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Self-Assembled Nanotubes in Organic Solvents

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Summary: Self-assembled nanotubes are formed spontaneously in alkane solvents by a simple diamide compound: the 3,5-Bis-(5-hexylcarbamoyl-pentyloxy)-benzoic acid decyl ester (BHPB-10). The tubular shape was proved by freeze fracture TEM and by SANS techniques. The tubes have a mean radius of 121 Å and a length of the order of a micron. BHPB-14, a homologue of this compound, bearing a longer ester chain (C14 instead of C10), self-assemble into flat ribbons under the same conditions. FTIR and UV spectroscopy showed that H-bonds between amide groups and π-π interaction between aromatic groups are involved in both kinds of aggregates and in the solid state as well. The nanotubes feature specific interactions between the ester carbonyls. Hence we show that ester, by its length and by the interactions between carbonyls determines the formation of nanotubes.

Keywords: gels; nanotubes; self-assembly

Introduction

The discovery of the carbon nanotubes by Iijima[1,2], and their applications in nanoscience, have motivated many groups for synthesizing tubular objects by supramolecular chemistry. Indeed, the self-assembly process can offer some advantages: easy formation, thermoreversibilty and high purity of the objects. In fact, the first molecules able to self assemble into tubular structures[3–5] were discovered twenty years ago, before the carbon nanotubes. These first examples of tubes have diameters of the order of a micrometer. But recently, one has discovered various compounds[6] that form tubes with diameters as low as 10 nm, which is close to the diameters of the multiwalled CNT (between 3 and 10 nm). They have very diverse chemical structures such as sugar derivatives,[7,8] peptides,[9,10] bolaamphiphiles,[11] lipids,[12–14] steroids,[15,16] or hexabenzocoronene derivatives.[17] The need for miniaturized structures in electronic devices has driven some groups into self-assembly approach: some self-assembled nanotubes have been used as template to synthesize inorganic nanotubes.[18–24] Some other applications of self assembled nanotubes arise from the possibility to design the constituting molecules to add functionality. It was done for instance by grafting biological ligands on lipids that are able to self-assemble in nanotubes. The resulting nanotubes can bind their proteins and form 2D crystals at their surface.[13,14] On the fundamental point of view, these objects have triggered much theoretical work by physicists.[25–28] These models, based on the molecular chirality and the elastic energy of a membrane describes the intrinsic bending of these membranes. But they do not provide insight at a molecular level and there is still no clear rule to design tube-forming molecules. It also explains that most of these compounds were discovered by serendipity. Therefore, gathering structural features at the molecular level is important to understand what are the important molecular parameters and interactions that govern the self-assembly of these molecules toward tubular structure.

We report a new compound that is able to form nanotubes in alkanes. We conducted different structural studies to characterize the tubular aggregates at two

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different levels: the geometry of the particles, and the interaction at a molecular level. We also compared the structures with other kind of aggregates to identify the important parameters determining the morphology of the aggregates.

We have been working previously on diamides as organogelators and we already showed that slight variations of their structures, preserve the gelation properties but lead to various shapes of the self-assemblies.[29]

Material and Methods

Synthesis of 1 and 2

The compounds were synthesized in two steps with the same methods as similar compounds.[29] Dihydroxybenzoic acid was esterified by decanol or tetradecanol (toluene, 0.05 equiv. APTS, 67 and 39% yield). The resulting dihydroxybenzoic acid decyl ester was alkylated with 6-bromohexanoic acid hexylamide (DMF, K_2CO_3, Bu_4NBr, 83 and 43% yield) to give the desired compounds.

Gel and Aggregates Formation

The aggregates were obtained by heating weighted amount of **1** or **2** in the desired amounts of solvent until a clear and isotropic solution was obtained, and by letting it cool down at room temperature.

IR spectra were recorded with a Bruker Vertex 70 spectrometer. The sample gels were placed in NaCl cells, and the cell was held by a thermostated cell-holder.

UV spectra were recorded in a quartz cell with an optical path of 0.1 mm, in a thermoregulated cell holder. Spectra were taken after the cell was translated to ensure that the gel was homogeneous throughout the cell. Several cooling-heating cycles lead to reproducible spectra during the heating phase.

