Experimental Report

Proposal: **9-11-1653** **Council:** 10/2012

Title: Hybrid materials: polymer/self-assembled systems

This proposal is a new proposal

Researh Area: Materials

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Samples: polystyrene (H and D), o-xylene (H and D)

Instrument	Req. Days	All. Days	From	To
D11	2	2	01/03/2013	03/03/2013

Abstract:

This paper examines the possibility of sheathing polymer nanofibrils, prepared from a tthermoreversible gel, by nanotubules, obtained through self-assembling of a complex ester. The method for preparing this hybrid system consists of cooling ternary solutions until gelation is achieved. The sheathing mechanism most probably occurs through heterogeneous nucleation: polymer fibrils act as heterogeneous nuclei, and so trigger the growth of nanotubules around them. The occurrence of the sheathing process is investigated by DSC, AFM, SAXS and SANS. In the latter case the contrast variation method is used.

HYBRID MATERIALS: POLYMER/SELF-ASSEMBLED SYSTEMS
(D11, exp: 9-11-1653)

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Recently, P. Mésini et al. have reported [1] the synthesis of oligomolecules capable of forming hollow nanotubules (fig.1). Scattering experiments have shown that the cross-sections of these nanotubules are well defined in view of the numerous oscillations observed (fig.1). They have an external radius of 12.7 nm and an inner radius of 9.5 nm.

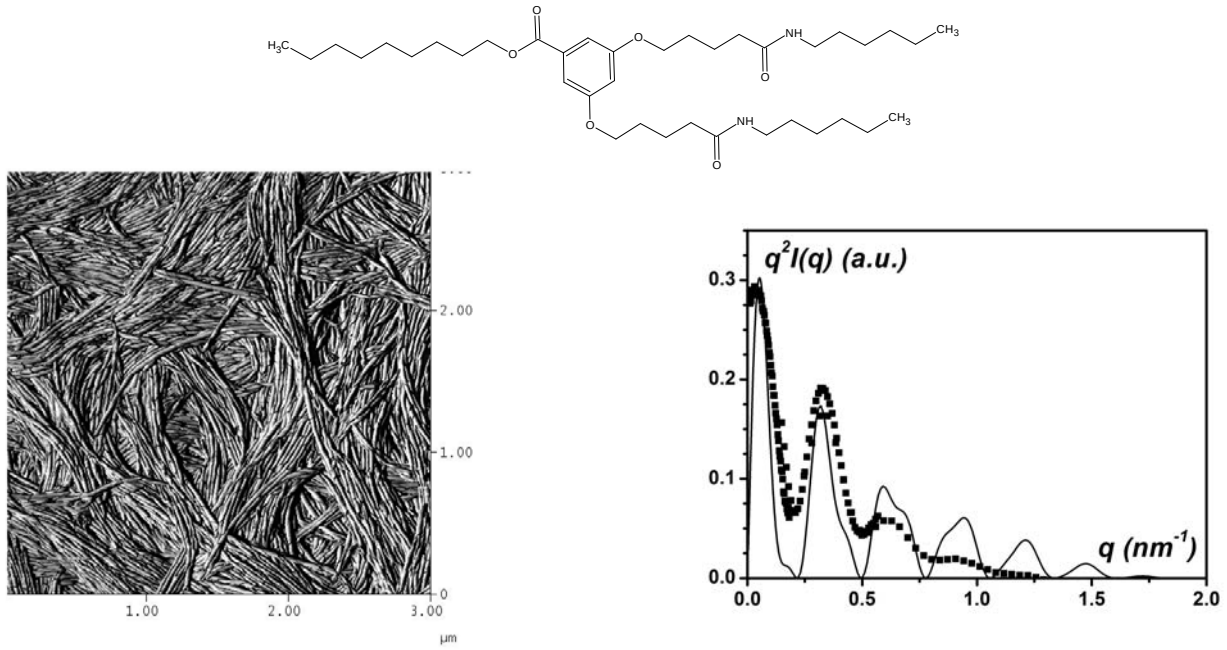

Fig.1: ***up****: chemical structure of BHPB-10;* ***left*** *AFM picture of nanotubules;* ***right*** *SANS scattering of 1% nanotubules in trans-decahydronaphthalene$_D$. Solid line is a fit by using equation for a hollow cylinder.*

Thermoreversible gels of isotactic polystyrene (iPS) consist of a micrometric array of randomly-dispersed fibrils of cross-sections in the range of 10 nm [2], namely values close to the nanotubules inner radius. This led us to contemplate the possibility of sheathing the polymer fibrils by these nanotubes through a heterogeneous nucleation process (fibrils act as heterogeneous nuclei for the growth of nanotubules).

