

# **Self-Assembly to create mesoporous materials**

Micelles

Polymers

Liquid Crystals

# Outline

1. What are they?
2. What are they useful for?
3. What are some of the theoretical aspects behind these materials?
4. How can we synthesize them?
5. What are the factors affecting their sizes, shapes and their existence ?

# What are mesoporous materials?

- Porous materials whose pores are between 2 and 50 nm in diameter.
- Silica based materials first synthesized by scientists at the Mobil Corporation in 1992.
- Non-silica mesoporous materials first reported at UC Santa Barbara in 1994.

# Applications

- Molecular sieves
- High surface area catalysts
- Gas sensors
- Dye sensitized photovoltaic solar cells

# Micelles

# Mesoporous materials are templated by amphiphilic molecules.



- An **amphiphilic molecule** has a hydrophilic (water loving) head and a hydrophobic (water loathing) tail.
- **Surfactant** is an amphiphilic molecule with a tendency to adsorb onto free surfaces and interfaces and to aggregate to form micelles
- **Micelle** is an association of amphiphilic molecules.
- **Mesoporous structures** are created by the ordered packing of micelles.
- Small molecules  $M_w \approx 100-1000$

# Questions to be answered about micelles

What are amphiphilic molecules?

Why do micelles form?

What factors determine the shape and size of the micelles?

What determines their packing geometry?

What are their properties?

How can we used them?

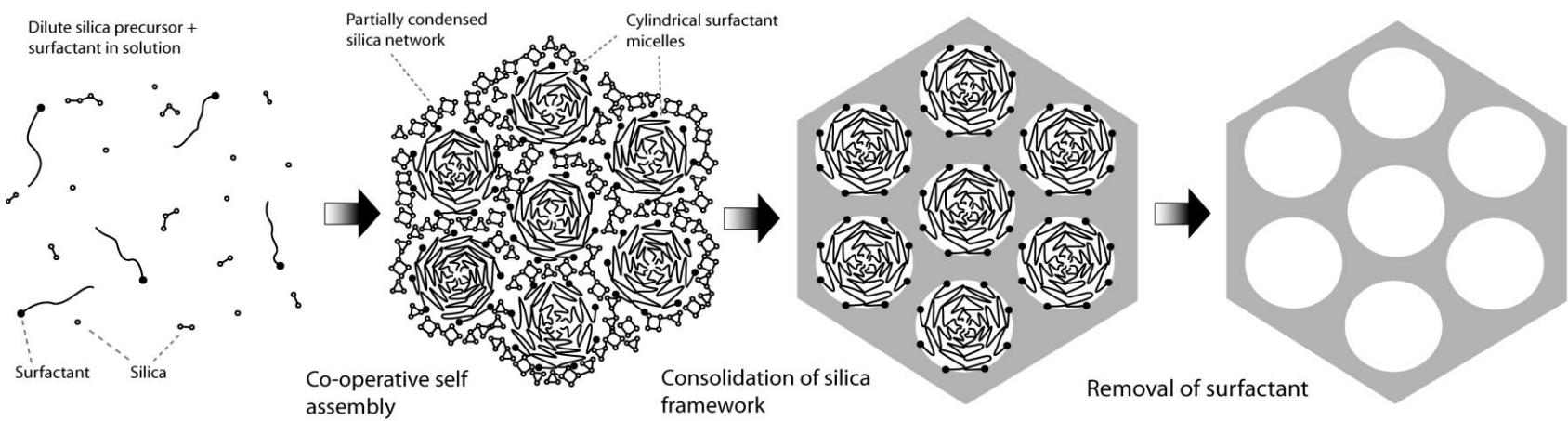
# Why do amphiphiles form micelles?

- Gibb's Free Energy ( $\Delta G$ ) is a thermodynamic quantity which predicts the spontaneity of a reaction. (A decrease in Gibb's Free Energy indicates a spontaneous reaction)
- Water molecules create structure by forming hydrogen bonds with one another.
- The hydrophobic tails of individual amphiphiles placed in solution force water molecules to associate in a particular way. This decreases the entropy ( $\Delta S$ ) of the system.
- When the hydrophobic tails associate to each other (form micelles) in order to minimize their interaction with water molecules they increase the entropy of the system.

$$\Delta G = \Delta H - T\Delta S$$

- An increase in entropy, decreases Gibb's Free Energy of the system therefore the reaction will occur spontaneously.

# How do we use micelles to form mesoporous metal oxides?



Courtesy of Brian Eggiman

# Shape of aggregates

**Self assembled structures are rich in phases:**

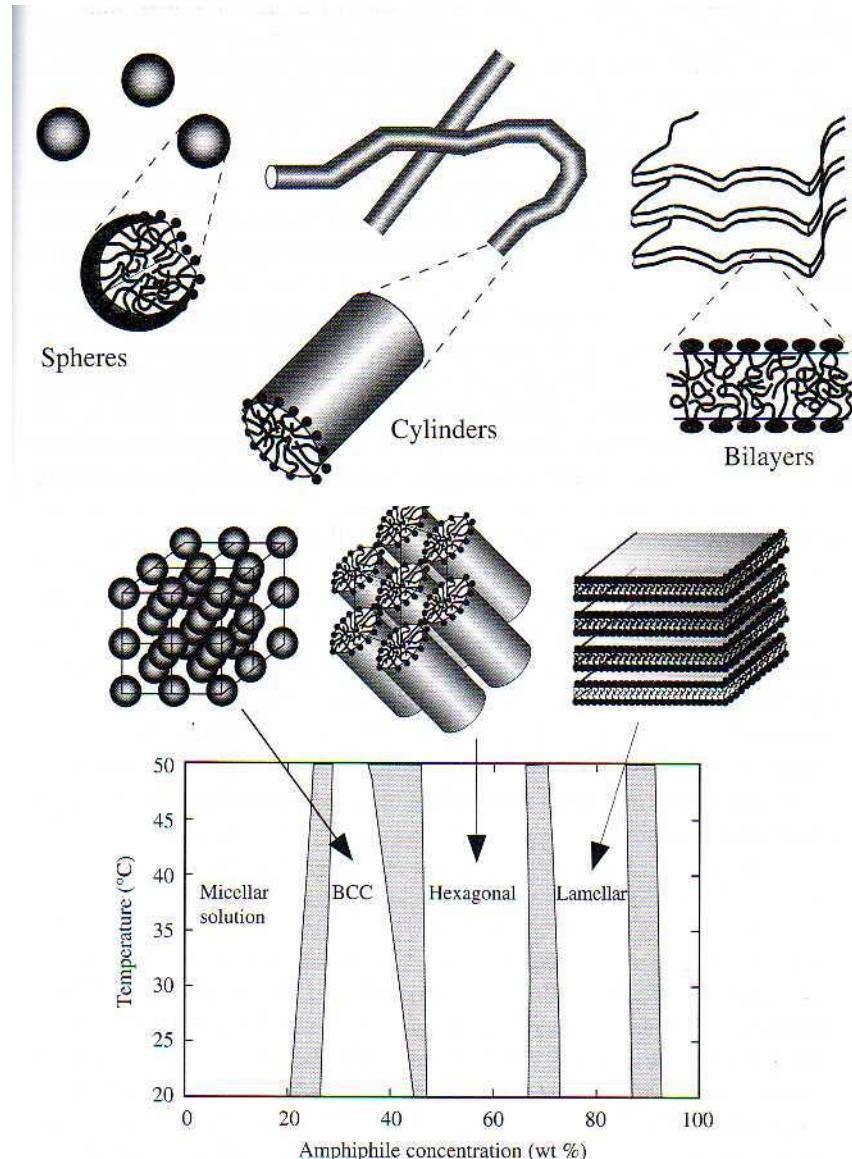
- response by changing size and shape and arrangement of micelles
- dramatic change in properties

**Basic shapes:**

- spheres
- cylinders
- bilayers
- vesicles

**Superstructures:**

- micellar crystals
- lamellar phases
- bicontinuous networks



# Packing Geometry of Aggregates: Attaining the desired Self-Assembled Structures considering Physico-Chemical aspects

- **Effect of surfactant concentration**

Surfactant conc  $\uparrow$ : lower hydration of head groups  $\rightarrow$

$$R = \frac{v}{a_0 l_c}$$

lower  $a_0 \rightarrow$  higher R  $\rightarrow$  lamellar structure

- **Effect of surfactant chain length**

If  $l_c$  increases, v increases, however if R increases too much, spherical  $\rightarrow$  lamellar

- **Effect of co-solvent**

- Polar solvents, like alcohols, tend to associate with head groups and reduce the tendency for the surfactant molecules to associate; CM may disappear,
- Non-polar solvents associate with hydrophobic chains of the surfactant increase v  $\rightarrow$  increase R  $\rightarrow$  less curved structures

- **Effect of salts and ionic species**

- On ionic surfactants, reduces repulsive energy between head groups, reducing  $a_0 \rightarrow$  larger R  $\rightarrow$  less curved structures

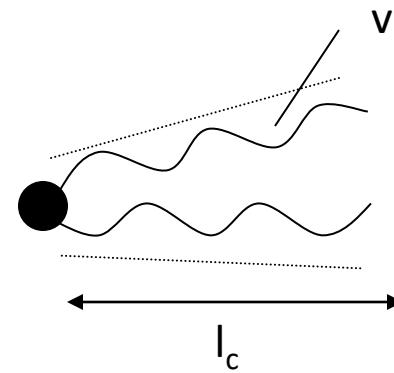
# Shape of the Aggregates: Optimum head group area (1), $a_0$

Factors determining the shape

- i) Optimum head group are,  $a_0$
- ii) Critical chain length,  $l_c$
- iii) Hydrocarbon volume,  $v$

$l_c$  - length of fully extended tail

$v$  - volume of the tail  
# of tails, side groups, ...

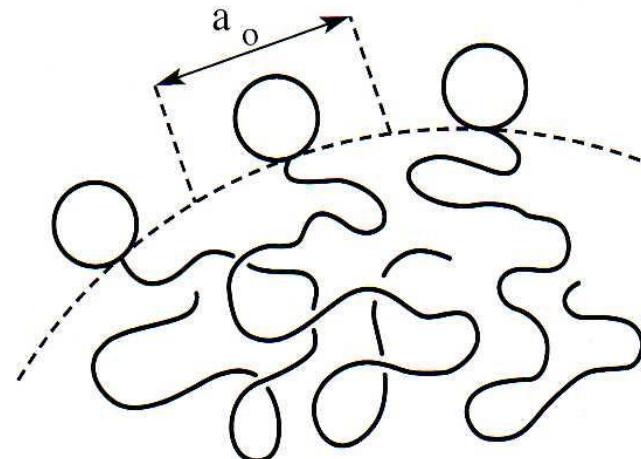
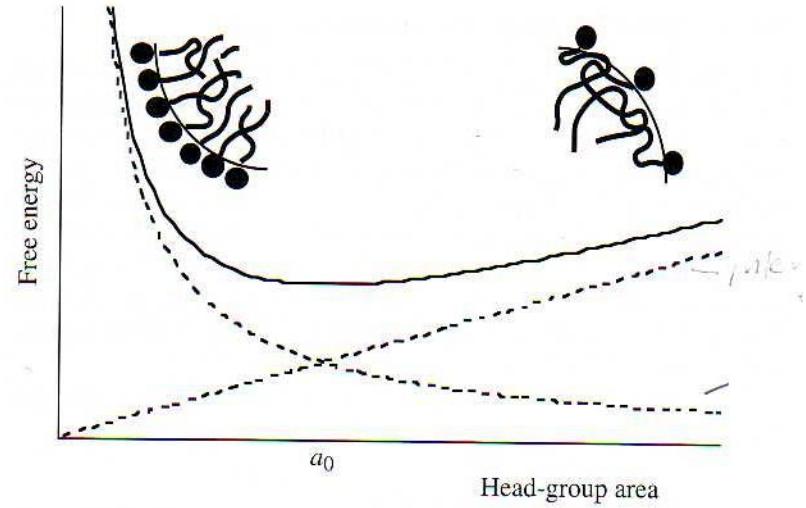


# Shape of the Aggregates: Optimum head group area (2), $a_0$

$a_0$  controlled by

*repulsive forces:*  
electrostatic or steric repulsion  
(can be altered by e.g.  
salt concentration)

*attractive forces:*  
protecting the tail



# Shape of aggregates: Volume considerations

Spheres - smallest area/volume

Volume:

$$4\pi r^3/3 = Nv$$

(N is the # of molecules in aggregate)

Surface area:

$$4\pi r^2 = N a_0$$

$$4\pi r^2 = 3 Nv/r$$

$$\rightarrow r = 3v/a_0$$

$$\text{but } r_{\max} \leq l_c$$

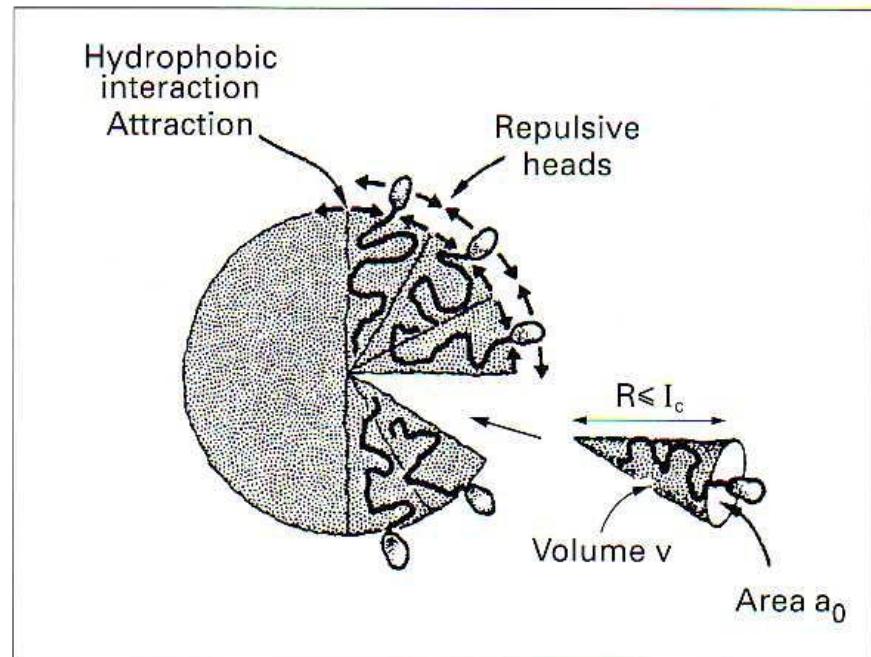
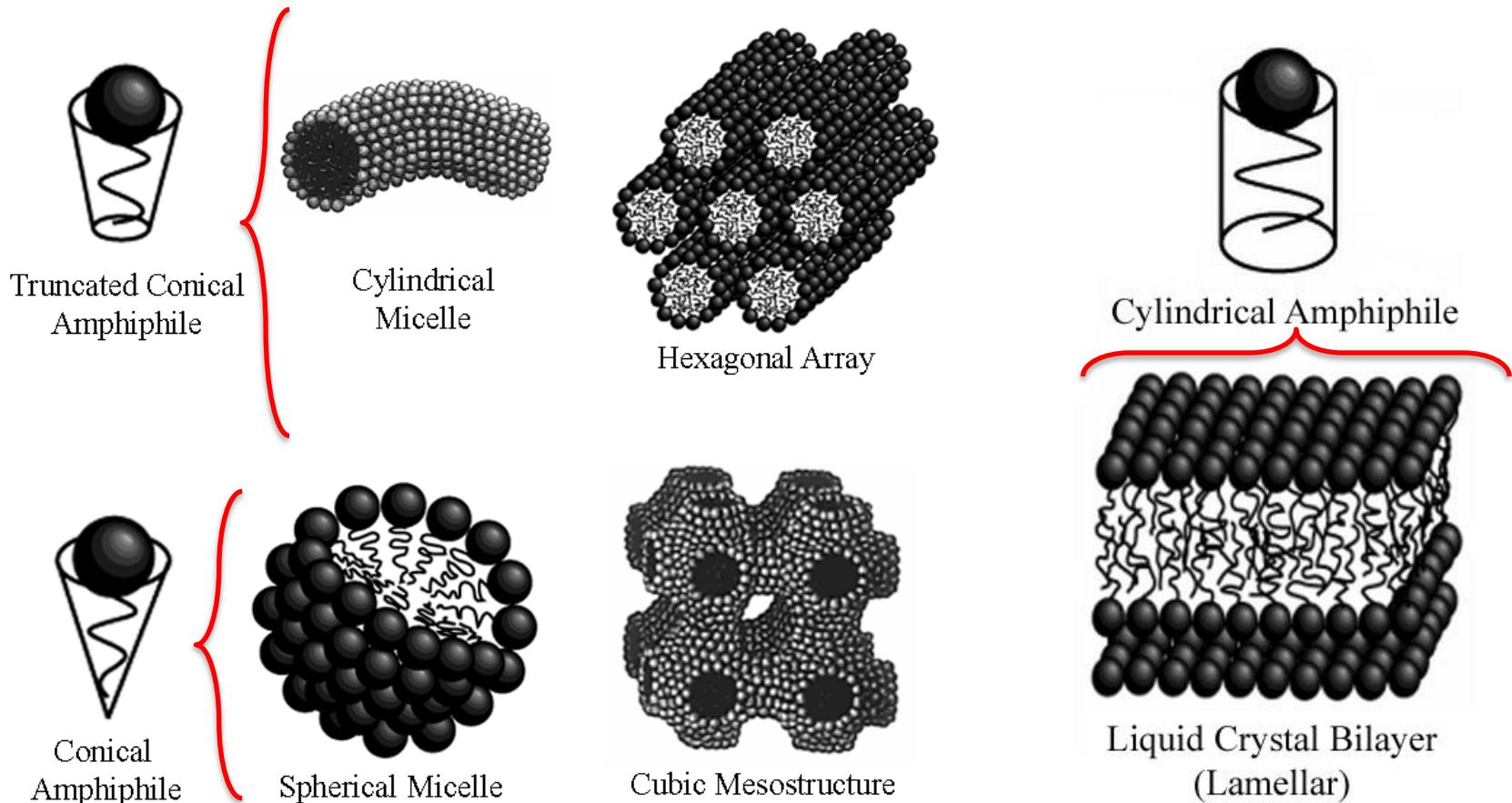


Fig. 4.4. Schematic diagram of a micelle

$$v/l_c a_0 \leq 1/3 \text{ for spherical micells}$$

# What determines the shape of the aggregates (1)?



Diagrams compiled from work by Brian Eggiman and Soler-Illia et al, "Chemical Strategies To Design Textured Materials: from Microporous and Mesoporous Oxides to Nanonetworks and Hierarchical Structures", Chem. Rev. 2002, 102, 4093-4138.

