

In-situ structural characterization of SWCNTs for probing polymer/nanorod interactions

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ABSTRACT

Assisted by the recently developed preparative ultracentrifuge method (PUM) - an in-situ structural characterization technique to determine the particle size and bundling states of single-walled carbon nanotube (SWCNTs) in dispersion, we investigated the probe diffusion behaviors of SWCNTs in semi-dilute polymer solutions - polyacrylonitrile (PAN) homo- and copolymer in dimethylacetamide (DMAc). With changing the polymer concentration to control the solution correlation length, the effect of topological constraints on the longitudinal diffusion of SWCNT probes in both PAN homo- and copolymer solutions was explicitly studied. It was found that the diffusion retardation of SWCNTs in polymer solution depends upon not only the topological constraints but also the chemical structures of polymer chain and the resulted SWCNT/polymer interactions.

Keywords: carbon nanotube, sedimentation, probe diffusion, dynamic light scattering, rigid rods

1 INTRODUCTION

Single-walled carbon nanotubes (SWCNTs) possess a variety of intriguing properties, such as, excellent mechanical robustness—high strength, stiffness, and toughness, extraordinary electrical and thermal conductivity, piezoresistive sensitivity, and versatile spectroscopic and optoelectronic characteristics [1, 2, 3]. This renders such a novel material great potential for developing SWCNT enabled multifunctional polymeric nanocomposites [4]. To establish the processing-structure-property relationship of SWCNT enabled multifunctional nanocomposites, a good understanding of the interactions between SWCNTs and polymer chains in SWCNT/polymer dispersion is necessary. In this regard, the structures of SWCNTs in the dispersion, such as, the length and diameter of SWCNT particles, their bundling states, and the side-wall defect density, etc., should be well characterized, since they played critical roles in dictating the interactions between SWCNTs and polymer chains [5]. With the structural characterization techniques recently developed by us - preparative ultracentrifuge method (PUM) [6] and the simultaneous Raman scattering and photoluminescence spectra (SRSPL) [7], such critical structural information of

SWCNTs in a dispersion can be quantified. The PUM method relies on inexpensive and easy-to-access instrumentation, namely, a preparative ultracentrifuge instrument and UV-VIS-NIR spectrometer, to experimentally determine the sedimentation function for a given carbon nanotube dispersion. Subsequent fitting of the sedimentation function based on hydrodynamic modeling gives rise to the bulk averaged length and diameter of carbon nanotubes. The SRSPL uses the simultaneously acquired Raman scattering and photoluminescence spectra to infer the percentage of individual tubes or the degree of exfoliation for a given SWCNT dispersion [7,8]. In addition, with the exact analytical solution derived by us [9] to relate the defect density of a defective SWCNT with its PL quantum yield, the SRSPL can also be used for quantitatively characterizing the SWCNT defect density. With assistance of PUM method to quantify the size of SWCNTs, in this paper, we experimentally explored the probe diffusion behaviors of SWCNTs in semi-dilute solutions of polyacrylonitrile (PAN) homo- and copolymer in dimethylacetamide (DMAc). This approach provides a convenient way for in-situ probing the topological and chemical/physical interactions between SWCNTs and the host polymer in the dispersion.

2 MATERIALS AND METHOD

2.1 Samples and sample preparation

Polyacrylonitrile (PAN) homo- and random copolymers were supplied by Japan Exlan Company Ltd. (Okayama, Japan). Both PAN homopolymer and PAN-methacrylic acid copolymer (4 wt% of MA) have a viscosity average molecular weight of 250,000 g/mol. Anhydrous N, N – dimethylacetamide (DMAc, 99.8 %, CAS Number: 127-19-5) was purchased from Sigma-Aldrich, Co., and used as received to prepare PAN solutions and SWCNT dispersions. Highly purified (low catalytic impurities) HiPco® SWCNT raw materials (batch no. SP0300, ~ 2 wt% catalytic impurities as determined by TGA) were supplied by the Continental Carbon Nanotechnologies, Inc. (CCNI). The SWCNT/DMAc dispersion with concentration of 10 mg/L was prepared by bath sonication (Branson 2510, 100W, 42 KHz) and characterized by PUM to determine the size of SWCNT particles. To investigate the probe diffusion behaviors of

SWCNTs in PAN/DMAc solutions, the as-sonicated SWCNT/DMAc dispersion was mixed with PAN/DMAc solutions at varied polymer concentrations to form SWCNT/PAN/DMAc ternary dispersions, in which the SWCNT concentration was maintained at 2.5 mg/L and the polymer concentration was varied from 4.5 g/L to 60 g/L.

