Growth Dynamics of Rosette Nanotubes in Solution as Observed via Small-angle X-ray Scattering

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Introduction

Rosette nanotubes [1-3] are a new class of nanotubular materials obtained via the hydrogen-bond-driven self-assembly of small molecules featuring hydrogen bonding of the Watson-Crick-type H-bond donor/acceptor found in the GC base pair of DNA. As illustrated in Fig. 1, six of these modules arrange themselves to form a planar assembly with a diameter of about 3 nm and a central cavity of about 1 nm. This assembly, which is stabilized in solution via 18 hydrogen bonds, is able to form stacks up to several micrometers long, as confirmed by transmission electron microscopy (TEM) and scanning probe microscopy (SPM). The surface of the tube can be decorated with almost any functional unit, such as those for amino acids or crown ethers, thereby allowing a wide spectrum of surface modification chemistry to control the assembly's size and its physical and chemical properties. The nanotubular assemblies show remarkable properties, such as entropically driven growth when they are annealing and control of the helicisity via chiral promoters [2]

Real-space analysis such as TEM or SPM can provide only indirect information about the morphology and dimensions of the assemblies originally formed in solution. The purpose of this research is to determine the influence of solvents and temperature on the structural formation of rosette nanotubes in solution. Currently we have very little information about the dynamics of the tube formation, aggregation, and degradation processes. The kind of side group (called backbone) that is attached to the exterior of the nanotube skeleton and the choice of solvent have a strong influence on the tube's dimensions, such as its diameter and aspect ratio, as well as on its stability and growth kinetics.
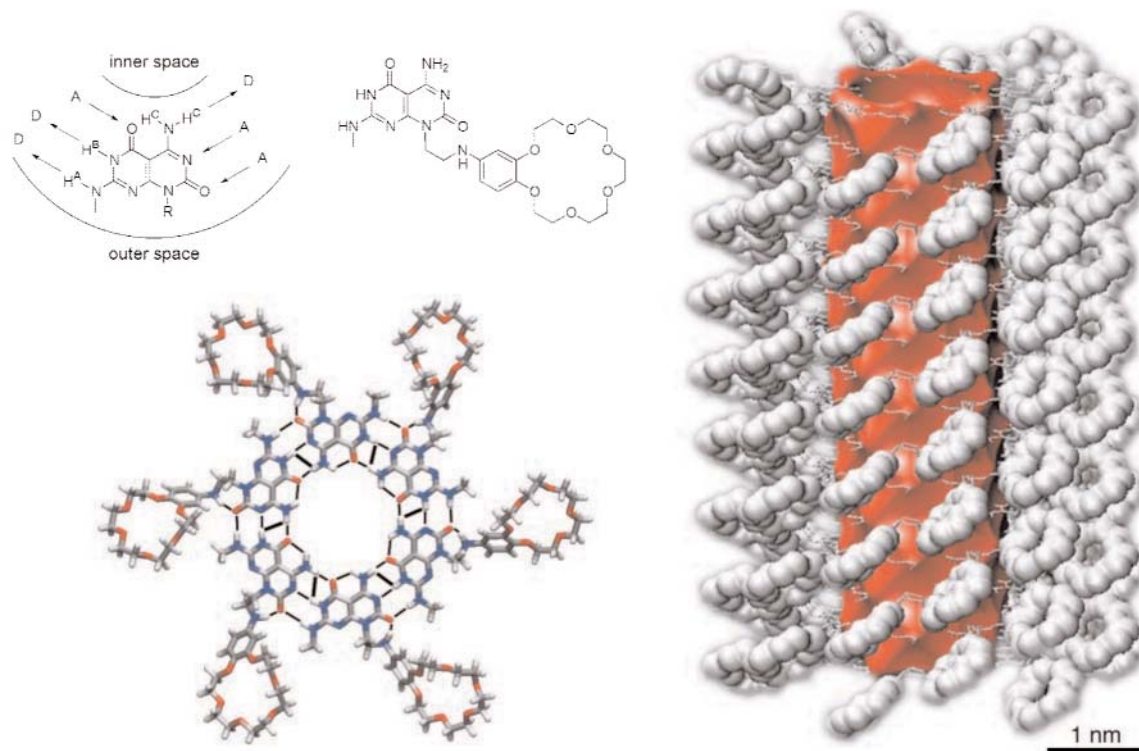