# What determines the shape of the aggregates (2)?

Spheres:  
 $v/l_c a_0 \leq 1/3$

Cylinders:  
 $1/3 \leq v/l_c a_0 \leq 1/2$

Bilayer:  
 $v/l_c a_0 > 1/2$

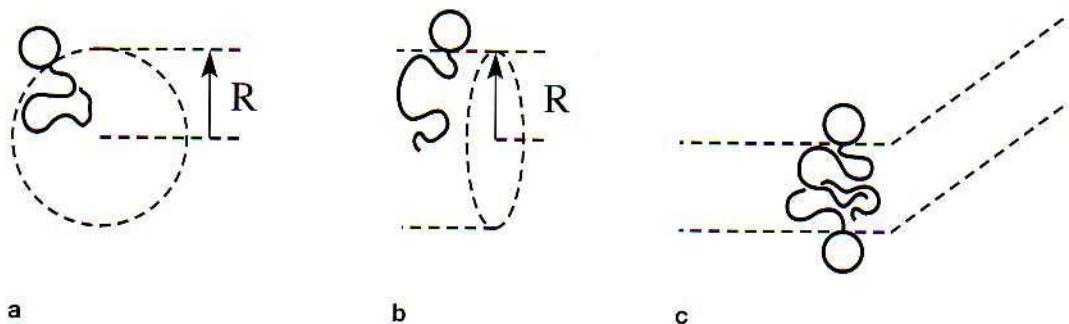
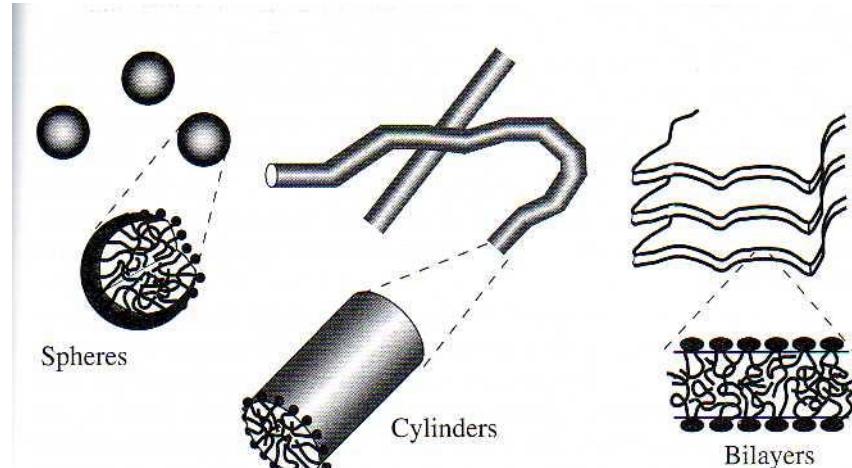


Fig. 5.4. Three possible morphologies, with their curvature. (a) Sphere, curvature  $1/R + 1/R = 2/R$ . (b) Cylinder, curvature  $1/R + 0 = 1/R$ . (c) Bilayer, zero curvature

# What determines the shape of the aggregates (3)?

Geometric packing parameter (shape factor)

$v$  = hydrocarbon chain volume

$a_0$  = optimal head group area

$l_c$  = critical chain length

$$R = \frac{v}{a_0 l_c}$$

R	< 0.5	> 0.5	> 1
structure	spherical-cylindrical	bilayers	inverse micelle

# Packing Geometry

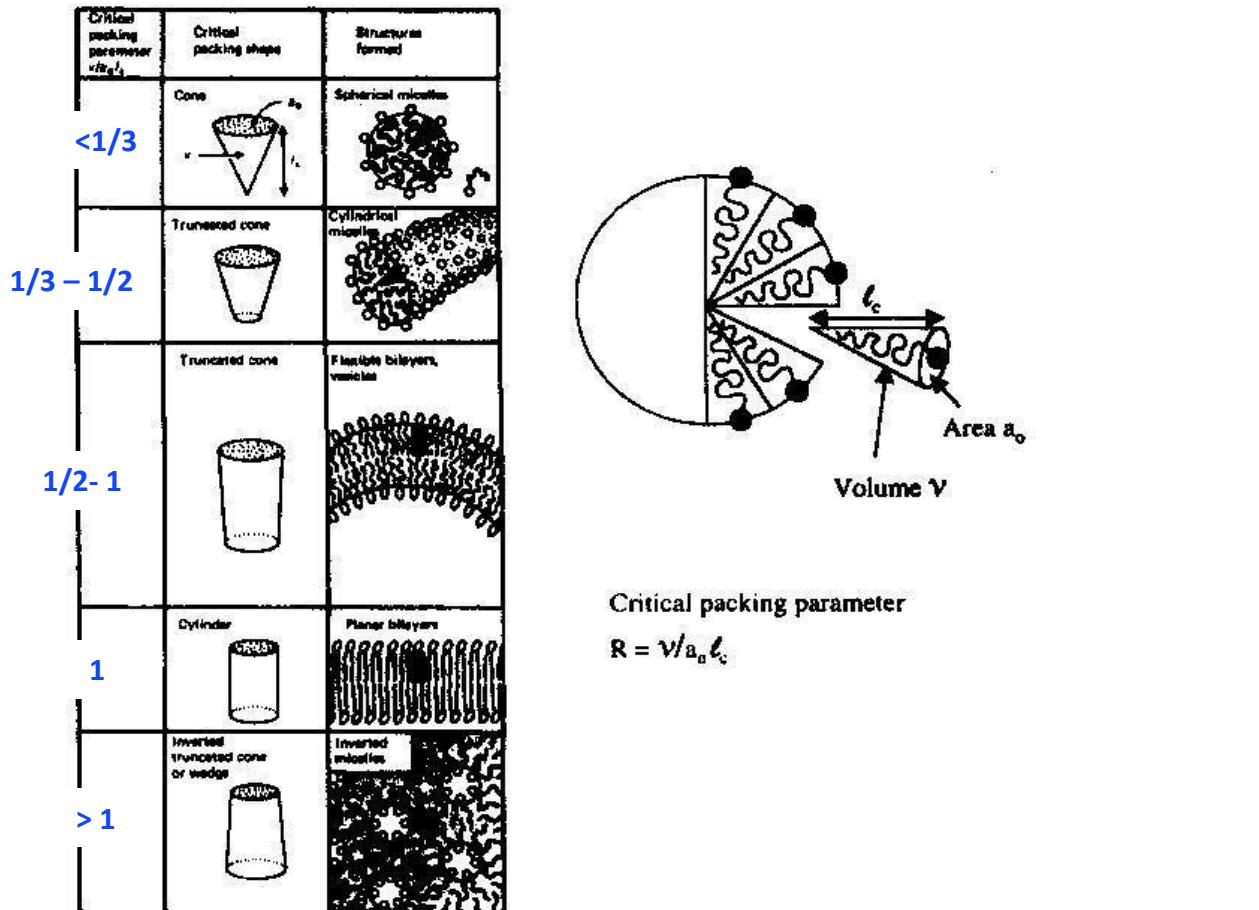
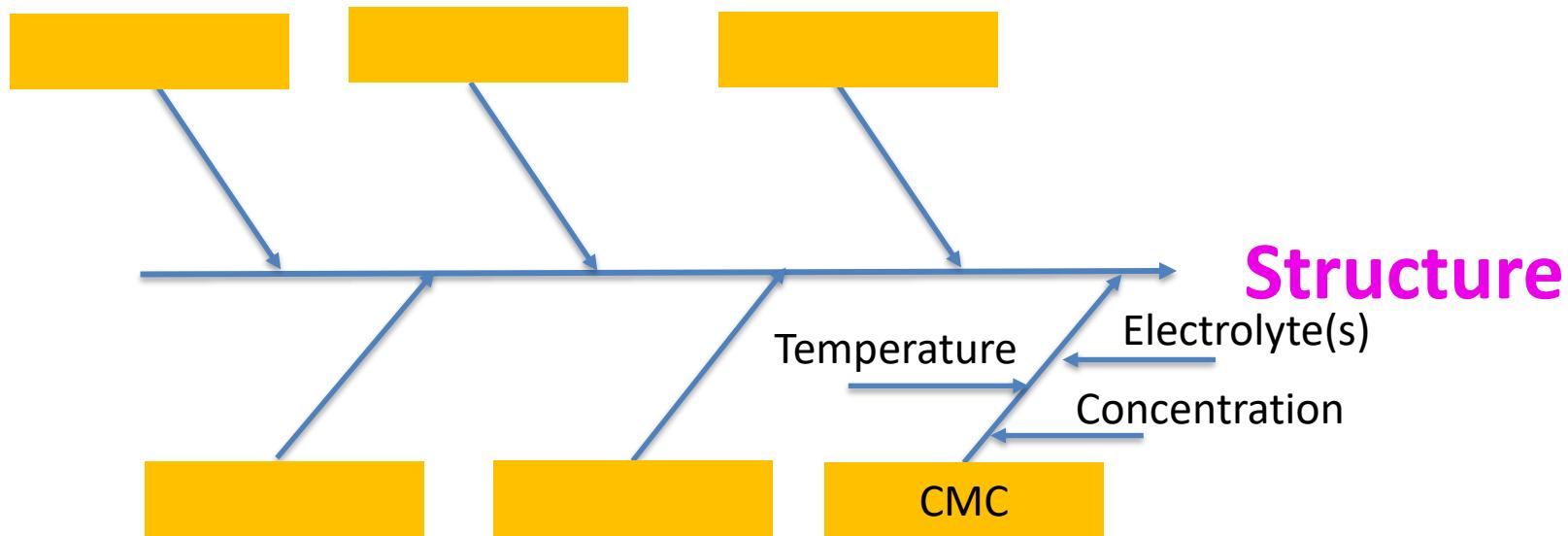


FIGURE 2.5. Relationship between the bilayer structures and the packing parameters (shape factors) (reproduced and adapted from Ref. 17 with permission from Academic Press).

Major driving forces for amphiphiles to form well-defined aggregates are:

- hydrophobic attraction at hydrocarbon-water interfaces and
- hydrophilic ionic or steric repulsion between head groups.

# Structure, also depends on:



# Surfactant characteristics

Head group charge, head group size, chain length, pH & ionic strength

## Cationic:

- long chain amines or ammonium salts are positively charged at pH<7,
- not charged at pH >7, then not active
- quaternary ammonium salts are charged and active at all pH's

## Anionic:

- Long chain carboxylic or sulfonic acids, are negatively charged at pH > 7,
- (at pH < 7 not ionized, not active)

## Non-Ionic surfactants:

- have the advantage in that pH, counter ions, or solvents do not affect their activity

## Surfactant Activity for ionic ones, depends on:

- pH, ionic strength of the solution
- Counter ions neutralize charges on surfactant head groups, and even cause its precipitation.

# Temperature Effects

(a) Gas (dispersed)  $\rightarrow$  Liquid (condensed)

under Van der Waals attraction forces

(b) Polymer gels (dispersed)  $\rightarrow$  Collapsed

polymer gel (condensed)

under rubber elasticity (entropy change),  
counter ions osmotic pressure, and  
electrostatic repulsive forces

