

# Generic Approach for Dispersing Single-Walled Carbon Nanotubes: The Strength of a Weak Interaction

Rina Shvartzman-Cohen,<sup>†</sup> Yael Levi-Kalisman,<sup>‡</sup> Einat Nativ-Roth,<sup>†</sup> and Rachel Yerushalmi-Rozen<sup>\*,†,‡</sup>

Department of Chemical Engineering and The Ilse Katz Center for Meso- and Nanoscale Science and Technology, Ben Gurion University in the Negev, 84105 Beer Sheva, Israel

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A generic noncovalent approach for dispersing high concentrations of individual single-walled carbon nanotubes (SWNT) in organic as well as aqueous solutions of synthetic block copolymers is presented. It is suggested that a weak, long-ranged entropic repulsion among polymer-decorated tubes acts as a barrier that prevents the tubes from approaching the attractive part of the intertube potential. The method opens a new route for utilization of block copolymers as compatibilizers for SWNT, improving the incorporation of de-agglomerated SWNT into target polymeric matrixes.

## Introduction

Single-walled carbon nanotubes (SWNT) currently attract scientific and technological attention because of their superior properties and emerging applications in nanoelectronics and in the field of nanocomposites.<sup>1</sup>

A major barrier for SWNT utilization in nanocomposites is their poor solubility and low dispersability in aqueous and organic liquids, leading to difficulties in their manipulation and incorporation into different matrixes. The resulting SWNT-based materials exhibit a strength, modulus, and conductivity much lower than expected.<sup>2</sup>

The low dispersability stems from the tendency of as-prepared SWNT to assemble into bundles or ropes that contain hundreds of well-aligned SWNT arranged in a close-packed triangular lattice,<sup>3</sup> due to van der Waals attraction. The over-micrometer-long ropes further entangle into networks. A recent calculation<sup>4</sup> suggests that the typical intertube attraction is on the order of 36 kT for every nanometer of overlap between adjacent tubes, leading to cohesive energy of a few thousands of kT per micrometer-long tubes. Unlike the case of classical colloids, the attraction is short-ranged and decays to a negligible value over a distance of a few nanometers.

Current approaches for dispersing and exfoliating bundled SWNT into individual tubes include covalent modifications,<sup>5–7</sup>  $\pi$ - $\pi$  interactions,<sup>8,9</sup> surfactant adsorp-

tion,<sup>10,11</sup> and more. Most of these methods are designed to reduce the short-range attraction between adjacent tubes via the introduction of a repulsive interaction of similar strength. Consequently, these treatments often lead to modification of the structural, electronic, and mechanical properties of the tubes.<sup>12–14</sup>

To overcome this problem, a significant effort was invested in the development of noncovalent dispersing methods,<sup>15</sup> mainly based on physical adsorption of polymers.<sup>16–18</sup> While quite a few examples were reported, the underlying mechanism in each of these studies was believed to rely on specific interactions between a given polymer and the SWNT. For example, it was suggested<sup>16</sup> that tight SWNT-polymer association (known as “wrapping”) leads to screening of the hydrophobic interaction in aqueous solutions and consequential dispersion of tubes.

Here, we present a generic, single-step method for dispersing individual SWNT in aqueous and organic liquids: a powder of as-prepared SWNT is sonicated in a solution of a synthetic block copolymer, forming a black inklike stable dispersion. While the gentle sonication leads to exfoliation of SWNT into individual tubes,<sup>19</sup> selective adsorption of the block copolymer triggers a repulsion among the polymer-decorated SWNT and stabilizes the exfoliated SWNT in the dispersion. X-ray scattering and

\* Corresponding author. E-mail: rachely@bgumail.bgu.ac.il.

<sup>†</sup> Department of Chemical Engineering, Ben Gurion University in the Negev.

<sup>‡</sup> The Ilse Katz Center for Meso- and Nanoscale Science and Technology, Ben Gurion University in the Negev.

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electron microscopy indicate that the SWNT do not bundle upon drying and may be redispersed in the pure solvent to form highly concentrated dispersions of individual SWNT and small bundles. We demonstrate that diblock and triblock copolymers of very different structures and compositions act efficiently as stabilizers and may be tailored so as to disperse the tubes in a variety of solvents.

### Experimental Section

**Materials.** SWNT. Two types of SWNT were used: select grade nanotubes (SWNT1) and AP grade (SWNT2), which were purchased from Carbolex, University of Kentucky, Lexington, KY, U.S.A. The nanotubes were synthesized by arc-discharge and used as received. According to the specifications by the manufacturer, the as-prepared select grade consists of 85 vol % pure SWNT, while the AP grade consists of 50–70 vol % SWNT. The samples contain graphite, carbon impurities, and catalyst (cobalt and nickel, ca. 20 nm in diameter), the average diameter of the tubes is 1.3 nm, and the typical length is in the range of hundreds of nanometers.