By toying with the contrast, we have been able to show that the nanotubules effectively sheathe those fibrils possessing a cross-section equal to their inner radius. To demonstrate this outcome we have used three systems: BHPB-10$_H$, iPS$_H$ or iPS$_D$ and *trans*-decahydronaphthalene$_D$ (H and D subscripts standing for hydrogenous and deuteriated). As can be seen in fig.2 oscillations typical of the nanotubules are seen for the system **BHPB-10$_H$/ iPS$_D$/ *trans*-decahydronaphthalene$_D$**. In this case the contrast of the polymer is zero and one only sees the BHPB-10$_H$ molecules. Conversely, these oscillations vanish for the system **BHPB-10$_H$/ iPS$_H$/ *trans*-decahydronaphthalene$_D$** where no distinction can now be made between the polymer and BHPB molecules. These conclusions are summarized by a sketch in fig.3.

<u>It is important to stress that neutron scattering is the only technique capable of demonstrating convincingly the sheathing process.</u>

iPS is essentially a case of study but applications are not expected with this polymer which offers no real interest in the bulk state. Conversely, syndiotactic polystyrene has a brighter future ahead as its properties in the bulk are interesting with respect to marketed polymers [3], and so is likely to be produced on an industrial scale. We are therefore pursuing our investigations with this polymer.

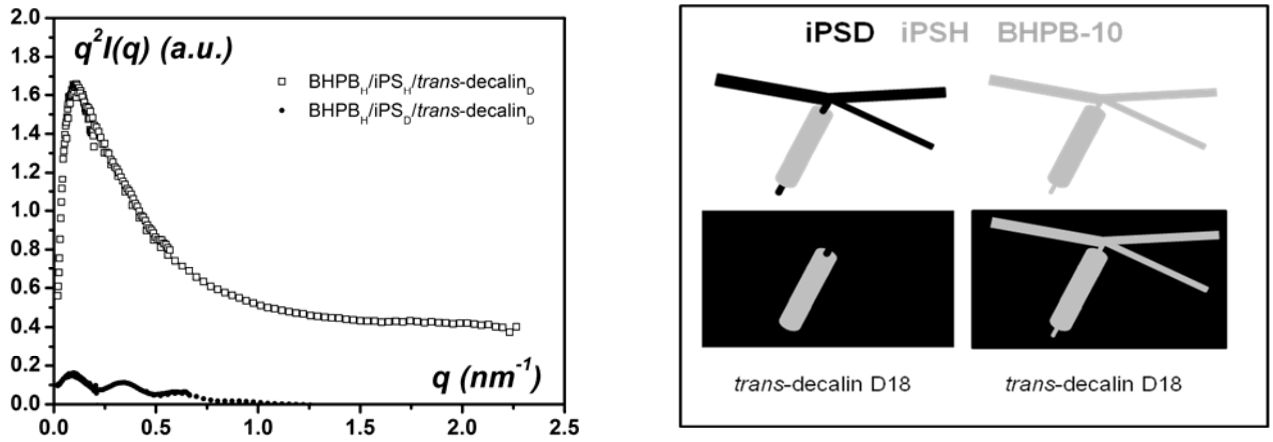

Fig.2: ***left****: SANS curves for the BHPB-10$_H$/ iPS$_D$/ trans-decahydronaphthalene$_D$ (upper curve), and BHPB-10$_H$/ iPS$_H$/ trans-decahydronaphthalene$_D$ (upper curve);* ***right*** *a sketch highlighting the effect of contrast. Oscillations are not seen in the second case because of the cross-section polydispersity of the system "polymer fibrils+BHPB-10$_H$" [2].*

These experiments are carried out as part of a study on hybrid materials prepared from polymers and self-assembling systems [5-7]

References

[1] N. Díaz, F.-X. Simon, M. Schmutz, M. Rawiso, G. Decher, J. Jestin and P. Mésini *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 3260

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