

Chromatographic Separation of Single Wall Carbon Nanotubes

Barry J. Bauer, Vardhan Bajpai, Jeffrey A. Fagan, Matthew L. Becker, and Erik K. Hobbie

Polymers, NIST, 100 Bureau Drive, stop 8541, Gaithersburg, MD, 20899-8541

ABSTRACT

Size exclusion chromatography (SEC) is shown to be an effective method to characterize single wall carbon nanotube (SWNT) dispersions. SEC separates nanotube dispersions by size, and measures the intrinsic viscosity on-line as a function of hydrodynamic size as is determined by Universal Calibration. This scaling contains information about the shape of the dispersed particles. This characterization method was tested on three representative dispersions: octadecyl amine functionalization in tetrahydrofuran (THF), butyl group functionalization in THF, and DNA wrapping in aqueous solution. Significant differences between the dispersions were found. Small angle neutron scattering (SANS) and atomic force microscopy (AFM) produced results consistent with the SEC method.

INTRODUCTION*

Single wall carbon nanotubes (SWNTs) have a variety of potential applications in materials, due to their outstanding mechanical, electrical, optical, and thermal properties¹. However, current SWNT synthetic methods produce bundles of nanotubes comprised of tubes with a distribution of lengths, chiralities and diameters, and they are unsuitable for most applications and characterization methods without further processing.

The dispersion of nanotubes in solution is necessary in order to achieve the goal of sorting and manipulating nanotubes by length and type and then to prepare high quality monodisperse samples. Monodisperse samples are required in order to properly characterize the optical, thermal and electrical properties of nanotube based materials. Several schemes have been developed to promote SWNT dispersion, which have demonstrated the ability to form stable suspensions that do not settle out over long time periods². Methods are necessary to assess the quality of the dispersions; for example, it must be known if the original bundles/ropes of nanotubes have broken down into isolated nanotubes. The nature of the dispersion and our ability to characterize the dispersion on a size scale comparable to the SWNTs is thus of great importance.

EXPERIMENTAL DETAILS

SWNTs were obtained from Carbon Nanotechnologies Inc.³ The butyl grafting reaction (SWNT-butyl) was carried out according to the procedure of Billups et. al.⁴ and was reported previously⁵. The octadecyl amine grafted samples (SWNT-ODA) were prepared according to the standard Procedure⁶. The aqueous DNA dispersions (SWNT-

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DNA) were prepared according to the procedure of Zheng et al.⁷⁻⁹. Dispersion was induced by sonication, and insoluble material was removed through centrifugation resulting in a SWNT concentration between (0.1 and 0.4) mg/mL as determined by UV absorption before and after centrifugation.

Size exclusion chromatography was performed on a Waters Alliance GPCV 2000 instrument using a refractive index and viscosity detectors. The SWNT-butyl and SWNT-ODA samples were run at 1.0 mL/min in THF using a Waters Styragel HMW 7E column. The SWNT-DNA sample was run in 0.2 mol/L NaCl, 0.04 M TRIS, pH = 7.0 at 0.5 mL/min using a SepaxCNT (SEC-1000 + SEC-300) column set. All columns were calibrated in THF with narrow polystyrene (PS) standards. All samples were passed through a 0.45 μm filter before injection.

Small angle neutron scattering was performed on the NG7 30 m instrument and the NG1 8 m instrument at the National Institute of Standards and Technology Center for Neutron Research. Tapping-mode atomic force microscopy measurements were conducted in air using a Nanoscope IV system (Digital Instruments) operated under ambient conditions with standard silicon tips (NanoDevices Metrology Probes; L, 125 mm; normal spring constant, 40 N/m; resonance frequency, 280-330 kHz).

The relative uncertainties reported are one standard deviation, based on the goodness of the fit or from multiple runs. Total combined uncertainties from all external sources are not reported, as comparisons are made with data obtained under the same conditions. In cases where the limits are smaller than the plotted symbols, the limits are left out for clarity.

RESULTS

Size exclusion chromatography (SEC) is an effective method to characterize SWNT dispersions; it takes advantage of the size polydispersity inherent in nanotube samples. Size exclusion chromatography (SEC) has been reported for a variety of SWNT dispersions^{6,7,10-17}, giving confidence that this method can be applied generally. Measurements of the scaling relationship between the intrinsic viscosity $[\eta]$, as determined by on-line detectors, and the hydrodynamic volume V_H , as determined by the universal calibration method¹⁸ were made. The shape of the nano-dispersion (for example tubes, spheres or coils) can be discerned from this scaling relationship. This characterization method is applied to three representative dispersion methods: octadecyl amine attachment to acid treated SWNTs, butyl grafting through free radical mechanisms (both dispersed in THF) and DNA wrapping in aqueous solution. Significant differences between the dispersions were found. Small angle neutron scattering (SANS) and atomic force microscopy (AFM) produced results consistent with the SEC method.

