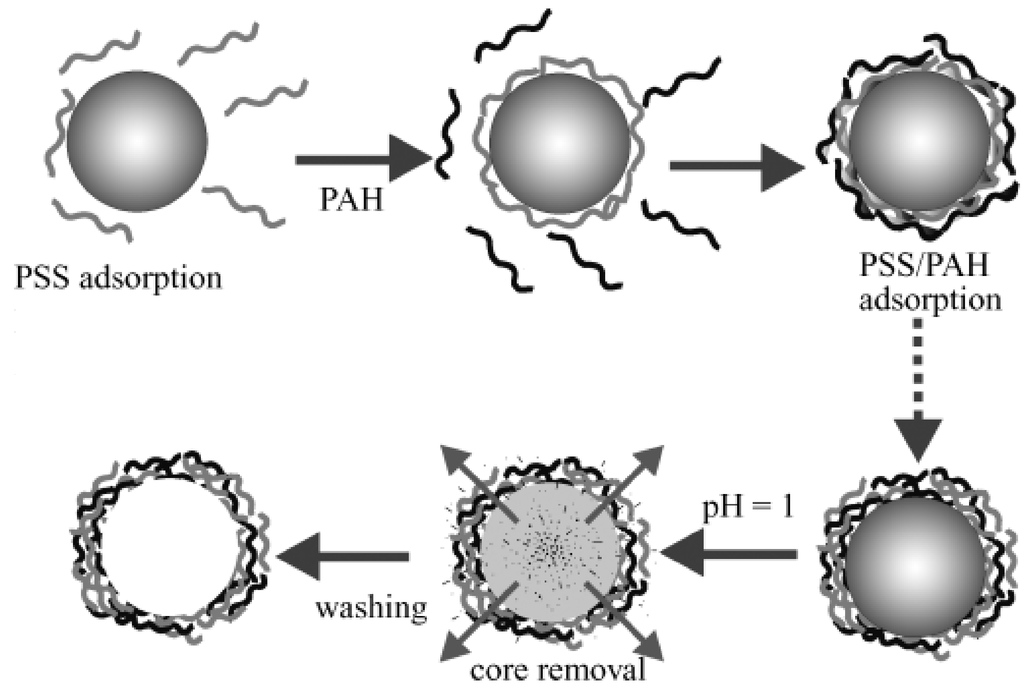


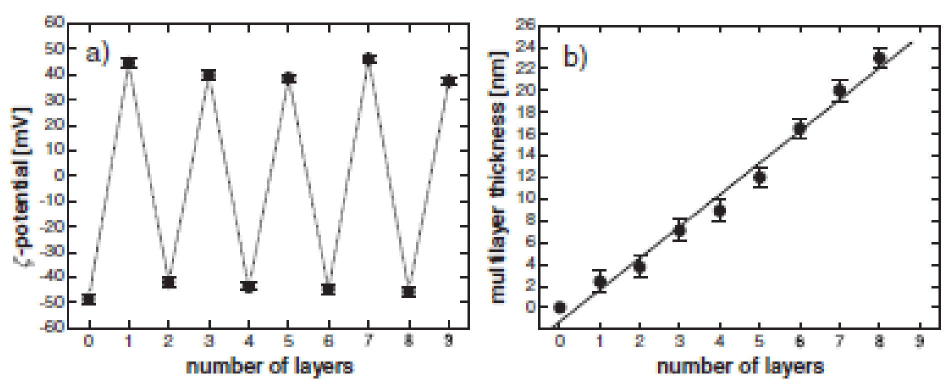
Fig. 4. Whey protein/gum arabic concentrated coacervate phase pored with a spoon. The coacervate is very viscous in nature.

Polyanion-Polycation complexes: layer-by-layer technologies

G. Decher, H. Möhwald, F. Caruso



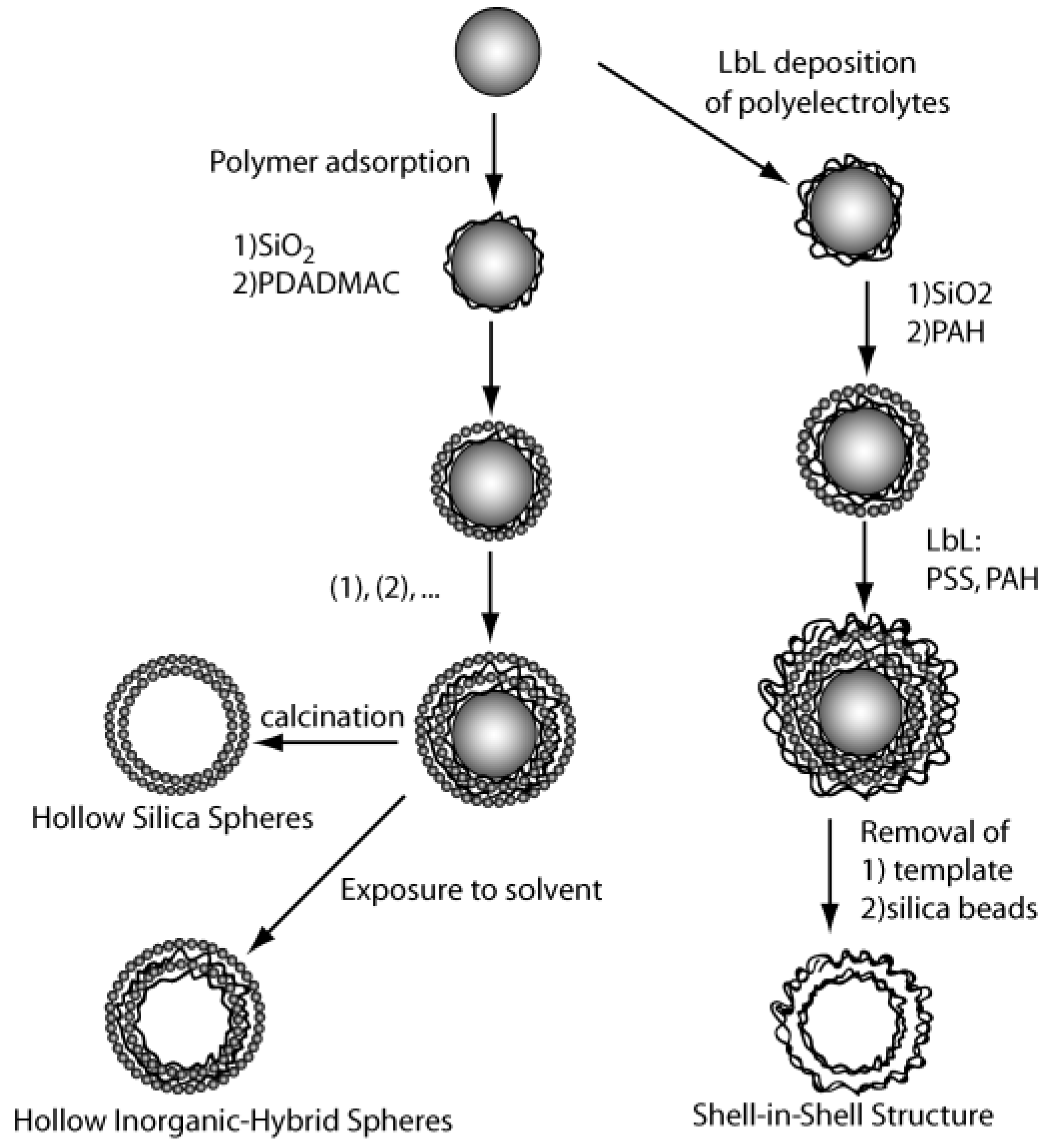




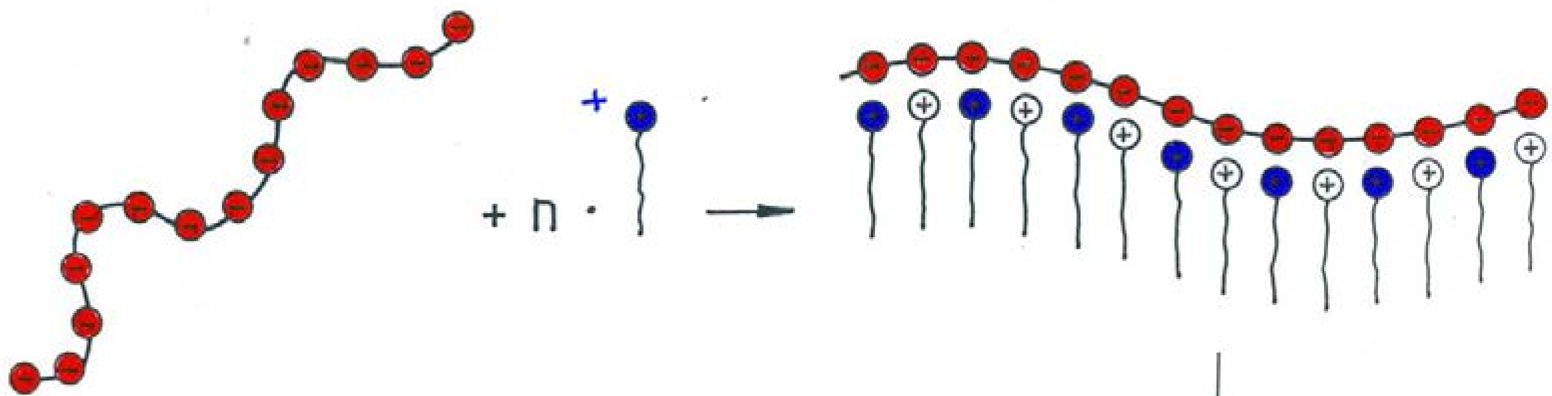
Polyanion-Polycation complexes: layer-by-layer technologies II

more complex structures,

Inorganic shells



Polyelectrolyte Surfactant complexes

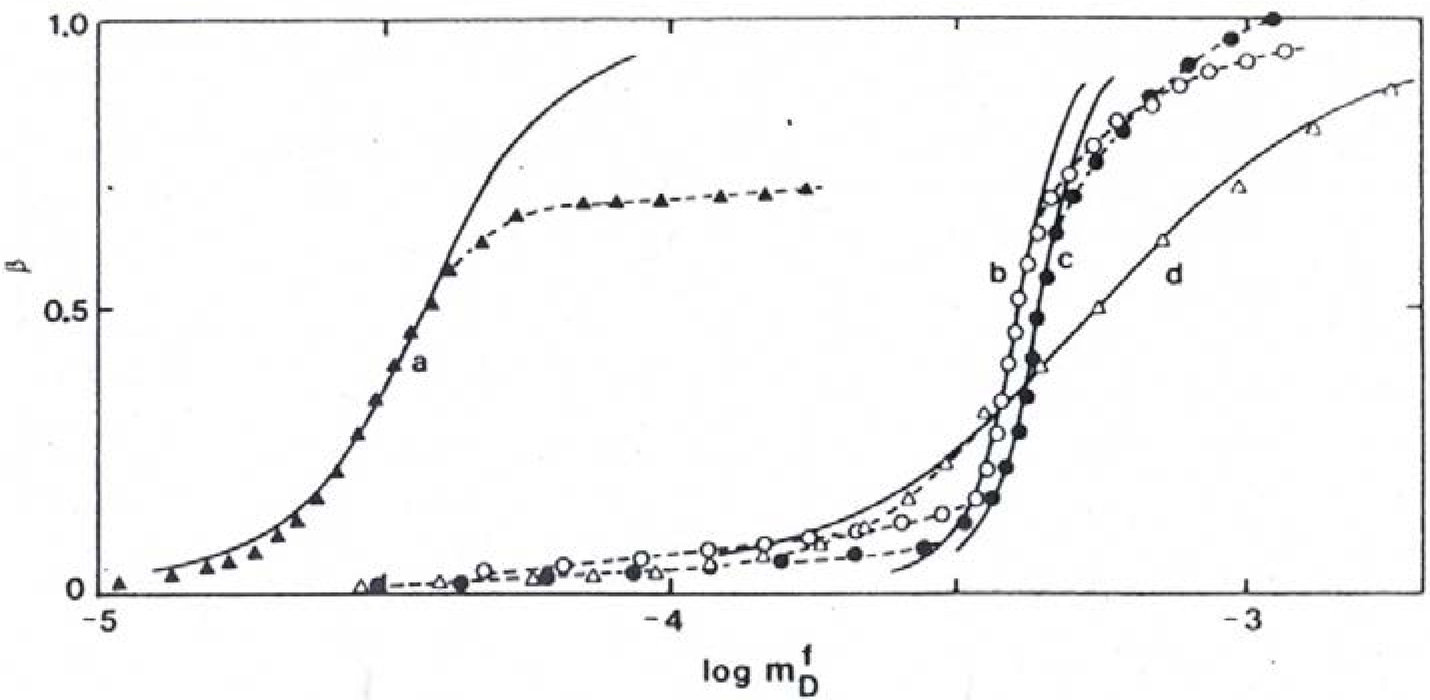


- formation highly cooperative
- 1: 1 complex
- dissolves in organic solvents
- film forming
- no Tg and softening