2.2 Preparative Ultracentrifuge Method

Optima™ MAX-XP ultracentrifuge instrument (Beckman Coulter, Inc.) with a fixed angle (30°) rotor was used to perform PUM on SWCNT/DMAc dispersion for determining the bulk averaged length and bundle diameter of SWCNT probes. Figure 1 shows the experimentally measured and theoretically fitted sedimentation function for SWCNT/DMAc dispersions sonicated respectively for 20 hrs and 80 hrs. The PUM results are given in Table 1, where the diffusion coefficients of SWCNTs in DMAc dispersion were measured by dynamic light scattering.

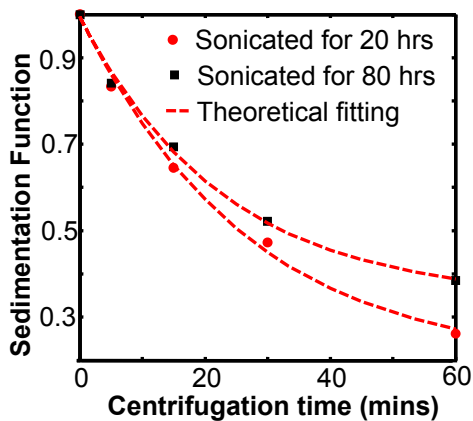


Figure 1: PUM determined (scattered data) and theoretically fitted (smooth dashed lines) sedimentation function for SWCNT/DMAc dispersion at centrifuge field of 65,000 g. The concentration of SWCNT/DMAc dispersion is 10 mg/L.

Table 1: PUM results of SWCNT/DMAc dispersions

| Sonication Time (hr) | Sedimentation Coefficient ($\times 10^{-12}$ sec) | Diffusion Coefficient ($\times 10^{-8}$ cm ² /sec) | Length (nm) | Diameter (nm) |
|----------------------|--|--|-------------|---------------|
| 20 | 6.52 | 1.14 ± 0.0445 | 2756 | 4.4 |
| 80 | 6.32 | 1.21 ± 0.0258 | 2580 | 4.3 |

2.3 Dynamic Light Scattering

Dynamic light scattering was used in our study to investigate the SWCNT probe diffusion behaviors in PAN/DMAc solutions. In DLS measurements [10], the time fluctuation of the scattered light intensity, $I_s(t)$, from a

dynamic system is recorded and the corresponding time correlation functions, $g_2(\tau)$, is determined by:

$$g_2(\tau) = \frac{\langle I_s(t)I_s(t+\tau) \rangle}{\langle I_s(t) \rangle^2} \quad (1)$$

which is further related to the time correlation function $g_1(\tau)$ of the scattered electric field:

$$g_2(\tau) = 1 + \gamma [g_1(\tau)]^2 \quad (2)$$

where γ is a constant determined by the experimental conditions. For a dilute particulate system, if the particles move according to diffusion motion, $g_1(\tau)$ is related to the distribution of the diffusion coefficients of the particles $G(\Gamma = Dq^2)$ by:

$$|g_1(\tau)| = \int G(\Gamma) \exp(-\Gamma \tau) d\Gamma \quad \Gamma = Dq^2 \quad (3)$$

where D is the diffusion coefficient of the particle; q is the magnitude of the scattering vector, which is related to the wavelength λ of the light in the medium and the scattering angle θ by $q = 4\pi \sin(\theta/2)/\lambda$. With the well-known CONTIN method [11] - a numerical algorithm for inverse-Laplace transform, $G(\Gamma)$ can be numerically determined from the experimentally measured $g_1(\tau)$.

Delsa Nano C (Beckman Coulter, Inc.) was used for performing the DLS measurements at 25°C on SWCNT/DMAc and SWCNT/PAN/DMAc dispersions. The intensity autocorrelation function, $g_2(\tau)$, was measured at a fixed scattering angle of 166° with a laser of 658 nm in wavelength. With the experimentally determined $g_2(\tau)$, the field correlation function $g_1(\tau)$ was calculated according to Eq. (2), to which the CONTIN algorithm was applied to extract the peak decay rate for calculating the corresponding diffusion coefficient by Eq. (3). As a representative example, Figure 2 shows the experimentally determined and CONTIN fitted field correlation function $g_1(\tau)$ for SWCNT/DMAc binary and SWCNT/PAN/DMAc ternary dispersion. Clearly, the $g_1(\tau)$ for the SWCNT/PAN/DMAc ternary dispersion shifts to longer delay time as compared to SWCNT/DMAc dispersion. This is an indication that the SWCNT probe diffusion is subject to retardation in polymer solutions. As discussed next, the diffusion retardation of SWCNT probes provides valuable information regarding the SWCNT/polymer interactions.

