Biomineral-inspired Materials Chemistry
Episode 2

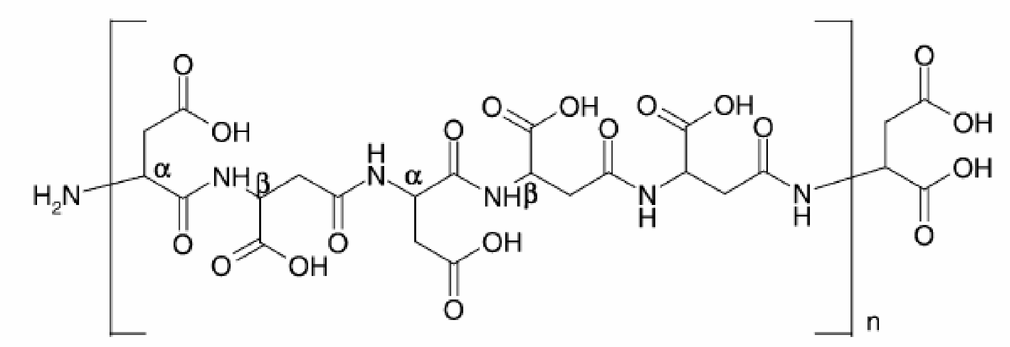
- *Inorganic-Organic composites*
- *Nanomaterials*
- *Funsctional materials and interfaces*
- *Oriented crystals*
- *Materials with complex morphologies*
- *Organized assemblies*
- *Hierarchical materials*

Biomineral matrices

Extraction of organic matrices and re-use for

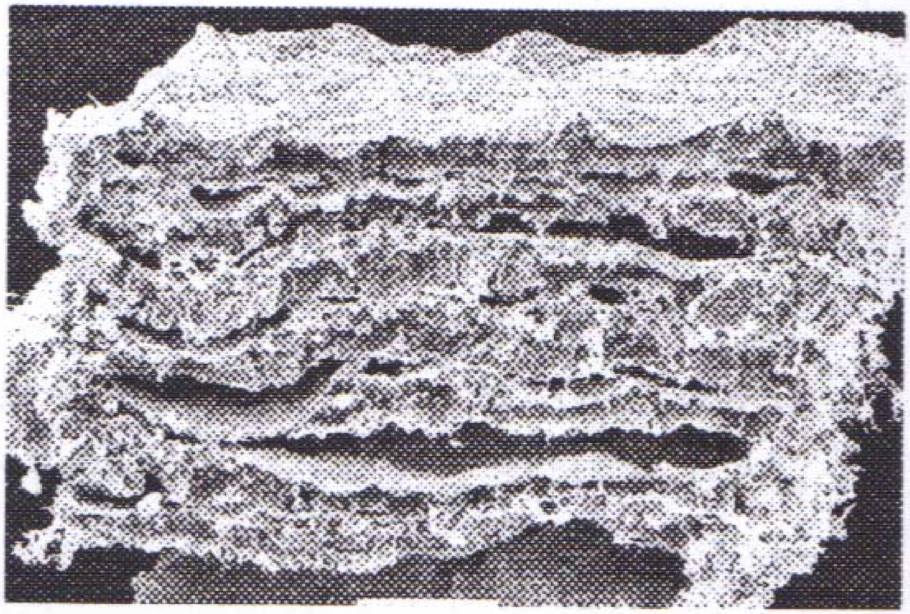
re-mineralization

Reactivation of chitin hydrophobic domains with polyaspartate to lead to oriented growth of calcite



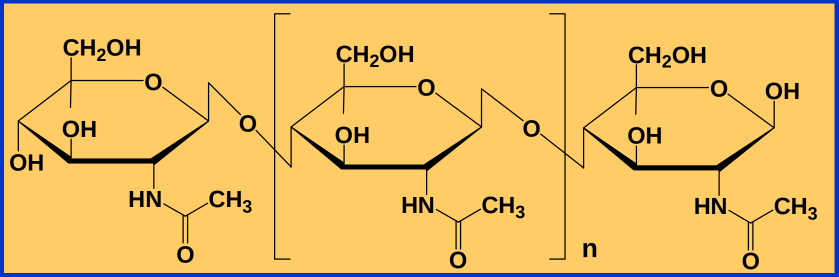
polyaspartate

Pure β-chitin from cuttlebone as a matrix



Intact sponge-like β-chitin matrix from demineralized cuttlebone. Scale bar, 500 μm.

Silica replicas can be obtained from β-chitin from cuttlebone



Silica replica of the *β*-chitin matrix of cuttlebone. Scale bar, 500 μm.

