Study of cyclodextrin nanotubes by transmission electron microscopy

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1. INTRODUCTION

The synthesis of cyclodextrin (CD) nanotubes has been first described by Harada in 1993[1]. Since then, few studies[2] have been reported concerning the synthesis and the characterization of these macromolecular structures by classical methods such as NMR[1]H, SEC and mass spectrometry[3]. Today, considering the progress made in microscopy, the analysis of these synthetic structures is conceivable with a resolution around the nanometer scale[4]. This study focuses on the characterization of several nanotubes obtained from two kinds of poly(ethylene oxide) (PEO) chains of variable length and polymolecularity, in order to check if the controlled synthesis of these nanotubes is affected by the choice of these parameters.

2. RESULTS

2.1 Description of the studied structures

The nanotubes are obtained according to the chemical pathway showed in figure 1 and are respectively synthesized from PEO chains of number average molar mass equal to 1000 and 1500 g.mol^{-1} with a lower polymolecularity index for the second one. The CD nanotubes are obtained by a reaction involving the hydroxyl functions of the CDs threaded on a polyrotaxane, and are then isolated after hydrolysis of the functions binding the bulky blocking groups to the polyrotaxane. The CD nanotubes can thus be isolated from the polymer chain illustrated as a black line in figure 1. The bare nanotubes can be modified with trimethoxysilane groups to obtain silylated nanotubes in order to limit the aggregation effect due to hydrogen bonding and to try to improve the contrast for the characterization by microscopy.

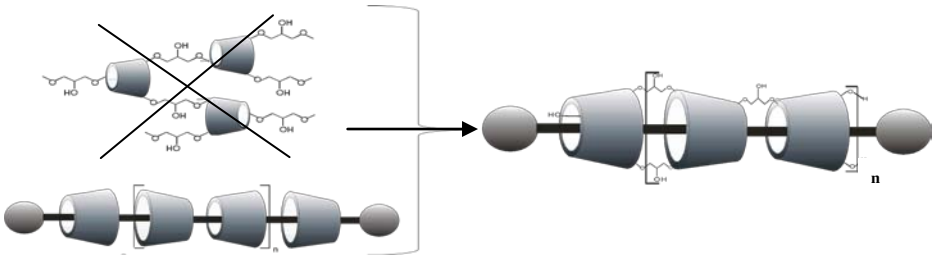

Figure 1 : Schematic synthetic route leading to the CD nanotubes

2.2 Experimental conditions

Aqueous solutions of each unmodified CD nanotubes (6 mg/mL) and a solution of silylated CD nanotubes in acetone (6 mg/mL) are prepared. A volume of 5 µL of each solution is deposited on a film made of pure carbon (Ted Pella grid, 01840-F 200 mesh). The thickness of the carbon film is around 20±5 nm. The deposited drop is dried at room temperature during an hour. The microscopy pictures are taken at 200 keV with a Jeol2200FS microscope equipped with an ultra-high resolution (UHR) polar piece and with a CCD Gatan US1000 camera. It was not necessary to work in « low dose » mode since the samples were not damaged by the irradiation.

2.3 Results

The transmission electron microscopy analysis enabled to confirm the presence of CD nanotubes (figure 2). Moreover, the number of CDs counted on the nanotubes matches with the theoretical values. Indeed, the maximal amount of CDs threaded on an isomolecular PEO chain is respectively 11 and 17 for a number average molar mass of 1000 and 1500 g.mol^{-1}.

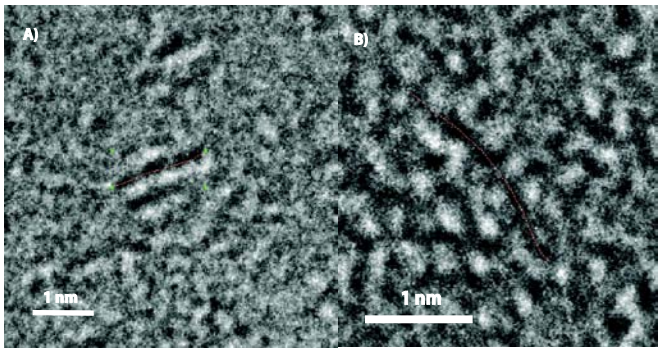

Figure 2 : HRTEM images of CD nanotubes obtained from A) 1000 g.mol^{-1} PEO and B) 1500 g.mol^{-1} PEO

We note that the number of CDs of a nanotube synthesized from a polymolecular PEO chain with a number average molar mass equal to 1000 g.mol^{-1} is equal to 6 CDs whereas a nanotube synthesized from a PEO chain with a lower polymolecularity and with a number average molar mass equal to 1500 g.mol^{-1} is composed of 11 CDs.

We observed that the modified nanotubes were desilylated under the electron beam, that's why we characterized them by cryo-TEM. Despite the change in solubility triggered by the chemical modification of the nanotubes, the images obtained (figure 3) highlight that the nanotubes are more flexible but are keeping the same aspect (number of CDs, length, diameter…) as the unmodified nanotubes.

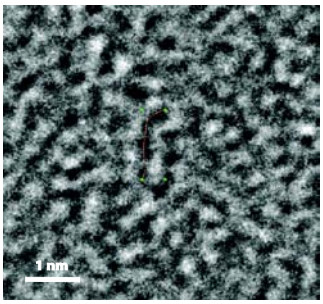

Figure 3.HRTEM images of silylated CD nanotubes obtained from 1000 g.mol^{-1} PEO

3. CONCLUSION

This study by transmission electron microscopy enabled to demonstrate that the synthesis pathway chosen for the formation of the CD nanotubes is at the origin of the control of their structural parameters, and thus their properties. These synthetic nanotubes can lead to electrophysiology and cytotoxicity studies.

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