3 RESULTS AND DISCUSSION

There is a long history of using trace amounts of Brownian particles as probes for interrogating the molecular motion of their host medium [12,13,14]. In particular, through studying the diffusion behavior of the probe particle in semi-dilute polymer solution, where the individual chains are overlap and interpenetrate each other, provide fundamental insights to understand the polymer chain dynamics, the solution microstructures and the

probe/polymers interactions [15,16]. The correlation length ξ is the key length scale to characterize the polymer solution structures [17,18]. Intuitively, a semi-dilute polymer solution can be considered as a transient network with mesh size of ξ , which is the key length scale to understand the diffusion behaviors of probe particles [12,19,20]. Based on scaling argument, a relationship between the correlation length ξ and the polymer solution concentration c has been well-established [18]:

$$\xi \approx R_g(0) \left(\frac{c}{c^*} \right)^{-0.75} \quad (4)$$

where $R_g(0)$ is the radius of gyration of polymer chain in dilute solution limit. c^* is the critical polymer concentration at which polymer chains begin to overlap. According to the dynamic light scattering measurements on the neat PAN/DMAc solutions at different concentrations, we arrived at an empirical scaling relationship for PAN/DMAc solution, which is given by:

$$\xi_{DLS} = 8.05 \times c^{-0.75} \quad (5)$$

When Eq. (5) is used to determine the correlation length of PAN/DMAc solution at a given polymer concentration, the concentration c should be in g/100ml. This then gives ξ in nm. Assisted by Eq. (5), we explicitly investigated the relationship between the correlation length ξ of and the SWCNT probe diffusion coefficient for both homo-PAN and PAN-copolymer solutions. The results are shown in Figure 3.

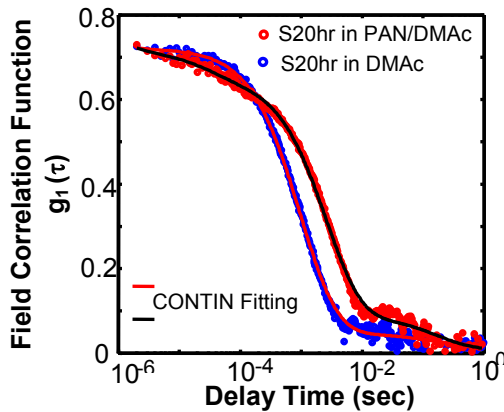


Figure 2: Experimentally determined (scattered data) and CONTIN fitted (smooth lines) field correlation function $g_1(\tau)$ for SWCNT/DMAc (10mg/L) and SWCNT/PAN/DMAc (2.5 mg/L + 9 g/L) dispersion. SWCNT probes were prepared by 20hr sonication.

Before discussing the results presented in Figure 3, a few remarks are necessary to clarify the nature of the diffusion coefficient measured by DLS for rigid rod particles. It is commonly known that, when DLS is used for examining the diffusion of spherical probes, the diffusion coefficient thus determined is a direct measure of the center-of-mass diffusion of the particles. However, the

