Helical tape as intermediate in nanotubes formation kinetics

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Nanotubular objects have attracted considerable attention due to the unique one-dimensionality as well as the potential applications utilizing nanoscopic channels. Besides, self-assembled helical supramolecular structures are widely found in nature and have also been observed in several systems based on synthetic amphiphiles. Synthetic nanotubes made up of self-assembly of amphiphilic precursors are generally formed when an isotropic solution of the precursor is cooled below the gel-to-liquid crystalline phase transition temperature. A synthesized amphiphile hexa-peri-hexabenzocoronene (HBC), consisting of a hexaphenylbenzene ring bearing two hydrocarbon chains at one side and two triethylene glycol (TEG) at the other have been reported to form nanotubes[1]. They are formed by cooling a tetrahydrofuran (THF) solution of the HBC from 50 °C to 20 °C, which is then kept at rest during 3 days. It was hypothesized that the HBC molecules self-assemble in a bilayer that rolls up forming the nanotubes. In the present work, both the kinetics of formation of these nanotubes and an equilibrated solution were studied *in situ* at the SAXS beamline of the synchrotron radiation facility Elettra. The solutions were cooled at a rate of 1 °C/min and 2D images were recorded every 160s. A cooled sample was kept at rest for 10 hours. In the curve of the equilibrated sample, five distinct minima show that the tubes are highly monodisperse. Although similar curves had been fitted by the assumption of infinitely long cylinders, straight cylinders form factor did not fit our data. Besides, the oscillations have asymmetries whose positions are consistent with a hexagonal packing. Previous transmission electron microscopy of objects formed by HBC in a mixture of THF with water showed a helical structure[1], thus we inferred that our sample could be in an intermediate stage during the rolling-up of the bilayer, forming helices. Based on a previous work concerning the form factor of helical filaments with a finite cross section, in the present work we generalized the helical form factor for a tape containing N layers and applied to our system, modeled as centrosymmetric bilayers containing 5 layers and including a hexagonal structure factor. These results were compared with that obtained using a model based on polydisperse cylinders, and it is shown that the full description with helical model and structure factor is the superior one.

After equilibration, the samples were heated and cooled again. The curves obtained during the cooling process have a constant minima position, showing that the nanotubes have constant radius. The variation of the integrated intensity with the temperature presented a hysteresis during the cooling process, but recovering the former intensity at 20 °C. These results show the fast kinetics of nanotubes formation, but emphasize the need of an aging time to reach a high level of monodispersity.

[1] Hill, J.P., Jin, W., Kosaka, A., Fukushima, T., Ichihara, H., Shimomura, T., Ito, K., Hashizumi, T., Ishii, N., Aida, T., *Science*, **304**, 1481-1483 (2004).

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