**Block Copolymers.** Details of the water-soluble polymers [poly(ethylene oxide)100-*b*-poly(propylene oxide)65-*b*-poly(ethylene oxide)100, PEO-PPO-PEO (F-108), of molecular weight 12 600 g/mol, and PE10,500, poly(ethylene oxide)-*b*-poly(propylene oxide), PPO-PEO, of molecular weight 6500 g/mol] are given in Supporting Information (Tables 1 and 2). The block copolymer soluble in organic solvents, poly(styrene-*b*-*tert*-butyl acrylate) diblock copolymer (P745: PS-*t*buAC), molecular weight of polystyrene 1900 g/mol and acrylate 31 900 g/mol, was purchased from Polymer Source, Canada. Poly(ethyleneoxide-*b*-poly(dimethylsiloxane)-*b*-ethyleneoxide) triblock copolymer (PEO-PDMS-PEO) was kindly donated by M. Gottlieb.<sup>20</sup> Each PEO block is of molecular weight 2000 g/mol, and the PDMS block is of 12 000 g/mol.

**Solvents.** Analytical grade organic solvents were used: heptane, ethanol, toluene, 2-propanol (Frutarom, Israel), and Millipore water ( $10^{18}$   $\Omega$ /cm).

**Methods.** *Preparation.* Dispersions were prepared by dissolving a block copolymer in a selective solvent (aqueous or organic) to form solutions of desired concentrations. A powder of as-prepared nanotubes was sonicated at very mild conditions (50 W, 43 kHz) for 15–20 min in the polymeric solution (these conditions were shown not to damage the tubes or the polymers).<sup>18,21</sup>

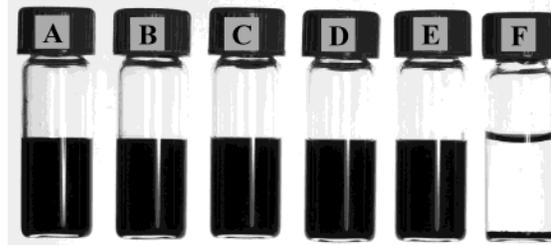
*Characterization. Electron Microscopy.* The dispersed SWNT were characterized via direct imaging of the aqueous dispersions using cryo-transmission electron microscopy (cryo-TEM).<sup>22</sup> Dried polymer-coated powders were imaged by high-resolution transmission electron microscopy (HRTEM).

In the cryo-TEM method, a drop of the solution was deposited on a transmission electron microscope (TEM) grid (300-mesh Cu grid) coated with a holey carbon film (Lacey substrate, Ted Pella, Ltd.). The excess liquid was blotted, and the specimen was vitrified by a rapid plunging into liquid ethane precooled with liquid nitrogen, in a controlled environment vitrification system. The samples were examined at  $-178$  °C using a FEI Tecnai 12 G<sup>2</sup> TWIN TEM equipped with a Gatan 626 cold stage, and the images were recorded (Gatan model 794 charge-coupled device camera) at 120 kV in low-dose mode.

*Wide-Angle X-ray Scattering (WAXS).* The measurements were carried out by a Philips X-ray powder diffractometer (PW-1050/70) at 40 kV/28 mA with Cu K $\alpha$  ( $\lambda = 1.54$  Å) radiation and a graphite monochromator. The scattering vector  $q = 4\pi/\lambda (\sin \theta)$ , where  $\theta$  is the scattering angle.

### Results and discussion

In Figure 1 we present black, macroscopically homogeneous dispersions obtained by sonication of as-prepared SWNT in different solutions of block copolymers (Figure 1A–E).



**Figure 1.** Dispersions of SWNT in polymeric solutions: 1 wt % SWNT1 in a 1 wt % solution of PS-*t*buAC (A) in ethanol and (B) in 2-propanol. SWNT2 in solutions of (C) 1 wt % PEO-PDMS-PEO in heptane, (D) 1 wt % PEO-PPO-PEO (F-108) in water, (E) 1 wt % PPO-PEO (PE10,500) in water, and (F) 1 wt % PEO-PDMS-PEO in toluene. Images were taken more than 2 months after preparation.

The observed dispersions are stable for months. The variety of polymers and solvents presented in this work demonstrates the versatility of the approach.

