Morphology and Dispersion of Nanotubes and Nanofibers: Investigation by Ultrasmall-angle X-ray Scattering

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Introduction

The carbon nanotubes discovered by Iijima [1] possess exceptional mechanical properties and fascinating electronic properties [2]. Carbon nanotubes occur in two forms. Single-walled nanotubes (SWNTs) are composed of a graphene sheet rolled into a cylinder, and multiwalled nanofibers (MWNFs) consist of multiple concentric graphene cylinders. SWNTs, which are prepared by laser vaporization, have very small uniform diameters (~1 nm) and can be curled or looped rather than straight.

Efforts have been made to incorporate the nanocarbons into polymers in order to take advantage of their exceptional properties. However, dispersion of nanocarbons in matrix polymers has proven to be extremely difficult, and the resulting composites do not show particularly enhanced properties.

In the absence of a suspending agent, nanocarbons do not disperse in solution, much less in a polymer matrix. The reason is simple enough. The extended pi-electron system leads to strong attractive van der Waals forces that are aggravated by the fact that tubes can interact over extended distances when aligned side by side.

With the aid of polyelectrolytes, nanocarbons can be suspended in water. Polyelectrolytes are known to adhere to surfaces of the opposite charge, and there is ample evidence that they will also cling to neutral surfaces, thus providing electrostatic colloid stabilization [3].

In this report, we show the successful characterization of dispersed nanocarbons by using scattering techniques to assess the morphology in solutions.

Methods and Materials

Preparation of Nanocarbon Suspensions

Polystyrene sulfonate and sodium salt (NaPSSO3) (molecular weight = 500,000) were used without further purification. One weight percent of this polyelectrolyte was dissolved in distilled water. The polyelectrolyte solutions were added to the SWNTs or MWNFs to make 0.1% nanocarbon total concentration. The mixtures were stirred for 5 min and then sonicated at a horn power of 10 W for 5 min more. No attempt was made in these experiments to control the pH of the polyelectrolyte solutions. As produced, the pHs of the polyelectrolyte solutions in water were 9 for NaPSSO3. The suspensions were then used in the scattering experiments.

USAXS

The structures of nanotubes and nanofibers suspended in polyelectrolyte solutions were investigated by using ultrasmall-angle x-ray scattering (USAXS), which covers the 0.1 Å$^{-1} \le q \le 10^{-4}$ Å^{-1} regime. In addition, light scattering was used to prove 10^{-6} Å$^{-1} \le q \le 10^{-3}$ Å^{-1}.

Results and Discussion

The combined light and USAXS results of nanotubes are illustrated in Fig. 1. The figure shows no signature of rodlike morphology at any length scale. This conclusion rests on straightforward fractal interpretation of the scattering data [4]. The length scales (radii of gyration, Rg) and power law exponents P are displayed in Fig. 1. For mass fractal objects $-1 > (P = -D) > -3$, the fractal dimension D = 1 for rods, 2 for disks, and 2-2.5 for

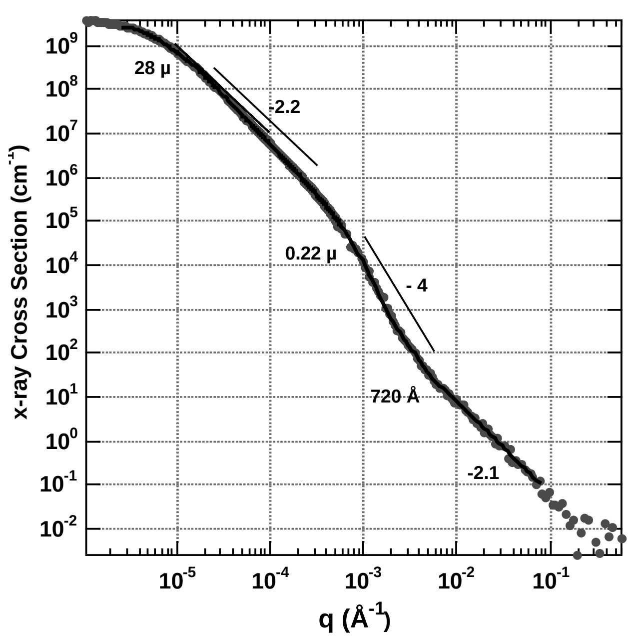

FIG. 1. Combined light and USAXS profile for SWNTs suspended with PSSO3.

branched polymers. When -3 > P > -4, P = Ds – 6, where Ds is the surface fractal dimension. Ds ranges from 2 for a smooth surface to 3 for a uniformly dense object that is all surface. The data in Fig. 1 are consistent with the existence of a branched, ropelike structure of bundled SWNTs. The length of 0.22 μm is considered a mean diameter of ropes. The power-law regime with P = -4 shows that the ropes have a smooth surface with Ds = 2. The origin of the power-law regime at high q is not clear at this point. Such a slope could imply that a small-scale meshlike network is present inside the ropes.

The combined light and USAXS results of nanofibers are presented in Fig. 2. The slope near -1 indicates a rodlike character on large scales for the nanofibers. The scattering profiles on the USAX regime show a crossover of 210 Å. At intermediate length scales, the dimensionality of the object is 2.80, whereas on shorter length scales, the object is uniformly dense (Ds = 2.7). This result is consistent with a hollow tube, since the wall of such an object is 2-D on scales larger than its thickness (and shorter than its length) and 3-D on scales smaller than the wall thickness.

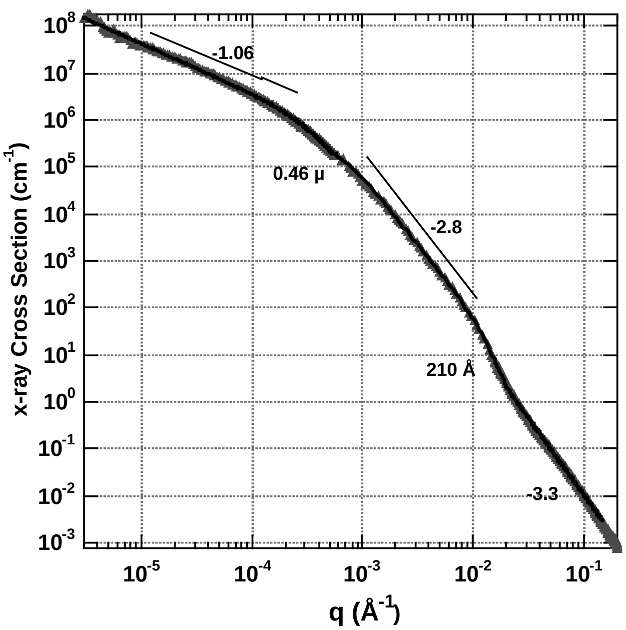

FIG. 2. Combined light and USAXS profile for MWNFs suspended with PSSO3.

Acknowledgments

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