(c) Colloidal particles (dispersed)  $\rightarrow$

self-assembled colloidal crystals and  
super lattice structures

(d) Surfactant packing transition

cubic, hexagonal, lamellar, solid

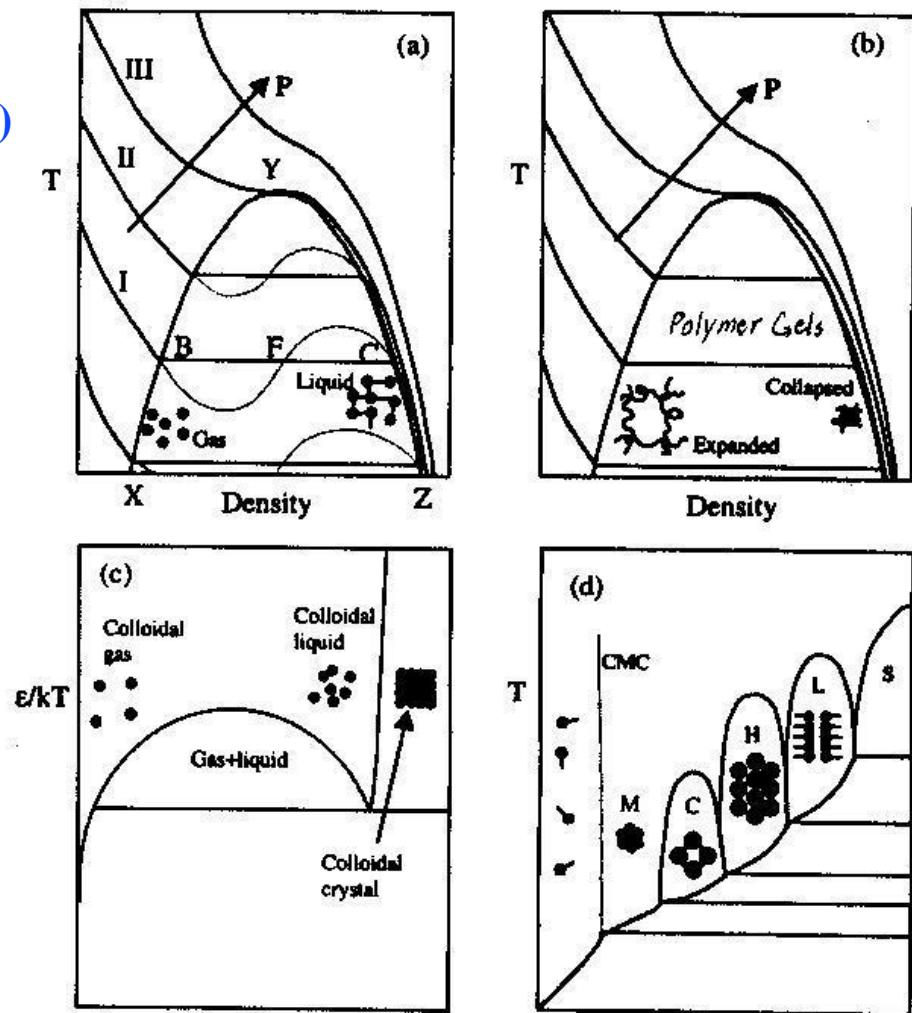
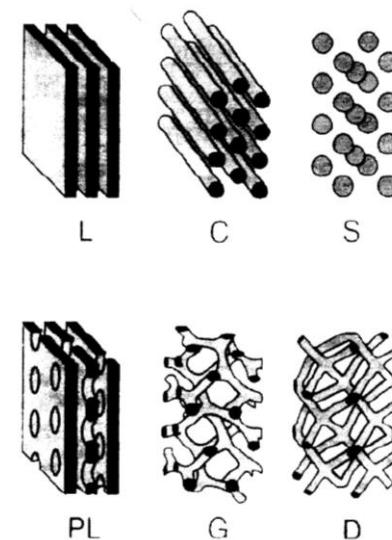
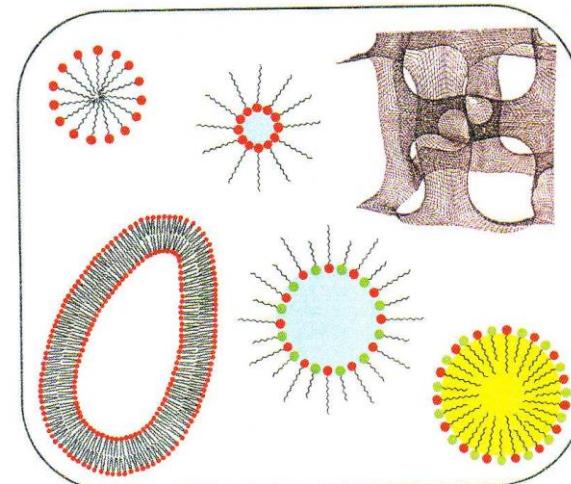
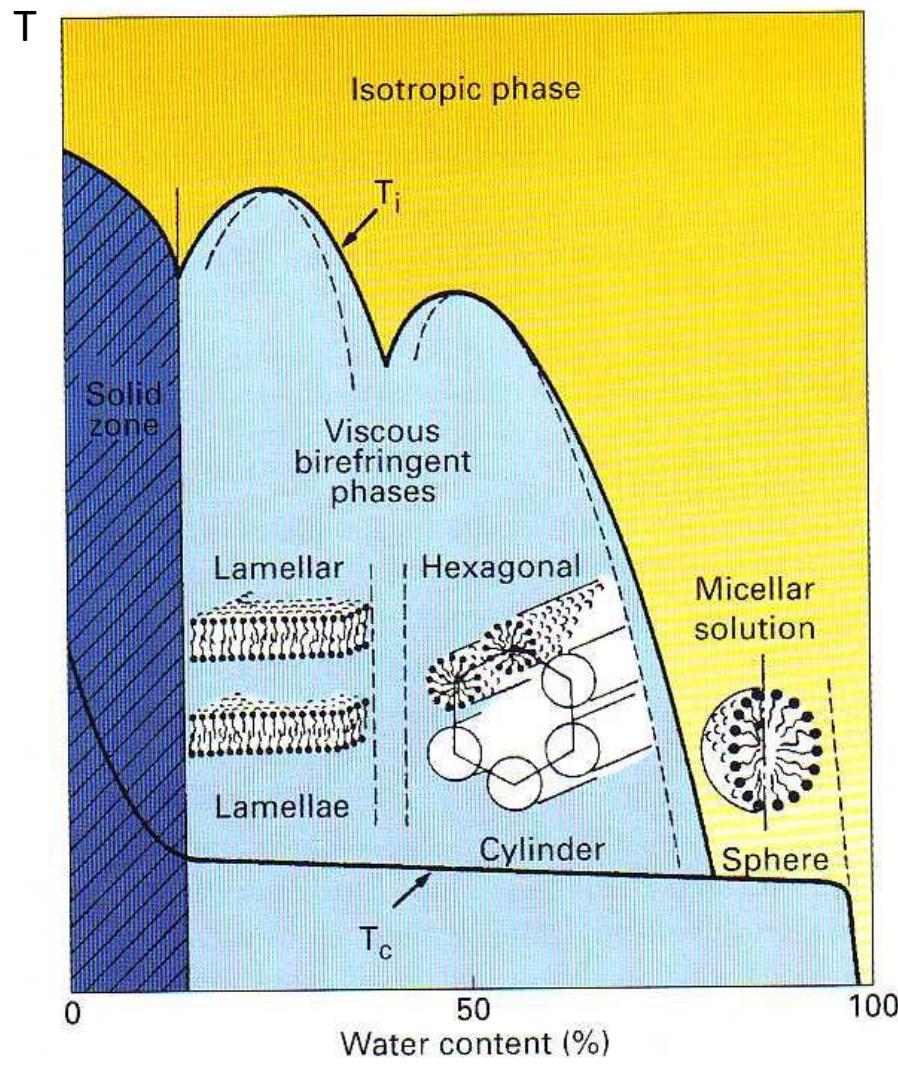
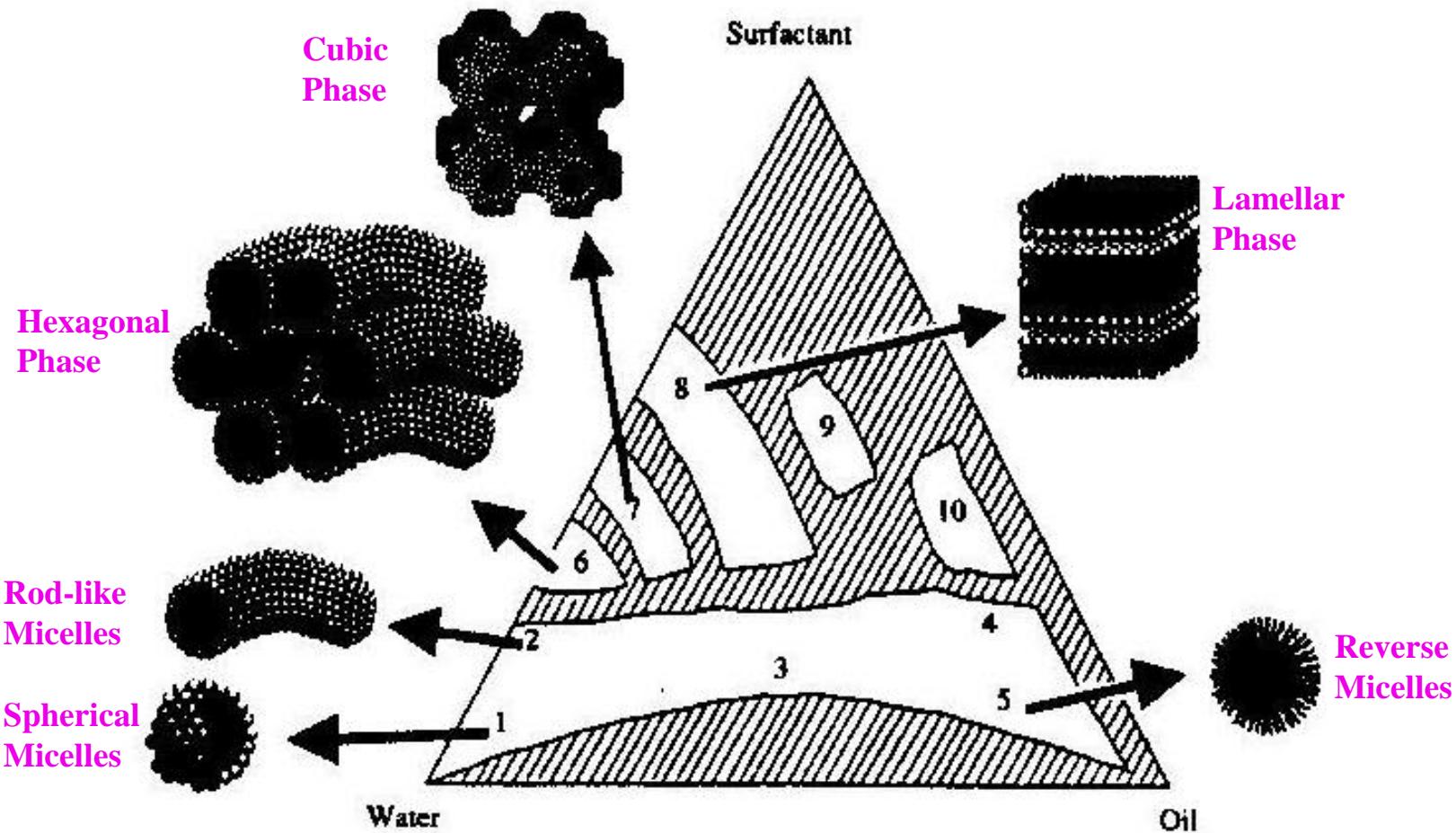


FIGURE 2.4. Phase diagrams of several systems showing the transition from dispersed states to condensed states. (a) Gas-liquid phase transition. (b) Swelling-deswelling in polymer gels. (c) Consolidation of colloidal crystals. (d) Surfactant phase diagrams. In Fig. 2.4(d) M, C, H, L, S represent micelles, cubic phase, hexagonal phase, lamellar phase, and solid phase respectively. Figures 2.4(a) and (b) are redrawn after Refs. 9, 10. Figure 2.4(c) is redrawn after Ref. 13. Figure 2.4(d) is redrawn after Ref. 16.

# Self-Assembled Structures vs. Temperature



# Surfactant concentration effects keeping constant other variables



**FIGURE 2.6.** Schematic phase diagrams of surfactant-water-oil systems. 1. Spherical micelles. 2. Rod-like micelles. 3. Irregular bicontinuous phase. 4. Reverse cylindrical micelles. 5. Reverse micelles. 6. Hexagonal phase. 7. Cubic phase. 8. Lamellar phase. 9. Reverse cubic phase. 10. Reverse hexagonal phase (Derived from Refs. 18 and 19 with permissions from the publishers).

Increase Surfactant Conc.: spherical micelles → rod-like micelles → cubic → lamellar

# Packing Geometry: Attaining the Desired Self-Assembled Structures

$$R = \frac{v}{a_0 l_c}$$

Increasing surfactant concentration, surfactant chain length,  
added high concentration salts and nonpolar solvent.

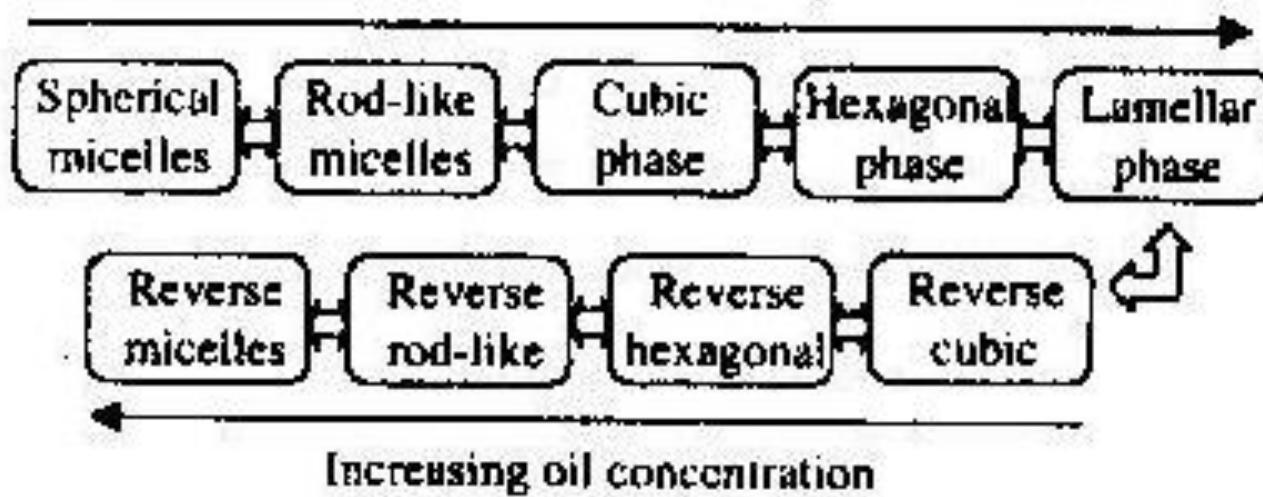
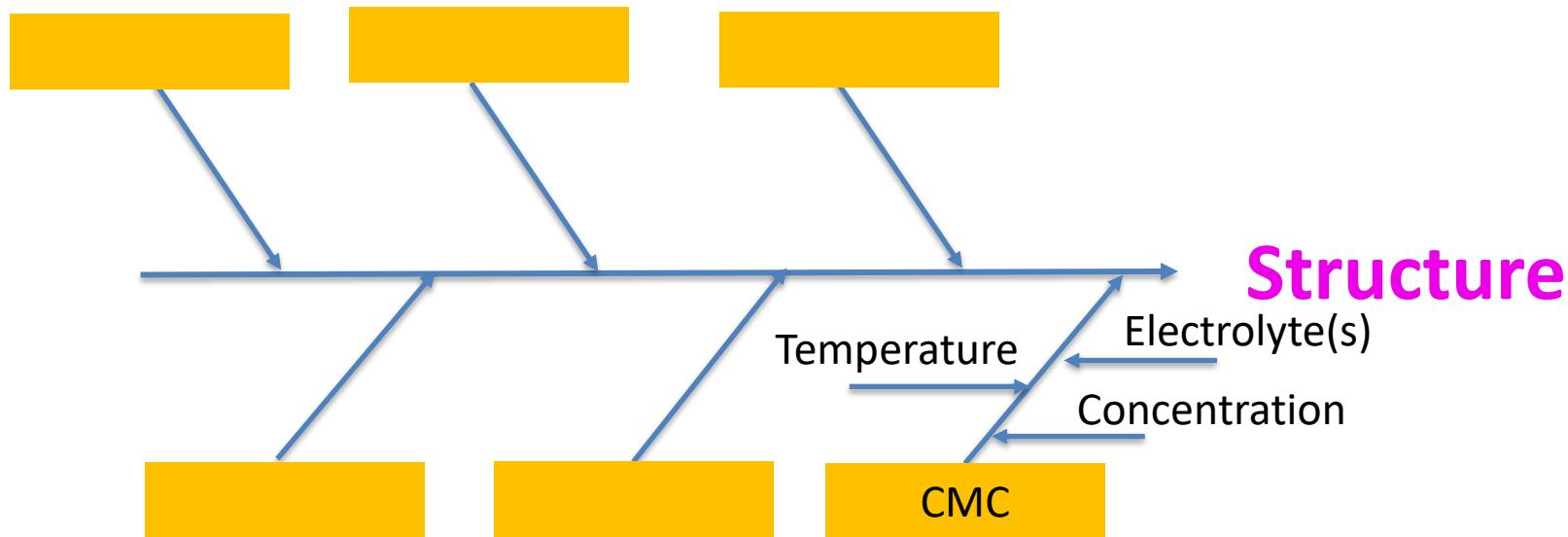


FIGURE 2.7. Phase structures as a function of external conditions.

