Sheathing Polymer Gels Fibrils with Nanotubules

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Summary: The aim of this preliminary study is to master the making of nanocomposites by physical processes. In particular, the sheathing of polymer fibrils by self-assembled nanotubules is examined. Nanotubules recently prepared from 3,5-Bis-(5-hexylcarbamoyl-pentyloxy)-benzoic acid decyl ester have been used for sheathing fibrils obtained by thermoreversible gelation of isotactic polystyrene. Investigations have been carried out by means of atomic force microscopy (AFM).

Keywords: AFM; isotactic polystyrene gels; nanotubules; sheathing

Introduction

In the field of nanomaterials, high aspect ratio objects such as supramolecular polymers, fibrils and nanotubules are interesting since they can form randomly-dispersed networks that can be easily oriented.[1,2] They can therefore display special properties such as transporting electrons or particles in a 1D fashion. The usual architecture of these molecules is rod-like or worm-like with a very large persistence length, and some of these are hollow, thus giving nanotubules.[3] Numerous molecules can self-assemble to form 1D objects such as ribbons or fibrils.[4] However, only a few of them are observed to form hollow tubes.[5] For some systems, such as lipids[6] the diameters are in the order of microns and are polydisperse. Recent work has led to the discovery of new self-assembled tubes with diameters that fill the gap between the micron scale and the diameter of the carbon nanotubes (1 to 3 nm) such as steroids,[7] peptides[8] hexabenzocoronene derivatives.[9] Such tubes are always found along with helical ribbons which are precursors to the closed tubes and that were already identified by Kunitake[10] in earlier work. Recently, one of us has succeeded in preparing nanotubules in organic solvents[11] from a diamide compound shown in Figure 1, namely 3,5-Bis-(5-hexylcarbamoylpentyloxy)-benzoic acid decyl ester (BHPB-10).

Another domain where fibrillar structures are formed is that of thermoreversible gels from covalent polymers.[12] Interestingly, it has been shown that self-assembling systems can be encapsulated in polymer fibrils by a heterogeneous nucleation process.[13,14] Clearly, nanocomposites can be prepared made up with covalent polymers and supramolecular polymers (self-assembled systems).

The nanotubules prepared from BHPB-10 have inner diameter of 21 nm which turns out to be in register with the fibrils cross-section of polymer thermoreversible gels.[11] It was therefore wondered whether one could sheath the polymer fibrils with these nanotubes, and thus gaining knowledge in the manipulation of these systems by using simple physical processes.

In this paper we present preliminary results obtained on isotactic polystyrene fibrillar gels with nanotubule-forming BHPB-10.

Experimental

Samples

The isotactic polystyrene(iPS) samples used in this study were synthesized by means of Natta's method.[15] The weight-average molecular weights as determined by SEC

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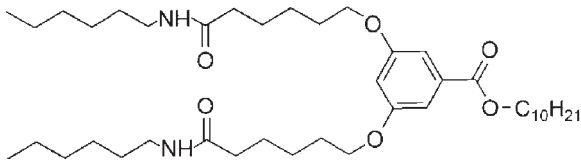

Figure 1.
Chemical structure of 3,5-Bis-(5-hexylcarbamoylpentyloxy)-benzoic acid decyl ester (BHPB-10). This molecule self-assembles into nanotubules.

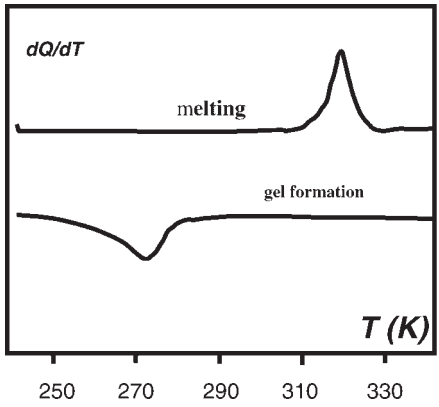

Figure 2.
DSC thermogrammes for iPS/trans-decalin gels. lower: formation exotherm, upper: melting endotherm.

in THF at 25 °C were found to be: Mw = 427 000 g/mol with Mw /Mn = 2:55. Hydrogenous trans-decalin was purchased from Aldrich and used without further purification. Thermoreversible gels were prepared at an iPS concentration of $C_{iPS} = 0.05$ g/cm^3.

3,5-Bis-(5-hexylcarbamoyl-pentyloxy)-benzoic acid decyl ester (BHPB-10) was prepared according to a described method.[11]

Techniques

AFM experiments were carried out at room sample in air using a Nanoscope III instrument (Digital Instruments, Snata Barbara, CA). The image was taken by means of tapping mode with a silicon nitride cantilever (Scientec, France) having a spring constant of 25–50 N/m and a rotating frequency of 280–365 kHz. The observation of the surface topography of the films was performed with a scannning rate varying from 1 to 2 Hz.

MicroDSC experiments were carried out with a MicroDSC III from SETARAM. Approximately 0.5 cm^3 of solution was used for performing the experiments. Cooling and heating rates of 0.5 C/min were used.