The stable dispersions may be dried (at ambient conditions) and the powder redispersed in the solvent to form an inklike dispersion of SWNT, in concentrations ranging from 0.5 to 30 wt % of polymer-coated SWNT in the solvent. The resulting suspensions are stable over a few months, and centrifugation (at 3500 rpm for 30 min) does not result in precipitation of the nanotubes.

The microscopic structure of stable SWNT dispersions was investigated using cryo-TEM, which is known to preserve the structures present in the bulk solutions<sup>22</sup> (Figure 2A). We observed that the length of the SWNT is well above 1  $\mu$ m and that the dispersions contain along with the tubes some carbonaceous residues and catalyst particles (Figure 2A). While cryo-TEM provides an overview of the solution composition, HRTEM (Figure 2B) allows one to probe the finer structural details of the dispersed species. The HRTEM images reveal that the structure of the individual SWNT is intact and that the most abundant species in the dispersions are well-separated individual tubes (of a diameter below 2 nm, Figure 2B) and small bundles comprising 2–3 tubes.

To test the aggregation state of dried SWNT, we performed X-ray scattering experiments. A typical WAXS pattern of a powder of high-purity as-prepared SWNT1 is presented in Figure 3A. A characteristic rope structure with peaks at the low- $q$  region (at  $q = 0.4, 0.85, 1.06,$  and  $1.50$  Å<sup>-1</sup>) indicates a two-dimensional triangular lattice with a lattice constant of 1.8 nm<sup>3</sup>. In addition, peaks of graphitic impurities are observed (at  $q = 1.88$  Å<sup>-1</sup>), in good agreement with previous observations. The WAXS spectrum of a dried SWNT1–polymer powder (Figure 3B) is quite different: peaks which result from intertube packing within the ropes in the as-prepared SWNT sample have disappeared, indicating that the dispersed-and-dried powders are composed of nonordered tubes of SWNT (for an additional example, see Supporting Information). The peaks at  $q = 1.30, 1.61,$  and  $2.35$  Å<sup>-1</sup> characterize the polymer. Redispersion of the powder results in the formation of a stable dispersion of individual SWNT (Figure 2).

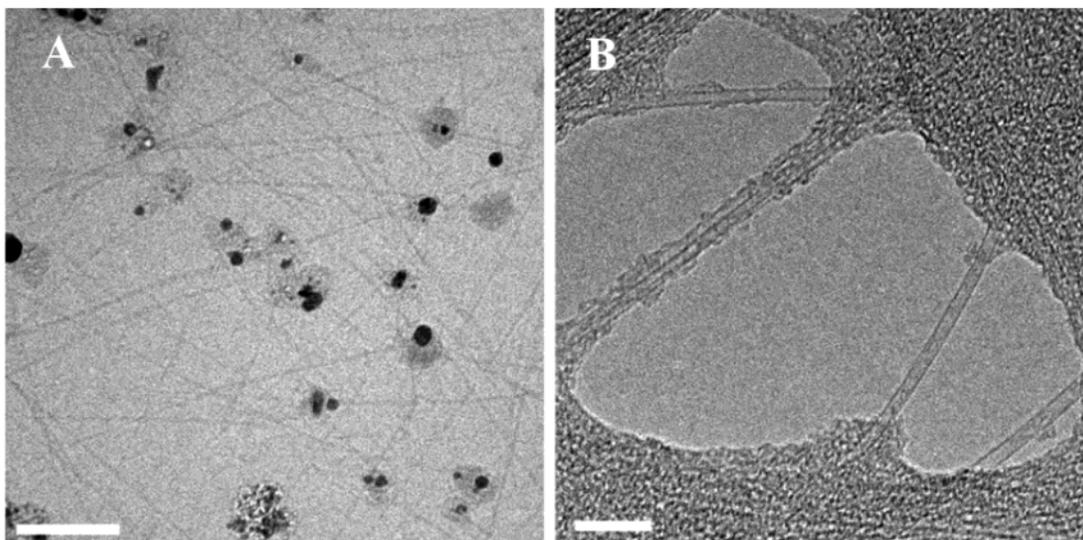
Redispersability is a well-known signature of a dispersion mechanism, known as steric stabilization.<sup>23</sup> The mechanism is based on the onset of entropic repulsion among polymer-decorated colloids. Block copolymers are among the more efficient steric stabilizers because they are comprised of chemically distinct and often mutually

