Mineralization of lipidic tubules

Abstract We describe the use of supramolecular assemblies of phospholipidic molecules as a support for the surface-mediated synthesis of inorganic nanoparticles. Diacetylenic phospholipids such as DC_{8,9}PC are known to form hollow tubular microstructures referred to as tubules. Mineralization of DC_{8,9}PC tubules is obtained by nucleation and growth of an iron oxyhydroxide on their surface. This leads to tubular organic–inorganic hybrid microstructures.

Key words Self-assemblies · Tubules · Phospholipids · Mineralization

Introduction

We report the use of self-assemblies of amphiphilic molecules as a support for the precipitation of anisotropic iron oxide nanoparticles. The organic template is a hollow cylinder made of tensioactive molecules. These molecules are phospholipids, namely diacetylenic phospholipid (DC_{n,m}PC). This phospholipid forms bilayers in water which have the specificity to roll themselves up into open-ended hollow tubes at room temperature, giving rise to so-called lipidic tubules (Figs. 1, 2) [1]. Tubule formation is driven by a reversible first-order phase transition from an intralamellar chain-melted L_{α} phase to a chain-frozen L_{α}^* phase [2], the tubule phase being the one in which the hydrocarbon chains are highly ordered [3]. The DC_{8,9}PC chain-melting transition temperature is approximately 43 °C [4]. Above this temperature DC_{8,9}PC forms liposomes in aqueous solutions.

Their rigidity, hollowness, high aspect ratio and resistance to a wide range of pH and ionic strength make the tubules suitable for technical applications and model bioinorganic template synthesis [5]. It was shown that lipidic tubules could be metallized by electroless deposition of copper [1] or permalloy [6] and mineralized by chemical precipitation of metal carbonates [7] or coated with pre-formed silica particles [8]. Archibald and Mann [9] described the coating of galactocerebrosides tubules with iron.

Despite their interesting morphology (high aspect ratio and hollowness) and their chemical resistance, DC_{8,9}PC tubules have not been used yet for the template precipitation of ferric species. After studying the interactions between iron oxide nanoparticles and DC_{8,9}PC tubules [10], our purpose is now to perform the mineralization of DC_{8,9}PC tubules that are easier to prepare than the galactocerebrosides ones. We shall refer to mineralization as to the surface-specific polycondensation of mono- or oligomeric species present in the bulk solution.

Experimental

The tubular lipidic microstructure were prepared with 1,2-bis[10,12-tricosadiynoyl]-sn-glycero-3-phosphocholine (DC_{8,9}PC) obtained from Avanti Polar Lipids and used as purchased. In order to get tubules, we used the so-called precipitation method firstly described by Georger et al. [4], which consists of the solubilization of the lipid in an appropriate solvent and the further precipitation by addition of water. Water was added to a solution of DC_{8,9}PC in ethanol, the water/ethanol ratio being about 40:60 (v/v) and the final concentration of lipids being approximately 1 g/l. A flocculent precipitate of tubules was observed. This precipitate was centrifuged at 6000 rpm for 15 min and the resulting pellet was dispersed in distilled water. The tubules obtained had a constant diameter of 0.5 μm and were multimellar. Their length ranged from a few microns to tens of microns.

According to Schur and coworkers [11] the self-assembly process of DC_{8,9}PC tubules begins with the formation of helical
prepared, then centrifuged. The heavy phase of the tubules (around 10 g/l) was then dispersed in an aqueous solution of iron chloride. On leaving the FeCl$_3$/DC$_{8,9}$PC tubule mixture at room temperature for aging, the hydrolysis of the ferric species drives the polycondensation process. It gives rise to a yellow-brown precipitate. The effects of the aging time, of the reactant concentrations and of the nature of the tubules (edged or smooth) were investigated. The ferric species concentration ranged from $10^{-4}$ to 1 mol$^{-1}$ and the tubule concentration ranged from 0.1 to 20 g/l$^{-1}$.

Optical microscopy and transmission electron microscopy (TEM) were performed in order to confirm the effective mineralization of the DC$_{8,9}$PC tubules. The nature of the inorganic species deposited on the tubules was indentified by electron scattering. TEM and electron scattering were performed using a JEOL 100CXII top-entry UHR electron microscope on samples deposited on carbon films and air-dried. Tubules without ferric precipitate were colored by negative stain with an aqueous solution of ammonium molybdate or uranylacetate (2 wt%). Mineralized tubules were observed without coloration.

**Results and discussion**

TEM photographs of the structures obtained are shown in Figs. 3 and 4. Two types of objects are observed: mineralized tubules (Fig. 3a), which are covered with iron oxyhydroxide microcrystals, and decorated tubules (Fig. 4), which bear discrete particles. These structure are never found together in the same sample. Moreover, the formation of one structure rather than the other only depends on the nature of the DC$_{8,9}$PC tubules.

The mineralized tubules are discernible by optical microscopy: they appear light brown and thicker than the uncoated tubules (Fig. 3b). Smooth tubules lead to large leaflike microcrystals that covers the entire surface of the tubules giving the latter a hairy shape (Fig. 3). The inorganic phase was identified by selected-area electron diffraction as lepidocrocite $\gamma$-FeOOH. The thickness of the inorganic coating ranged from 0.1 to 0.3 $\mu$m in the samples observed. Edged tubules exhibit small rice-bean-shaped particles that are very specifically deposited on the DC$_{8,9}$PC ribbon edges (Fig. 4). The iron oxyhydroxide particles were identified as poorly ordered akaganeite $\beta$-FeOOH and were about 70-nm long and 20-nm wide, on average. In our case the particles are monodisperse in size and their binding to the ribbon edges is obvious on the TEM pictures.