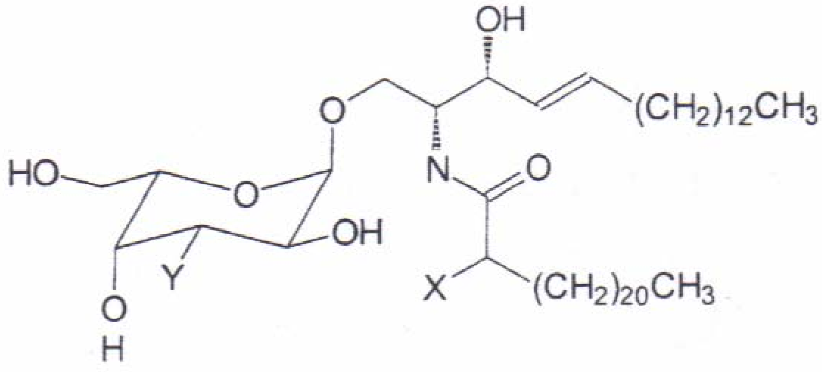
Lipid Tubules

Biomineral organic matrices are not easy to obtain in large amounts, so synthetic analogs with functionalized surfaces are often used for inorganic nucleation

Lipid tubules are multi-lamellar structures formed by the supramolecular assembly of chiral amphi-philic molecules

In the initial stages molecules pack in bilayer sheets separated by solvent. But the molecular chirality induces formation of long strings of strongly-interacting chiral amphiphiles.