# Structure, also depends on:

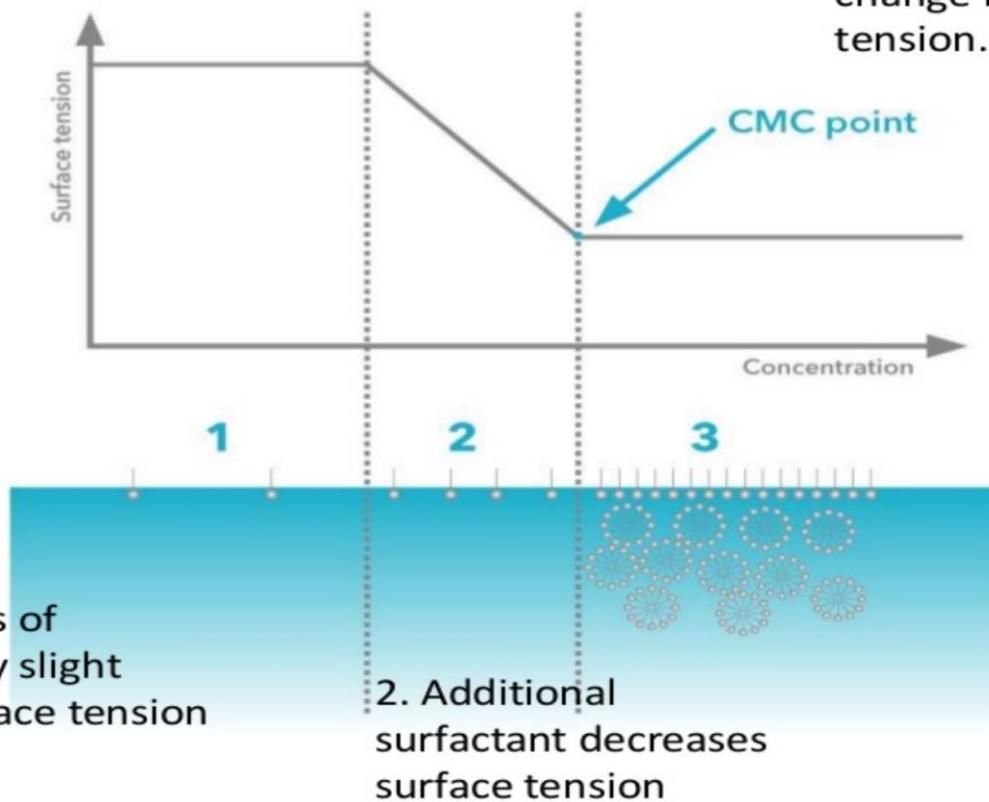


# Critical Micelle Concentration

Micelles are formed at the critical micelle concentration (CMC) and at that concentration some of the properties have an inflection point:

- Surface tension
- Conductivity
- Turbidity

# Surface tension



# Critical Micelle Concentration

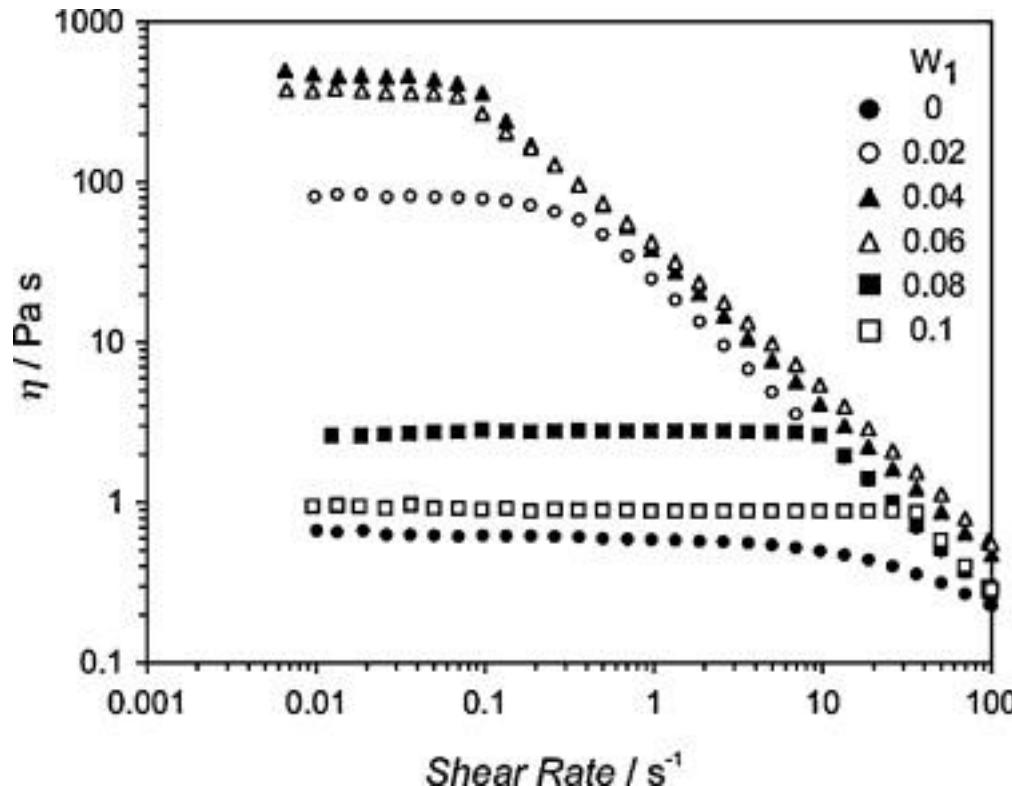
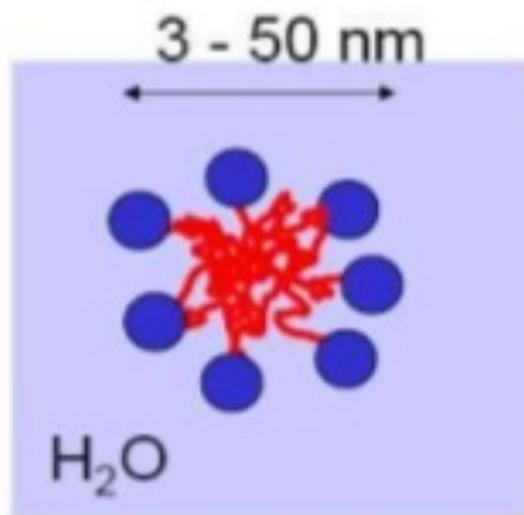


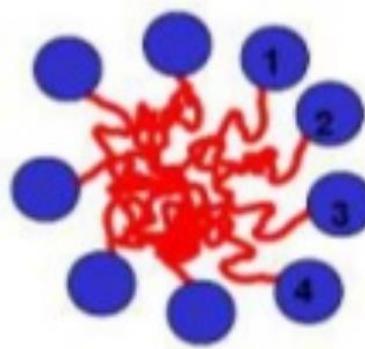
Fig. 1. A plot of viscosity for micellar solutions of the water/ $C_{16}SE/LA$  system at 30 °C against shear rate at various weight fractions of LA in total amphiphiles ( $W_1$ ) is shown. Weight fraction of water in the whole system is fixed at 0.9. Sucrose monopalmitate ( $C_{16}SE$ ) lauric acid (LA)

# Sizes

Micelle size:



Aggregation number:



Ionic surfactants  
 $z_A = 10-170$

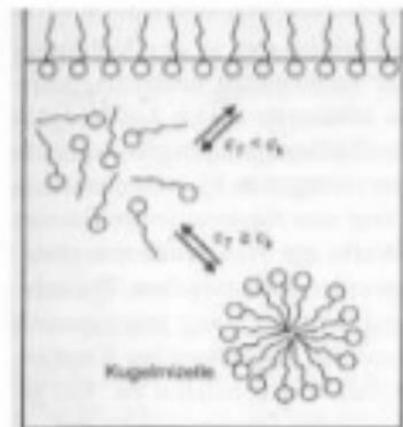
Nonionic surfactants  
 $z_A = 30-10.000$

Critical micelle concentrations (CMC):

cmc of **ionic** surfactants  
is generally **higher**  
compared to nonionic surfactants

Ionic surfactants  
 $cmc = 10^{-3} - 10^{-2} M$

Nonionic surfactants  
 $cmc = 10^{-4} - 10^{-3} M$

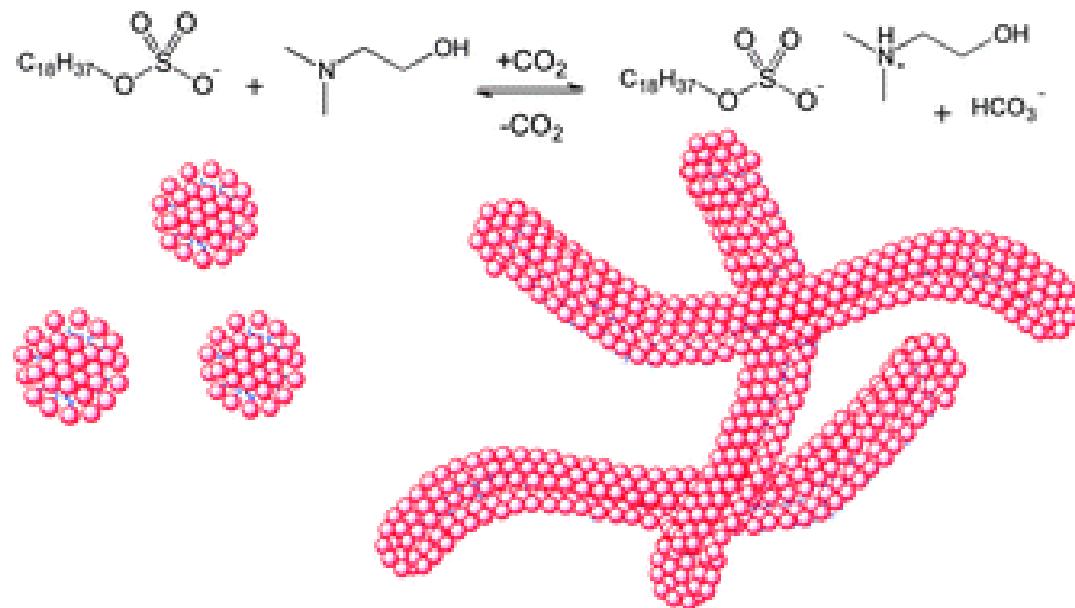


**Switchable viscosity triggered by CO<sub>2</sub> using smart worm-like micelles†**

Xin Su,<sup>a</sup> Michael F. Cunningham<sup>\*ab</sup> and Philip G. Jessop<sup>\*a</sup>

**Abstract**

We report two CO<sub>2</sub>-responsive aqueous solutions having switchable viscosity. The solution of sodium octadecyl sulfate and 2-(dimethylamino)ethanol forms viscoelastic worm-like micelles in the presence of CO<sub>2</sub> but not in its absence at 60 °C. Another solution of sodium stearate and sodium nitrate has high viscosity only if CO<sub>2</sub> is absent.



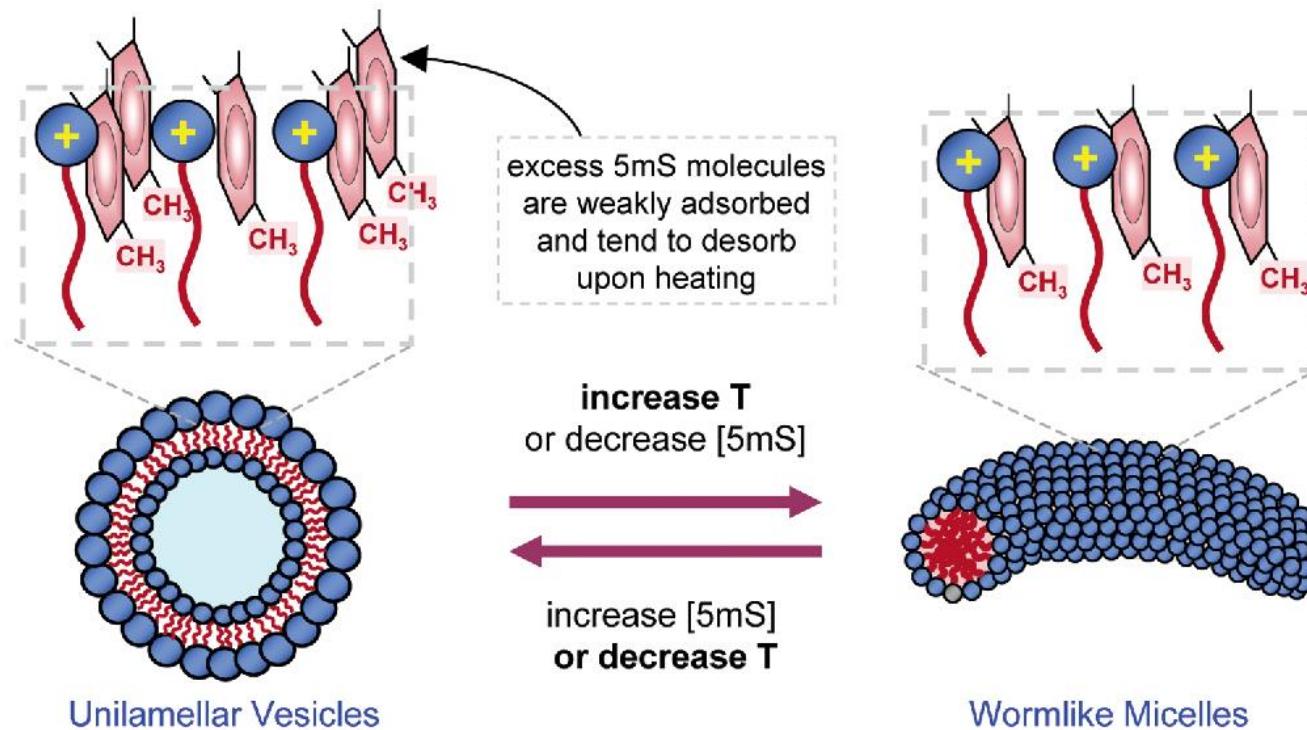
## Chemistry, Medicine

Published in Journal of the American Chemical Society 2006 DOI:[10.1021/ja060021e](https://doi.org/10.1021/ja060021e)

**Self-assembly of surfactant vesicles that transform into viscoelastic wormlike micelles upon heating.**

Tanner S Davies, Aimee M. Ketner, Srinivasa R. Raghavan

Unilamellar vesicles are observed to form in aqueous solutions of the cationic surfactant, cetyl trimethylammonium bromide (CTAB), when 5-methyl salicylic acid (5mS) is added at slightly larger than equimolar concentrations. When these vesicles are heated above a critical temperature, they transform into long, flexible wormlike micelles. In this process, the solutions switch from low-viscosity, Newtonian fluids to viscoelastic, shear-thinning fluids having much larger zero-shear viscosities



# ***Self Assembly***

- **Self-assembly** is the fundamental principle which generates structural organization on all scales from molecules to galaxies. It is defined as reversible processes in which pre-existing parts or disordered components of a preexisting system form structures of patterns. Self-assembly can be classified as either static or dynamic.
- <http://en.wikipedia.org/wiki/Self-assembly>

# **Molecular Self-Assembly**

- Molecular self-assembly is the assembly of molecules without guidance or management from an outside source. There are two types of self-assembly, **intramolecular** self-assembly and **intermolecular** self-assembly, although in some books and articles the term self-assembly refers only to intermolecular self-assembly.
- Intramolecular self-assembling molecules are often complex polymers with the ability to assemble from the random coil conformation into a well-defined stable structure (secondary and tertiary structure). An example of intramolecular self-assembly is protein folding.
- Intermolecular self-assembly is the ability of molecules to form supramolecular assemblies (quaternary structure). A simple example is the formation of a micelle by surfactant molecules in solution.

# Self Assembled Monolayers

- **SAMs – Self Assembled Monolayers**
  - Alkane Thiol complexes on gold
  - C10 or longer, functionalized end groups
- Can build ***multilayer*** / complex structures
- Used for creating biosensors
  - Link bioactive molecules into a scaffold
- The first cells on earth formed from **SAMs**

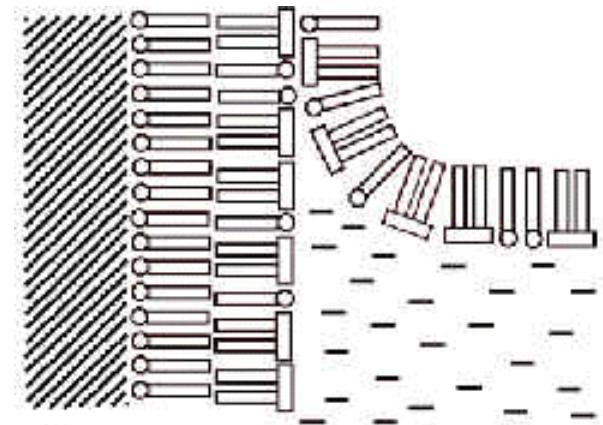
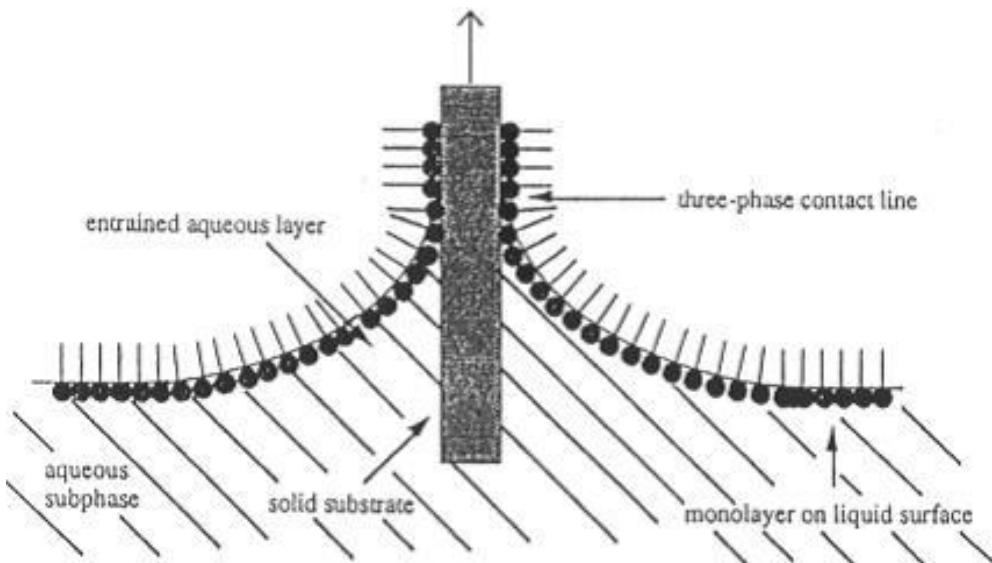
# Langmuir-Blodgett Films

- Definition of LB films
  - History and development
- Construction with LB films
- Building simple LB SAMs
- Nano applications of LB films
  - Surface derivatized nanoparticles
  - Functionalized coatings in LB films

# Langmuir-Blodgett Films

- A **Langmuir-Blodgett film** contains of one or more monolayers of an organic material, deposited from the surface of a liquid onto a solid by immersing (or emersing) the solid substrate into (or from) the liquid.
- A monolayer is added with each immersion or emersion step, thus films with very accurate thickness can be formed.
- Langmuir Blodgett films are named after Irving Langmuir and Katherine Blodgett, who invented this technique.
- An alternative technique of creating single monolayers on surfaces is that of self-assembled monolayers.