precipitates from water,

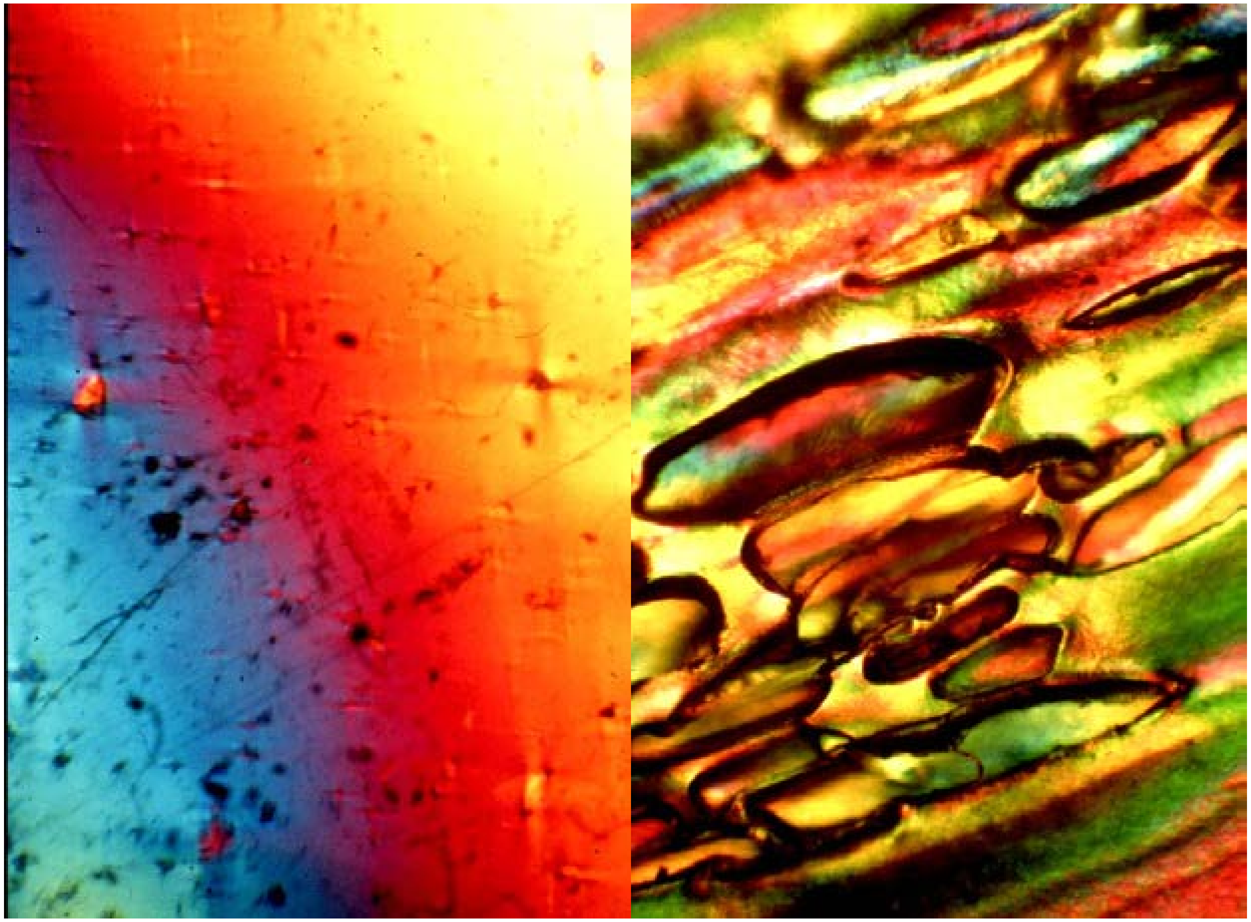
easy synthesis

Cooperativity of binding of PEs and surfactants



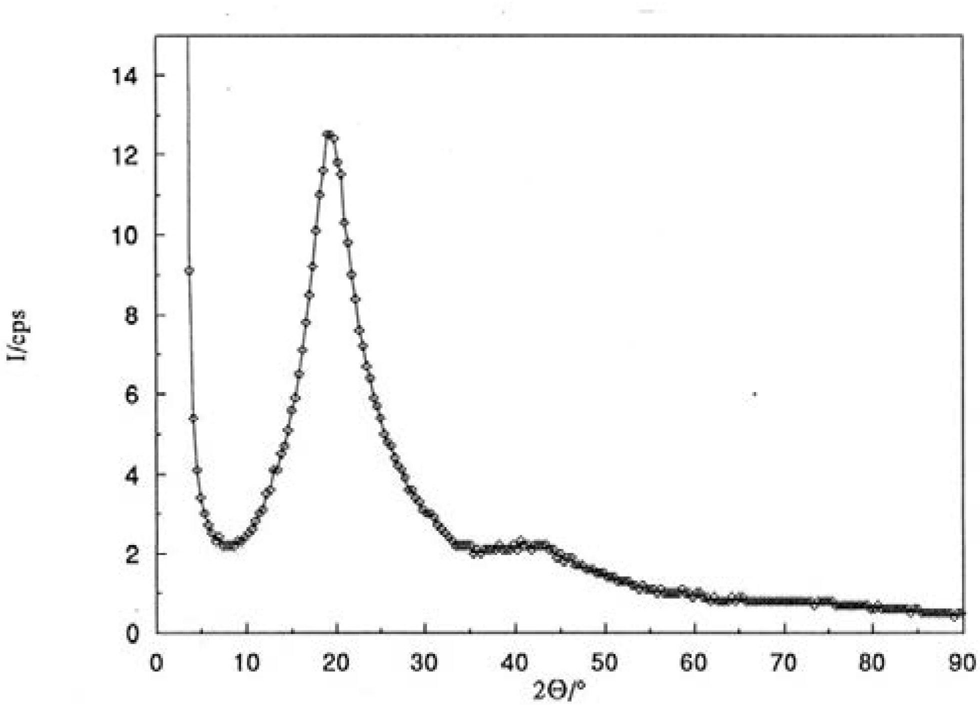
Binding isoterms of DTAB on a) polyacrylate;
b) alginate; c) pectate; d) CMC

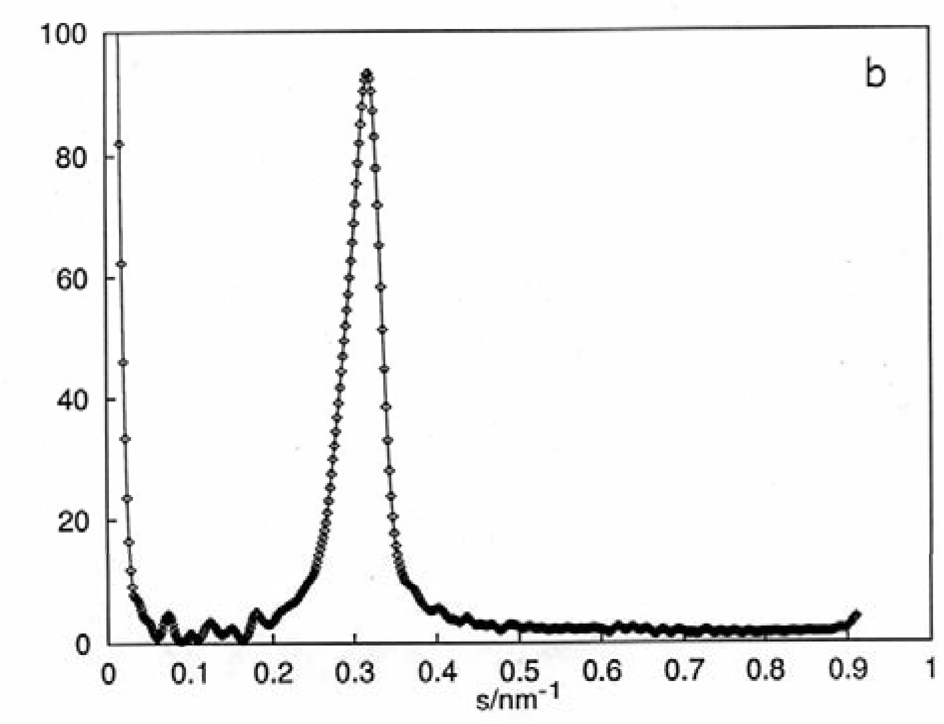
Polyelectrolyte complex films self-organize !



X-ray characterization of films

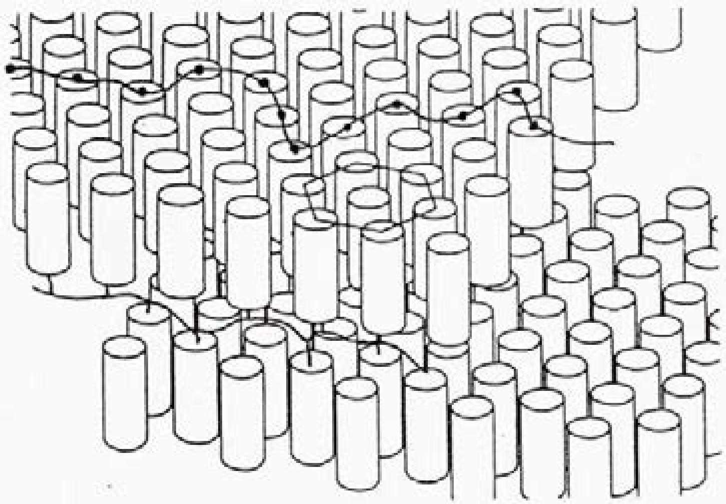
Na-PSS plus DTA-Br

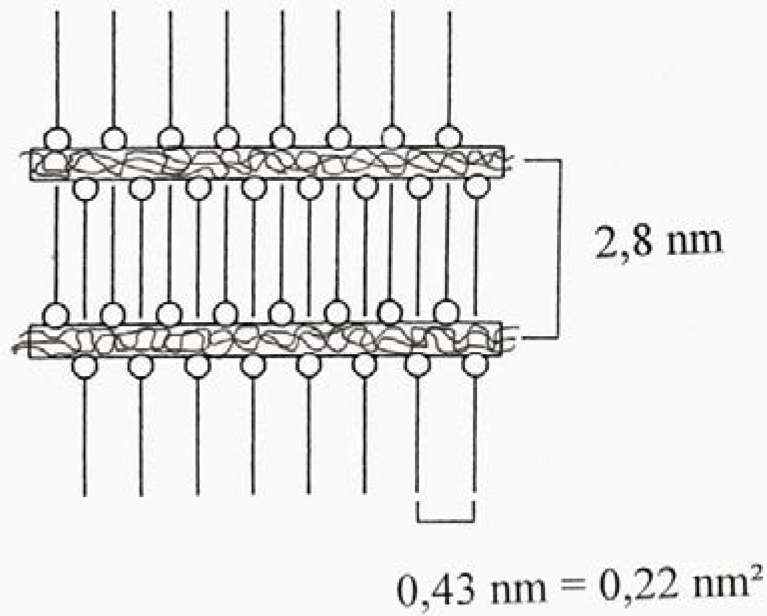




→The product is a highly oriented lyotropic liquid crystalline polymer !

Structure model



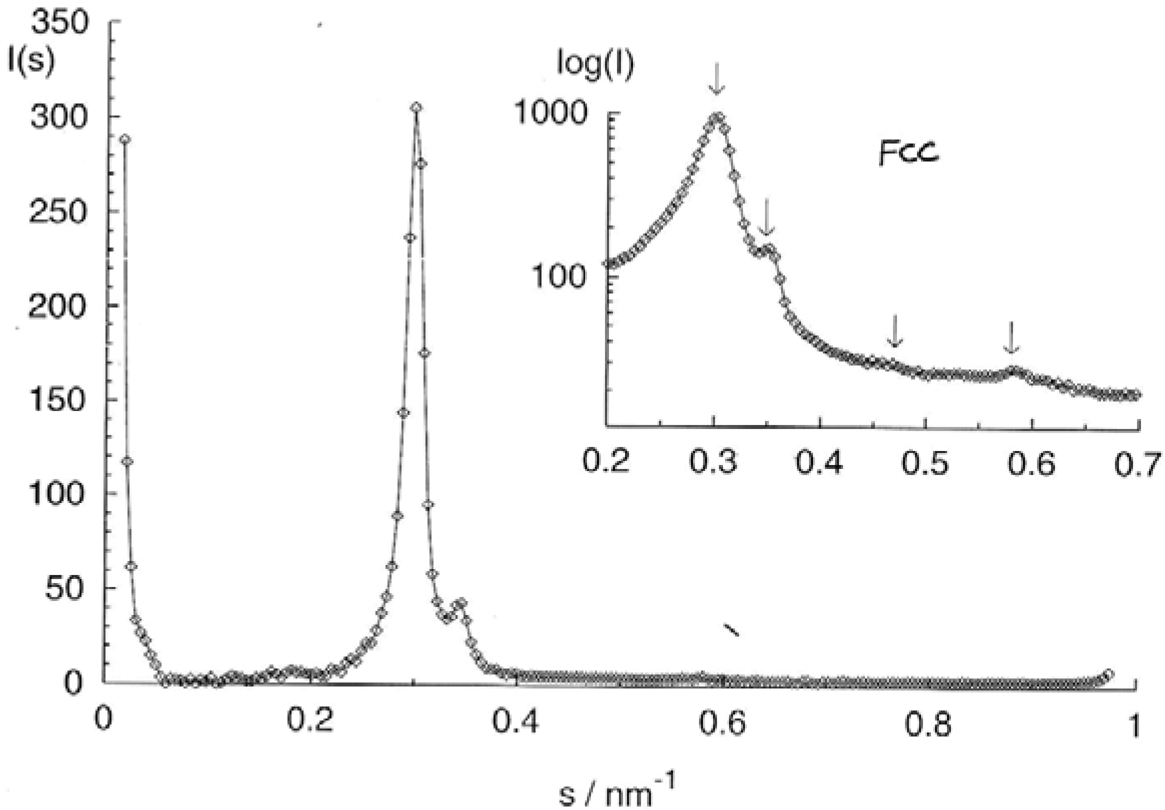


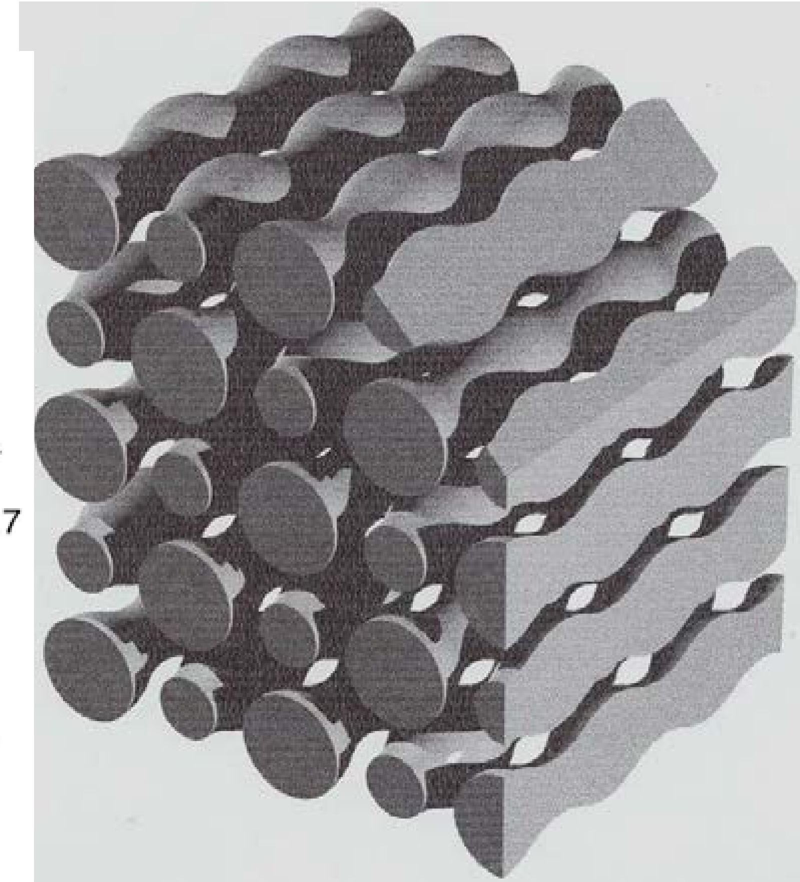
smectic S_A-phase:

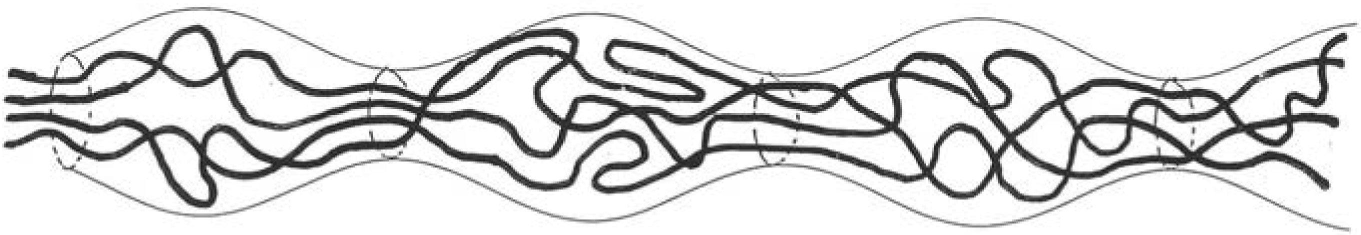
one flexible alkyl phase

one glassy ionic polymer phase

Structure of PAA with hydrophobic counterions

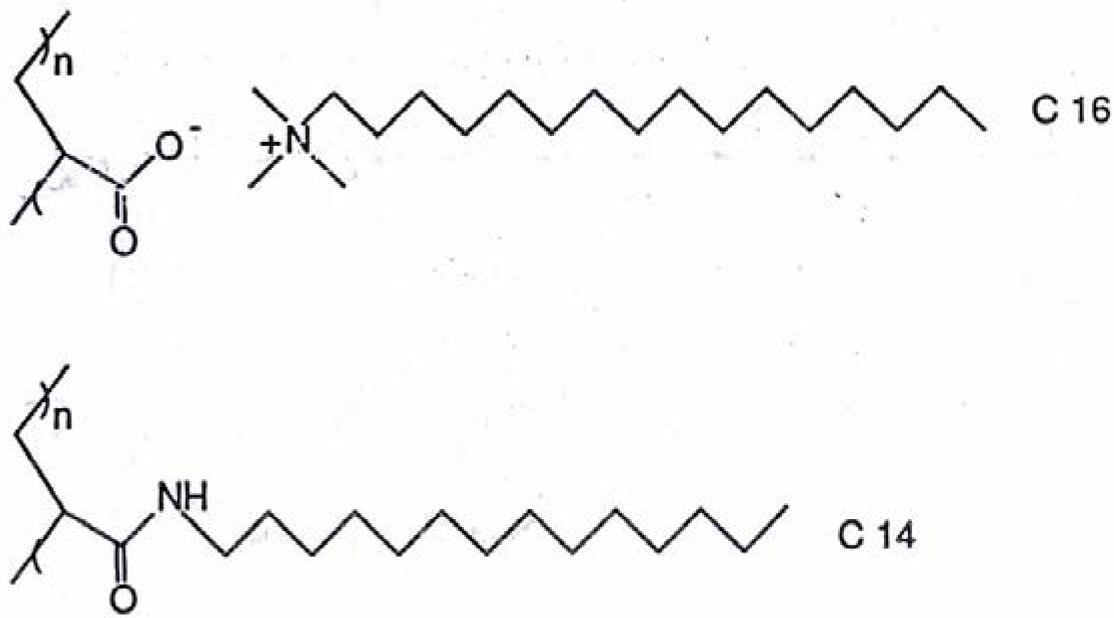






Conformation of single chains

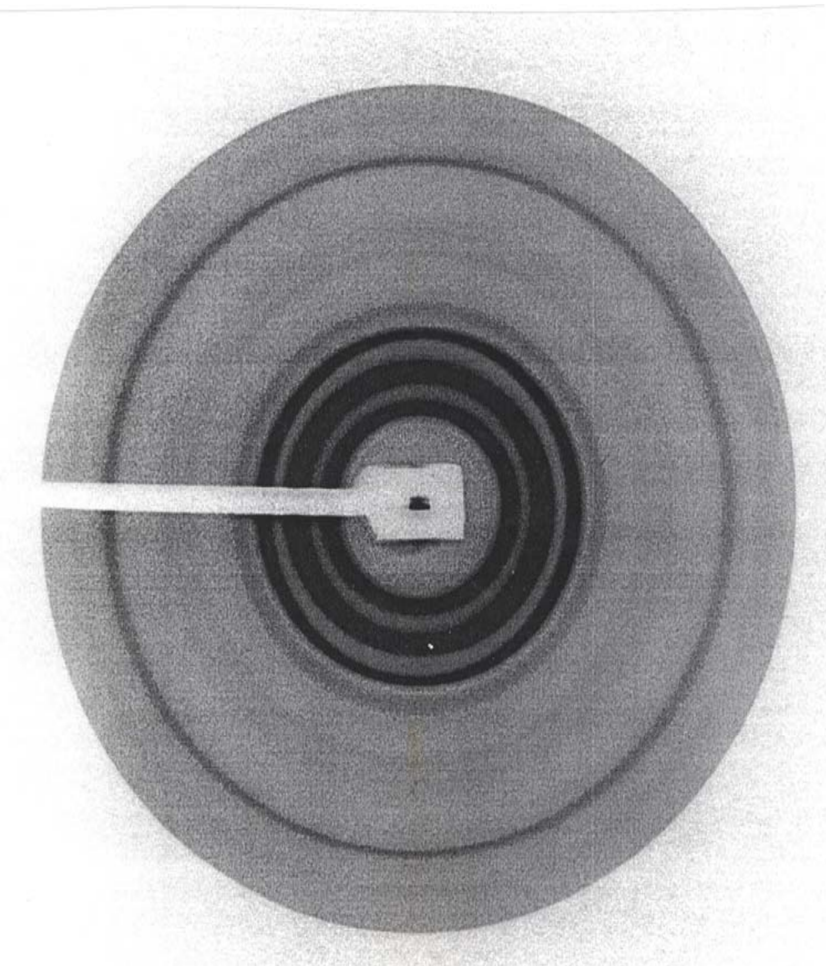
Thermoplastic PE-Surf complexes by copolymerization

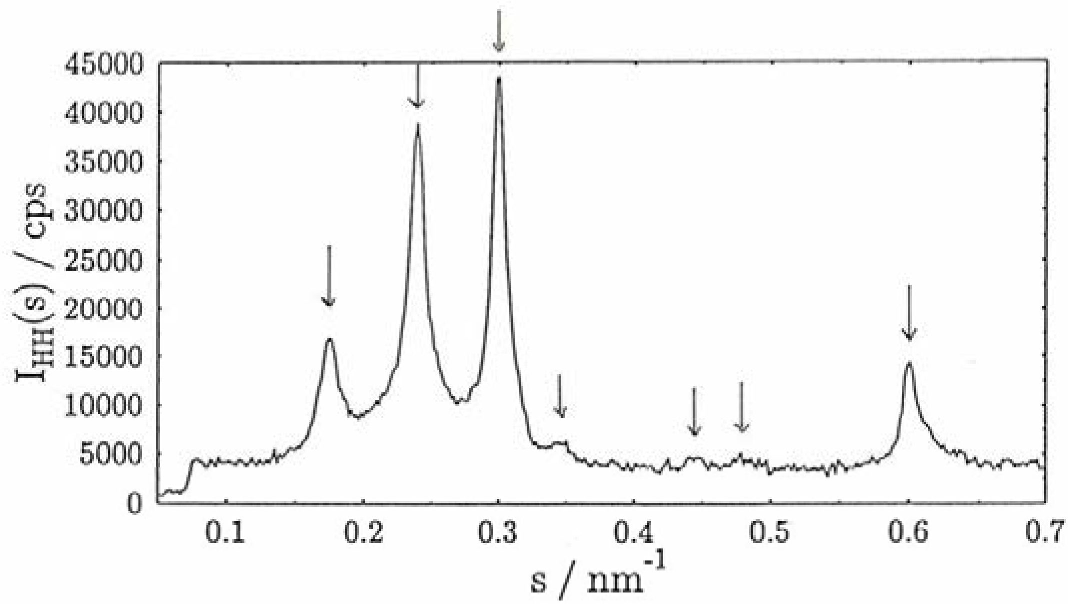


Choice of comonomers;