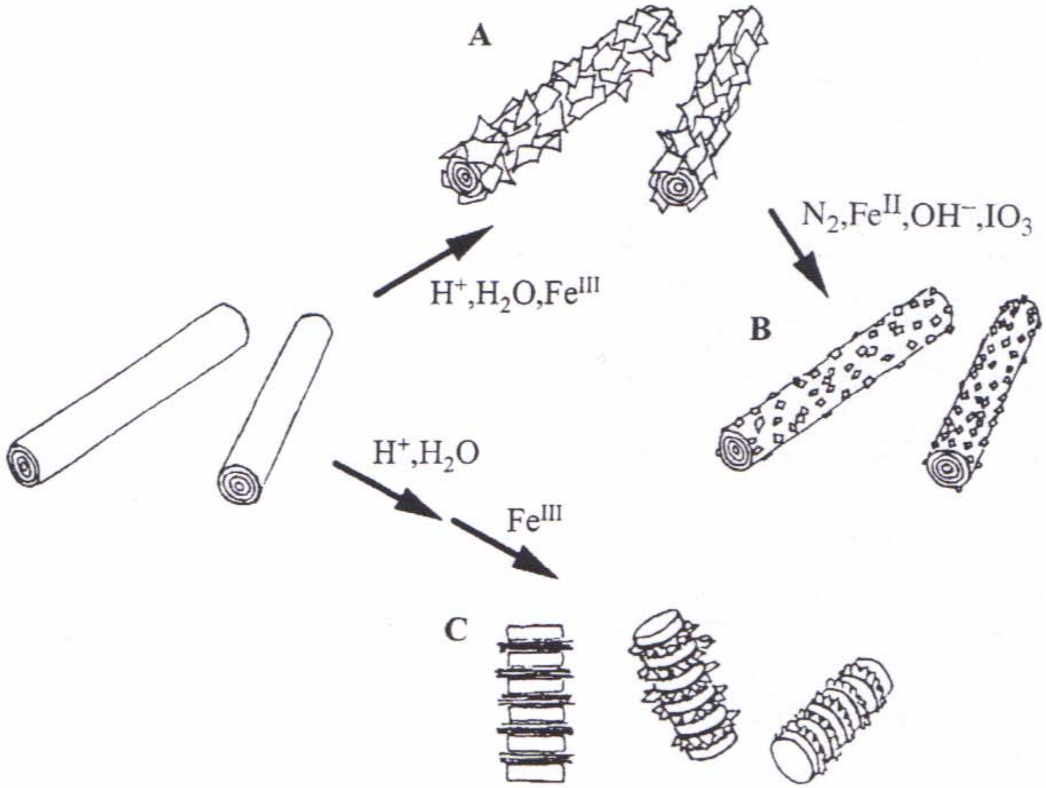
Lipid Tubules



X = OH	Y = OH	HO – Cer
X = H	Y = OH	H – Cer
X = OH, H	Y = OSO_3^-	S – Cer

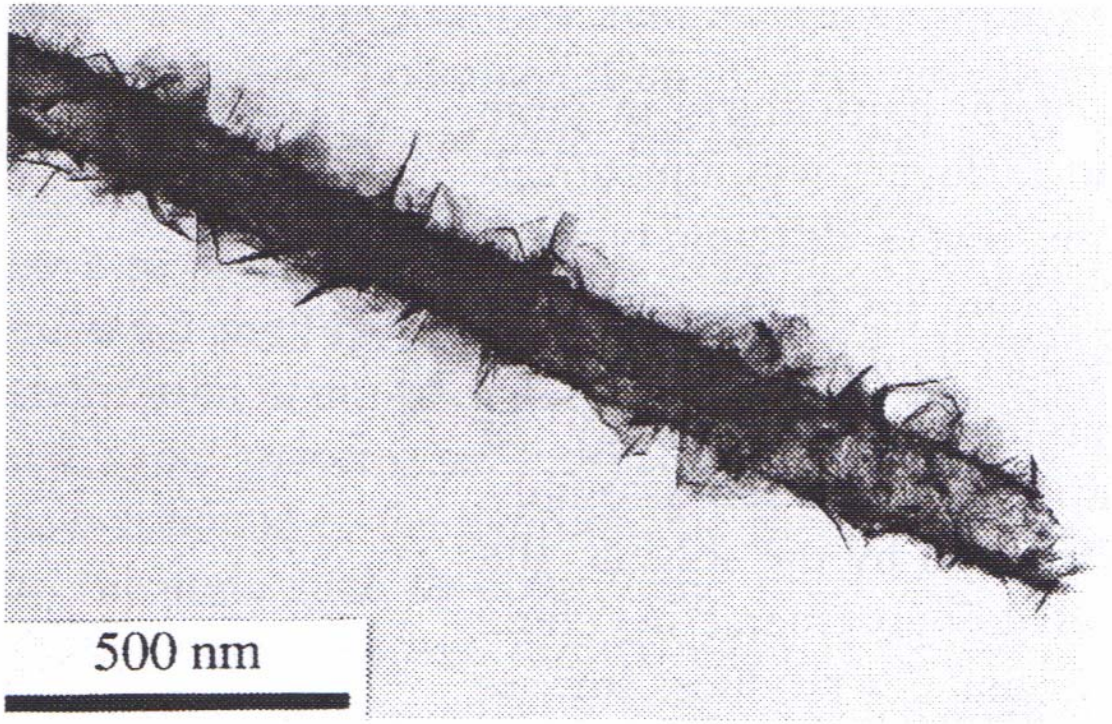
Molecular structure of galactocerebroside lipid and three derivatives.

Formation of rod-like iron oxide composites



Use of galactocerebroside lipid tubules in the template-directed synthesis of iron oxides.

FeOOH formation on lipid tubule

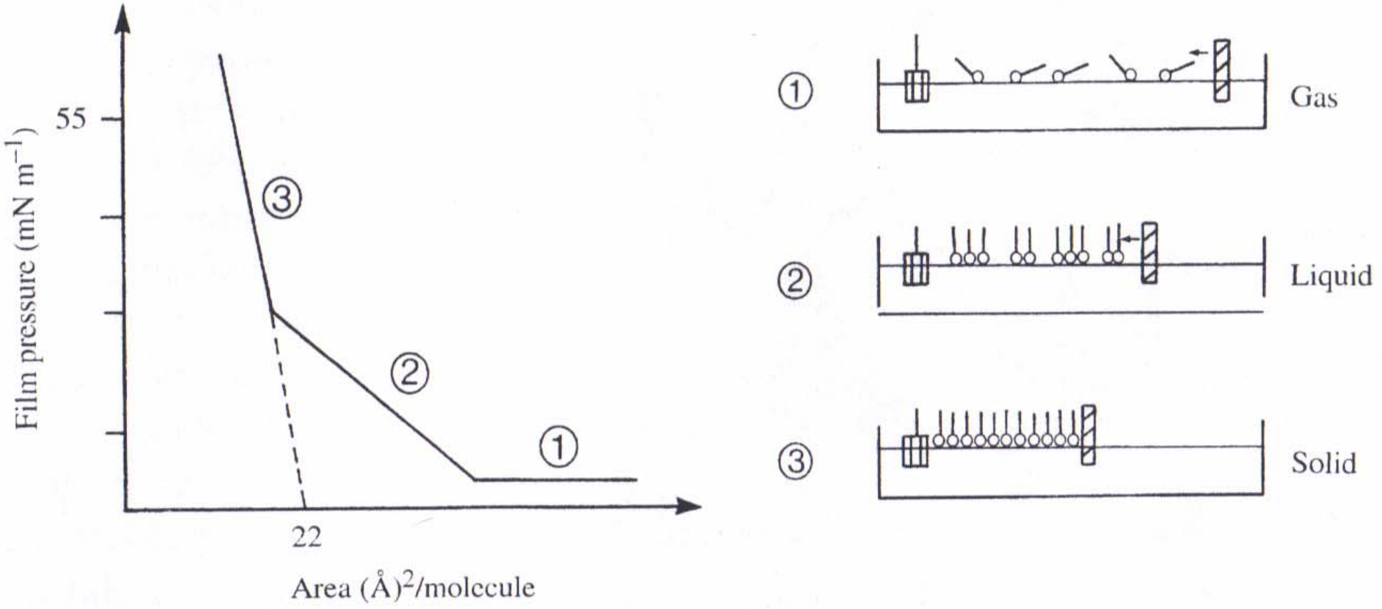


Galactocerebroside lipid tubule coated with lepidocrocite (γ-FeOOH).