# Langmuir-Blodgett Films



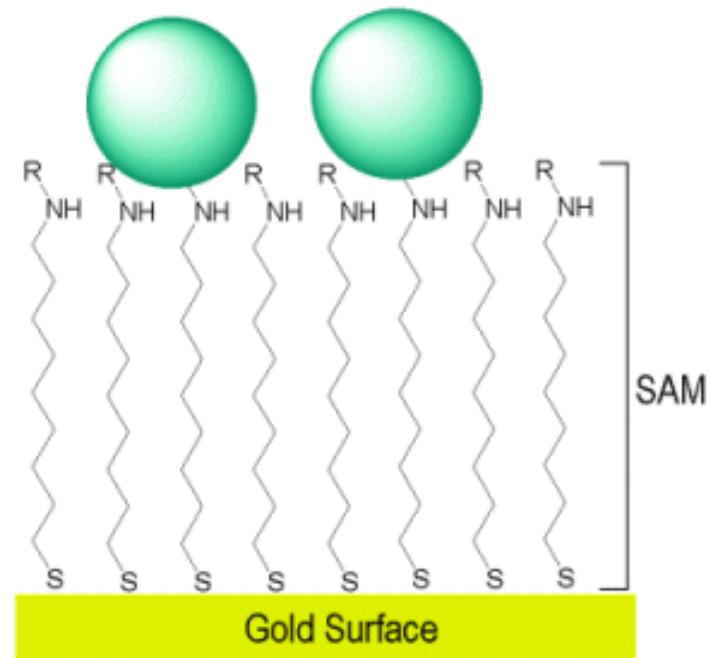
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[http://www.ksvlt.com/pix/keywords\\_html\\_m4b17b42d.jpg](http://www.ksvlt.com/pix/keywords_html_m4b17b42d.jpg)

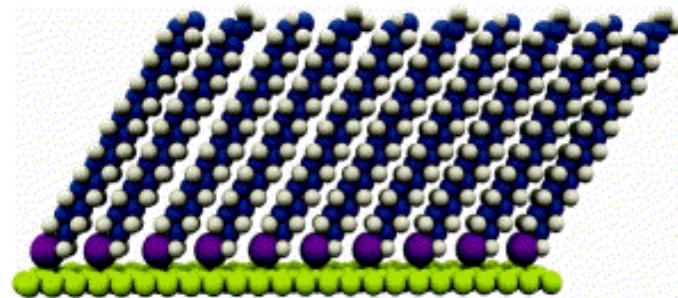
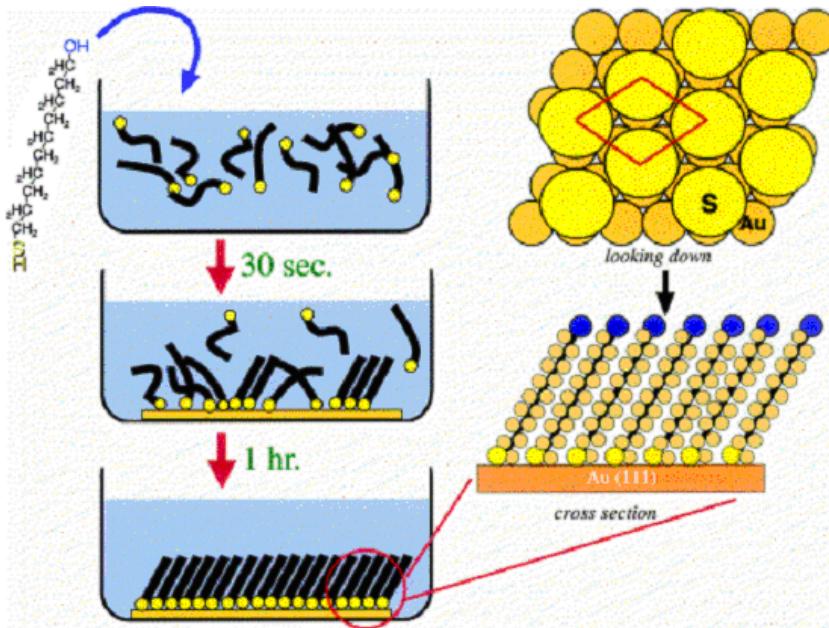
**Deposition of Langmuir-Blodgett molecular assemblies of lipids on solid substrates.**

# SAM Technology Platform

- SAM reagents are used for electrochemical, optical and other detection systems. Self-Assembled Monolayers (SAMs) are unidirectional layers formed on a solid surface by spontaneous organization of molecules.
- Using functionally derivatized C10 monolayer, surfaces can be prepared with active chemistry for binding analytes.



# An example of Self-Assembly Process



A schematic of SAM (*n*-alkanethiol  $\text{CH}_3(\text{CH}_2)_n\text{SH}$  molecules) formation on a Au(111) sample.

The self-assembly process. An *n*-alkane thiol is added to an ethanol solution (0.001 M). A gold (111) surface is immersed in the solution and the self-assembled structure rapidly evolves. A properly assembled monolayer on gold (111) typically exhibits a lattice.

# Co-Assembly of Liquid Structures and Inorganic Materials

Self-assembled liquid crystals from surfactants act as a **template** to support the growth of ceramic materials. These ordered structures are cross-linked together through the condensation of the aluminosilicate ions. Subsequently, the surfactant molecules can be removed by thermal or chemical treatment without collapsing the ordered structure (2-50 nm tunable).

Self-assembled periodic structures can be further used as a structural frame work to develop new materials:

1. by incorporating functional molecules and active sites into the porous channels (e.g. nanoporous silica)
2. by using the periodic nanoporous structures as a template (e.g. for carbon or metals)
3. by physically confining a new material in the organized nanostructures.

# Co-Assembly of Liquid Structures and Inorganic Materials

Interactions between cationic surfactants and Anionic Silicates

Mesoporous materials: mixing aluminosilicate precursors (e.g. sodium aluminate, tetramethyl ammonium silicate, and silica) in a surfactant solution (e.g.  $\geq 1$  wt% cetyltrimethyl ammonium bromide (CTAB))

Inorganic ions play an important role in the self assembly process

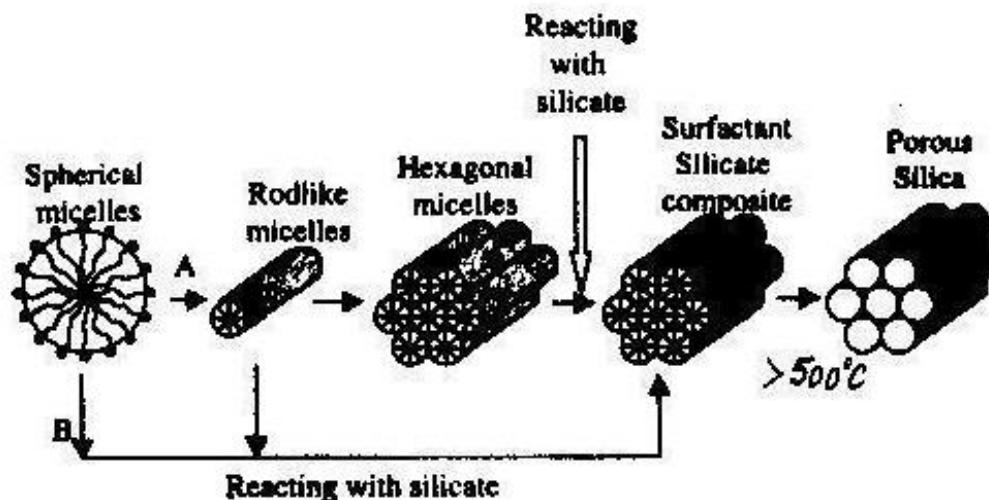
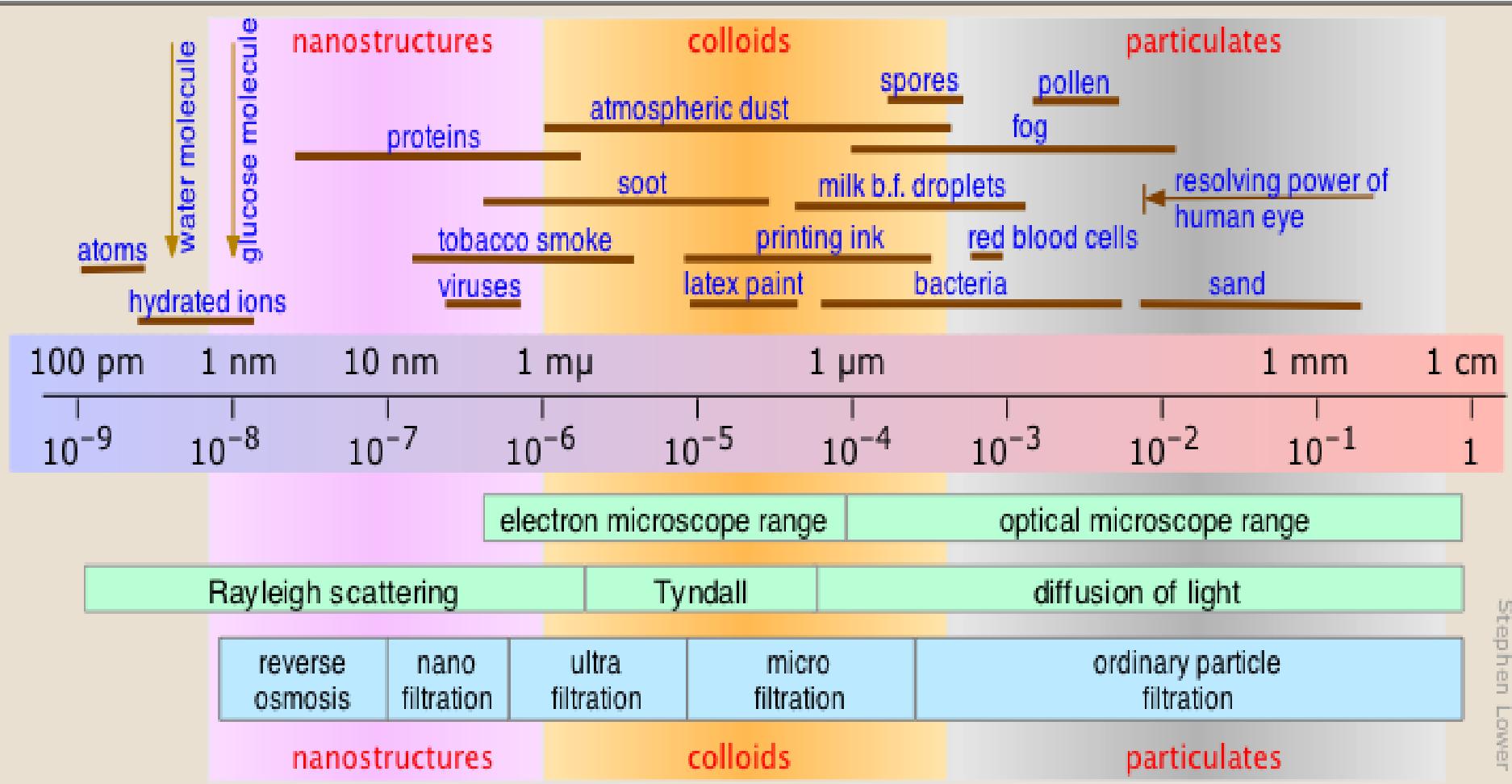
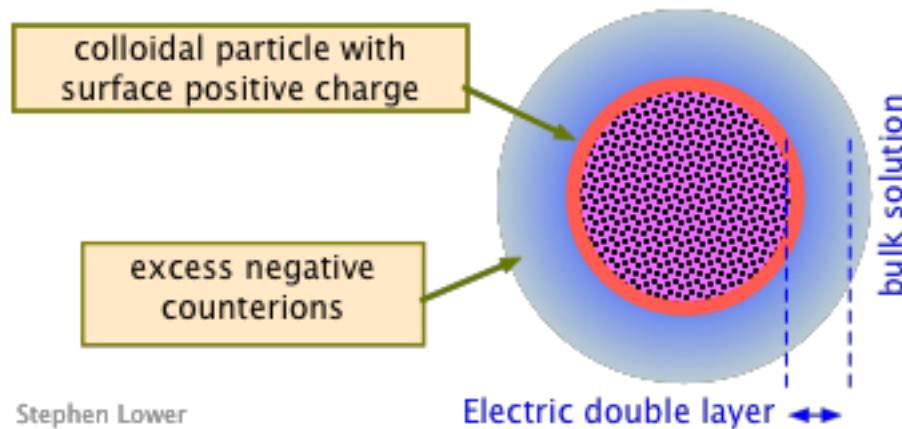


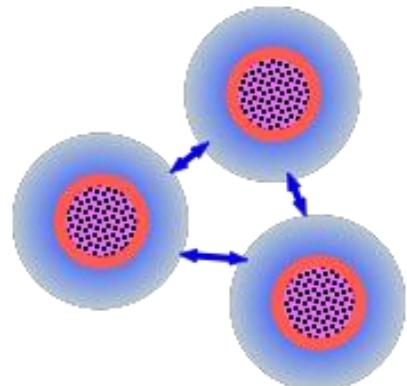
FIGURE 2.11. Liquid crystalline templating mechanisms initially suggested for the formation of ordered nanoscale materials (redrawn after Ref. 23).