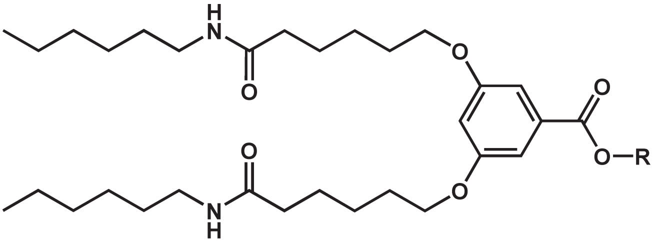
Electron Microscopy

The gels were held between two copper cupules and rapidly frozen with liquid N_2. They were fractured in a freeze-fracture apparatus (developed by J.-C. Homo, at the IGBMC, Strasbourg) and shadowed by a rotary evaporation of Pt under an angle of 45° and C under an angle of 90°. The replica were rinsed with $CHCl_3$, deposited on grids and observed with a CM12 Philips Microscope operating at 120 kV.

SANS experiments were performed at the LLB in Saclay with the PAXE spectrometer. Correction, reduction and normalization of the data were carried out as described previously.[30]

Results and Discussion

When compound **1** is heated in cyclohexane until complete dissolution and when the



1: R = $nC_{10}H_{21}$

2: R = $nC_{14}H_{29}$

Figure 1.
Structure of the studied compounds **1** and **2**.

solution is cooled back at 25 °C, the solution thickens to yield a gel. This process can be observed for concentrations as low as 0.05 wt %. This process is thermoreversible and reheating of the gels yields a sol. The same experiment can be conducted with **2**. This macroscopic behavior clearly designs both compounds as low mass organogelators.[31–33] In this class of compounds, the gel properties are due to the self-assembly of small molecules into fibrillar aggregates, which form a 3D network.

The inner structure of the gels of **1** and **2** has been explored by freeze-fracture electron microscopy. Figure 2A shows the structure of the gels of **1** in cyclohexane. The micrograph shows that the gel comprises mainly cylindrical objects. Their widths are about 20–30 nm with little dispersity and their lengths are of the order of a micrometer and polydisperse. In some pictures the end of the tubes can be observed and their section shows they are hollow objects (Figure 2A, arrows).

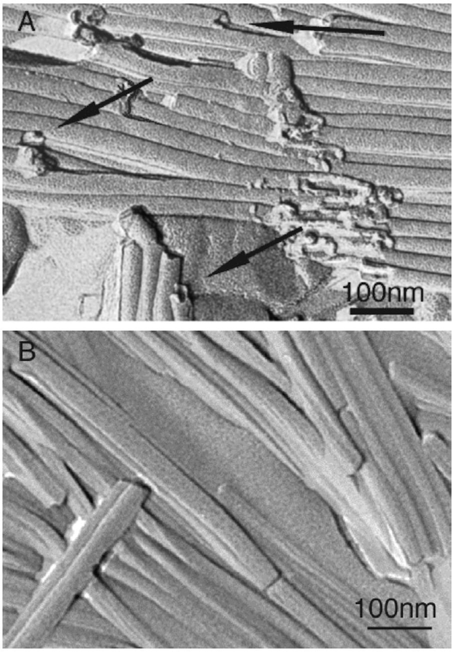


Figure 2.
Electron microscopy of freeze fractured gels in cyclohexane (2% wt). A: **1**, nanotubes; arrow: end of an aggregate, showing the inner void space. B: **2**, flat ribbons.

In the gels of **2**, the self-assembled aggregates have a different morphology. They form flat ribbons with a 40 nm width and several micrometers long (Figure 2B). On a topological point of view, the difference between both morphologies is due only to the curvature of the ribbons. A ribbon without curvature remains flat, whereas an intrinsic curvature bends it into helical tapes, and nanotubes. Experimentally, the tubes are often observed along with helical ribbons that were assumed in very early work[4] as the precursors of the tubes. This hypothesis was proved to be correct by the theoretical models.