The scaling is based on the Mark-Houwink-Sakurada (MHS)¹⁸ equation

$$[\eta] = KM^a \quad (1)$$

which relates the intrinsic viscosity, $[\eta]$, to molar mass, M through the MHS parameter a , which varies with extension and branching of the polymer or nano-particle. $\eta(\phi)$ is the viscosity of a solution with nanotube concentration ϕ , and η_s is the viscosity of the solvent. Table 1 lists the MHS values of a for six different structures ranging from rigid rods ($a = 2$) to dense spheres ($a = 0$).

Standard SEC methods that have been developed for polymer solutions have been applied to nanotube dispersions. In SEC, a porous column packing material is used to separate dissolved polymer molecules by size. The polymers partition between the flowing mobile phase and stationary phase that is incorporated within the pores of the column. The smaller polymers have a larger partitioning coefficient inside of the pores than the larger ones. This results in the larger polymers spending a larger fraction of time in the mobile phase, hence, eluting from the column before the smaller ones¹⁸.

The partitioning of the polymers will depend on their characteristic volume, which is commonly associated with their hydrodynamic volume. Universal Calibration¹⁹ is a technique that assumes that elution time is a function of the hydrodynamic volume alone. Therefore, a column can be calibrated with a set of polymers having known hydrodynamic volumes and then used to measure other polymers or nanoparticles with unknown sizes and shapes. While it is an empirical method, it is valuable for estimating the relative structure of dissolved or suspended material.

SEC with Universal Calibration is used to measure the MHS parameter of unknown polymers by calibration of a column with a known polymer and by measuring the $[\eta]$ on-line by employing a viscosity detector along with a concentration detector such as refractive index or ultraviolet absorption¹⁸. When properly calibrated, $[\eta]$ at any elution time can be compared with the hydrodynamic volume from the calibration step. The hydrodynamic volume, V_H , is related to the $[\eta]$ and molecular mass through a power law relationship

$$V_H = [\eta]M = KM^{a+1} \quad (2)$$

Thus, a plot of measured on-line $[\eta]$ as a function of V_H from a calibrated column on a log-log scale has a slope of $a/(a+1)$. By applying the strategy described above to the case of nanotube dispersions, the MHS parameter can be measured to determine the nature of the dispersion.

Figure 1 is a plot of $[\eta]$ measured using on-line SEC with columns calibrated with narrow Polystyrene (PS) standards. The calibration used a literature value of MHS parameters of $K = 0.011 \text{ mL/g}$ and $a = 0.725$ ²⁰. The a value from a broad PS mixture is 0.73 ± 0.02 which is in agreement with the literature value used in the calibration. The three SWNT dispersions have considerably different slopes in the plots, and the extracted values of a are listed in Table 1. The SWNT-ODA and SWNT-butyl dispersions had very weak viscometer signals, resulting in sizable uncertainty limits as is shown in the symbols to the right of the plotted data. The SWNT/DNA gave stronger viscometer response, indicating a more open structure.

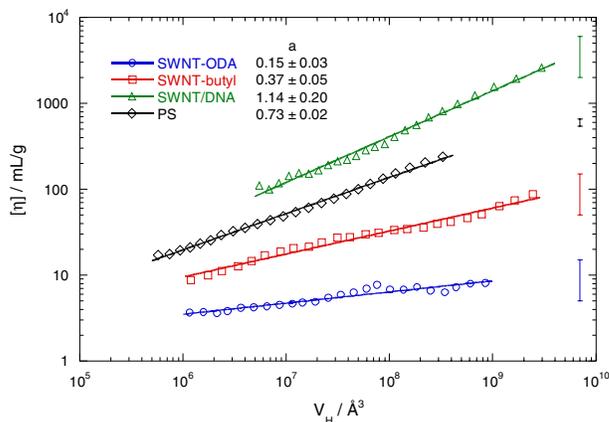


Figure 1. Intrinsic viscosity measured on-line by SEC. V_H from Universal Calibration using columns calibrated with PS standards.

AFM images provide complementary information. Figure 2 shows AFM images of SWNTs dispersed by the three methods. SWNT-ODA shows irregular spheres with high polydispersity (A), SWNT/DNA shows individual stiff rods (B), and SWNT-butyl grafted shows branched clusters of many tubes (C). The micrographs ($5 \mu\text{m} \times 5 \mu\text{m}$) are representative of each sample type and clearly place each in a different class.