Different phases between $0 < x < 1$

An interesting phase for the 40:60 mixture

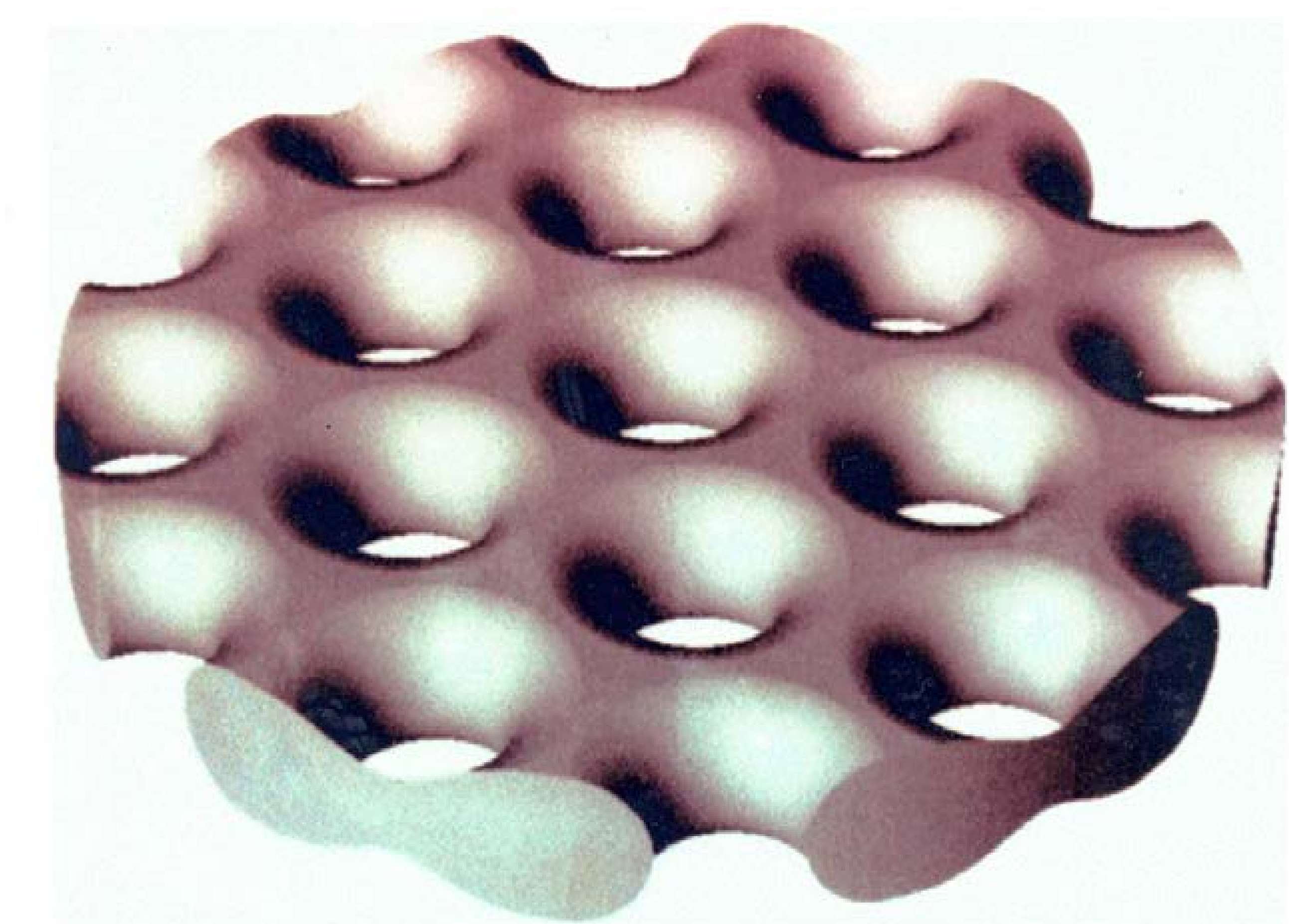




indexing according to cubic morphology, but in-plane oriented

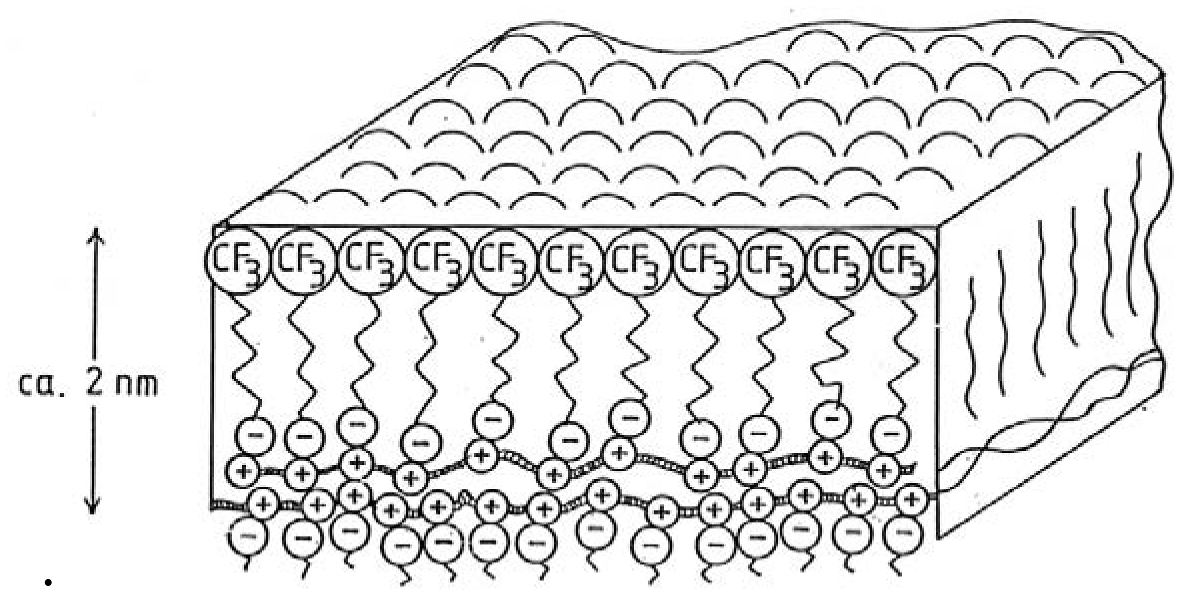
Synchroton radiation

The HPL phase



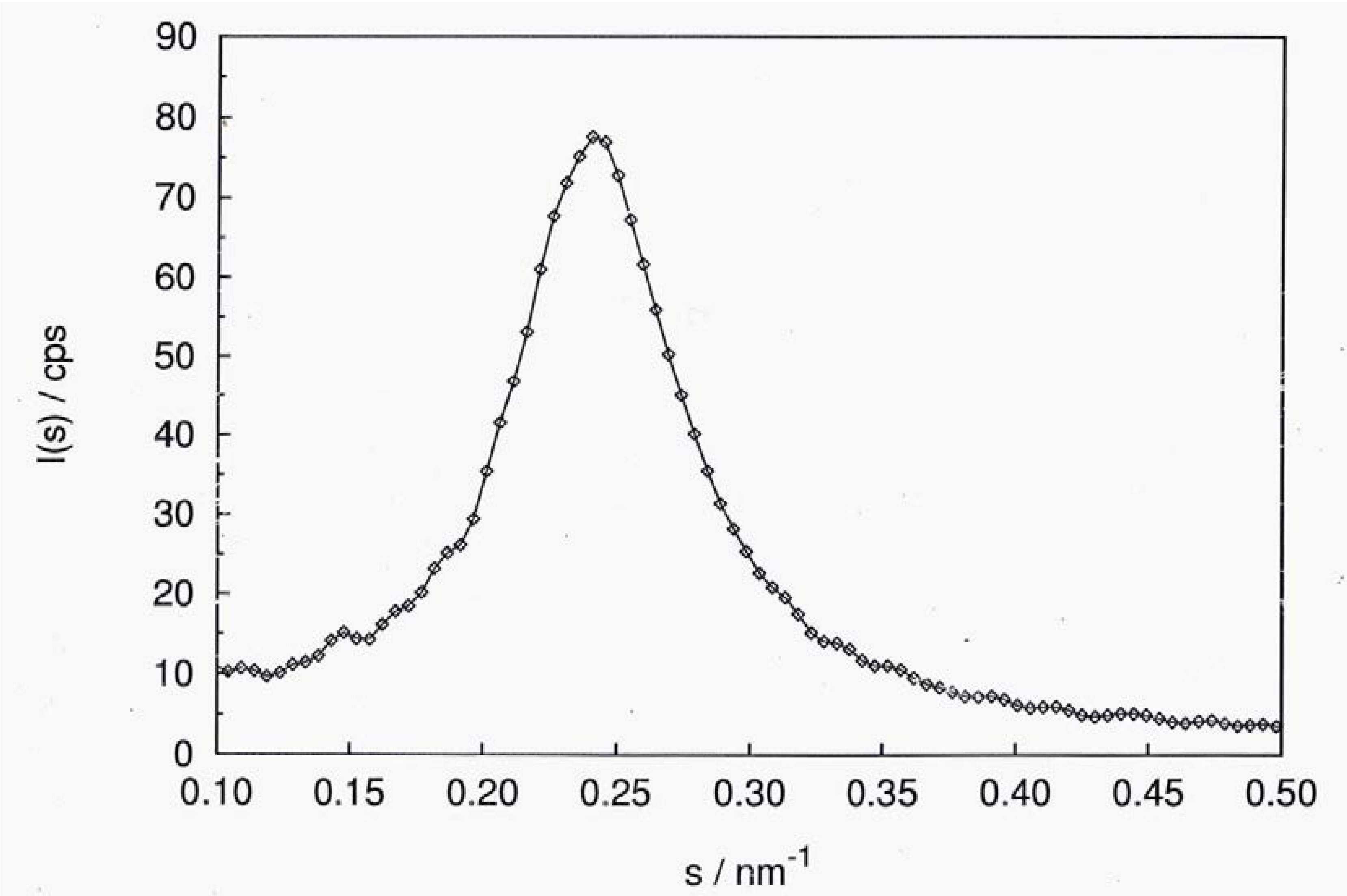
A polymeric molecular sieve film …

Fluorinated PE-Surfs: Coatings with ultralow surface tension

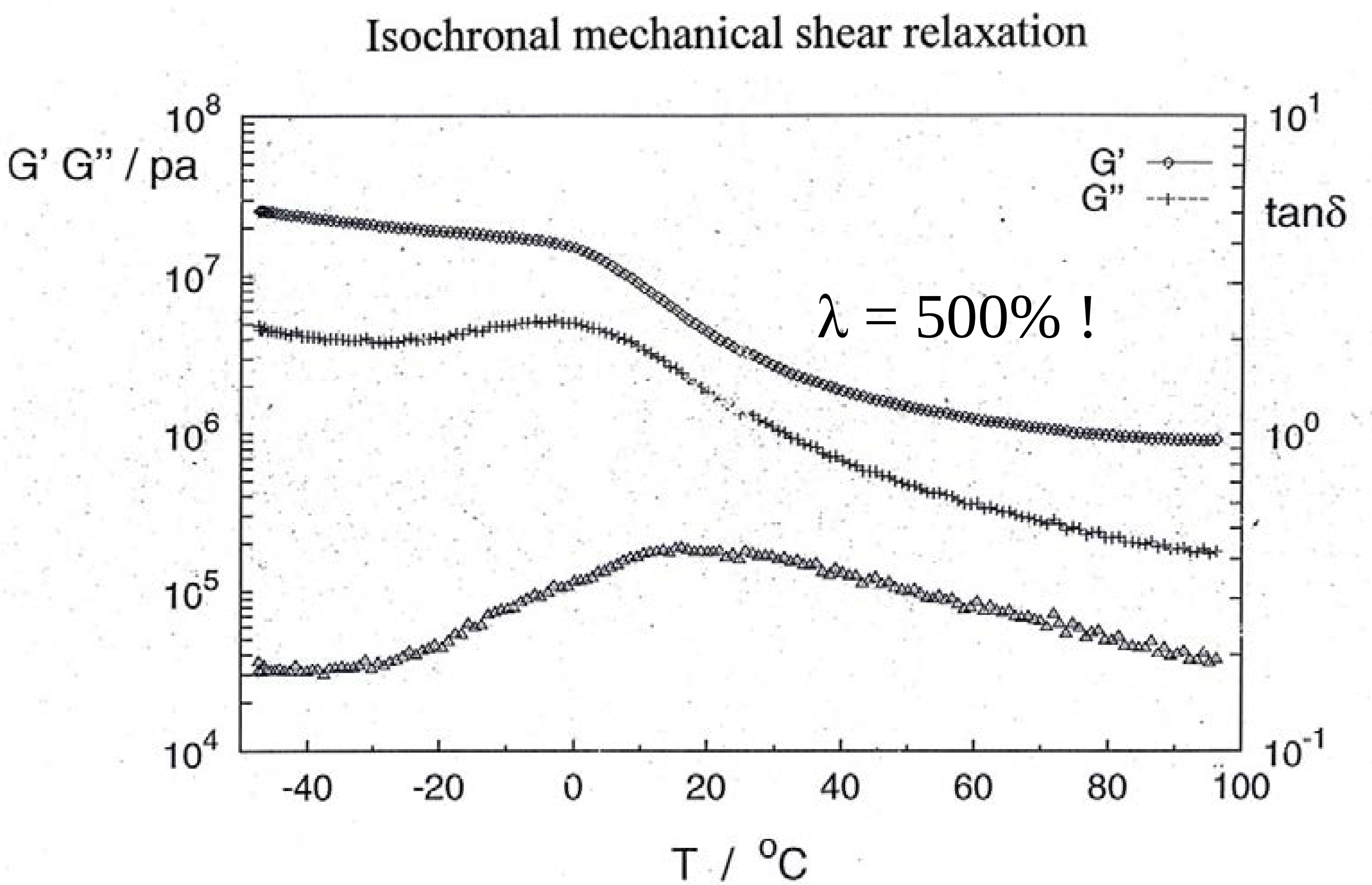


Surface energies against $C_{16}H_{34}$:	
Wool	50 mN/m
Iron	50 mN/m
PS	36 mN/m
PDMS	22,8 mN/m
PTFE	20,3 mN/m
PDA-K12	12,7 mN/m

PE-Lipid complexes: high end rubbers



Mechanical characterization



Qantitative evaluation of the SAXS data:

From the scattering data, the normalized autocorrelation function of the radial density γ (r) is calculated. This can be expanded as:

$$\gamma(r) = 1 - \frac{1}{l_P} \cdot r + \frac{b}{l_P} \cdot r^3 + O(r^4)$$

The Porod length l_p is easily transformed into a wavyness:

$$\frac{A}{A_0} = \frac{2d_1 \cdot d_2}{d \cdot l_p} = \left\langle \frac{1}{\cos\alpha} \right\rangle_{s_0}$$

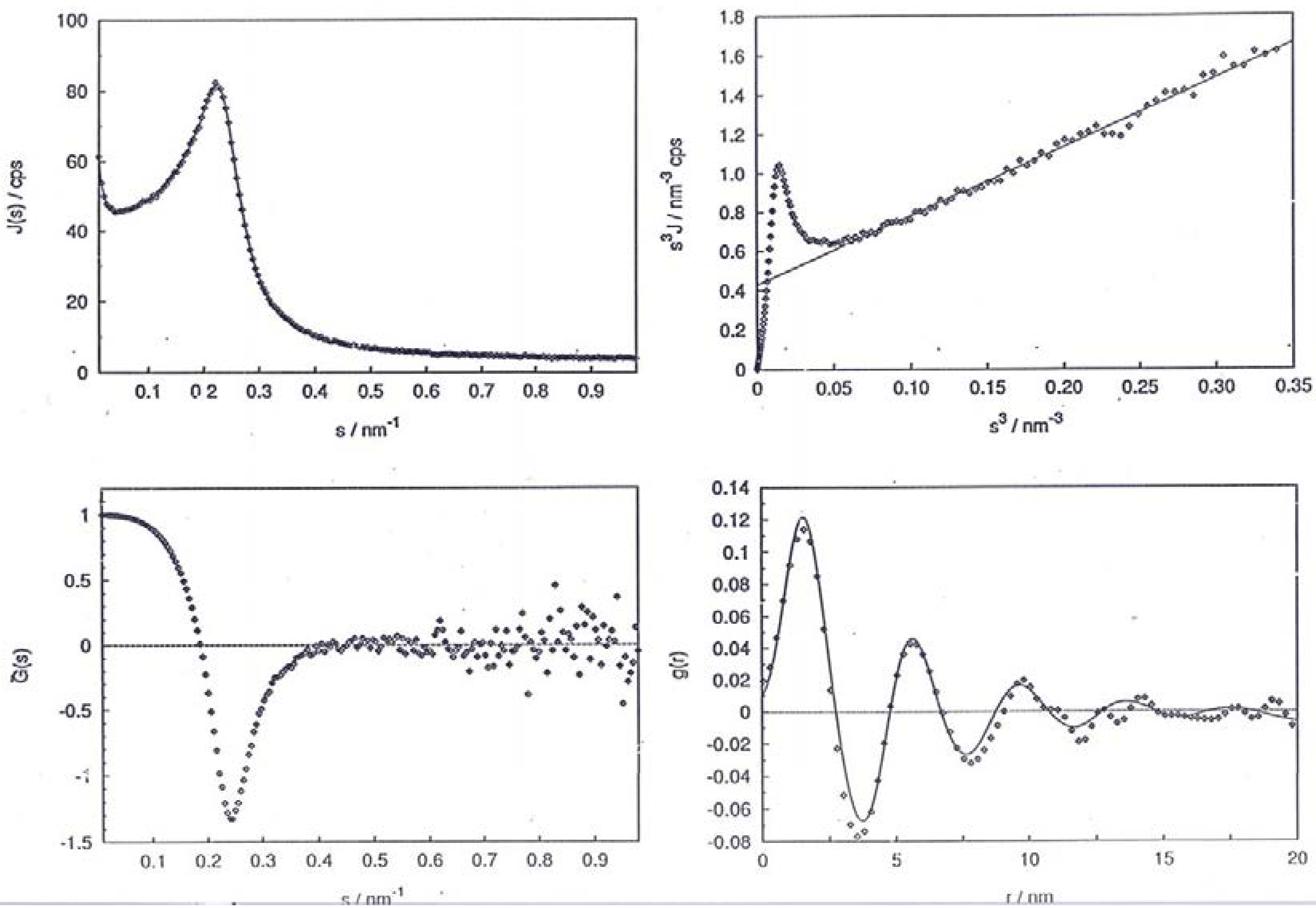
The cubic term is a measure for the interface curvature:

$$b = \frac{1}{8}\langle H^2 \rangle - \frac{1}{24}\langle K \rangle$$

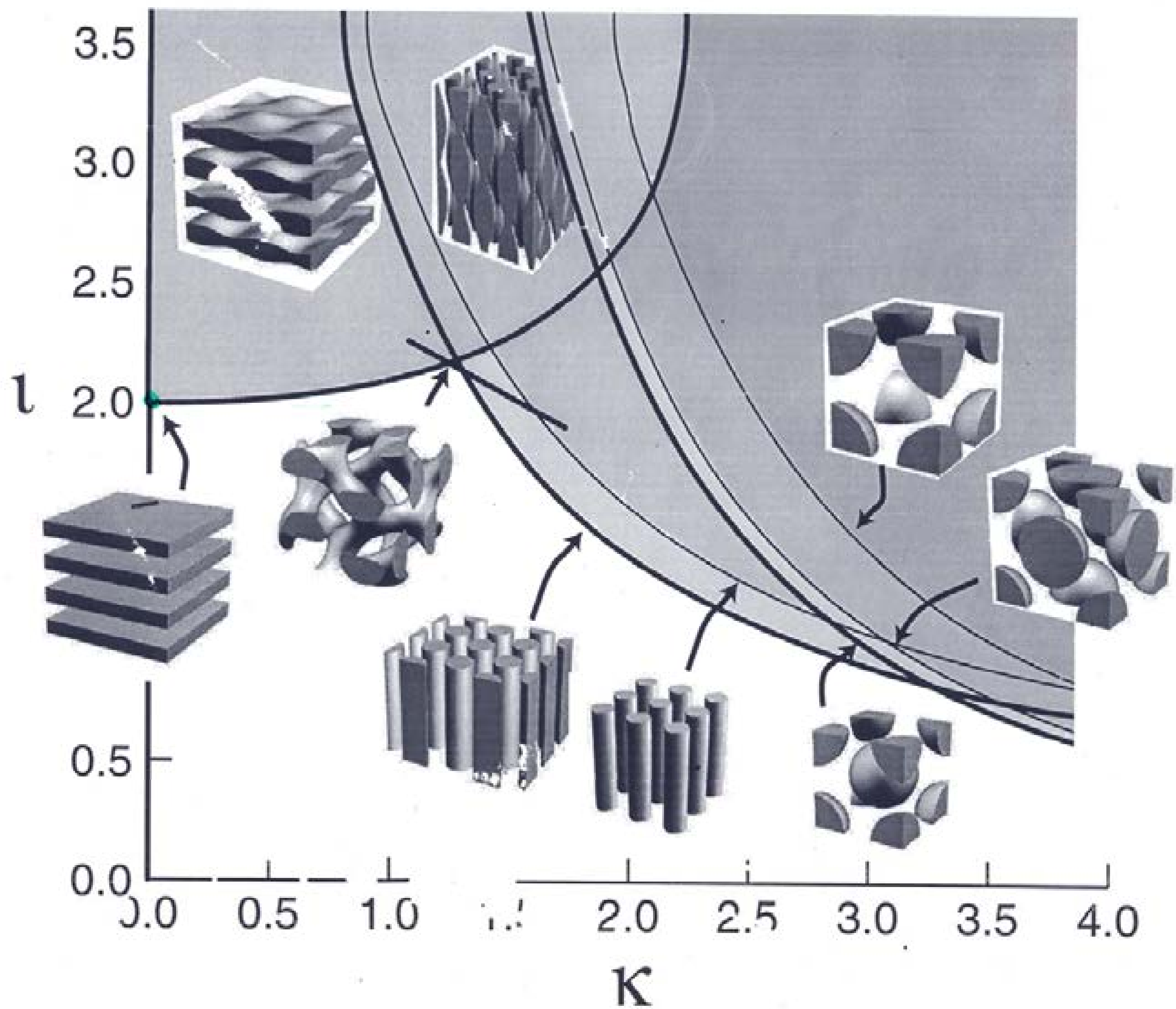
with b the Kirste - Porod - parameter, <K> the mean Gaussian curvature, and $<H^2>$ the mean square of the averaged curvature.

Procedure relies on good measurements at high s !

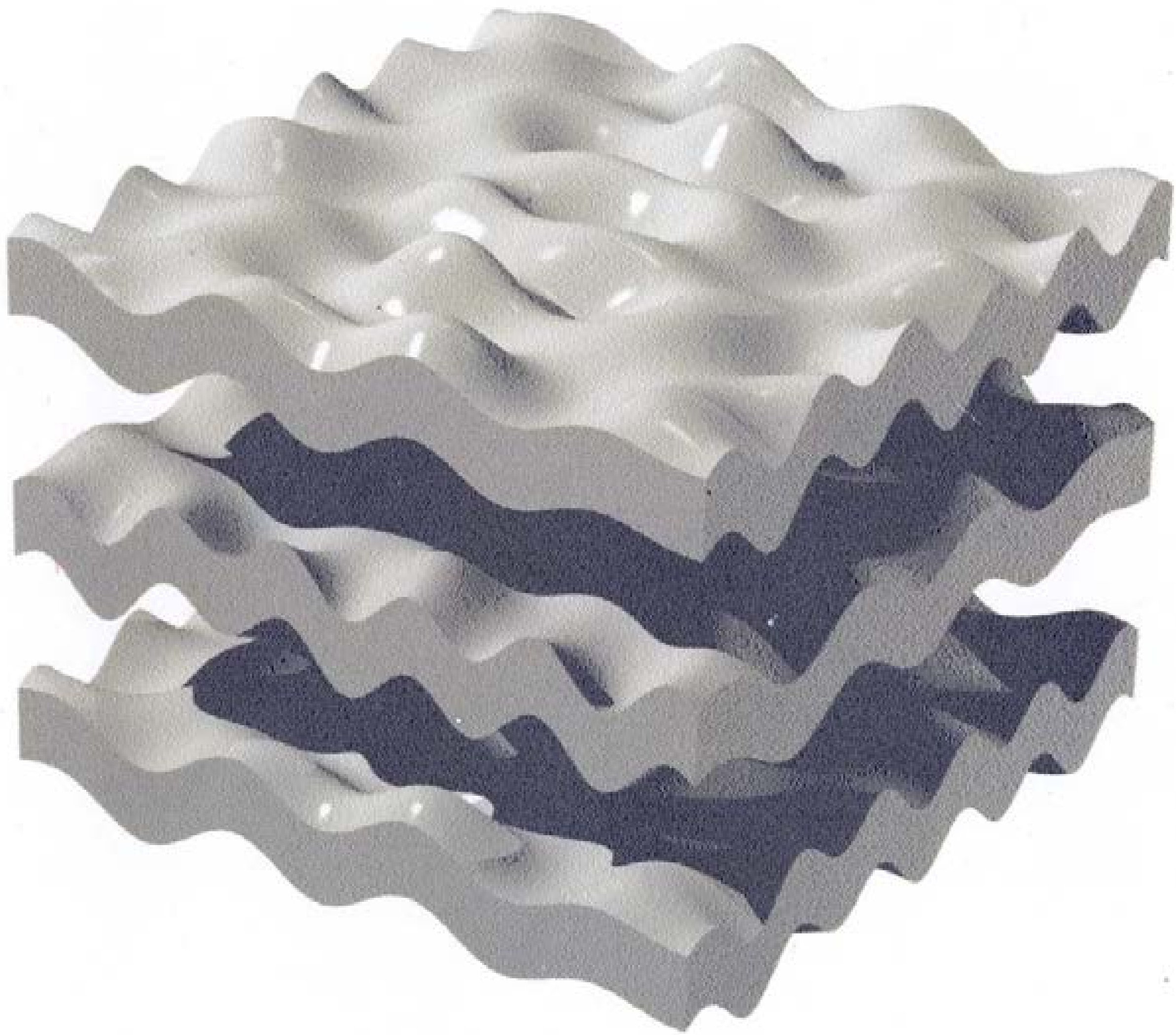
A walk through data evaluation….