FIG. 1. *Molecular structure of D-108 and model of rosette nanotube assembly.*

Methods and Materials

A number of samples carrying various backbones were studied by small-angle x-ray studies at the APS. This report highlights a measurement series that sheds light on the temperature-dependent tube growth process that is based on a molecule carrying a crown ether backbone (Fig. 1) called D-108. The measurements were done in a 1-wt% water solution at a temperature range of 20° to 70°C. A modified Gunier analysis of the scattering profiles allowed a very accurate determination of the tube diameter when a model for rodlike structures was used [4]. The evaluation is based on the following equation:

$$I(Q) = Q^{-1} \times I_c(0) \times \exp(-Q^2 \times R_c^2/2) \qquad (1)$$

where R_c is the cross-sectional radius of gyration and is related to the rod radius by $r = \sqrt{2} \times R_c$.

Results and Discussion

The background-corrected scattering profiles of D-108 plotted as Q^2 versus ln $[Q \times I(Q)]$ and the modified Gunier fits are plotted in Fig. 2. In the initial state at 20°C, the measured tube diameter was 4.6 nm, which is close to the calculated diameter of a single rosette nanotube. After the sample was heated to 70°C, the tube diameter increased to 11.5 nm, which is about three times the value determined at 20°C, suggesting the formation of bundles of about seven rosette nanotubes.

After the sample was cooled back to 20°C, we observed a decrease in diameter to 11.1 nm at 40°C and to 7.1 nm at 20°C. In separate experiments, we observed that the growth as well as the degradation of the assemblies is time dependent, meaning that the growth or degradation does not stop after the set temperature is reached. This indicates that the growth or degradation kinetics of the assembly process are slower than the experimentally applied heating or cooling rates (1°C/min and 2°C/min, respectively). The observed aggregation hysteresis is in agreement with data obtained from dynamic light scattering (DLS) and TEM measurements [2].

References

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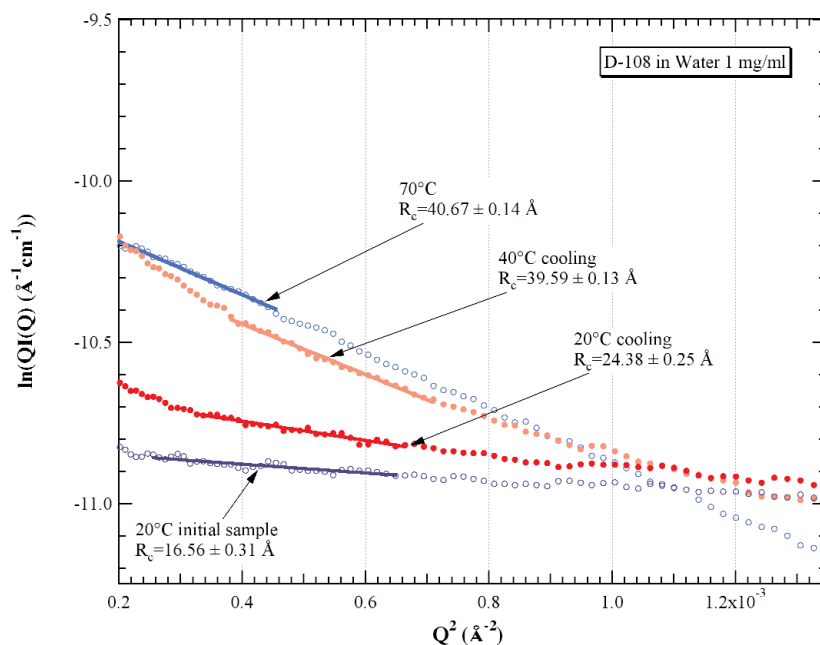[4] O. Kratky and G. Porod, J. Colloid Sci. **4**, 35 (1949).

FIG. 2. *Modified Gunier analysis of scattering behavior of 1-mg/mL D-108 solution in water. Measurement time was 10 seconds. The overall tube diameter d is related to R_c via $d = \sqrt{8} \times R_c$.*