situation becomes more complicated when DLS is used for examining the diffusion behaviors of rigid rod particles, e.g., SWCNTs. For rod-like probes [21,22,23], the shape anisotropy imparts the unique anisotropic diffusion of the probe particles, which is manifested by the faster diffusion along the longitudinal direction than that in the transverse direction. Moreover, the translational diffusion of the rod is coupled with its rotational Brownian motion. Because of complication of the anisotropic diffusion and the related translation-rotation coupling effect, the diffusion coefficient of rigid-rod measured by DLS is not simply a direct measure of mass-of-center diffusion. Instead, on the basis of the theoretical framework developed by Maeda et al [23], the numerical simulation studies [24] suggested that the physical nature of the diffusion coefficient measured by DLS for rigid rods depends on the value of qL – the product of the scattering vector q and the rod length L . When the DLS measurement is carried out in a weak translation-rotation coupling regime ($qL < \sim 4.0$), the diffusion coefficient determined by DLS is a measure of the center-of-mass diffusion of the rod; however, when the DLS measurement is performed in a strong translation-rotation coupling regime ($qL > \sim 20.0$), the diffusion coefficient measured by DLS is the longitudinal diffusion coefficient of the rod. Since the qL value for the SWCNT probes in our DLS experiments is greater than 70, according to the criterion mentioned above, it is clearly that the SWCNT probe diffusion results shown in Figure 3 is a reflection of the longitudinal diffusion of SWCNT particles. Clearly, as shown in Figure 3a and 3b, with increasing the polymer concentration or decreasing the correlation length of polymer solution, the SWCNT probe diffusion is subject to an increased retardation in both homo-PAN and PAN-copolymer solutions. The observed phenomenon can be understood in terms of the transient network structures of polymer solutions. When the polymer concentration is increased, the network mesh size ξ decreases. It then makes the SWCNT probes more difficult sieve through the meshes along their long axis to cause the observed retarded longitudinal diffusion. The topological constraints formed by polymer chain entanglements are not the only factor to dictate the retarded diffusion of SWCNT probes. The detailed chemical structures of polymer chains and the resulted SWCNT/polymer interactions also play important roles. As evidenced in Figure 3a and 3b, the SWCNT probe diffusion in homo-PAN and PAN copolymer solutions show different functional dependence on the correlation length of the polymer solution. In homo-PAN polymer solution, the SWCNT probe diffusion coefficient shows a power-law dependence on the correlation length; in PAN copolymer solutions, an exponential function gives a better description on the relationship between the SWCNT probe diffusion coefficient and the correlation length. The different chemical structures for PAN homo-polymer and copolymer are presumably responsible for the observed different diffusion retardation behaviors of SWCNTs probes. In particular, the methacrylic acid co-monomers in

PAN copolymer could form hydrogen-bonding with the carboxylic acid groups of the SWCNTs that were introduced during purification process. However, there is a lack of such hydrogen-bonding interaction in the dispersion of SWCNTs in PAN homopolymer solutions. The dispersion stability testing results (insets of Figure 3a and 3b) provide further evidence to corroborate this point. It has been observed that, the SWCNT/homo-PAN dispersion is much stable than SWCNT/PAN copolymer dispersion.

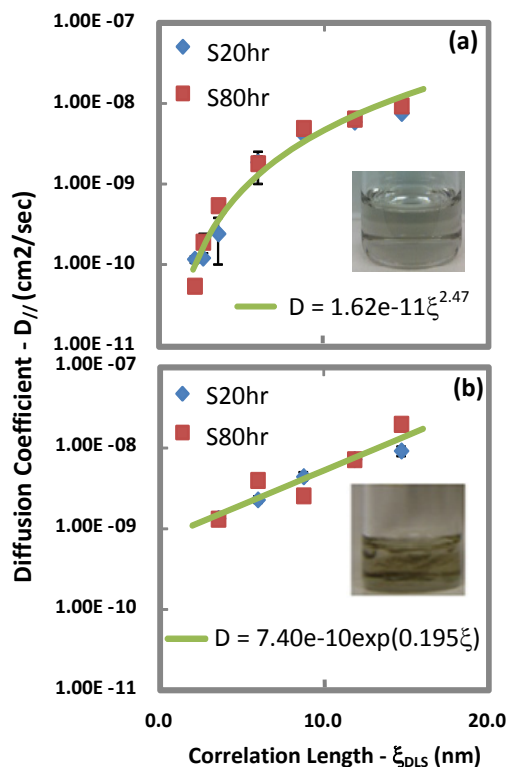


Figure 3: Diffusion retardation behaviors of SWCNT probes in (a) homo-PAN/DMAc solutions (inset: SWCNT/Homo-PAN/DMAc dispersion aged for 2 weeks) and (b) PAN-methacrylic acid copolymer/DMAc solutions (inset: SWCNT/PAN copolymer/DMAc dispersion aged for 2 weeks)

4 CONCLUSIONS

With the recently developed characterization techniques – preparative ultracentrifuge method (PUM) to quantify the size of SWCNT probes, we investigated the probe diffusion behaviors of SWCNTs in semi-dilute solutions of polyacrylonitrile homo- and copolymers in dimethylacetamide. With varying the polymer concentration and thus to control the correlation length, the role of polymer solution structures on the retardation of longitudinal diffusion of SWCNT probes has been investigated. It was identified that the topological constraints formed by polymer chain entanglements as well as the detailed polymer chain chemical structures both play

important role in dictating the SWCNT probe diffusion behaviors. Our findings indicate that the interaction information between SWCNTs and polymer chains in the dispersion can be readily acquired through studying the SWCNT probe diffusion behaviors by DLS.

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