Oriented formation on soap films

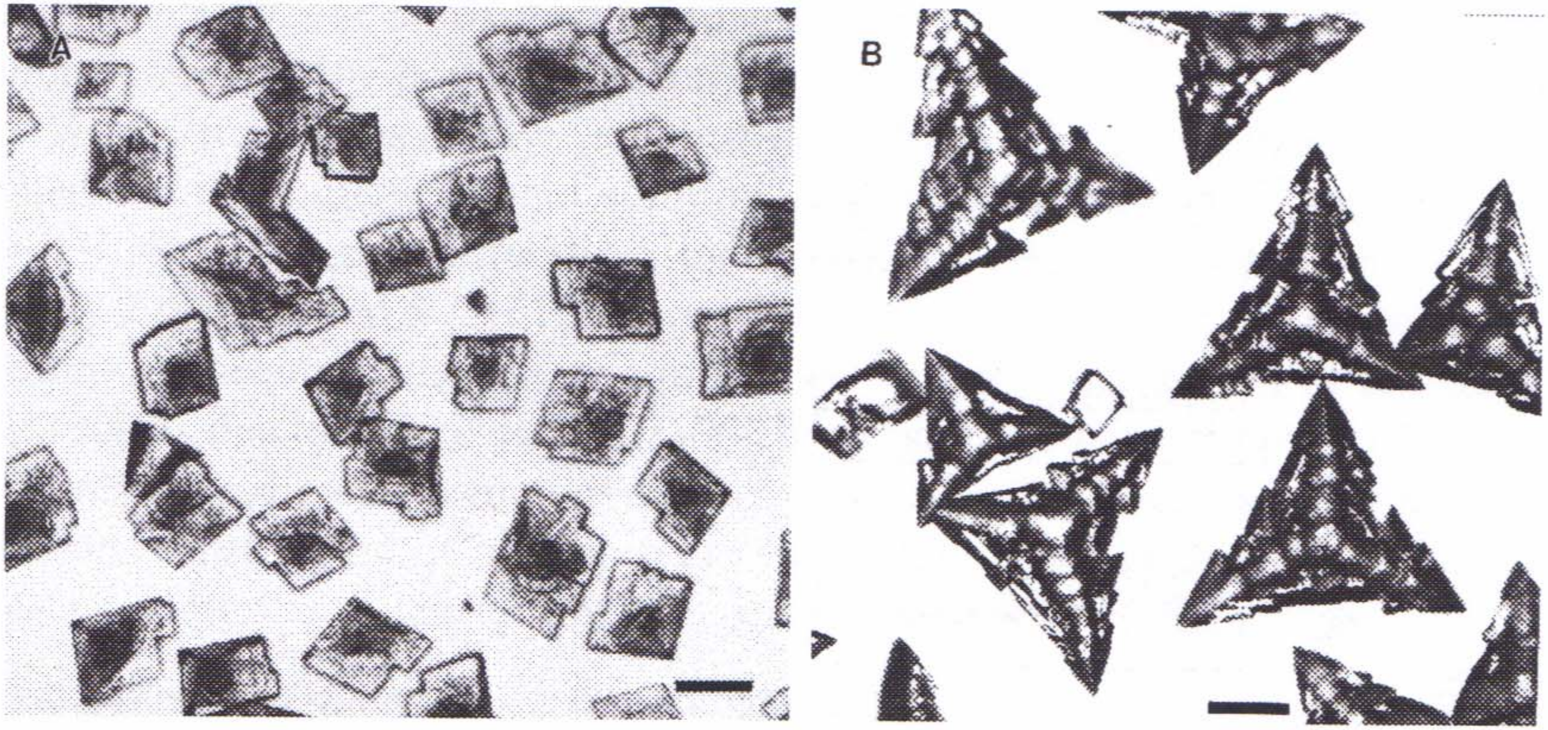
Controlled crystallization of inorganic solids on compressed monomolecular films of insoluble surfactants, spread at the air-water interface

Langmuir monolayers



Idealized plot of film pressure against area per molecule for a surfactant undergoing compression at the air–water interface. The corresponding gas, liquid and solid states of the monolayer are also shown.

Formation of calcium carbonate under Stearic acid Langmuir monolayers



Calcite crystallization under compressed Langmuir monolayers: (A) stearic acid film with {1$\bar{1}$0} oriented crystals, scale bar, 50 μm; (B) *n*-eicosyl sulfate film with {001} oriented crystals, scale bar, 20 μm.