The κ-ι- diagram



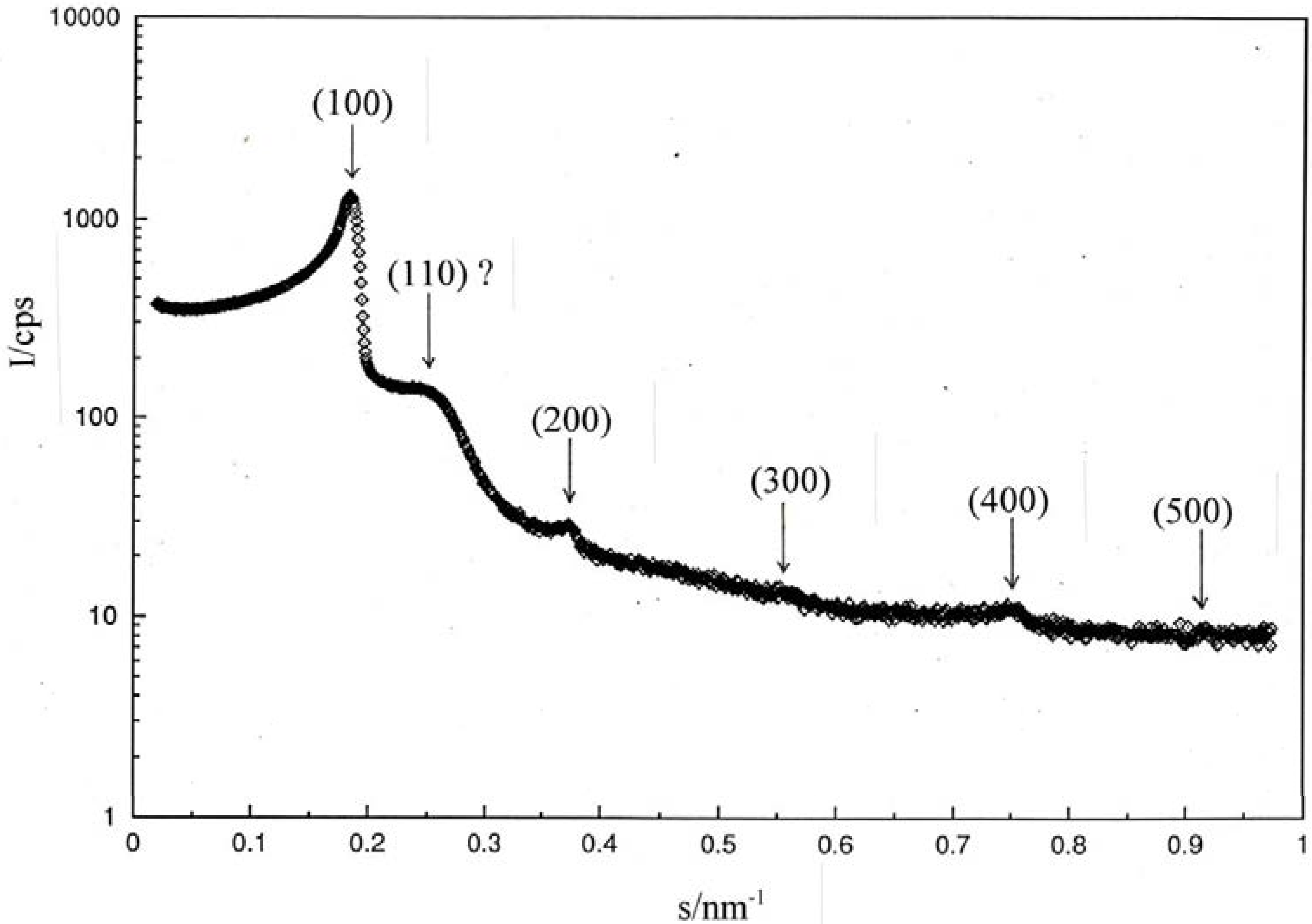
Solution: the super-undulated phase

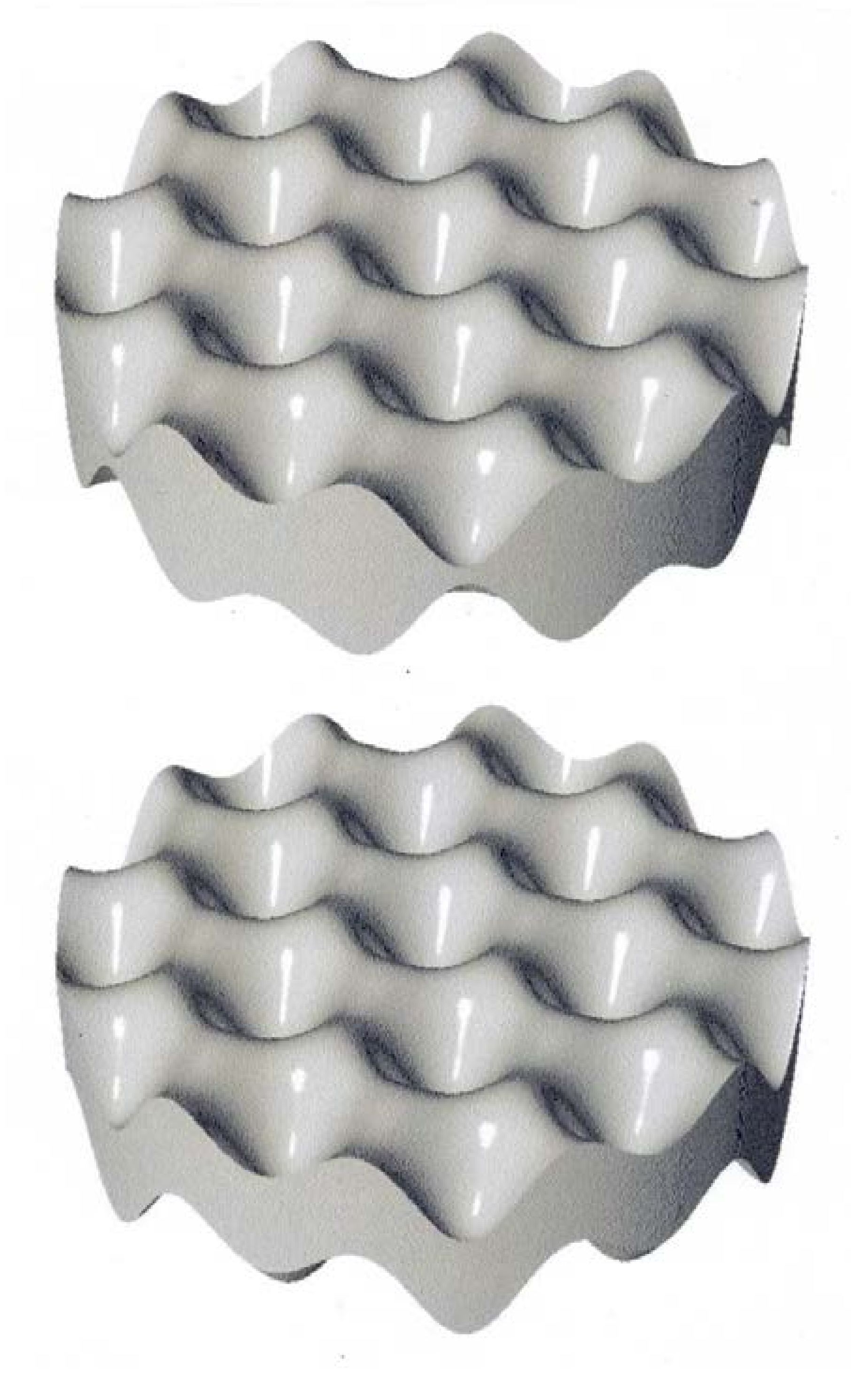


predicted by

Helfrich

Variation of lipid composition: increase ionic lipids

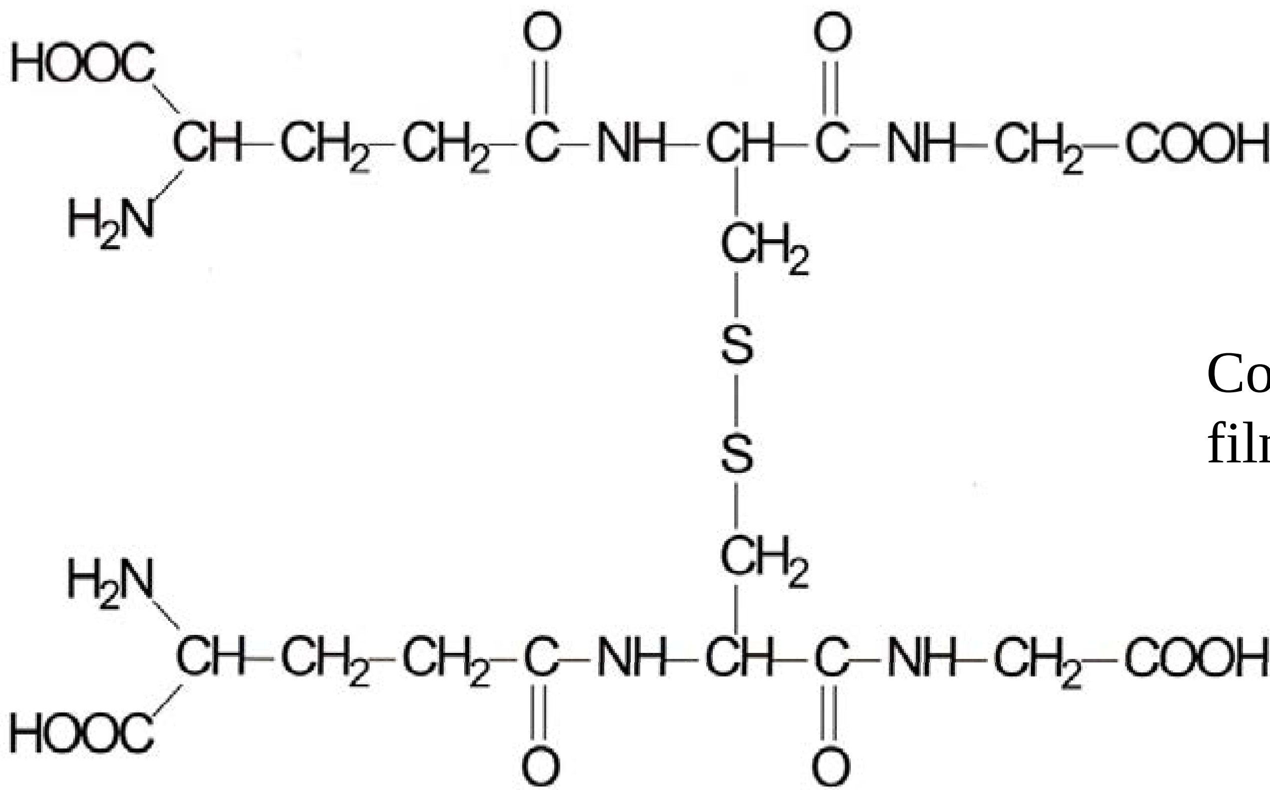




the corrugated lamellar phase

(a very close relative of the superundulated phase)