The shape of the self-assembled structures formed by **1** in cyclohexane was studied more accurately by small angle neutron scattering experiments. The same tubes were formed in deuterated cyclohexane to obtain sufficient contrast between the solvent and the aggregates. The intensity of neutron scattering was recorded between 0.008 Å^{-1} and 0.6 Å^{-1}. The interparticle correlations were assumed to be negligible. In these conditions, the scattered intensity can be simply written as in Eq. 1, where Φ_v is the volume fraction of the particles, $\Delta\varphi^2$ is the contrast of the particles and V_p is the volume of the particles. P(q) is the form factor of the particle and depends only on the geometry of the particle. The form factor of a long cylinder is given by Eq. 2,[34] where L is the length of he cylinder, R_o and R_i are respectively the outer and inner radii, and J_1 represent the Bessel function of order 0.

$$I(q) = \Phi_v \Delta\varphi^2 V_p P(q) \tag{1}$$

$$P(q) = \frac{\pi}{qL} \times \frac{4(R_o J_1(qR_o) - R_i J_1(qR_i))^2}{q^2(R_0^2 - R_i^2)^2} \tag{2}$$

Figure 3 shows the intensity normalized to the contrast and the volume fraction. This curve can be fitted only with close values of

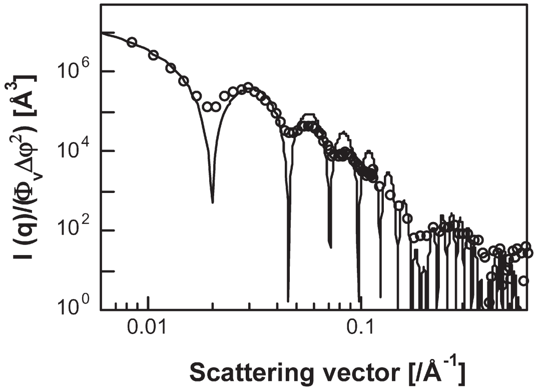


Figure 3.
Small angle neutron scattering of a gel of **1** in C_6D_{12} (2% wt). The intensity is normalized to the volume fraction and to contrast. o: experimental; line: fit with equation 2, $R_i = 10.4$ nm, $R_o = 13.7$ nm.

R_o and R_i, which strongly supports the fact that these objects are hollow.

The curve yields a measurement of the mean diameter ($R_o + R_i$) with a good accuracy: 24.2 ± 0.3 nm. The curve was fitted with $R_e = 10.4$ nm and $R_i = 13.7$ nm. The found outer diameter 27.4 nm is in good agreement with what is observed in electron microscopy. The thickness of the wall of the cylinder ($R_e - R_i$) is 3.3 nm. This has to be compared with the length of the fully stretched molecule that is 3.6 nm from field calculations.

The nature of the interactions in the aggregates has been investigated by simple spectroscopic techniques. IR spectroscopy was performed on gels of **1** in cyclohexane at different temperatures. Figure 4 shows the spectra in the area of the NH stretching bands. The major peak is found at 3312 cm^{-1}, which is consistent with the fact that the amide groups are linked by H-bonds. The comparison can be made with the spectra of **1** in $CHCl_3$, in which **1** is soluble in all proportions. In these solutions, the major peak is located at 3450 cm^{-1}, which is