Mechanism of formation

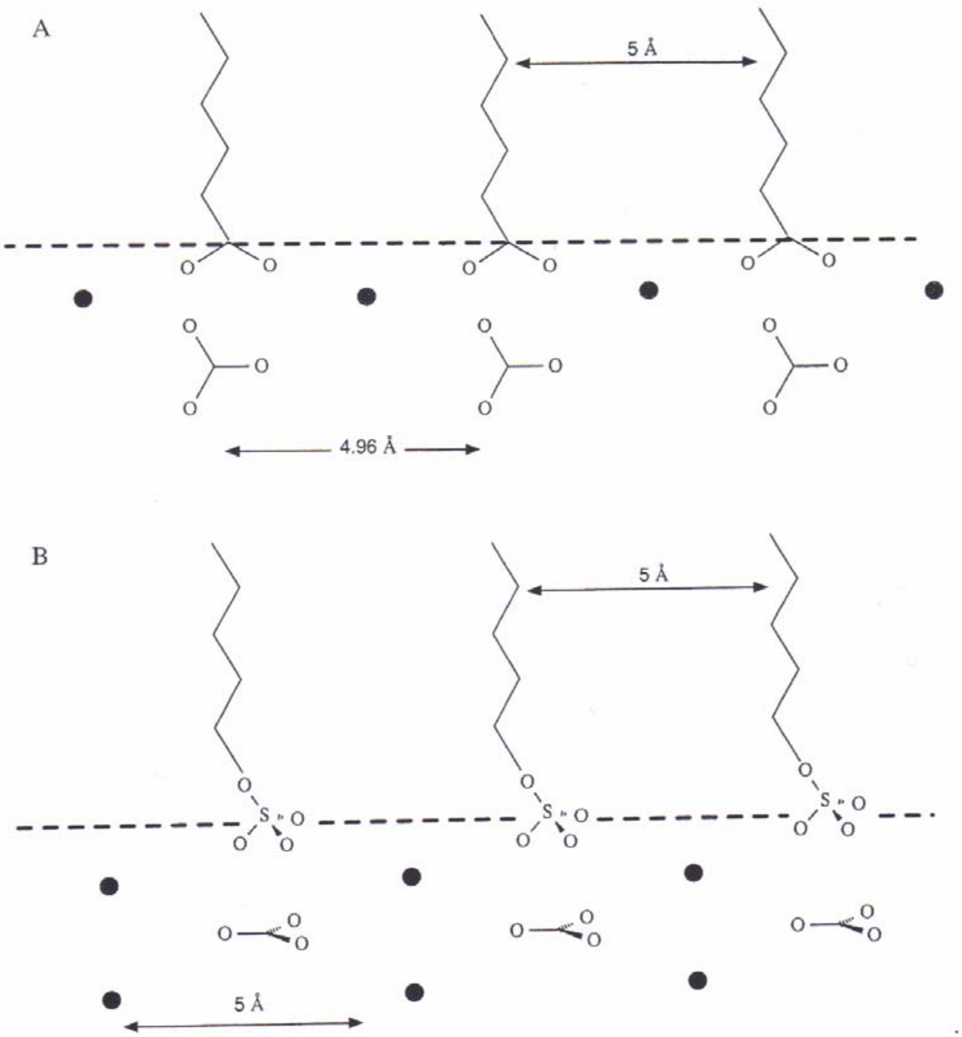
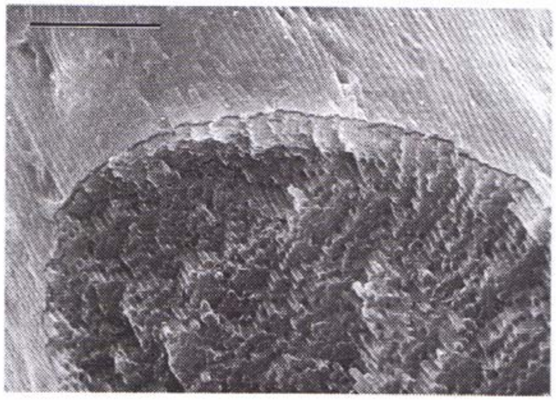


Fig. 9.22 Interfacial recognition under Langmuir monolayers and oriented calcite nucleation for: (A) carboxylate monolayers and the $\{1\bar{1}0\}$ face; (B) sulfate monolayers and the {001} face.