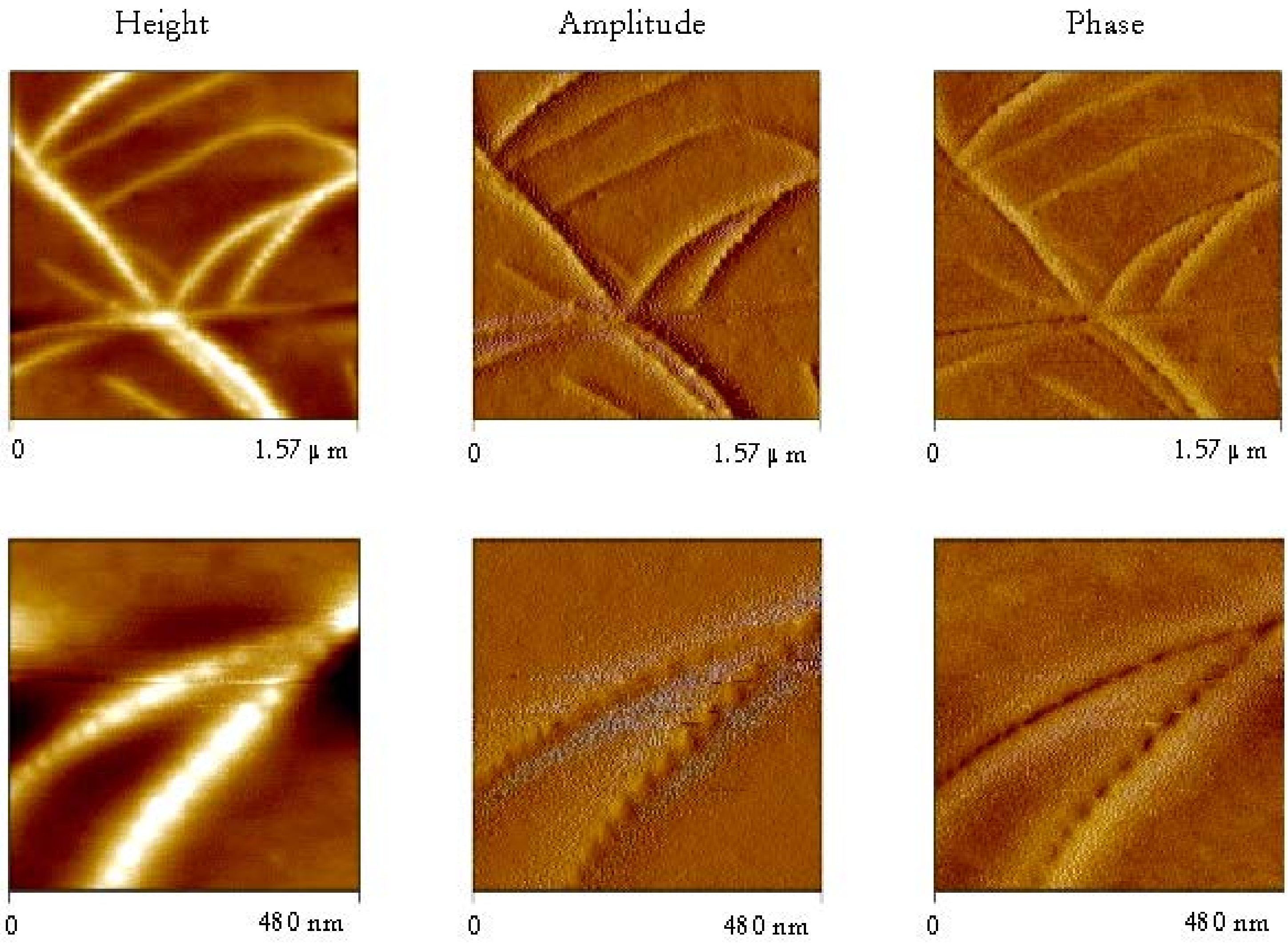
Complexes with oligopeptide



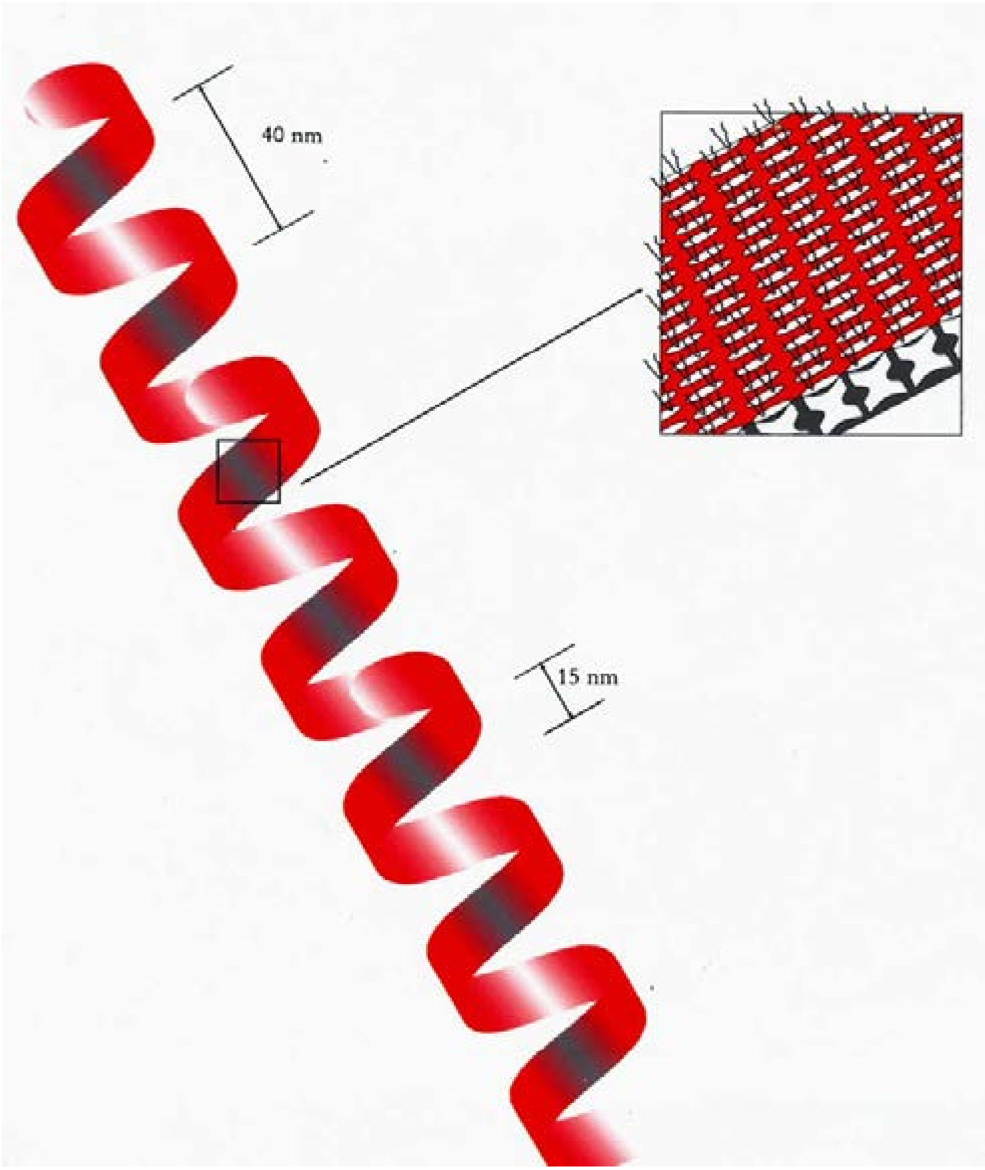
Complexes organosolv,
film forming !!

ox. Glutathione: a model peptide

AFM characterization of glutathione-lecithine complexes



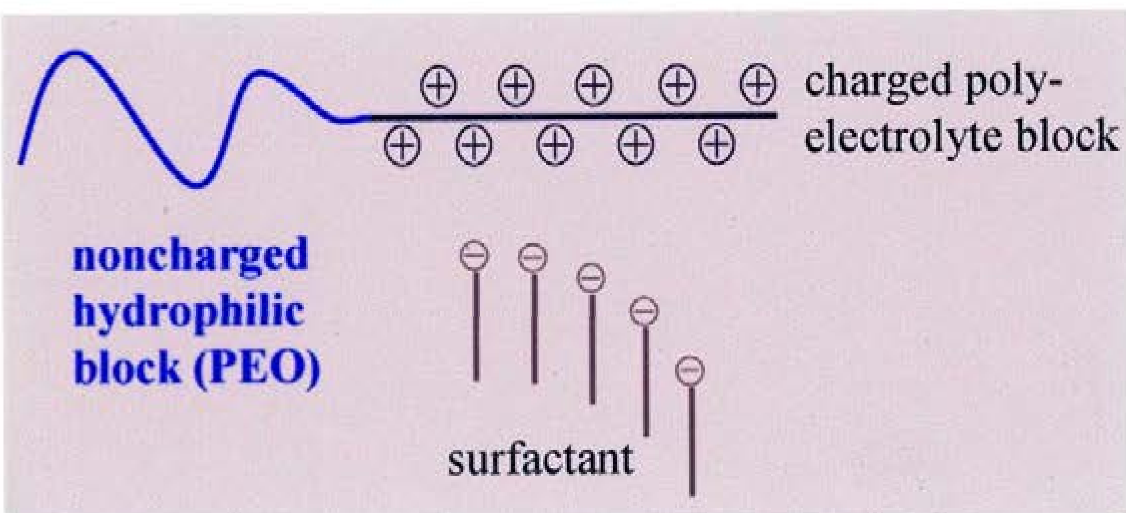
Structure Model

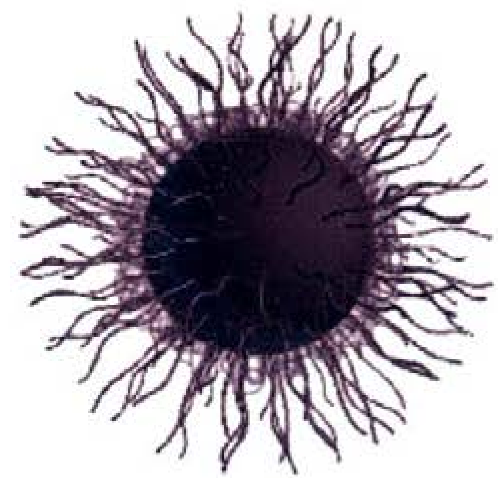


Complex structure with elements on three different length scales !

Complexes from double-hydophilic block copolymers
(S. General)

- stable nanoparticles by surfactant or drug complexation
- supramolecular approach to new polymer systems
- hierarchical superstructure

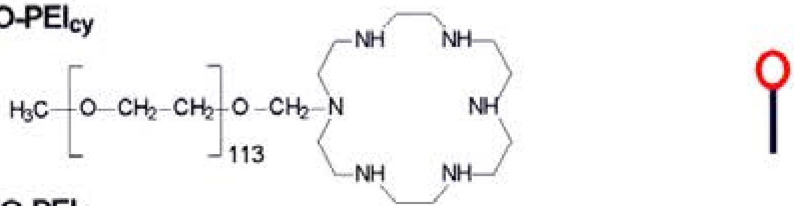




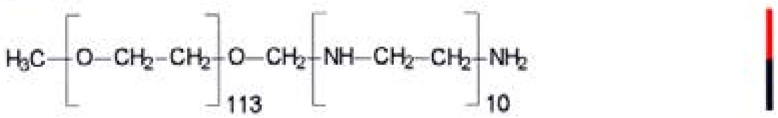
Materials

Poly(ethylene oxide)-*block*-poly(ethylene imine) as double-hydrophilic block ionomers

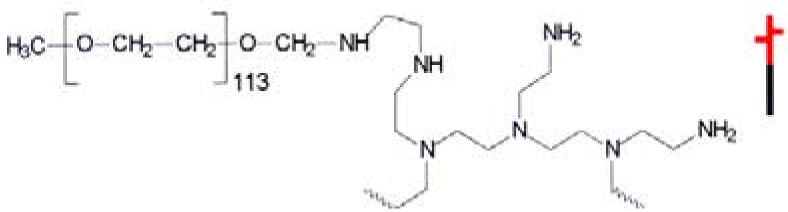
PEO-PEI$_{cy}$

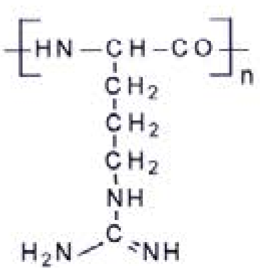


PEO-PEI$_{li}$

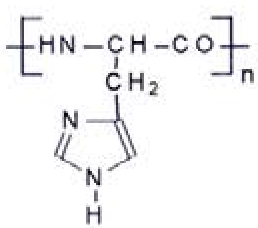


PEO-PEI$_{br}$

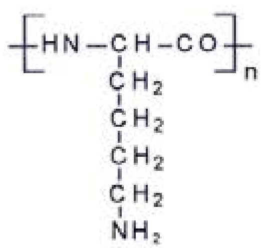




poly (*L*- Arginine); pK_a~12

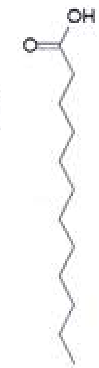


poly (*L*-Histidine); pK_a~6.8

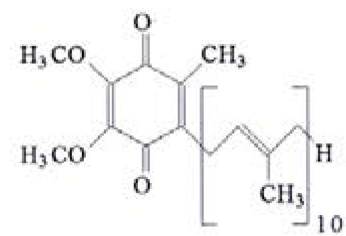


poly (*L*-Lysine) pK_a~10.1

dodecanoic acid (C12) as surfactant



Coenzyme Q_{10} as model drug

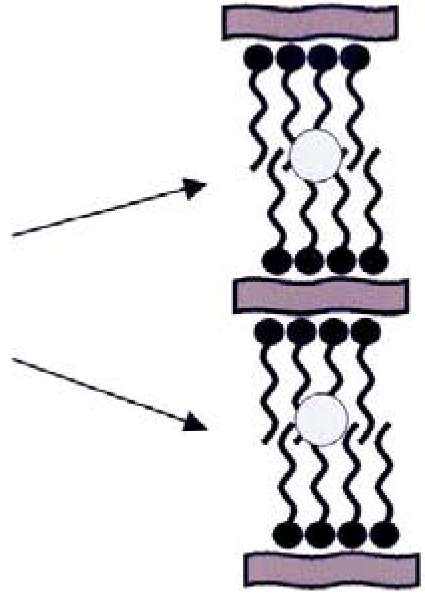


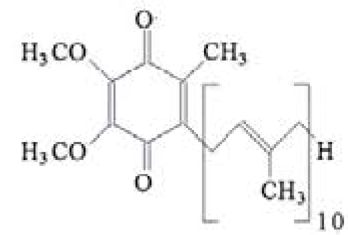
13 wt% incorporated !

Loading and local structure of the Drugs

Incorporated drugs

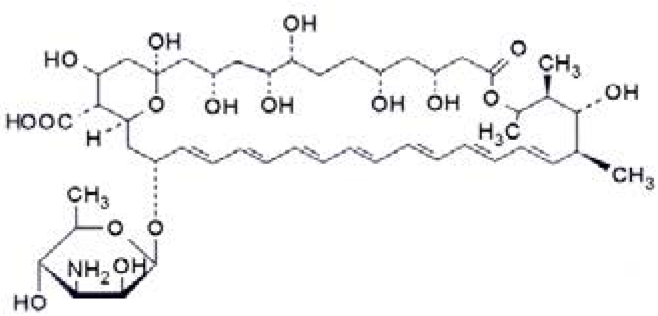
	uptake %[w/w]
Coenzyme Q_{10}	20 %
Estradiol	1-10 %
Triiodothyronine	15 %
Amphotericin B	~ 90 %
Azelaic acid	~ 50 %

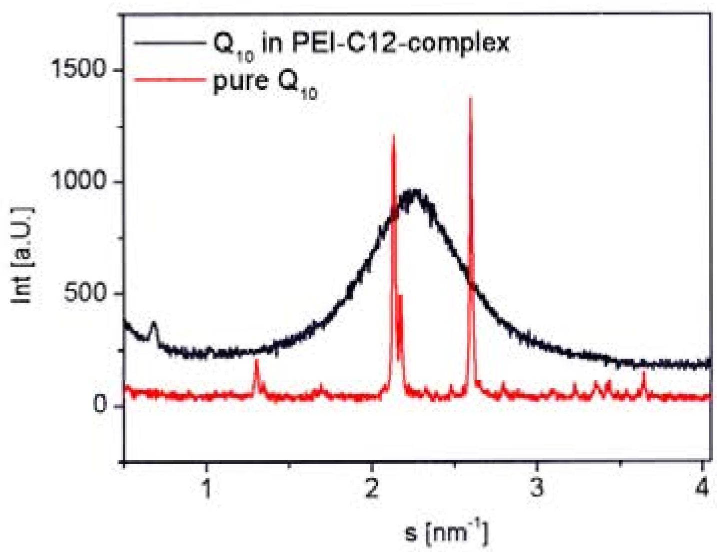




Q_{10}

determined with homopolymers



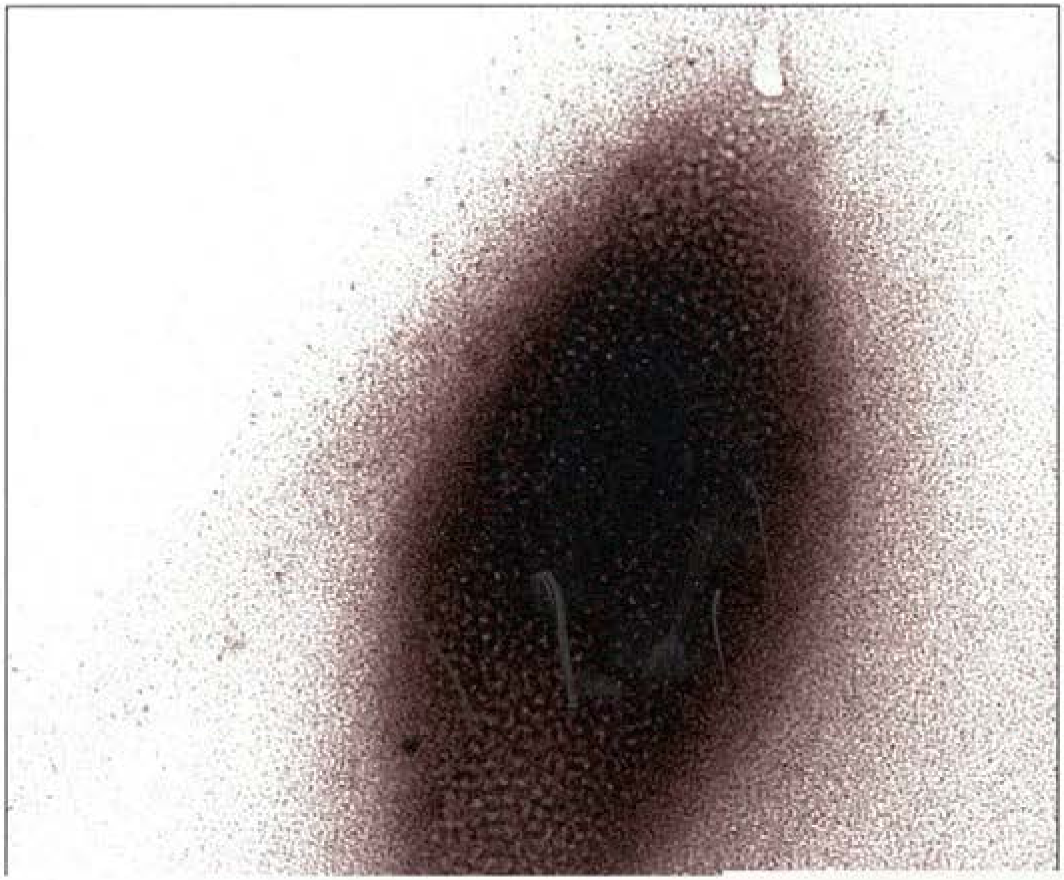


WAXS; 20 % [w/w] Q_{10} incorporated in PEI-C12-complex

after a storage period of 150 days

Inner Structure of Nanoparticles

Inner structure: characteristic graining of ~ 3 nm.