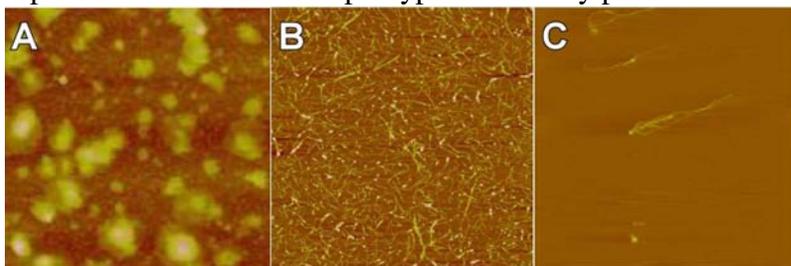


Figure 2. Representative AFM micrographs ($5 \times 5 \mu\text{m}$) depicting the results from the three preparative methods described in the text: SWNT-ODA (A), SWNT/DNA (B), and SWNT-butyl (C).

Figure 3 shows the SANS results from the butyl, the ODA and DNA SWNT dispersions. The butyl and ODA dispersions show power law behavior over a range of q . Table 1 indicates the power law exponents, α , expected from typical structures, in a fashion analogous to the viscosity power laws. The SWNT-butyl has an extended power law region of -2.4 ± 0.2 ⁵, the SWNT/DNA shows an extended power law region of -1.5 ± 0.1 . The SWNT-ODA has a broad curvature typical of large polydispersity with a slope of 3.9 ± 0.5 at the highest q as reported in Table 1.

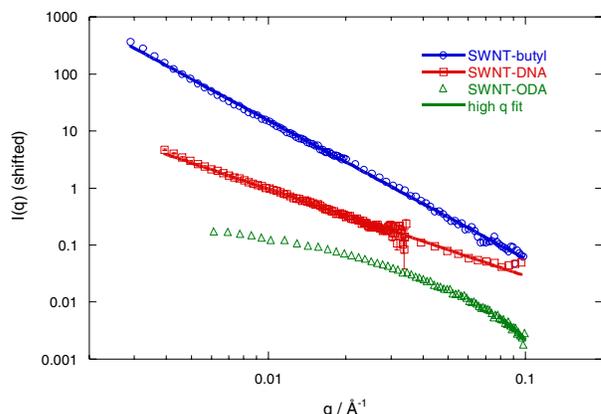


Figure 3. SANS from SWNT dispersions. SWNT-butyl has a wide power law region of -2.5 ± 0.2 , SWNT/DNA has a wide power law region of -1.5 ± 0.1 , and the SWNT-ODA has a curved region with a power law of 3.9 ± 0.5 at the highest q region measured.

The SEC with on-line detection is clearly able to measure the large differences between the three dispersions, as seen in the summary of results at the bottom of Table 1. SEC indicates that the SWNT-butyl is a branched structure, and it indicates that the SWNT/DNA is a semi-flexible rod, stiffer than a self-avoiding walk, but more flexible than a rigid rod. The SEC result from the SWNT-ODA tells us the eluent is a dense object, close to spherical in nature, most likely comprised predominately of carbonaceous masses. These results are consistent with those seen in the AFM images. SANS provides a complementary result, as shown in Table 1.

Table 1. Power law relationships for ideal structures and measured dispersions

Structure / Dispersion Method	viscosity power law $[\eta] \propto M^a$	scattering power law $I(q) \propto q^{-\alpha}$
rigid rod	2	1
flexible rod	0.8 to 2	1 to 1.67
self-avoiding random walk	0.8	1.67
gaussian random walk	0.5	2
branched	< 0.5	2 to 3
dense sphere	0	4
SWNT-ODA	0.15 ± 0.03	3.9 ± 0.5
SWNT-DNA	1.14 ± 0.20	1.5 ± 0.1
SWNT-butyl	0.37 ± 0.05	2.5 ± 0.2

The choice of the three dispersion methods used in this study was intended to represent a variety of typical techniques. SEC separations of SWNT-ODA have been reported previously^{6;14;16}. Reports have found an initial fraction containing dispersed SWNTs followed by fractions of primarily carbonaceous impurities and other reports using acid purified SWNTs also found considerable carbonaceous impurities^{14;16}. Our

measurements are consistent with the presence of a significant amount of this carbonaceous impurity. A published report of SEC of SWNT/DNA dispersions describes good dispersions, which is consistent with our findings⁷⁻⁹. The SWNT-butyl SANS and AFM results have been previously reported⁵.

Chromatography is becoming an important method of purifying and sorting SWNT types. The use of size sensitive on-line detection can provide important information on the nature of the dispersion. All three of the dispersions described in this manuscript formed dark, black liquids even after centrifugation and passing through a 0.45 μ m syringe filter. SWNT dispersions that can pass through a SEC column may still have components of clustered nanotubes or non-SWNT carbon.

CONCLUSIONS

A method for quantifying dispersion using SEC with concentration and viscosity detection has been demonstrated with three dispersions of SWNTs. Employing an additional on-line size sensitive detection method such as multi-angle light scattering will prove valuable, since it measures radius-of-gyration and molecular mass. This will allow for a more direct characterization of dispersion type, which can supplant Universal Calibration.

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