

# Measurement of Nanotube Dispersion by Scattering, Chromatography, and Microscopy\*

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## INTRODUCTION

Single wall carbon nanotubes (SWNTs) are tubular structures made from what is effectively a rolled graphic sheet. The tubes are approximately 1 nm in diameter and can be from hundreds of nm to many  $\mu\text{m}$  in length. They are proposed for a variety of potential applications in materials, due to their outstanding mechanical, electrical, optical, and thermal properties [1]. However, as-produced SWNTs are masses of nanotubes that need to be separated from each other to produce individual nanotubes that can be sorted and manipulated.

Many of the potential applications of SWNTs require dispersion in liquid or solid matrices [2]. Three general methods of dispersion have been developed: surfactant dispersion, wrapping with long chain polymers, and covalent attachment of organic groups. The covalent attachment method promotes dispersion in organic solvents or polymeric media, and is widely studied. All methods can produce stable suspensions that do not settle out over long time periods. The nature of the dispersion on a size scale comparable to the SWNT size is of great importance since manipulation of individual tubes into devices is the ultimate goal.

Techniques such as microscopy can show the existence of individual tubes, however small angle scattering is capable of determining the average distributions of large collections of dispersed tubes. Small angle x-ray scattering (SAXS) and small angle neutron scattering (SANS) have been used to measure the structure of SWNT dispersions. The exponent  $\alpha$  in the scattering is  $\alpha = 1$  for individual rods and is between 5/3 and 2 for individual semi-flexible chains.

$$I(q) \sim q^{-\alpha} \quad (1)$$

Most previous work has found power law scattering in the region  $q < 0.01 \text{ \AA}^{-1}$  with  $2 < \alpha < 3$ . This is characteristic of branched or aggregated rods or chains. Schaefer et al [3-4] describe "network of tubes". The reported scattering seems dominated by clusters, even though individual chains may also be present in the mix. The clusters could either be remnants from the synthesis that have never become separated by the dispersion process, or associations in dynamic equilibrium with individual tubes. SANS can use the "high concentration" method to extract single particle scattering from clusters of nanotubes [5]. Two samples are prepared, one in which deuterium has replaced the hydrogen of the structure. SWNTs themselves contain no hydrogen, so this technique cannot be used on them alone. However, several methods of covalently attaching hydrocarbons have been reported. Billups [6] uses free radical chemistry to attach alkyl groups that supply the required hydrogen for the high contrast technique. While this could conceivably change the shape and association of the nanotubes, it is the only practical way of labeling the tubes for the high concentration method.

Scattering from concentrated mixtures have contributions from single chain correlations,  $P(q)$ , and inter-chain correlations,  $Q(q)$ .  $P(q)$  contains information on molecular mass, size, stiffness, etc., and  $Q(q)$  contains information on clustering, ordering, etc. For a mixture of identical SWNTs with differing contrast factors,  $\sigma_H$  and  $\sigma_D$ , dispersed in a medium with contrast factor  $\sigma_S$ , for a SWNT mixture with a molecular mass of  $M$  and a mole fraction of  $H$  and  $D$  of  $x_H$  and  $x_D$  and a total volume fraction in the medium,  $\phi$ , the scattered intensity,  $I(q)$  is:

$$I(q) = K M((x_D(\sigma_D - \sigma_S)^2 + (x_H(\sigma_H - \sigma_S)^2)P(q) + (x_D\sigma_D + x_H\sigma_H - \sigma_S)^2\phi Q(q) \quad (2)$$

By varying the relative amounts of the SWNT-d and SWNT-h, the single particle and inter-particle contributions can be calculated independently. A series of scattering experiments are carried out at constant  $\phi$ , but varied  $x$  to produce a series of equations to fit both  $P(q)$  and  $Q(q)$ .

