Monodisperse Steroid Nanotubes in Water: Kinetics of Formation and Ordering

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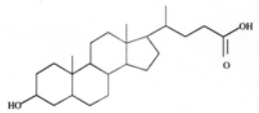
Introduction

Soft condensed matter is known to exhibit well-defined 1-D supramolecular assemblies such as thread-like micelles, fibres and tubules. Tubular architectures presenting the dual property of a cross-sectional monodispersity and a propensity to an easy orientation are promising candidates for numerous applications such as catalysis, selective separations, sensors, conducting devices in nanoelectronics, opto- or iono-electronics. We present here such an example of nanotubes obtained from a low-cost biological steroid, lithocholic acid in alkaline aqueous solutions.

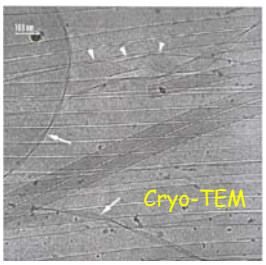


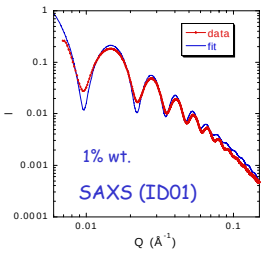
Building Block = Lithocholic Acid

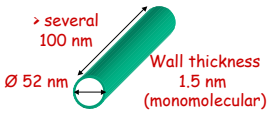
- low-cost biological molecule
- chiral

Suspensions of highly monodisperse Nanotubes

Lithocholic Acid in alkaline aqueous solution (NaOH):





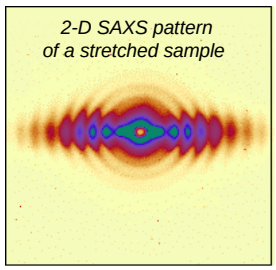


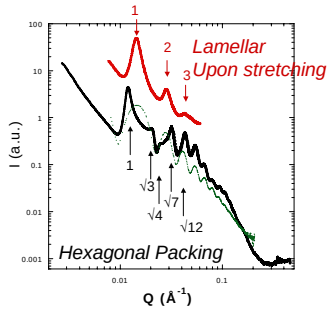
$$QI_F(Q) \propto \left[\left(\frac{J_1(QD_0/2)}{QD_0/2}\right) - \left(\frac{D_i}{D_0}\right)^2 \left(\frac{J_1(QD_i/2)}{QD_i/2}\right)\right]^2$$

form- factor of a tube

Nanotubes Ordering

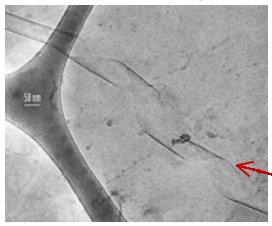
Example of Ordering : 8% SLC in NaOH 0.25 M

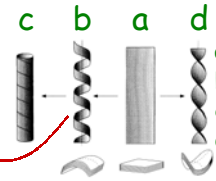




2-D Hexagonal Packing of Nanotubes with N.N. distance = 60.5 nm (indpd. of concentration between 6 and 10 % wt.): Oriented domains
Transition from hexagonal to lamellar ordering upon stretching

Theoretical point of view





a: membrane
b: helicoidal ribbon
c: cylinder
d: twisted ribbon

As suggested by cryo-TEM images and described by theories[2] based on molecular chirality (lithocholic acid, as a steroid, is chiral) the mechanism of formation of the tubules may involve intermediate species such as helicoidal ribbons

Kinetics of Formation

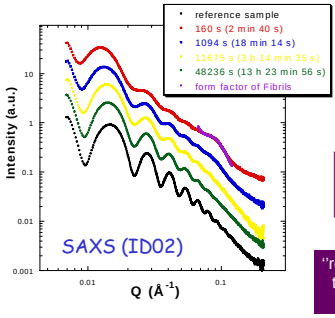
SAXS curves at different times after sample preparation

Shift towards larger Q

↘ of cross-section of rod-like intermediate

Amplitude of the oscillations ↗

↘ of size distribution



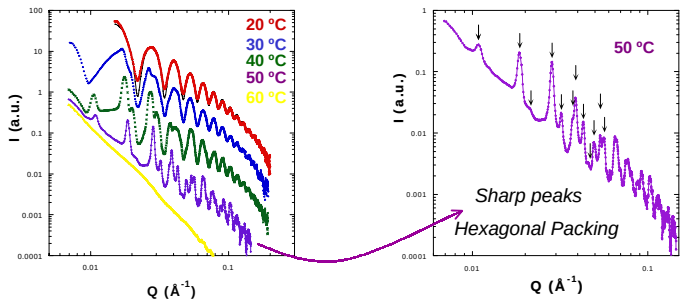
Large-Q component disappears

''reservoir'' of fibrils or tapes used to form tubules

All the molecules are aggregated before t_d = 160 s
Kinetics = redistribution of matter into different structures (fibrils, tapes, ribbons and nanotubes)
Fast kinetics towards stable objects

Nanotubes in NH_3 : towards a perfect system

1% Lithocholate suspension in NH_3



T = 20 °C : very narrow size distribution (12 oscillations, very good fit)
T = 50 °C : highly ordered Hexagonal phase (at least up to the 12th order)

Conclusion and perspectives

Spontaneous formation of highly monodisperse nanotubes in alkaline solutions of a common steroid bile salt
SAXS characterization as a function of time, temperature, concentration, chemical base
Complex mechanism of tube formation via redistribution of molecules in different structures (fibrils, tapes, ribbons and nanotubes)
Ordering into well-defined 2-D hexagonal phase with concentration (in NaOH) or temperature (in NH_3)
Easy orientation of the nanotubes → deposition on substrates

(2) Selinger J.V., MacKintosh F.C. and Schnur J.M. *Phys. Rev. E* **53**, 3804-3818 (1996)
(1) Terech P., de Geyer A., Struth B., Talmon Y. *Advanced Materials* (in press)