# Particles

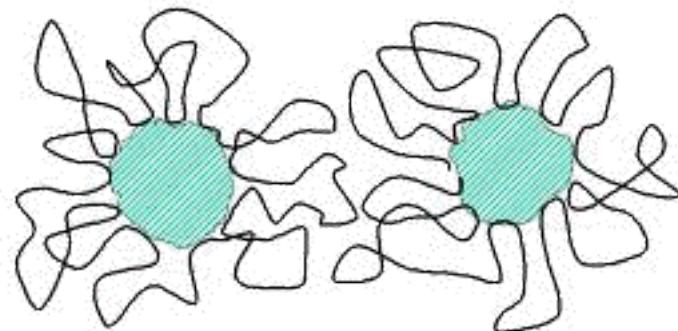




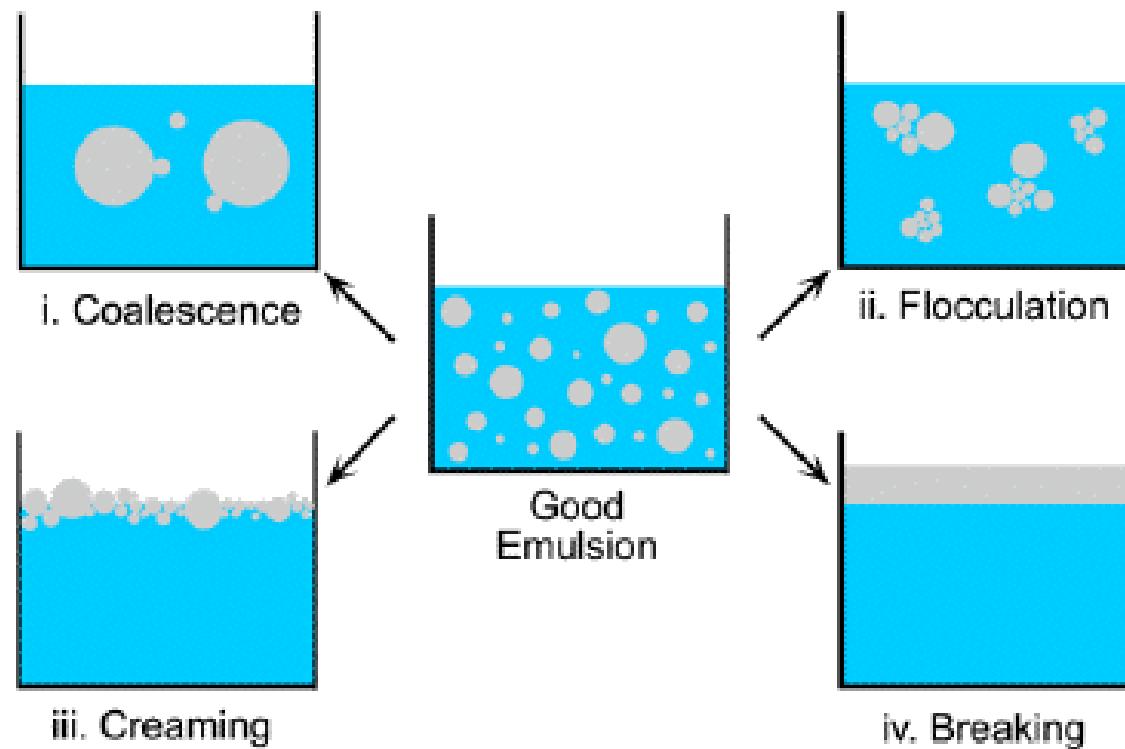
## Electrostatic Stabilization



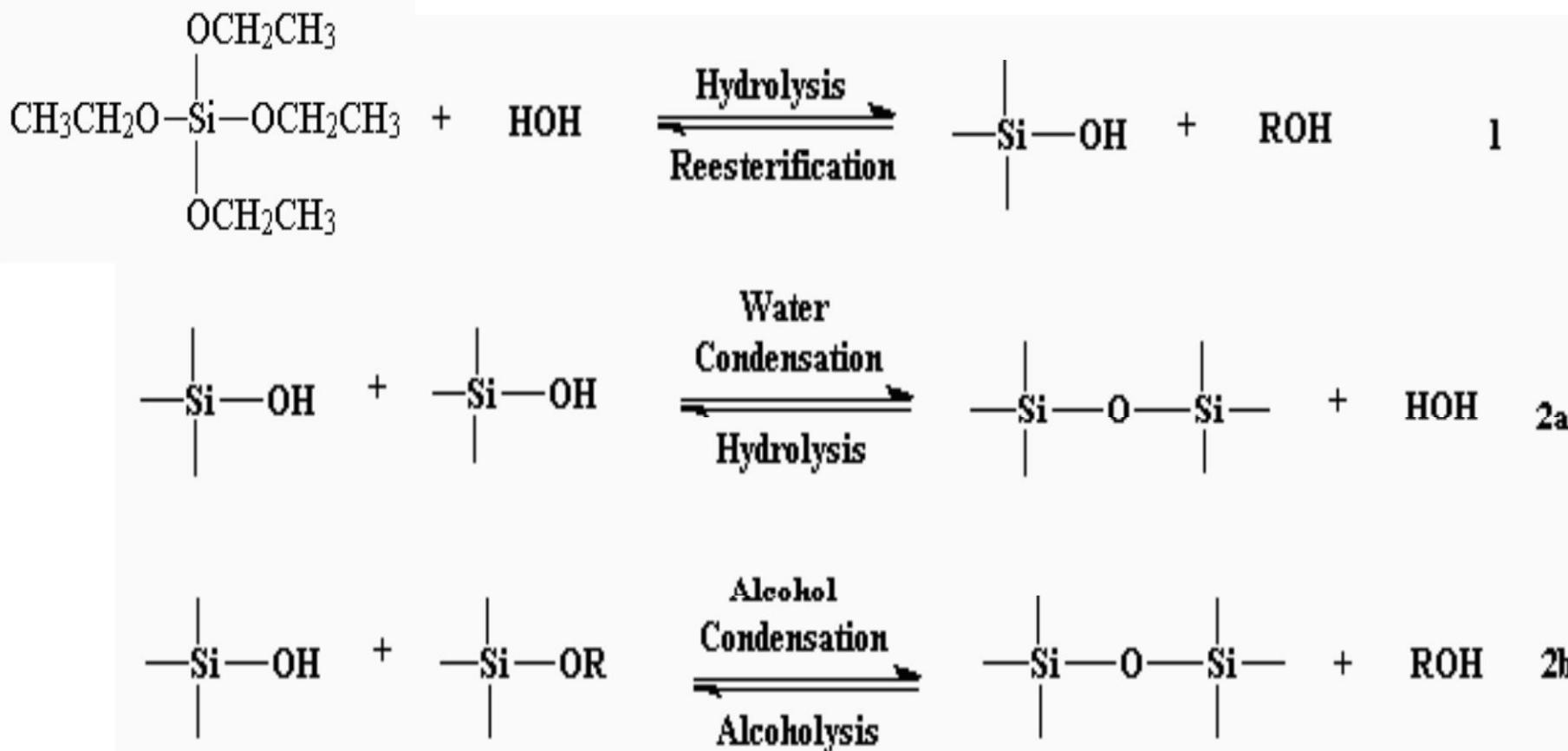
## Steric Stabilization



M. Hubbe



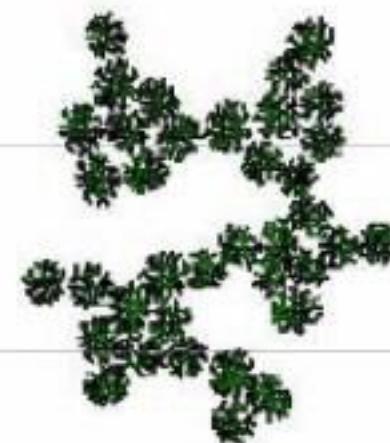
# In-Situ Generation of Nanophases



TEOS Hydrolysis/condensation

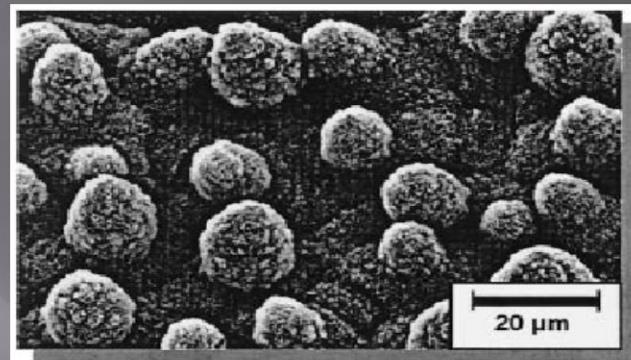
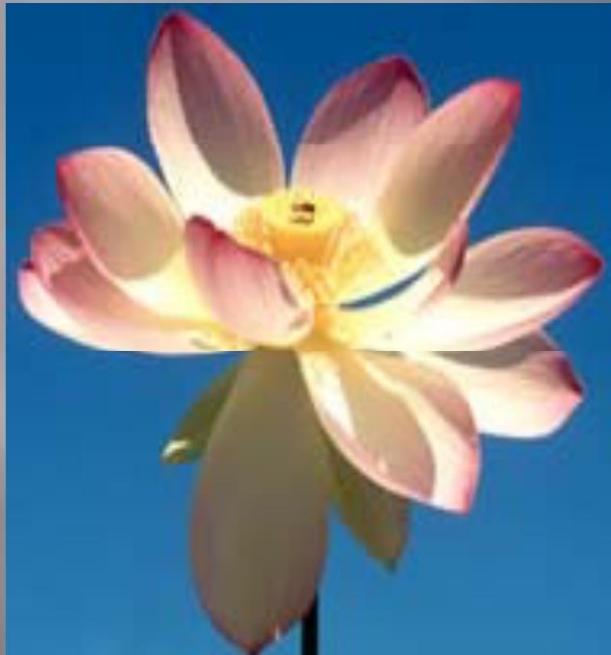
# Sol-gel derived silicon oxide networks

- Acid-catalyzed
  - yield primarily linear or randomly branched polymer
- Base-catalyzed
  - yield highly branched clusters



# Lotus Effect

Rainwater cleans lotus leaves because of their bumpy surface.



Abramzon, et al., Chemistry & Life (1982)  
Barthlott et al., Annals of Botany (1997)

# Nano-Structuring Methods

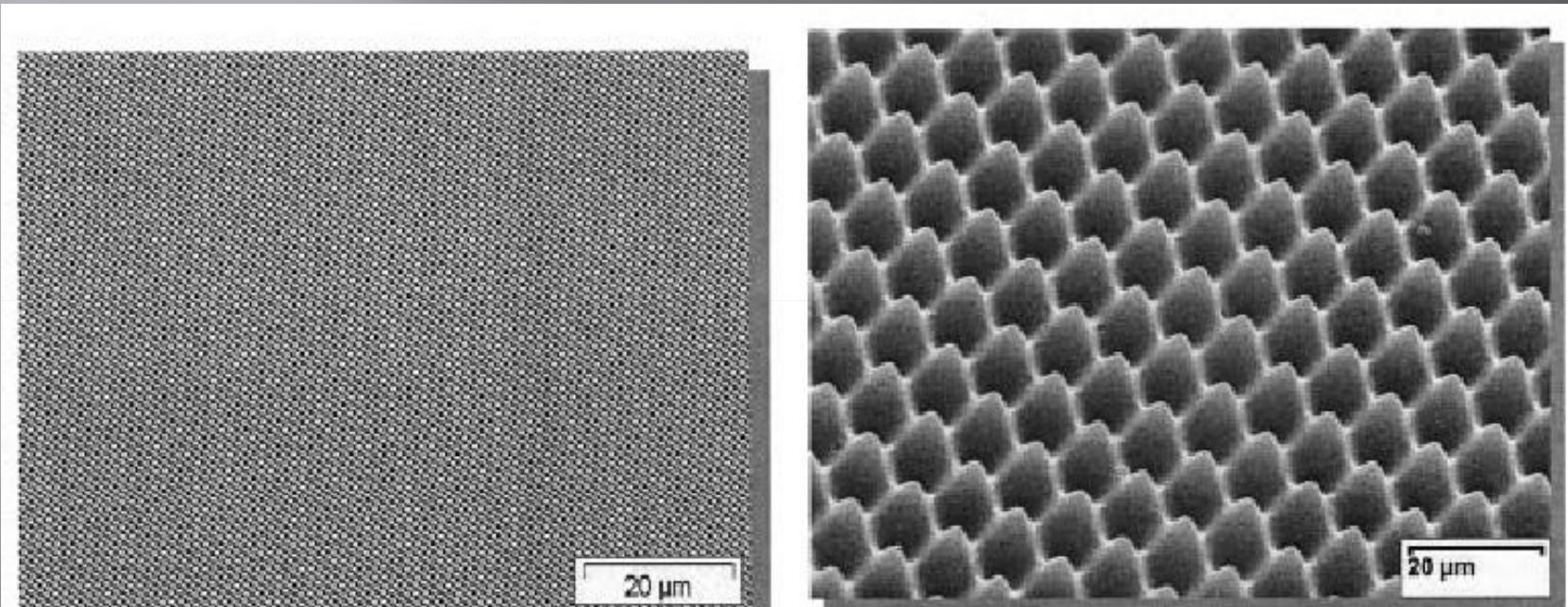


Figure 2. SEM image of self-cleaning surfaces with different structure size

Nun, Oles, & Schleich, Macromol. Symp., 187, 677-682 (2002)

“Nanostructured superhydrophobic surfaces”, H. M. Shang, Y. Wang, K. Takahashi, G. Z. Cao, D. Li, and Y. N. Xia, J. Mater. Sci., 40, 3587, 2005

# Homework 4

**Read, make a 200 word Abstract and propose a method to produce the surface indicated in the paper**

## Transformation of a Simple Plastic into a

**Superhydrophobic Surface** H. Yıldırım Erbil<sup>1,\*</sup>A. Levent

Demirel<sup>2,\*</sup>Yonca Avcı<sup>1</sup>, Olcay Mert<sup>1</sup>

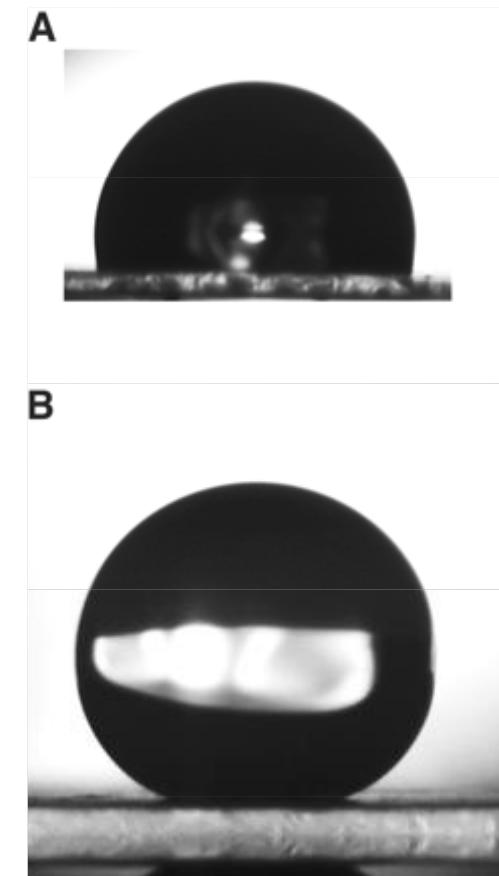
*Science* 28 Feb 2003:

Vol. 299, Issue 5611, pp. 1377-1380

DOI: 10.1126/science.1078365

### Abstract

Superhydrophobic surfaces are generally made by controlling the surface chemistry and surface roughness of various expensive materials, which are then applied by means of complex time-consuming processes. We describe a simple and inexpensive method for forming a superhydrophobic coating using polypropylene (a simple polymer) and a suitable selection of solvents and temperature to control the surface roughness. The resulting gel-like porous coating has a water contact angle of 160°. The method can be applied to a variety of surfaces as long as the solvent mixture does not dissolve the underlying material.



# Homework

Langmuir-Blodgett Trough Tutorial - Part I: Introduction

<https://www.youtube.com/watch?v=9Sm8MvIYINg>

Langmuir-Blodgett Trough Tutorial - Part II: Cleaning and preparation

<https://www.youtube.com/watch?v=XEjdjtSkyIU>

Langmuir-Blodgett Trough Tutorial - Part III: Monolayer formation and taking an isotherm

<https://www.youtube.com/watch?v=orV-xtM4lxI>

Langmuir-Blodgett Trough Tutorial - Part IV: Deposition of a monolayer

[https://www.youtube.com/watch?v=NQ6H3ys6\\_o](https://www.youtube.com/watch?v=NQ6H3ys6_o)

# Uses

- As small chemical reactor to obtain:
  - zero dimension nanoparticles
- As templates to create stable mesoporous materials
  - Molecular sieves
  - High surface area catalysts
  - Gas sensors
  - Dye sensitized photovoltaic solar cells
  - Nanotubes

**May you want to know more, this**

# **ANNEX 1**

**is for you**

# Methods of Measuring Surface Tension

<i>Method</i>	<i>Pure Liquids</i>	<i>Solutions</i>
Wilhelmy Plate	quick and easy to operate	Good, suitable when ageing occurs
Du Nu��y Ring	Satisfactory	n/a
Sessile Drop	Very Good	Good when surface ageing occurs
Drop Weight	Suitable	Poor when surface ageing occurs
Capillary Height	Very Good	n/a if $\theta \neq 0$
Bubble pressure	Very Good	Good when ageing occurs

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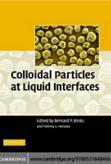
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Contenido

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Mis notas

### Colloidal Particles at Liquid Interfaces



**Autor:** Horozov, Tommy S., Binks, Bernard P.

**Fecha:** 2006

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### Interfaces, Surfactants and Colloids in Engineering

Editors

H. -J. Jacobasch

Book

288

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## Journal of Polymer Science Part C: Polymer Symposia

Article

**Time-temperature superposition in ultimate behavior of heterogeneous gels with varying microstructure**

M. Raab, Z. Pelzbauer, J. Janáček, M. Štol

First published: 1972 | <https://doi.org/10.1002/polc.5070380118> | Citations: 2
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**Abstract**

If water is present in a volume concentration higher than about 0.5 during the crosslinking copolymerization of poly(2-hydroxyethyl methacrylate), porous heterogeneous systems are formed. Samples of poly(2-hydroxyethyl methacrylate) obtained by polymerization in the presence of various concentrations of water and, therefore, exhibiting different heterogeneity, were swollen in water to equilibrium and used to investigate the ultimate behavior. Heterogeneity was characterized by the volume fraction of swollen polymer in the heterogeneous system and morphology was determined by electron and light microscopy. For all samples, the dependence of time to break on tensile stress, and tensile strength and strain at break at various temperatures have been measured. While the rupture stress of homogeneous samples is very temperature sensitive, the effect of temperature is much less pronounced in the case of highly porous samples. This phenomenon has been ascribed to the temperature-independent coulomb friction which participates in the rupture process of heterogeneous gels.