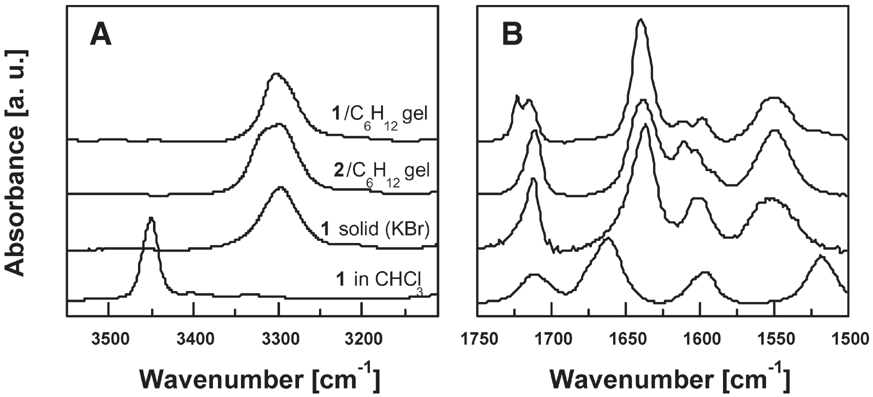


Figure 4.
IR spectra; from top to bottom: gel of **1** in cyclohexane (2% wt); gel of **2** in cyclohexane (2% wt); solid (KBr); solution in $CHCl_3$ (5% wt). **A**: amide A band; **B**: form left to right: ester carbonyl, amide I, aromatic ν_{CC}, amide II bands (see text).

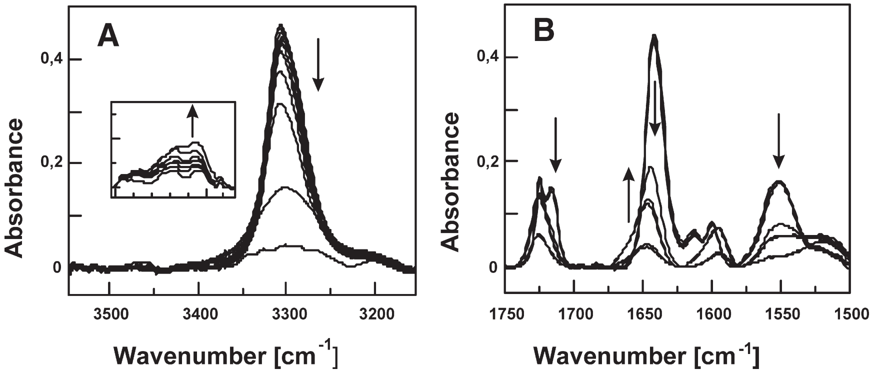


Figure 5.
IR Spectra of gels of **1** in cyclohexane (2% wt) at different temperatures, from 26 °C to 64 °C. A: amide A band; B: ester carbonyl, amide I and amide II bands.

characteristic of H-bond free NH groups. Similar difference can be observed in the band I area: in the **1**/cyclohexane gels, the band I maximum is at 1642 cm^{-1}, whereas it is at 1663 cm^{-1} in the $CHCl_3$ solutions. In the solid **1** (after recristallization in EtOAc) and in the gels of **2**, the bands A, I and II have the same intensities and frequencies as those of the nanotubes.

These spectra show that the H-bonds between the amide groups are involved in the self-assembly. However, these interactions are not specific of the nanotubes, since the same interactions can be observed in the solid or in the flat ribbons formed by **2**. The most intriguing signal is the CO stretching band of the ester. The maximum of this band is at 1712 cm^{-1} in the solid and in solution in $CHCl_3$. In the nanotubes, the CO stretching band is split in a doublet at 1716 and 1724 cm^{-1}. The presence of this doublet can be due to the presence of two sets of carbonyls, for instance two different orientations of the carbonyls inside the nanotubes. The doublet can also arise from a coupling between two neighboring ester groups. Although the explanation for this doublet is not yet well understood, this signal is specific of the nanotubes. It suggests that there are interactions between carbonyls. When the gels are heated gradually above the gel-to-sol transition, the peaks characteristic of the amides that are bonded via H-bonds decrease while those characteristic of isolated amide groups increase (Figure 5). However, the peaks do not disappear at the higher temperatures (64 °C), showing that even in the sol, many H-bonds between amides remain. The molecular spectra of the gels in cyclohexane were also recorded at different temperature and compared with the solutions in $CHCl_3$ (Figure 6). The major absorption bands at 223 nm and 258 nm shift to the blue, at 207 nm and 251 nm respectively when the gel melts. This experiment shows that π-π interactions

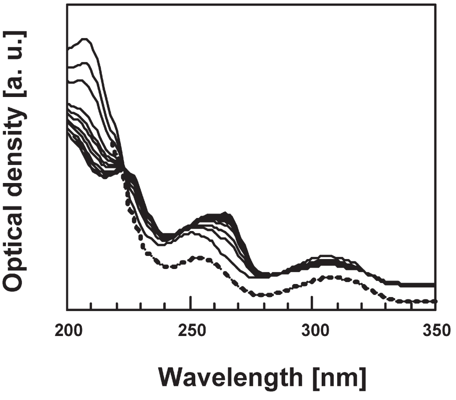


Figure 6.
Molecular spectra of **1**. plain line: gel in cyclohexane (0.3% wt) form 25 °C to 62 °C. dotted line in solution in $CHCl_3$.