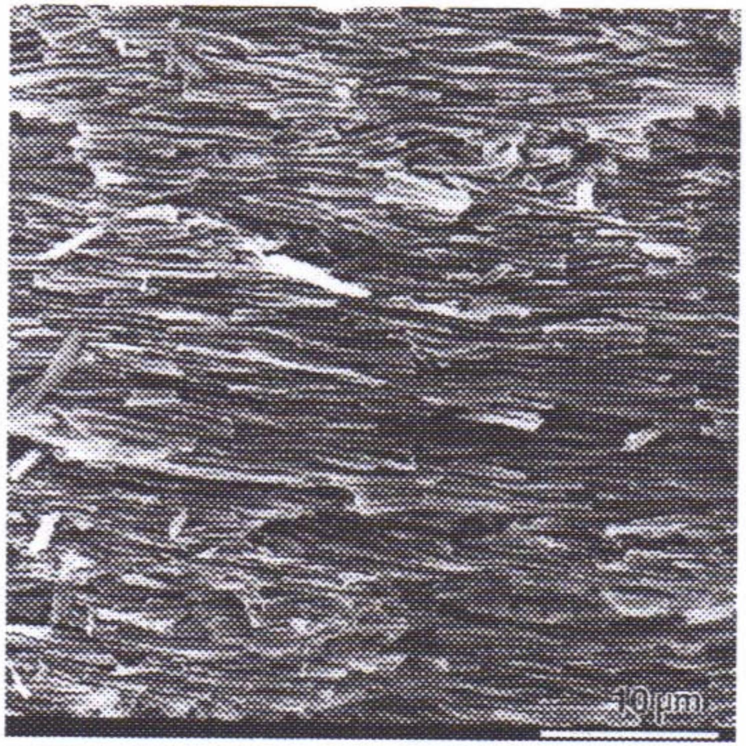
Morphosynthesis of biomimetic form

One major challenge in biomineral-inspired materials chemistry is the synthetic reproduction of analogous structures, using an approach called MORPHOSYNTHESIS

Physical patterning with supramolecular templates

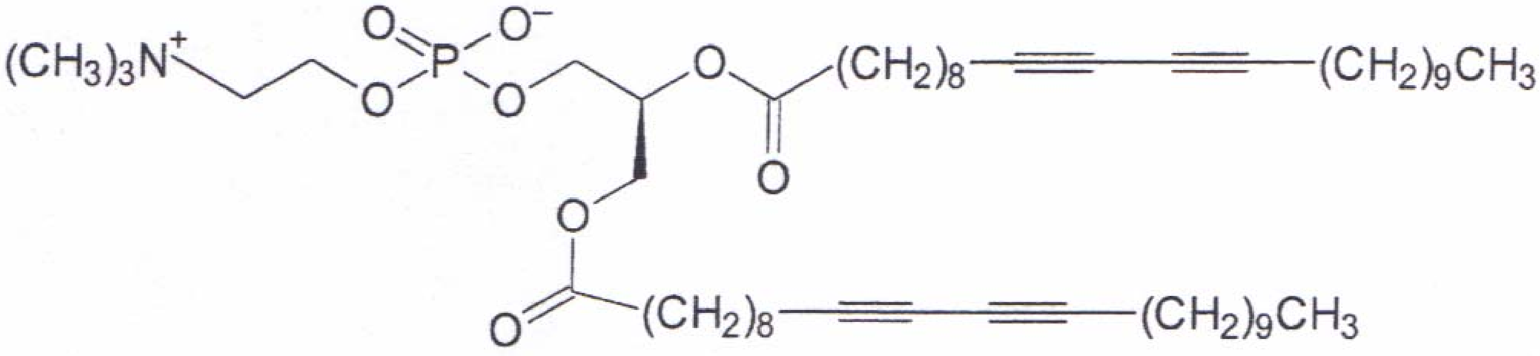


Sectioned bacterial thread showing internal hexagonal superstructure of coaligned multicellular filaments. Scale bar, 10 μm.



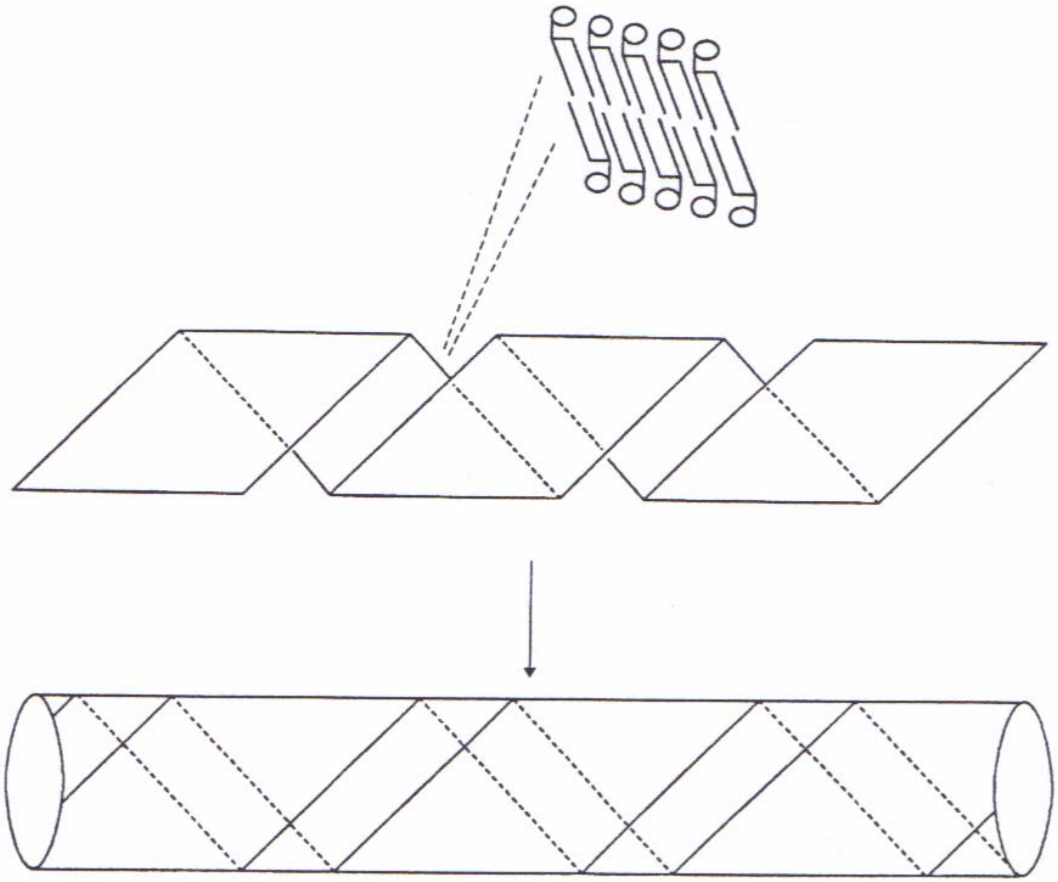
Section cut parallel to the long axis of a silica-infiltrated bacterial thread after removal of the multicellular filaments, showing co-aligned channels. Scale bar, 10 μm.