Diffusion and Sheathing Process

There is a large variety of common solvents where this can be achieved. We have used here trans-decalin wherein both iPS thermoreversible gels and BHPB-10 nanotubules are obtained.

A piece of gel obtained beforehand is immersed in an excess of solution containing the BHPB-10 molecules at a temperature above the nanotubules formation but well below the gel melting point. BHPB-10 can thus diffuse within the gel.

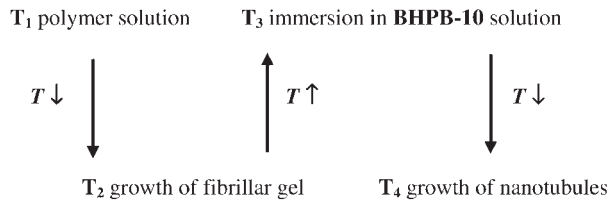

Figure 3.
The diffusion process: T2 = iPS gelation temperature, T3 = 30 °C. T4 = 20 °C.

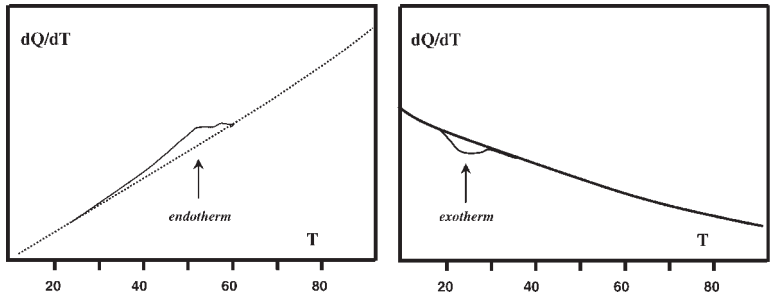

Figure 4.
DSC thermogrammes for BHPB-10 nanotubules. *left*: formation exotherm, *right*: melting endotherm.

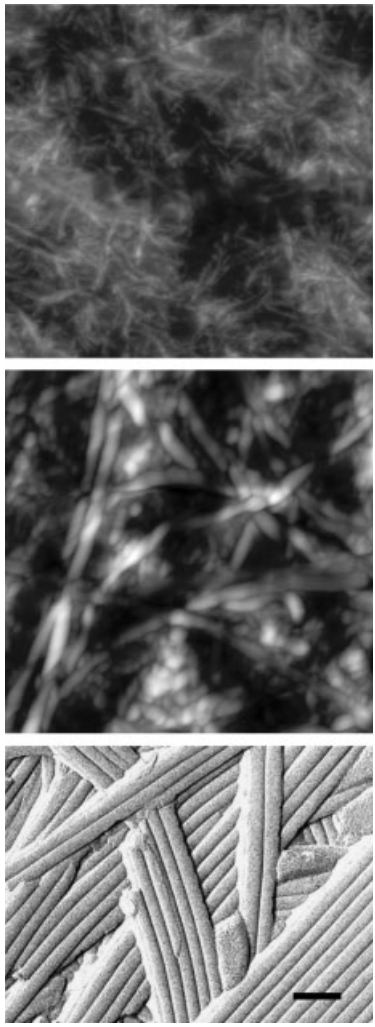

Figure 5.
AFM images of 5% iPS/trans-decalin gel (top) and 5% iPSgel + 0.05% BHPB-10 (middle). The size of the images is 1μm × 1μm. *Bottom*: electron micrograph of nanotubules from BHPB-10, bar = 100 nm.

After exposure of the gel to this solution for 48 hrs, the temperature is lowered to allow for nanotubules formation. The diffusion process must be carried out just above the gelation temperature in order to alter as little as possible the gel structure. At higher temperature partial melting may occur.

The preparation process is schematized in Figure 3.

As is shown in Figure 4 by means of microDSC, nanotubules formation proceeds through 1st order transitions so that formation exotherm as well as melting endotherms can be seen. We have found that $T_3 = 30\,^{\circ}C$ is an adequate temperature for performing the diffusion process. In *trans*-decalin nanotubules form below this temperature for a concentration of BHPB-10 of 0.05%.

Results

The iPS gel morphology and the structure resulting from the incorporation process of BHPB-10 within the gel have been examined by AFM. The nanotubules obtained by BHPB-10 have been observed by electron microscopy. The results are presented in Figure 5.

As can be seen, the gel structure has been dramatically altered after incorporation of the BHPB-10 molecules. These results seem to indicate that BHPB-10 molecules have wrapped around the iPS gel fibrils to form sheathed structures as expected. These are preliminary results that need now to be confirmed.

Concluding Remarks

Preliminary investigations have shown that wrapping polymerfibrils with self-assembled nanotubules is feasible through physical process. We suspect that the mechanism is similar to aheterogeneous nucleation process: fibrils trigger the growth of the nanotubules. Further experiments are now needed for confirming the effect and obtaining more information of the sheathing process.

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