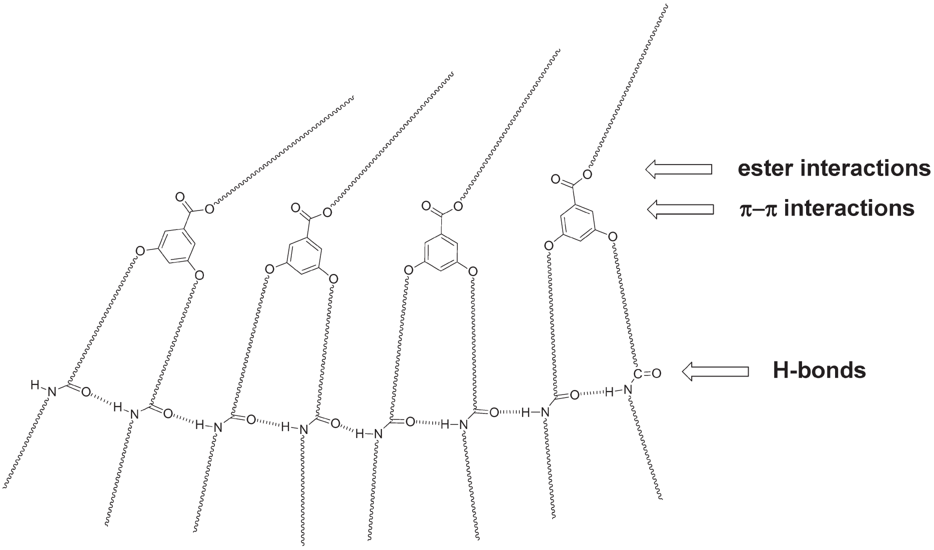


Figure 7.
Summary of the intermolecular interactions in the nanotubes.

between aromatic rings also participate to the cohesion of the aggregates.

The WAXS spectrum of the nanotubes was also recorded and Braggs peaks at wide angles were observed[35]. This is evidence that the inner structure of the tubes is crystalline.

Figure 7 summarizes the interactions that have been experimentally showed in the course of these studies. The interactions between the esters determines the morphology of the self-assembly of **1**. In cyclohexane, the ester-ester interactions, combined to the aromatic interaction and the H-bands between the amides leads to the formation of the tubes. At this stage of our work, we cannot propose an accurate model of the molecular array of the molecules inside the wall of the cylinders. It is more complex than a simple monolayer, as preliminary phase variations SANS experiments have shown it.

Compound **2** self-assembles in straight ribbons with no curvature, and the ester band, in IR spectra, is the same as in the solid state or as in chloroform solution. This result proves again that the ester plays a major role in determining the type of self-assembly. The size of the ester chain is the molecular parameter that can enable or preclude the interactions between the esters and hence the formation of the nanotubes. This can be interpreted as a different steric demand of 14 carbon atoms, instead of 10, that leads to a different type of molecular packing. This rough explanation needs to be refined in theoretical models.

Conclusion

We have found a new compound forming nanotubes in organic solvents by self-assembly. The nanotubes have an outer diameter of 28 nm as measured by SANS. Spectroscopic methods were used to identify many non-covalent interactions involved in the self-assembly. The comparison with the solid state or with analogues, enabled us to identify an unusual interaction between esters, which is the most characteristic of the molecules forming nanotubes. We found that one molecular parameter, the ester chain length, strongly influences the morphology of the self-assemblies. Further analogues are under studies and their comparison with the abovementioned compounds will serve as basis for a theoretical model.

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