Synergism in the assembly of DCPC



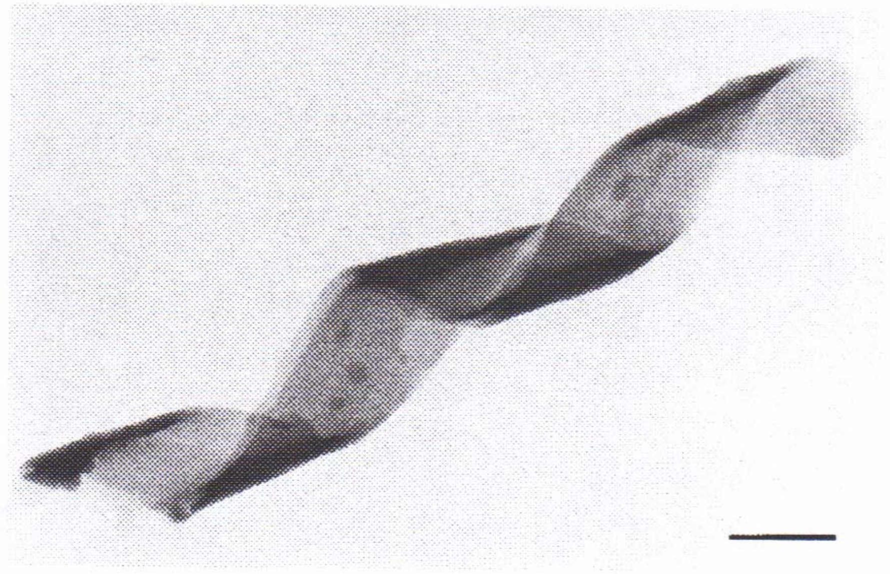
Molecular structure of diacetylenic phosphatidyl choline (DC$_{8,9}$PC)

Multilamellar helical ribbons



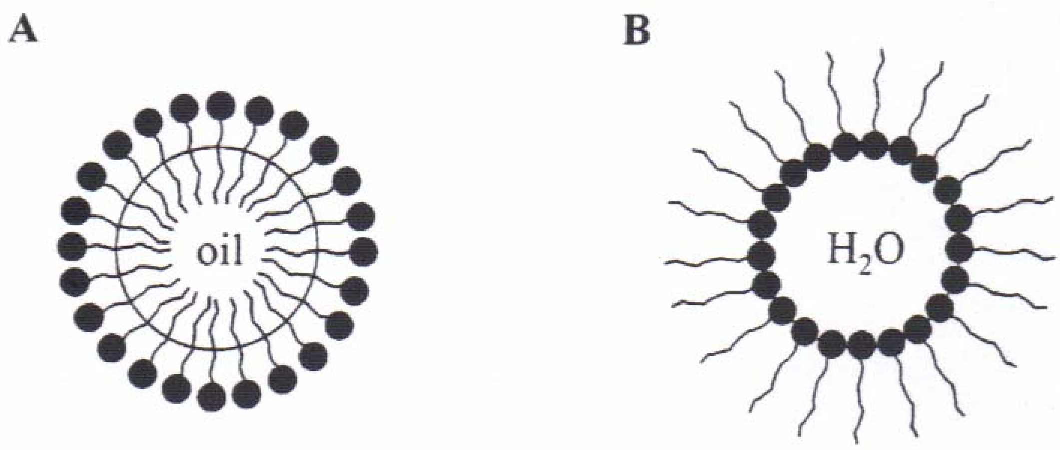
Multilamellar helical ribbon and helical tube of $DC_{8,9}PC$.