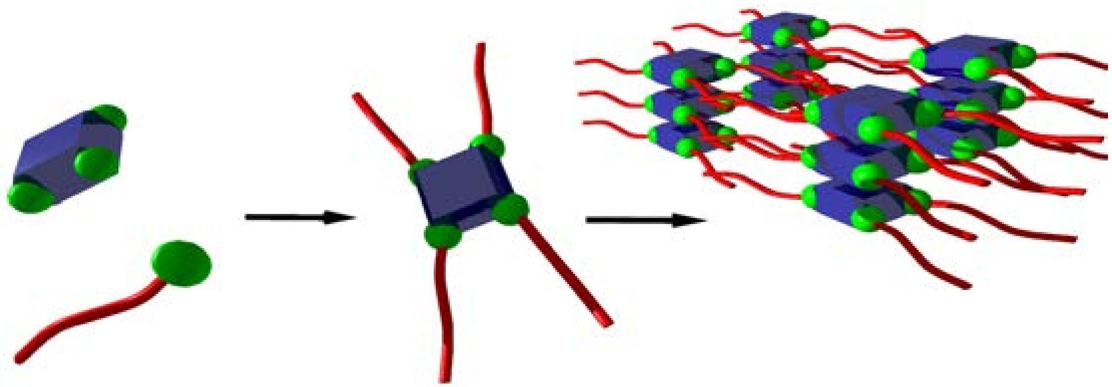


Dye-Surfactant Complexes via Ionic Self-Assembly

Ionic Self-Assembly

(ISA)

- Oligoelectrolyte-surfactant complexes

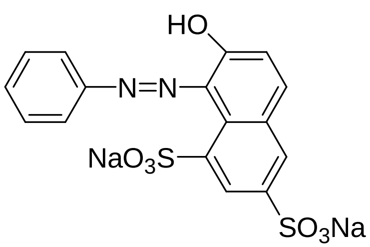


- Electrostatic interactions to drive the organisation of matter
- Modular approach: multiple non-covalent interaction strategy

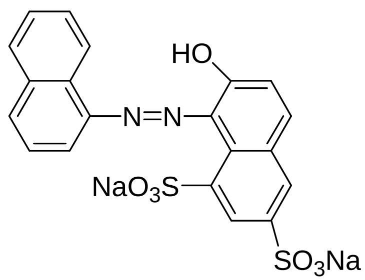
π-Toolbox

- Shape-rigid, -defined tectonic units

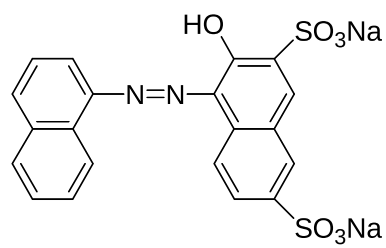
Orange G (OG)



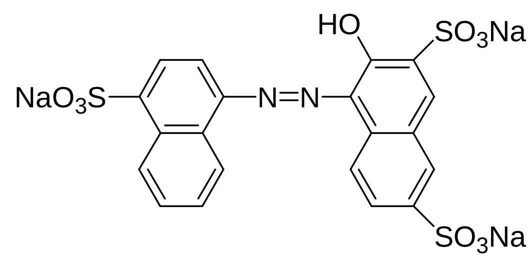
Crystal Scarlet (AR44)



Bordeaux R (AR17)

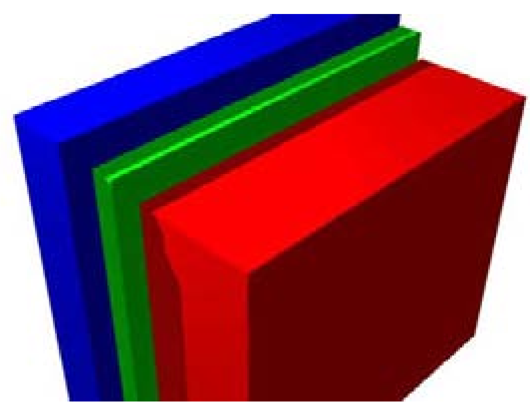


Amaranth (AR27)



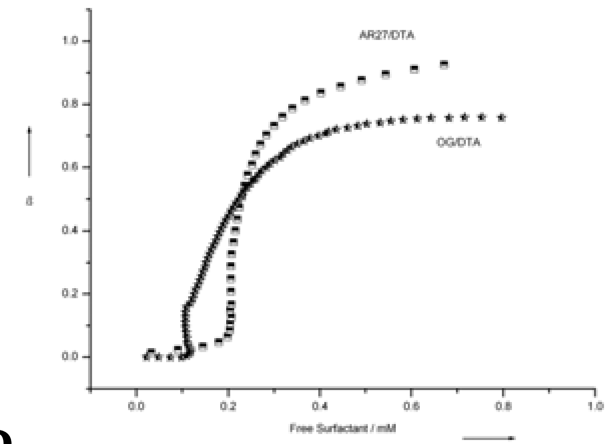
Commercially available dyes

- Subphase formation?

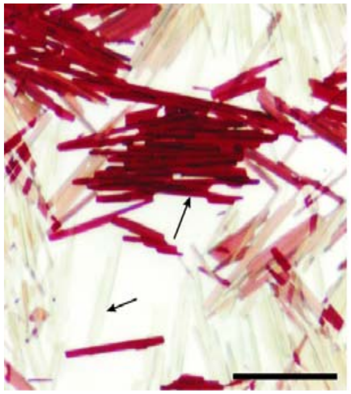


Binding?

- Binding studies – cooperativity?
  - Surfactant selective electrode
  - Titrino 720 / Dosimat 765 Combination
  - 20 °C ± 0.1 °



- Aggregate formation
- Precipitated complex – 1:1 ratio?
  - EA & ICP-AES
- Properties

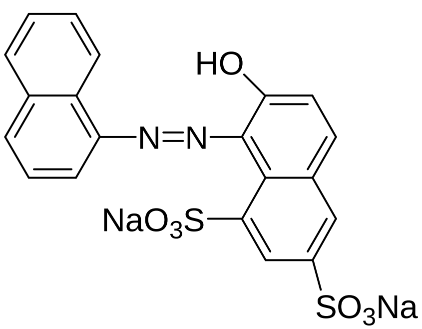


Chem. Eur. J., in press

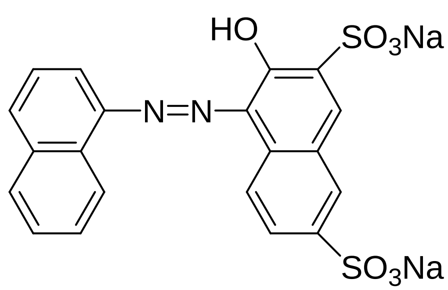
Structure?

- What is to be expected?
  - Crystalline / LC materials?
  - Lamellar / columnar / other phases?
  - Internal organisation of dye subphase?

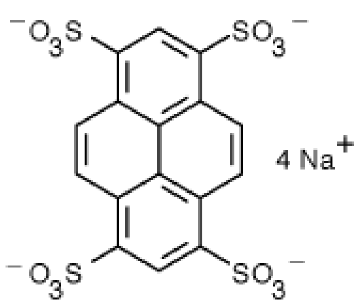
Crystal Scarlet (AR44)



Bordeaux R (AR17)



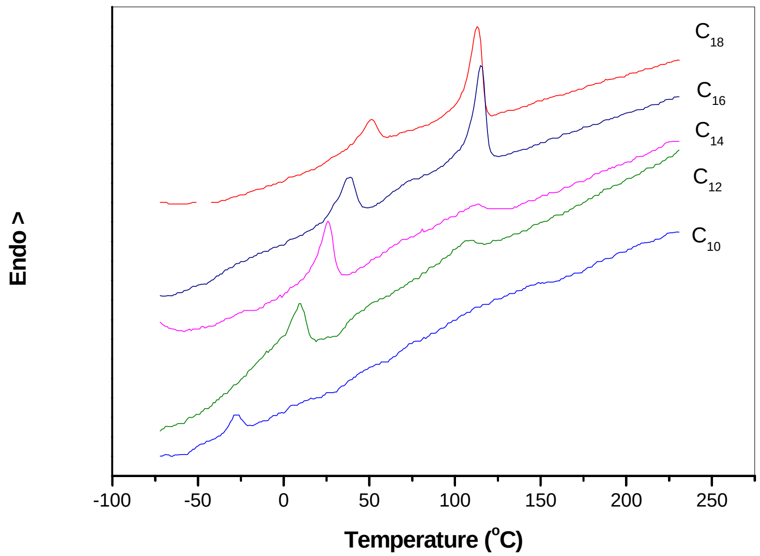
Pyrene tetrasulfonic acid (PTSA)

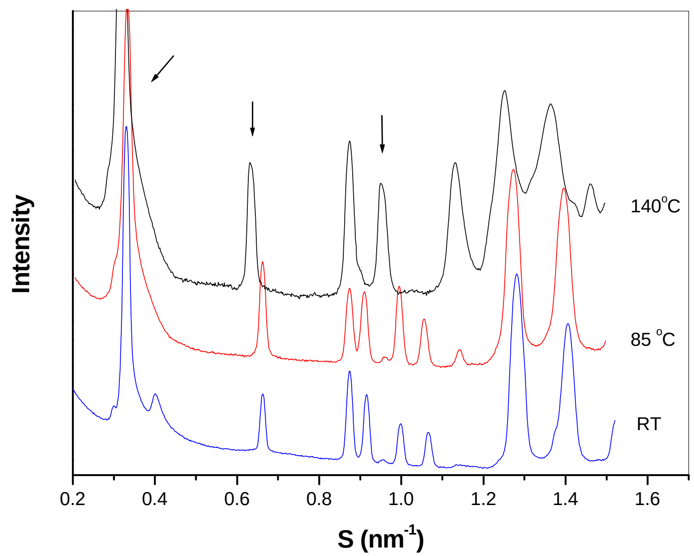


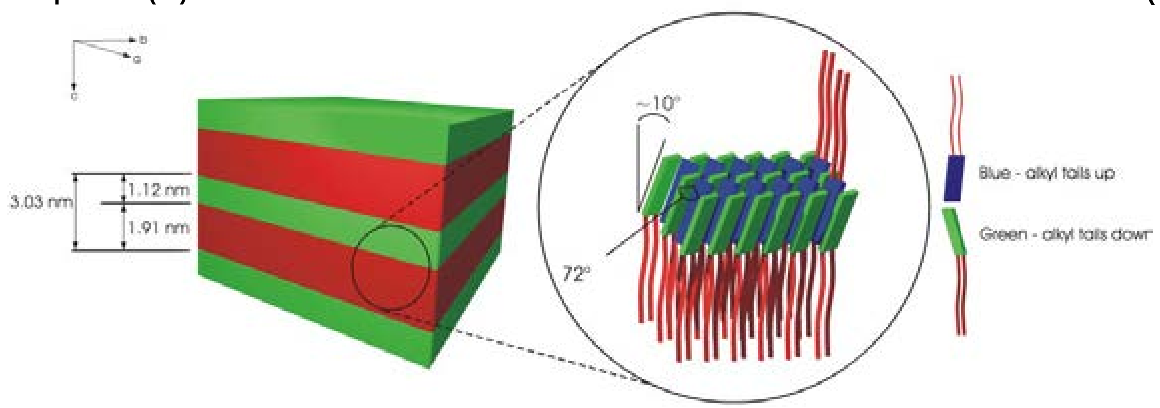
Structure

(cont'd)

- AR44 / AR 17 + single / double tail surfactants





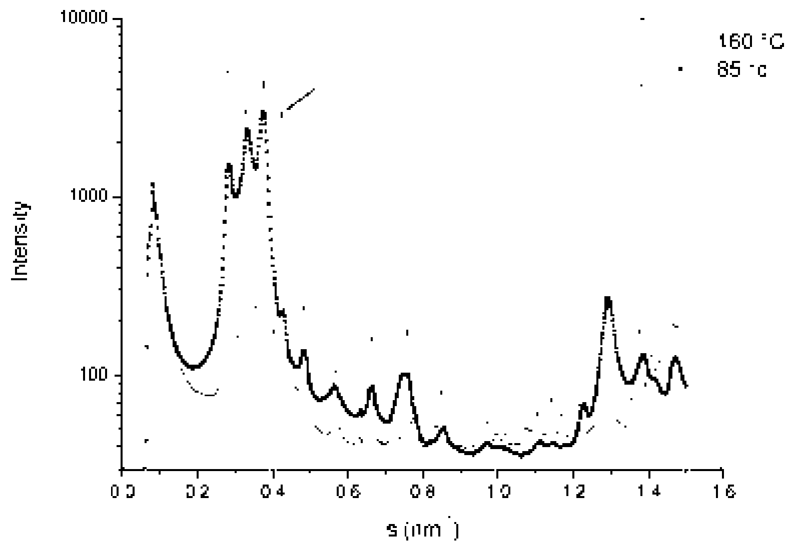


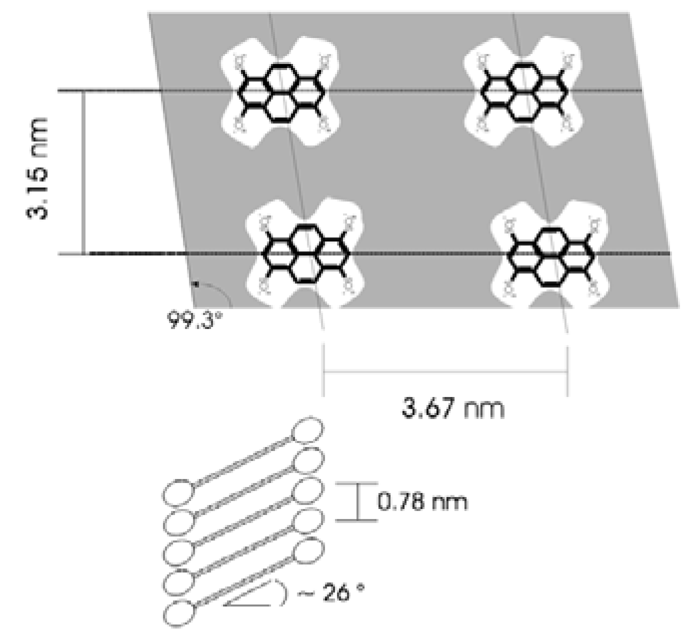
Langmuir, accepted

Structure

(cont'd)

- PTSA as a discotic system

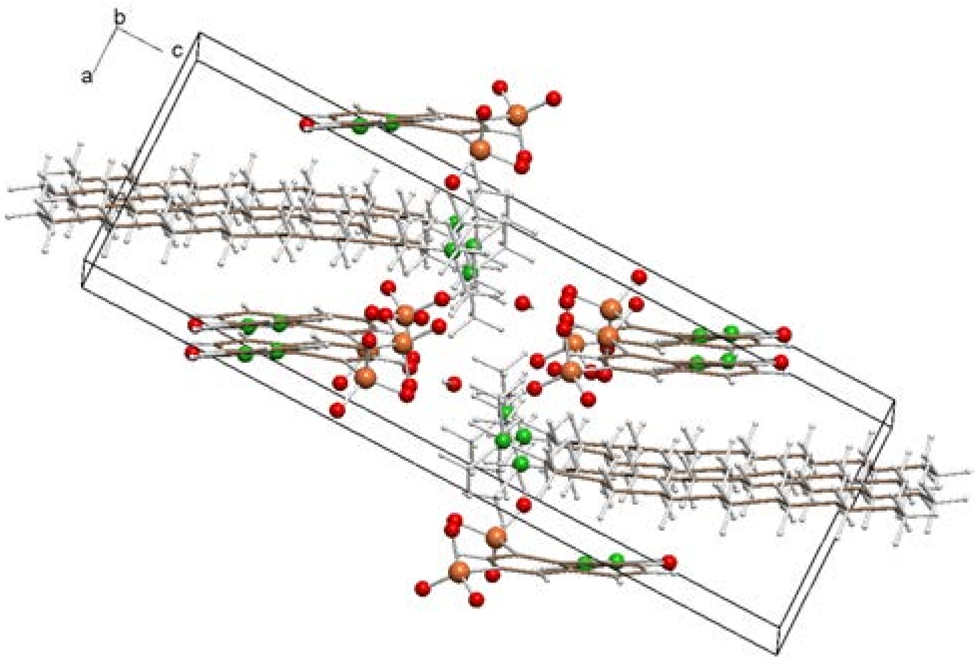




Structure

(cont‘d)

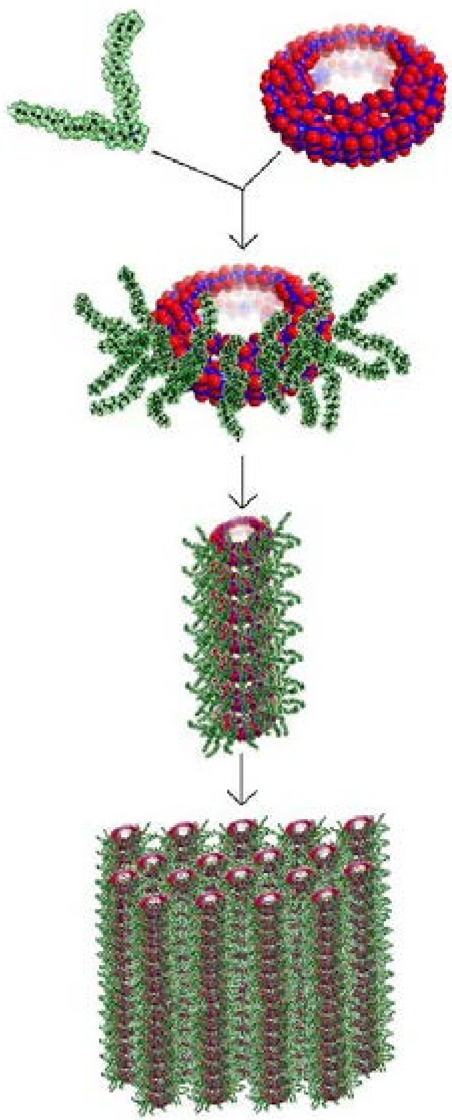
- Nano-phase separation that simple?
- 3 Subphases a reality?