Chromatography of dispersed SWNTs has also described [2]. Size Exclusion Chromatography (SEC) separates by molecular size with the elution time being a monotonic function of hydrodynamic volume,  $V_H$ . The "universal calibration" [7] technique relates  $V_H$  to the intrinsic viscosity,  $[\eta]$ , and the molecular mass,  $M$  as

$$V_H = [\eta] M \quad (3)$$

Therefore an SEC column is calibrated with a polymer with known intrinsic viscosity - molecular mass relationship. If a concentration detector and a viscosity detector are used to measure the eluent, the molecular mass can be determined. The intrinsic viscosity - molecular mass relationship follows a power law over a considerable range known as the Mark-Houwink relationship:

$$[\eta] = K M^a \quad (4)$$

where the power law exponent,  $a$ , is a measure of the structure of the molecule. Therefore, two measurements, SANS and SEC, each have characteristic power laws describing the structure. Table 1 gives power laws for a variety of structures.

**Table 1. Power Law Exponents for Various Fractal Structures**

Structure Type	Viscosity Power Law = $a$	Scattering Power Law = $\alpha$
Rod	$\sim 1.3$	1
Self Avoiding Walk	0.8	5/3
Random Walk	0.5	2
Branched	$< 0.5$	2 to 3
Dense	0	4

## EXPERIMENTAL<sup>#</sup>

**Sample Preparation.** SWNTs were obtained from Carbon Nanotechnologies Inc. The chemical modification reaction was carried out according to the procedure of Billups et al. [6] using iodobutane to form butyl grafts. Dispersions for SANS were made by sonicating the grafted tubes in a 1 % by mass fraction solution of sodium lauryl sulfate-d23 (SLS) in  $D_2O$  at 1 mg/mL SWNT concentration. The dispersions were centrifuged for 10 min and the top layer was removed. Dispersions for SEC were obtained by extraction of 100 mg of butyl grafted SWNT with methylene chloride. The extract was dried and redissolved in tetrahydrofuran (THF) at 1 mg/mL. The solution was filtered through a 0.45  $\mu\text{m}$  Teflon filter.

**SANS, SEC, and AFM.** Small angle neutron scattering (SANS) was performed on the 30 m NG7 instrument at the National Institute of Standards and Technology (NIST) Center for Neutron Research (NCNR). The SEC was performed on a Waters Alliance GPC2000 using a Styragel 6E column with THF as a mobile phase. Calibration was made with narrow mass distribution polystyrene (PS). Tapping-mode atomic force microscopy (AFM) measurements were conducted in air using a Nanoscope IV system (Digital Instruments). Uncertainties are one standard deviation and are not plotted when smaller than symbols.

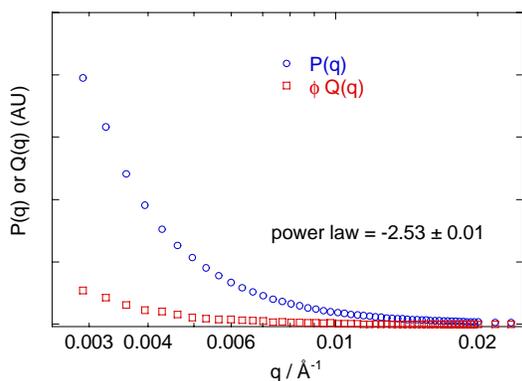
<sup>#</sup> Certain commercial equipment and materials are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by NIST nor does it imply that the material or equipment identified is necessarily the best available for this purpose.

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## DISCUSSION

Dispersions of grafted SWNTs were prepared both in organic solvents and in aqueous surfactant dispersions. Both methods had similar results, but the surfactant dispersions were studied in most detail and are reported here. SANS measurements were made on two samples containing 100 % SWNT-H and 100 % SWNT-D. The SLS has the same neutron scattering contrast as the D<sub>2</sub>O and does not add to the scattering of the labeled SWNT. Plots of I<sub>H</sub>(q)/I<sub>D</sub>(q) vs q were flat indicating a good match in SWNT structure. The ratio of scattered intensities gives  $(x_D\sigma_D + x_H\sigma_H - \sigma_s)^2$  and the match point compositions,  $x_H = 1 - x_D$  can be calculated. A mixture is made of nanotubes at this composition so that the scattering from equation 2 has a Q(q) prefactor of zero producing only P(q). Three sets of scattering data are fit with equation 2 to produce values of both P(q) and Q(q).