Silica helical ribbon



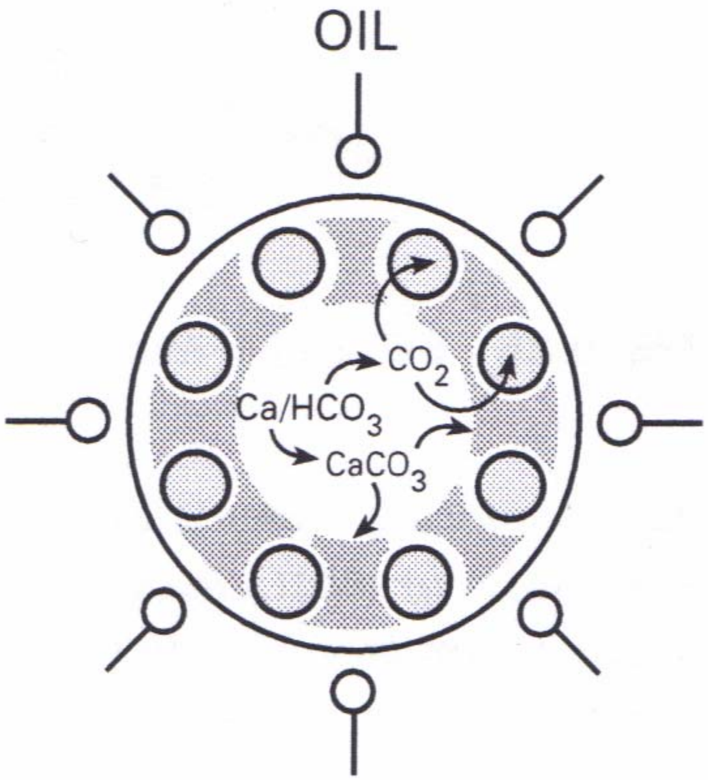
Silica–lipid mineralized helical ribbon. Scale bar, 400 nm.

Inorganic solids formed in reverse microemulsions



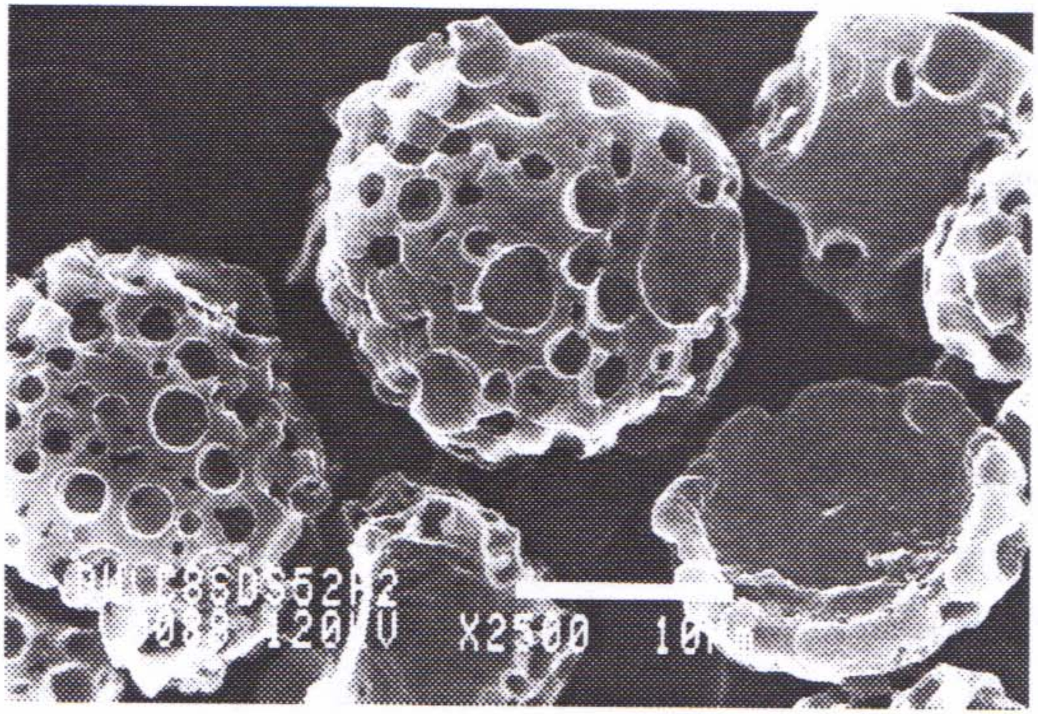
(A) Oil-in-water microemulsions; (B) water-in-oil reverse microemulsions

$CaCO_3$ formed in reverse microemulsions



Growth and patterning of calcium carbonate hollow shells in reverse microemulsions.

$CaCO_3$ formed in reverse microemulsions



Calcium carbonate hollow shells with surface pores. Note also the presence of a broken shell. Scale bar, 10 μm.