Journal of the Korean Ceramic Society  
Vol. 56, No. 3, pp. 211–232, 2019.<https://doi.org/10.4191/kcers.2019.56.3.02>**Review****Wet Foam Stability from Colloidal Suspension to Porous Ceramics: A Review**Ik Jin Kim \*, Jung Gyu Park\*, Young Han Han\*\*,  
Suk Young Kim\*\*\*, and James F. Shackelford\*\*\*\*

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(Received March 4, 2019; Revised March 21, 2019; Accepted April 1, 2019)

**ABSTRACT**

Porous ceramics are promising materials for a number of functional and structural applications that include thermal insulation, filters, bio-scaffolds for tissue engineering, and preforms for composite fabrication. These applications take advantage of the special characteristics of porous ceramics, such as low thermal mass, low thermal conductivity, high surface area, controlled permeability, and low density. In this review, we emphasize the direct foaming method, a simple and versatile approach that allows the fabrication of porous ceramics with tailored microstructure, along with distinctive properties. The wet foam stability is achieved under the controlled addition of amphiphiles to the colloidal suspension, which induce *in situ* hydrophobization, allowing the wet foam to resist coarsening and Ostwald ripening upon drying and sintering. Different components, like contact angle, adsorption free energy, air content, bubble size, and Laplace pressure, play vital roles in the stabilization of the particle stabilized wet foam to the porous ceramics. The mechanical behavior of the load-displacements curves of sintered samples was investigated using Herzian indentations testes. From the collected results, we found that microporous structures with pore sizes from 30 μm to 570 μm and the porosity within the range from 70% to 85%.

**Key words :** *Colloidal suspension, Surfactants, Wet foam stability, Direct foaming, Porous ceramics*

# Critical Micelle Concentration

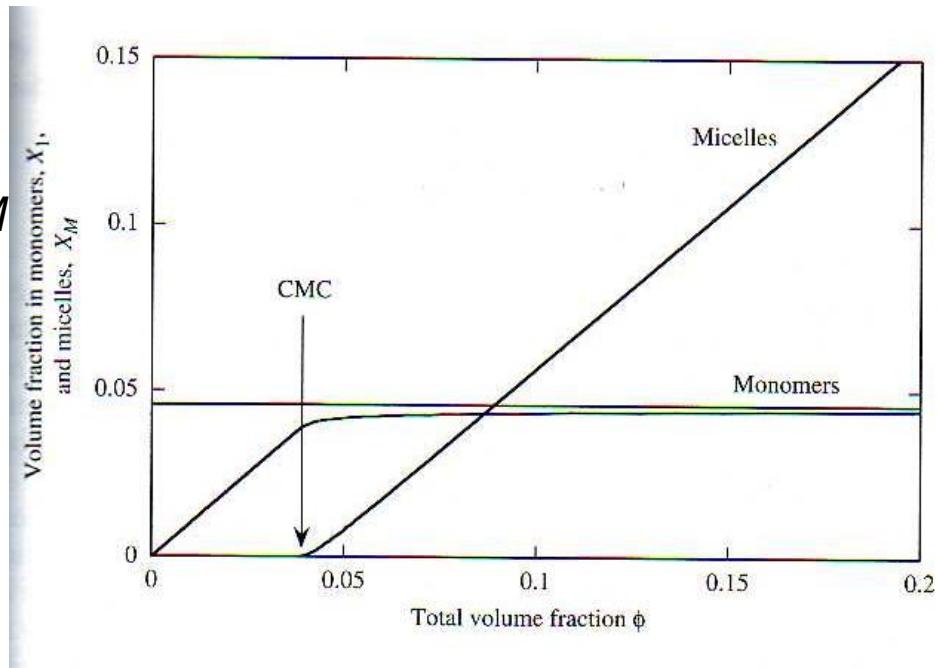
$\phi$  volume fraction of amphiphile

$\phi < \phi_c$  monomers

$\phi > \phi_c$  micelles of average size  $M$

$$X_M = M \left[ X_1 \exp\left(\frac{\Delta\varepsilon}{k_B T}\right) \right]^M \quad \Delta\varepsilon = \varepsilon_1 - \varepsilon_M$$

$$\phi_c = \exp(-\Delta\varepsilon/k_B T) \quad (\text{CMC})$$



# Spherical micelles

Spheres formed when:

$$v/l_c a_0 \leq 1/3$$

Size of micelles finite ->

$\varepsilon_N$  has a minimum value at an optimum number M

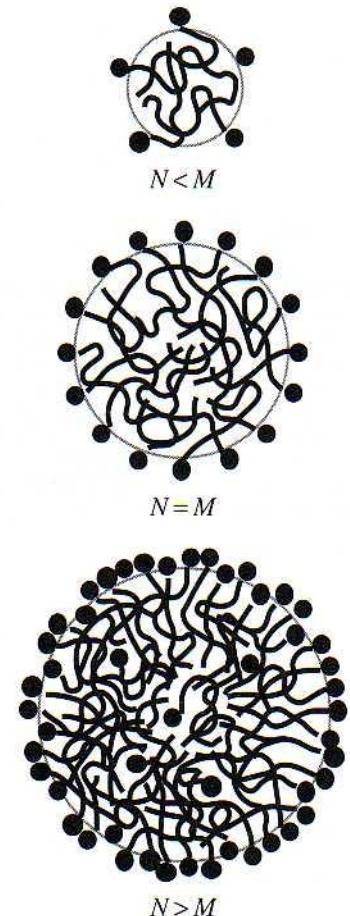
$$\varepsilon_N = \varepsilon_M + \Lambda(N - M)^2$$

$$X_N = N \left[ \frac{X_M}{M} \exp\left(\frac{-M\Lambda(M-N)^2}{k_B T}\right) \right]^{N/M}$$

$X_N$  - volume fraction of micelles  
with N molecules

$$\langle |N - M|^2 \rangle = \frac{k_B T}{2M\Lambda}$$

↑  
size distribution



**Fig. 9.3** The optimum aggregation number,  $M$  for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the hydrophobic core.

# Macro vs. micro phase separation

Simple liquids (water & oil):

$$\varepsilon_N = \varepsilon_\infty + \frac{\alpha k_B T}{N^{1/3}}$$

$$\alpha k_B T = 4\pi\gamma(3v/4\pi)^{2/3}$$

free energy when a molecule joins an aggregate  
 $N$  - number of molecules in the aggregate  
 $\gamma$  - interfacial energy,  $v$  - molecular volume

$\varepsilon_N$  - monotonic decreasing function of  $N$

-> infinite aggregates - macroscopic phase separation

Amphiphiles:

-> finite size of aggregates - microscopic phase separation

Why?

# Macro vs. micro phase separation

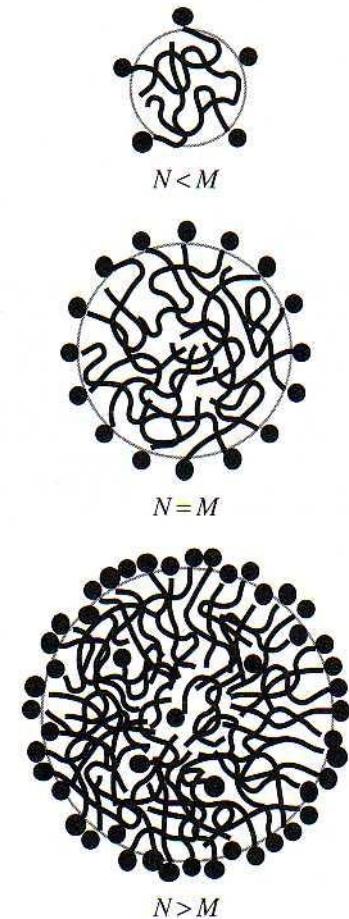
Amphiphiles:

- > micro-phase separation
- > finite size of aggregates
- > entropic considerations more important



**Why?** Balance between protecting the hydrophobic tail and keeping the head in contact with the water

associating tails vs. repulsion of head groups



**Fig. 9.3** The optimum aggregation number,  $M$  for a spherical micelle. Micelles containing a smaller number of molecules have too large an area for each head-group, causing unfavourable water/hydrocarbon interactions, while in micelles larger than the optimum number some head-groups are forced inside the hydrophobic core.

# Cylindrical micelles

Spheres formed when:

$$1/3 < v/l_c a_0 \leq 1/2$$

Size of micelles finite but  $\varepsilon_N$  has a no minimum - energy of a molecule in the cylinder is independent of the size -> only  $2\Delta E_{end}$

-> forming larger micelles leads to energy gain, but a loss in entropy

$$\varepsilon_N = \varepsilon_\infty + \frac{\alpha k_B T}{N} \quad , \quad \frac{\alpha k_B T}{N} = \frac{2\Delta E_{end}}{N}$$

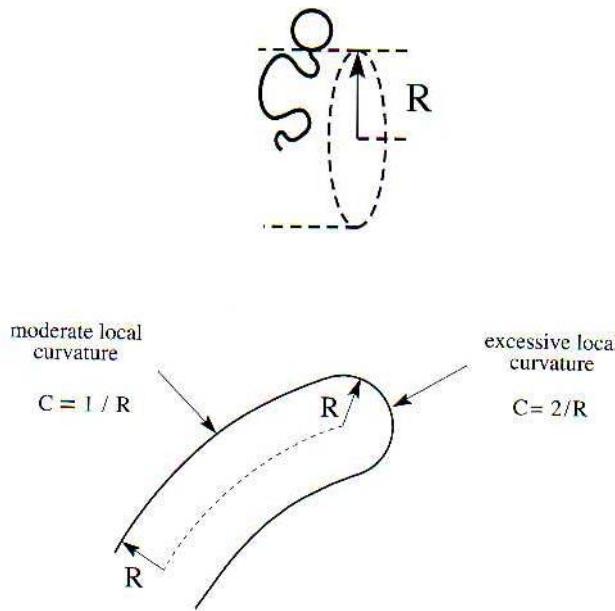


Fig. 5.11. To isolate its hydrophobic interior from water, a more or less hemispherical surface must form at the two ends of a giant cylindrical micelle

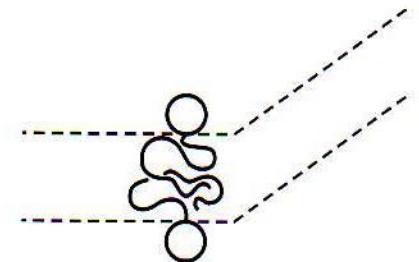
# Bilayers

Bilayers formed when:

$$v/l_c a_0 > 1/2$$

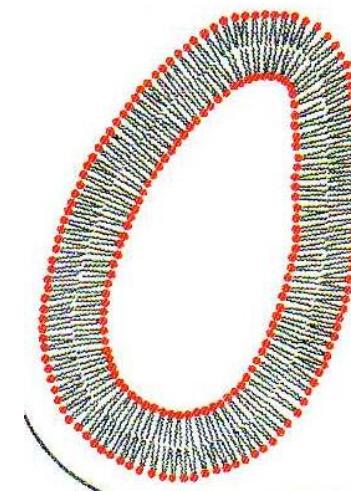
$$\Delta E_{\text{edge}}(A) \propto A^{1/2} \quad (\text{A - area of a layer})$$

dependent on the size of the bilayer  
-> formation of infinite layers



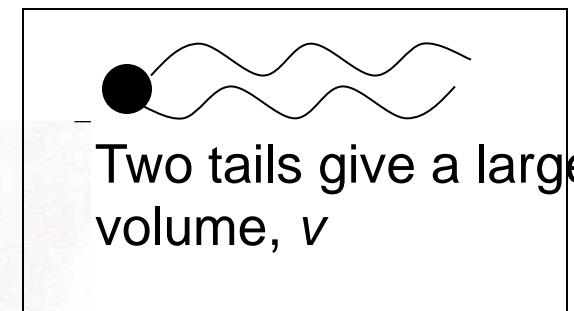
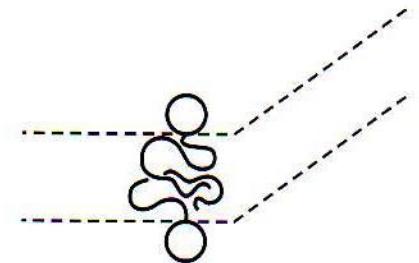
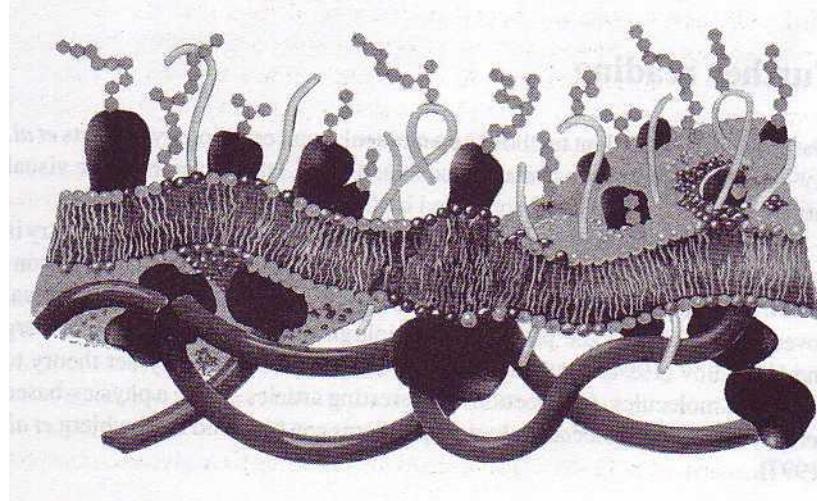
Vesicles - closed surface by a bilayer

- > model for cell membranes
- > drug delivery systems
- > colloidal behaviour



# Bilayers

Cell membranes - phospholipid bilayers



Two tails give a large volume,  $v$

$$v/l_c a_0 > 1/2$$

**Fig. 10.11** A schematic diagram of the cell membrane of a eukaryotic cell. The basic structural element is a lipid bilayer; the bilayer is decorated by a number of protein molecules. On the inside of the membrane (below) a network of actin filaments is anchored by protein molecules, while the outside of the membrane is decorated by carbohydrate chains. Reproduced with permission from Mouritsen and Andersen (1998).