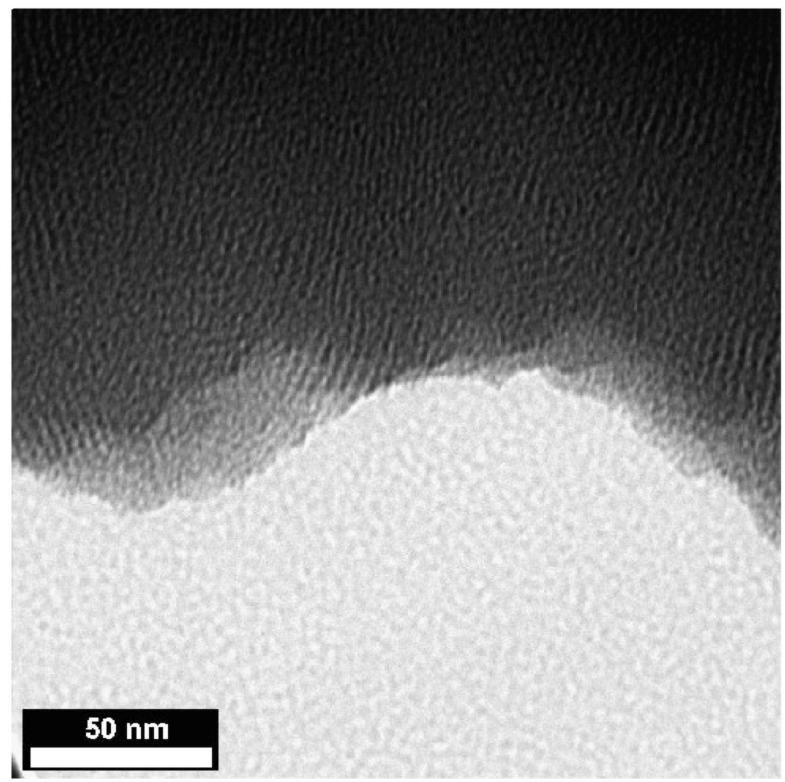
Single crystal analysis
OG + C_{14}TAB

Nature surprises us!

Giant-Polyoxometallates

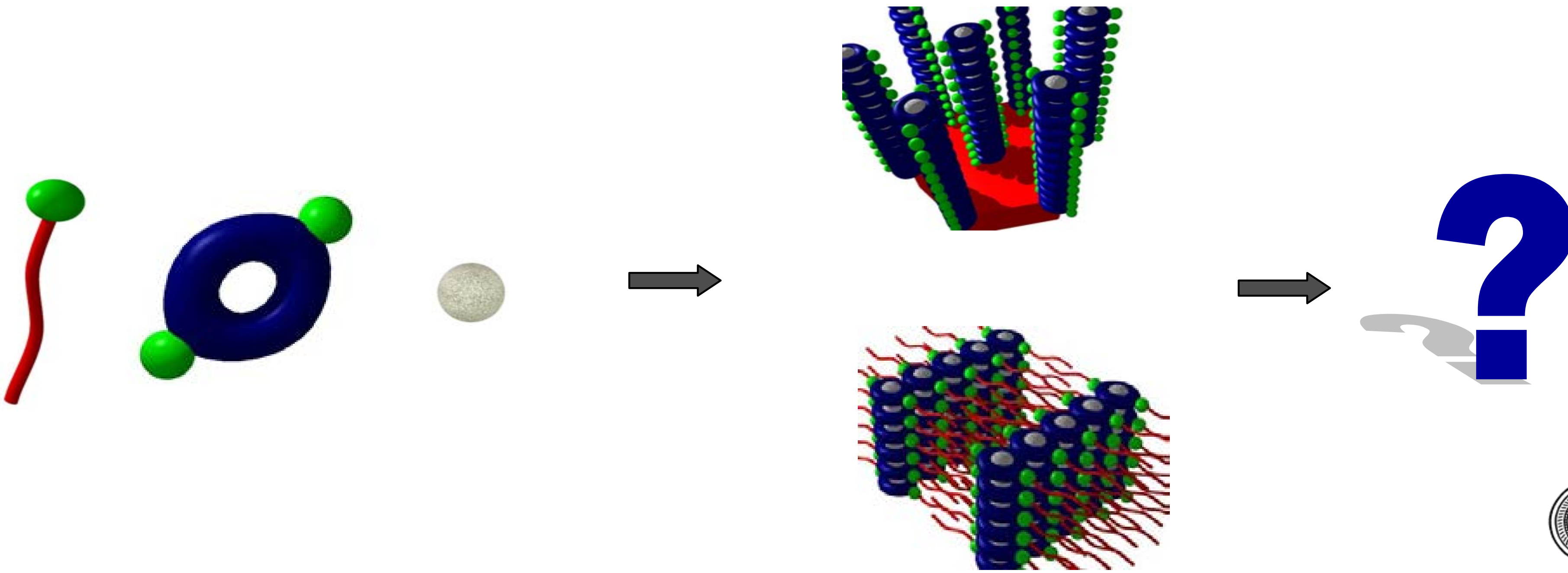


The „ferris wheel“ /A. Müller



Expanding modular approach

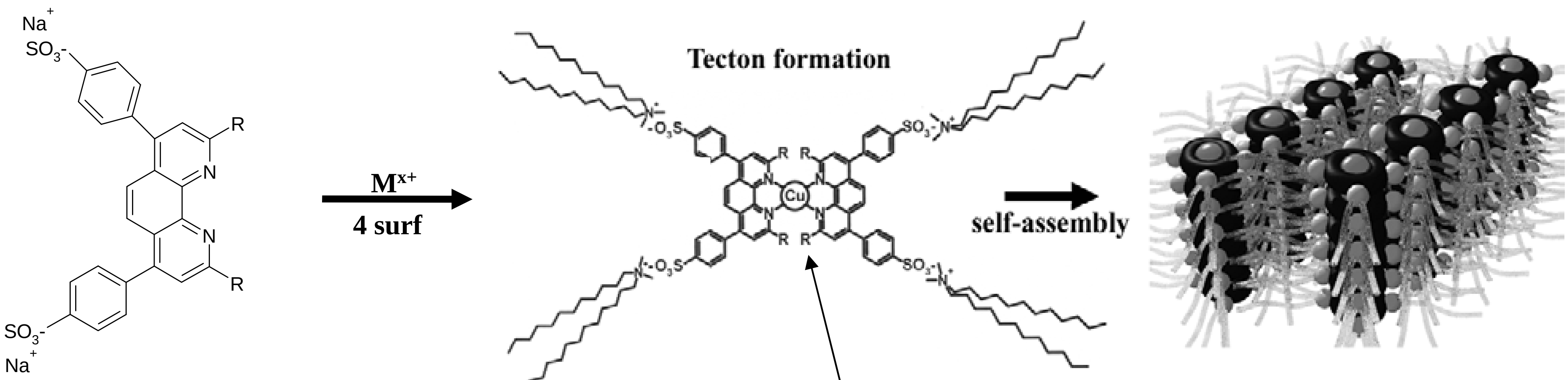
- Surfactant, codon, metallic species
- Multiple interaction strategy



Modular Approach

(cont'd)

- Complexes based on stepwise noncovalent interactions

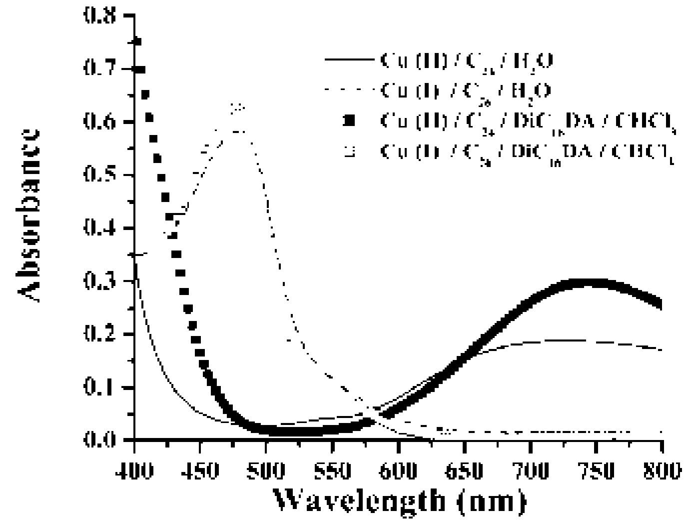


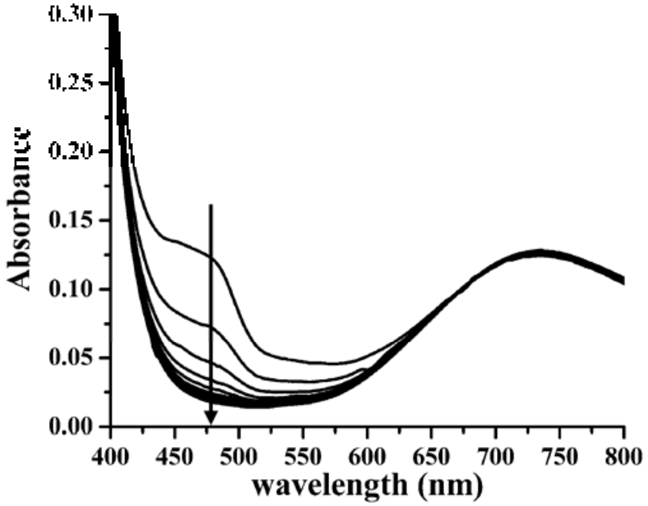
R	H	CH_3
$CuCl_2$	green	red

Camerel, Strauch, Antonietti, Faul, Chem Eur J, **2003**

Cu(I) / Cu (II)

- Behaviour of copper species?
- Colour change with complexation
- Cu(II) to Cu(I) via complexation



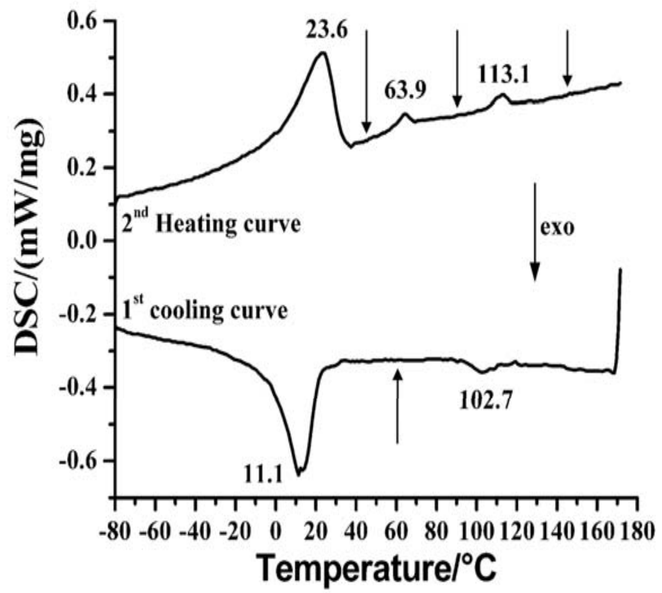


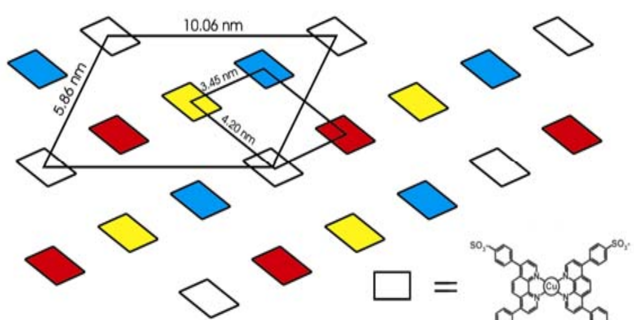
- Heating of green Cu(II) complexes
- Films turn black
- Back to green via dissolution

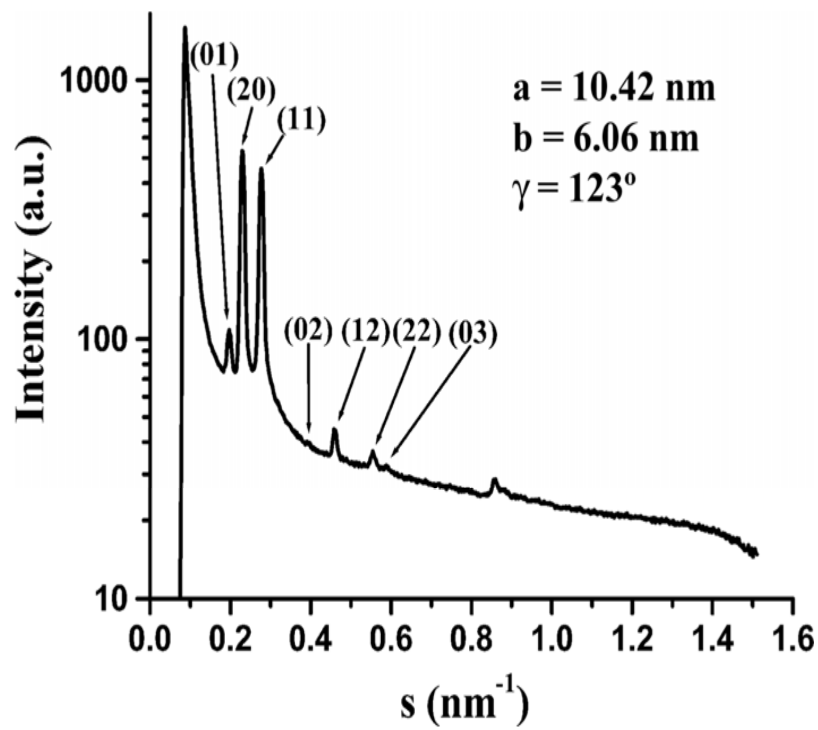
Materials Properties

(Cu(I) / C(II))

•$CuCl_2$ / C_{24} / DiC_{18}







Oblique columnar phase

Conclusion

- ISA is a facile route to organise matter
- Coacervation, symplexes, LbL-structures
- Objects turn into nanos, films and materials
- Partly solubility in solvents
- Multiple interaction strategy
- Organisation of oligoelectrolytic π-systems
- Exciting mechanical & optical properties
- Structures and organisation into subphases