Figure 1 gives the SANS results. The single particle scattering can be fit with a power law of  $-2.53 \pm 0.01$ , which is the same as the power law of whole sample. This indicates that the structure of the scattering entity is a branched collection of SWNTs. The mixing and sonication of the clustered samples does not appear to break up the clusters, rather there appears to be mixing only at a scale larger than the individual SWNT. There is not a dynamic equilibrium that randomizes the tubes on an individual level. The relative magnitude of the interchain scattering is small in comparison to the single chain scattering. Therefore, the scattering at these concentrations is dominated by the scattering from clusters.

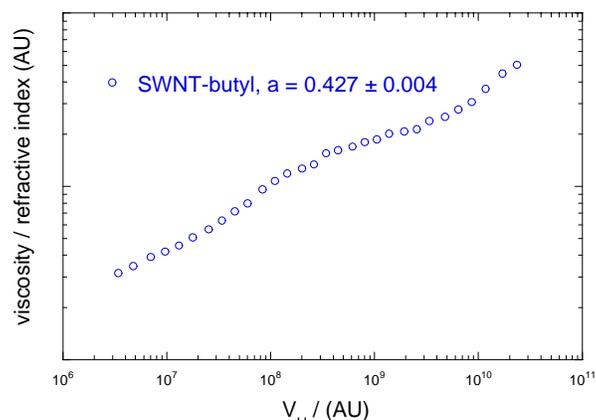


**Figure 1.** Single particle scattering function, P(q), and interparticle scattering function, Q(q) for grafted nanotubes.

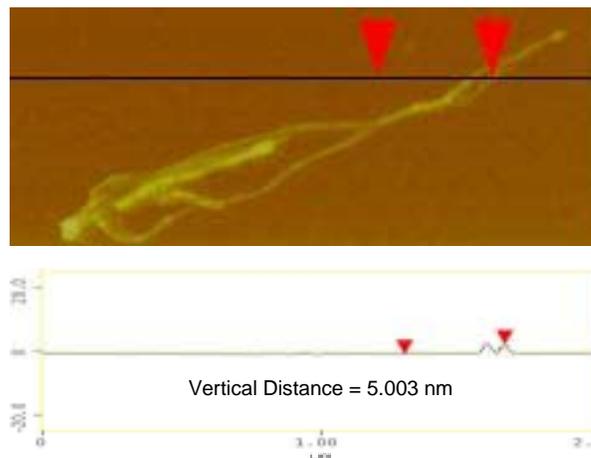
The SEC results are shown in figure 2. The characteristic viscosity power law exponent is  $0.427 \pm 0.004$  over a considerable range of molecular size. Rigid rod structures such as poly( $\gamma$ -benzyl- $\alpha$ -L-glutamate) have a viscosity power law of 1.3 and follow universal calibration [8]. The grafted nanotubes clearly do not exhibit the behavior of rigid rods. The power law exponent of 0.427 is more consistent with branched structures.

Further evidence is supplied by AFM measurements. Figure 3 depicts a clustered and folded collection of SWNTs that was common for this series of samples, and provides a reasonable interpretation for the data collected via the respective scattering techniques. The height measurements provided by section analysis suggest a wrapping of multiple SWNTs or a SWNT suspended over the surface.

In conclusion, SANS power law,  $\alpha$ , of 2.53 and SEC power law,  $a$ , of 0.427 are consistent with structures consisting of many nanotubes. AFM measurements also find such structures. While these conclusions are valid for the particular materials reported here, we have not demonstrated that it is a typical case. Other dispersal schemes or even different sample preparations of covalently attached SWNTs may produce different results. However, the combination of scattering, chromatography, and microscopy can be applied to a wide variety of SWNT dispersions, providing multiple independent measurements of dispersion efficiency.



**Figure 2.** Intrinsic viscosity  $[\eta]$  vs.  $V$  for grafted nanotubes in THF from SEC.



**Figure 3.** AFM image of grafted nanotubes showing a clustered and folded collection of SWNTs.

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