# Bilayers

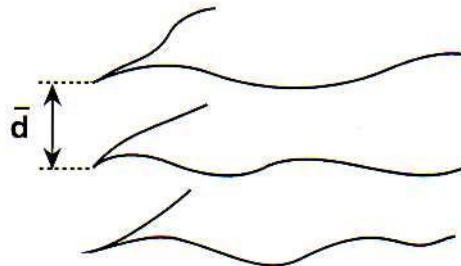
Bilayers are not flat - highly crumpled

Persistence length:

$$\xi_k = a \exp\left(\frac{4\pi k}{\alpha k_B T}\right)$$

$k$  - bending modulus of membrane

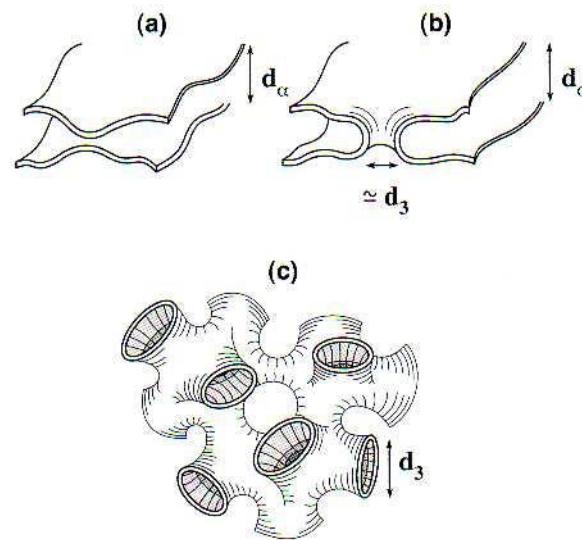
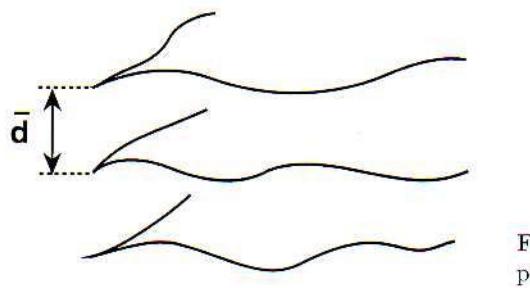
For  $r > \xi$  direction in membrane is lost



Lamellar phases can anyway be obtained with very large  $d \rightarrow$  confinement between two adjacent planes leads to loss in entropy

# Bilayers

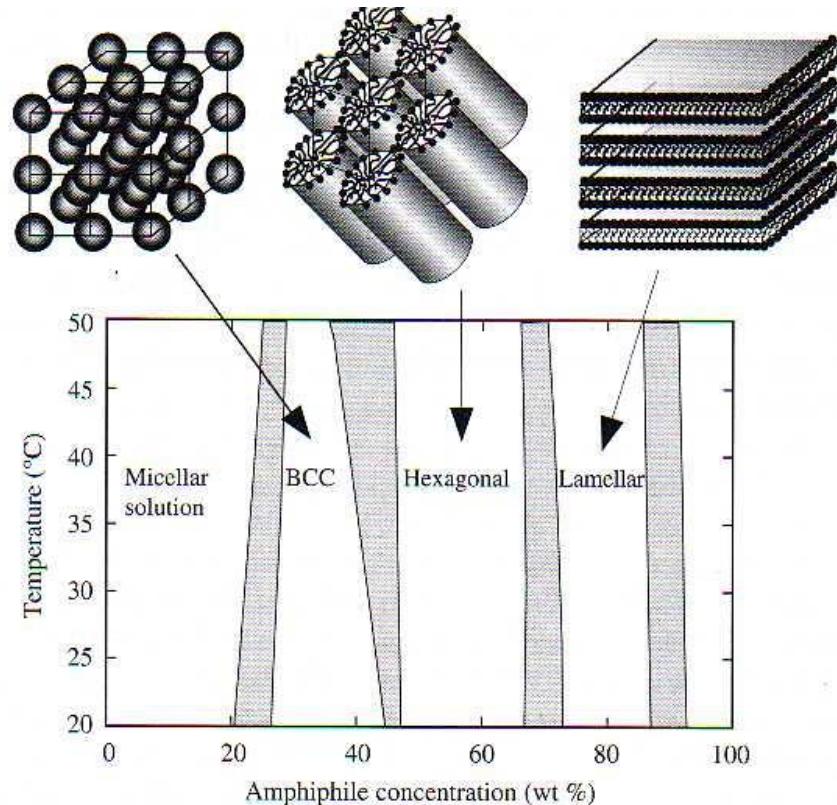
Lamellar phase can be distorted by fluctuations forming complex geometries



**Fig. 5.21.** Structure of the sponge phase.  
**(a)** Two bilayers in the lamellar phase.  
**(b)** Formation of an elementary passage.  
**(c)** Proliferation of passages, leading to the sponge phase  $L_3$

# Phase behaviour

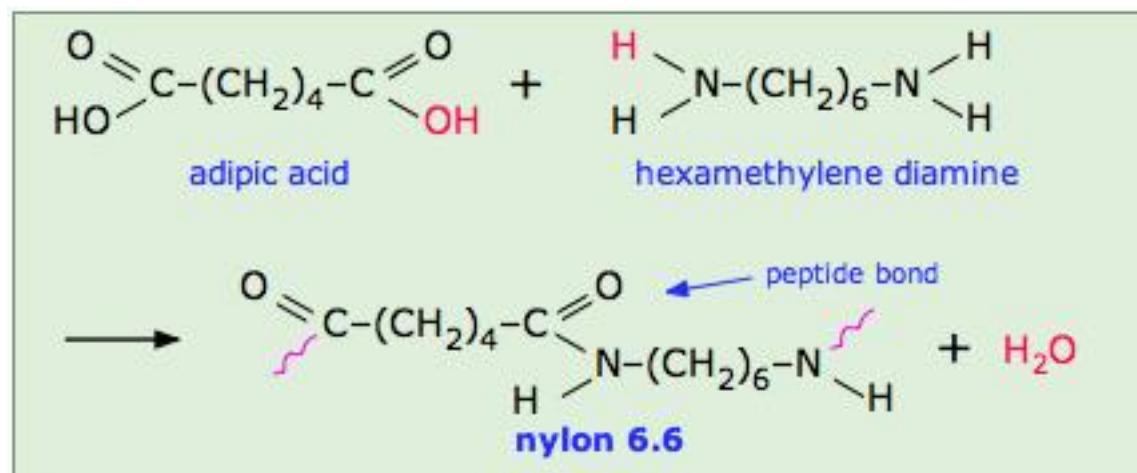
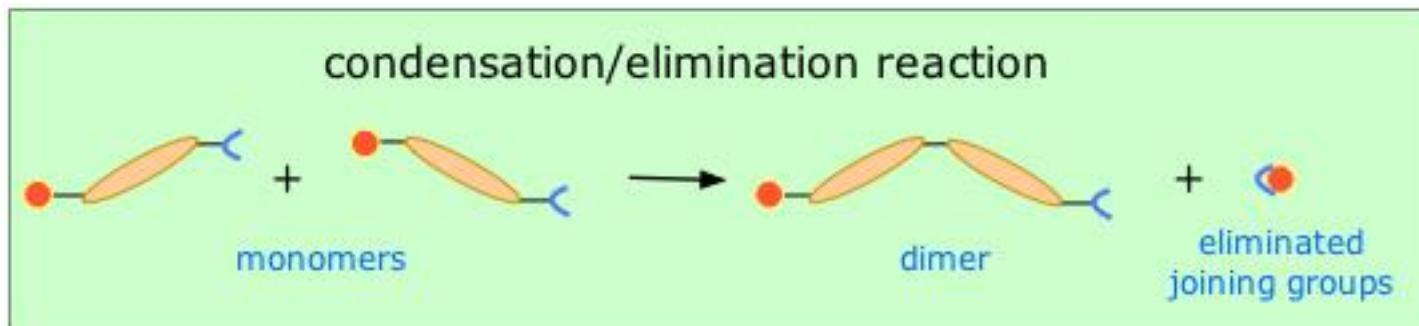
Self assembled structures are rich in phases  
-> response by changing size and shape and arrangement of micelles  
-> dramatic change in properties



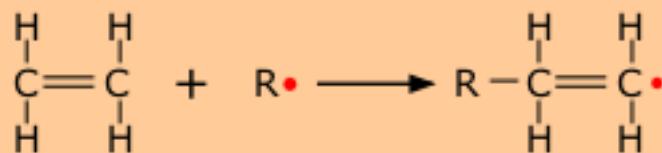
**Fig. 9.7** The phase diagram of an amphiphilic copolymer in water, showing schematically the structures of the ordered phase. The material is a short triblock copolymer of ethylene oxide (EO) and propylene oxide (PO), with the structure  $(EO)_{37}(PO)_{58}(EO)_{37}$ . Data from P. Alexandris, D. Zhou, and A. Khan, *Langmuir*, **12**, 2690 (1996).

# Polymers

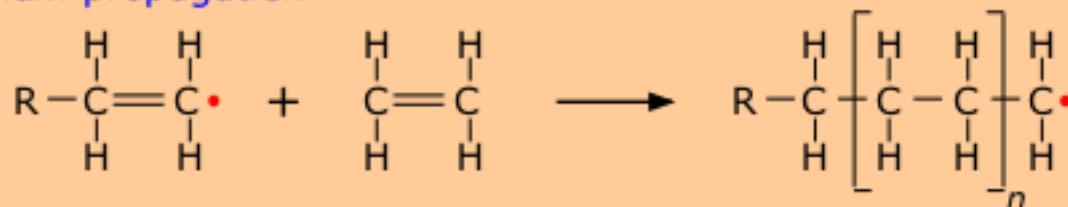
# Condensation



chain initiation



chain propagation



chain termination



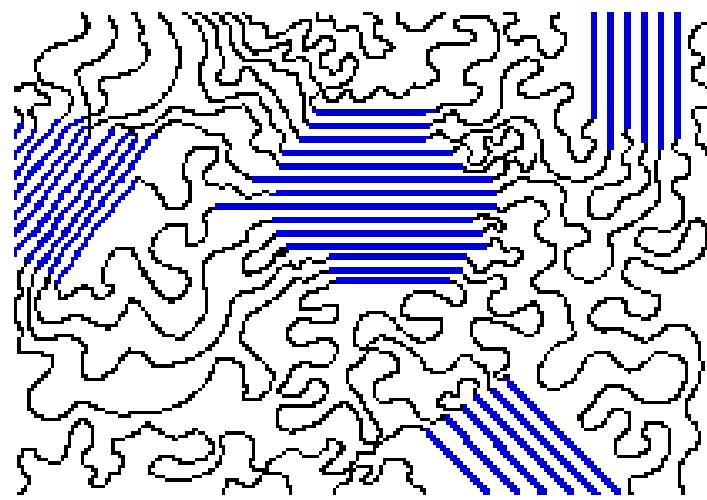
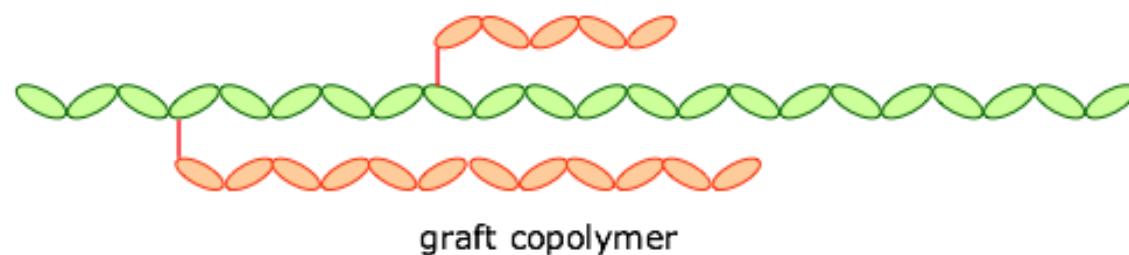
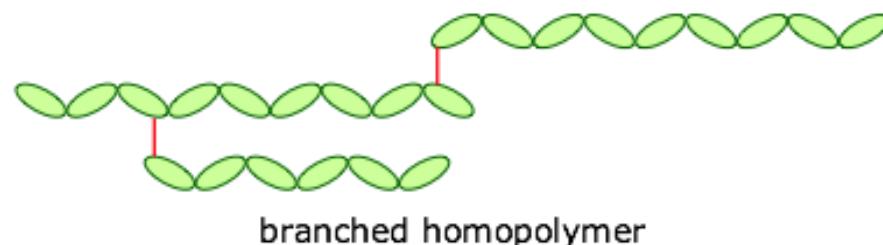


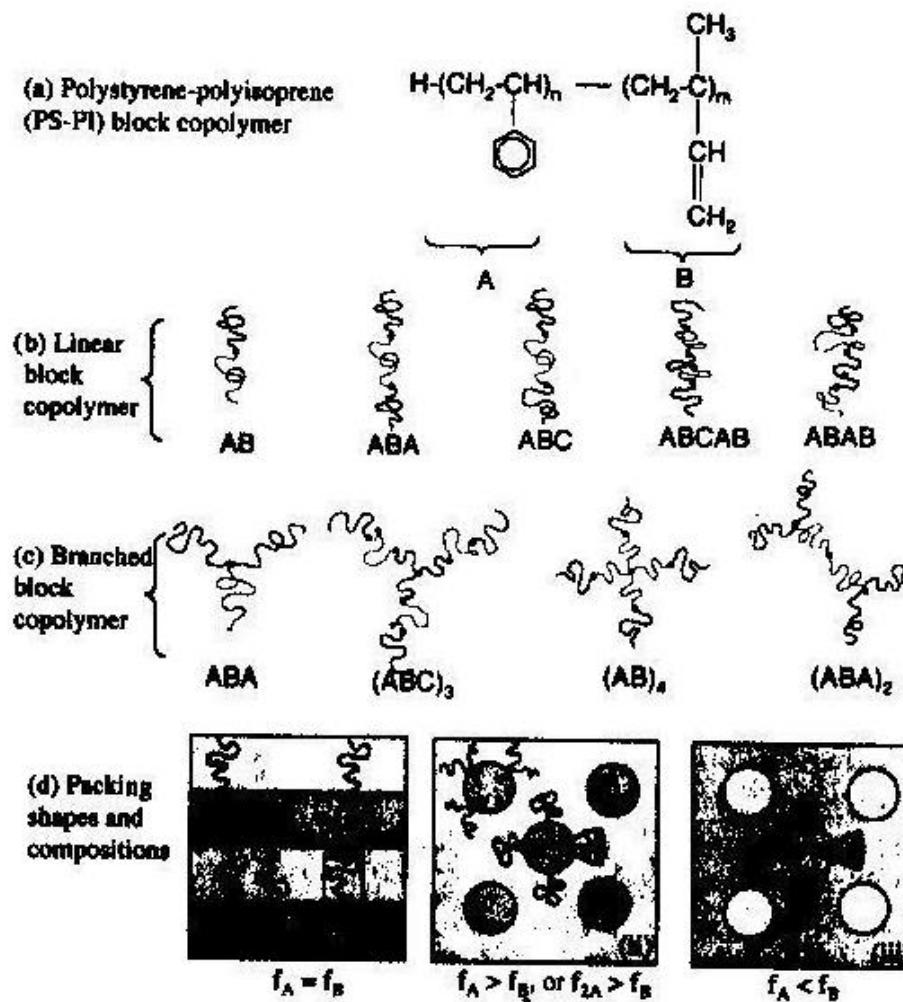
Figure 7.11.3: The crystalline parts of this polymer are shown in blue



# **Self-assembled Block Copolymer Nanostructures**

- ✓ **Block copolymers are amphiphilic molecules containing distinctively different polymer segments (blocks):**
  - polystyrene and poly isoprene block copolymer
  - polystyrene and poly butadiene block copolymer
  - polyethylene and poly propylene block copolymer
- ✓ **Different blocks in a single polymer chain are covalently bonded.**
- ✓ **The phase separation occurs on the nanometric scale, as determined by the dimension of the blocks.**
- ✓ **Factors: monomer type, composition and molecular size, and molecular configuration.**

## **2.5 Self-assembled Block Copolymer Nanostructures**



**FIGURE 2.8.** Variations of block copolymer configurations and the consequences on the packing geometry of the nanostructural ordering. (a) A common block copolymer, polystyrene-polyisoprene (PS-PI). (b) Linear block copolymers. (c) Branched block copolymers. (d) Packing shapes as a function of the compositions or molecular compositions (redrawn from Ref. 22).

## 2.5 Self-assembled Block Copolymer Nanostructures

Flory-Huggins segment-segment interaction parameter  $\chi$ :

$$\chi = \frac{E_{AB} - 1/2(E_{AA} + E_{BB})}{k_B T}$$

$[\chi > 0]$  phase separation is favored

E: Interaction Energy

**f = volume fraction**

$f_A = f_B \rightarrow$  straight cylinder  $\rightarrow$  lamellar phase

$f_A > f_B \rightarrow$  cone structure  $\rightarrow$  B phase dispersed in A phase as spherical micelles

$f_B > f_A \rightarrow$  cone structure  $\rightarrow$  A phase dispersed in B phase as spherical micelles