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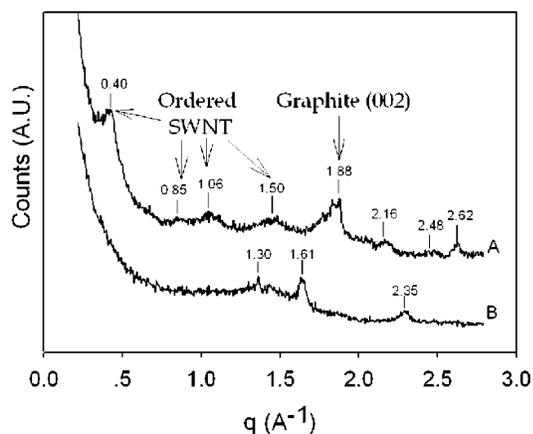
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**Figure 2.** TEM micrographs of concentrated SWNT dispersions prepared by redispersing a powder of the dried dispersion in the pure solvent. (A) Cryo-TEM image of a vitrified aqueous dispersion (1:2.5 wt % of SWNT2/PE10,500). Scale bar = 100 nm. (B) HRTEM image of a dried SWNT2 dispersion prepared by redispersion in ethanol, a dry powder of PS-tbuAC diblock-copolymer-coated SWNT (1:1 wt % SWNT2/PS-tbuAC). Scale bar = 10 nm.



**Figure 3.** WAXS spectra of a dry powder of a stable dispersion. (A) As-prepared SWNT1 powder exhibiting a typical rope structure. (B) A powder prepared by drying an aqueous dispersion of SWNT1 in a solution of a diblock copolymer (1 wt % SWNT1 in 2.5 wt % of PE10,500).

incompatible moieties (designated A-B and A-B-A for diblocks and triblocks, respectively) that are covalently bonded.<sup>24</sup> A typical scenario for steric stabilization via block copolymers relies on the dual action of the polymer: while one of the blocks (B) anchors the chain to the surface, the other block (A) dangles into the solvent and repels other polymer-decorated objects. It is well-known in the field of colloidal science<sup>23</sup> that the crucial parameter determining the dispersion ability of different block copolymers is solvent selectivity: A selective solvent that acts as a “good solvent” for one of the blocks (i.e., A) dissolves the polymer readily and increases the spatial dimensions of the polymeric chain, while simultaneously acting as a “poor solvent” for the other block (B) that adsorbs onto the colloid.<sup>25</sup>

To test the role of solvent selectivity in SWNT stabilization, we performed two sets of control experiments. In

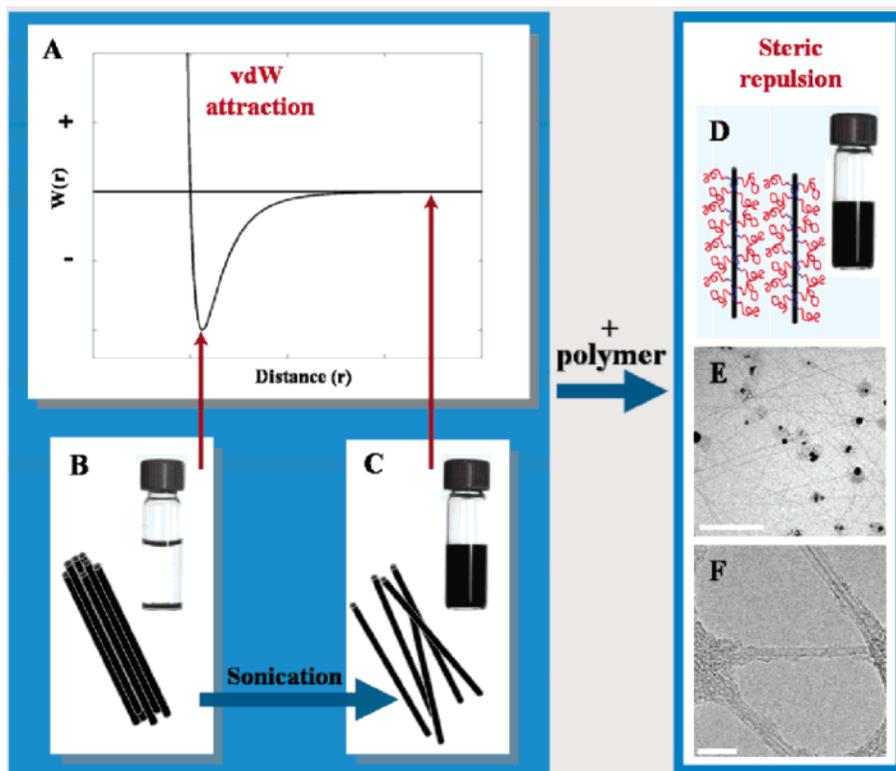
the first, we examined the behavior of block copolymers in a nonselective solvent (a good solvent for both blocks). For example, the triblock copolymer PEO-PDMS-PEO was dissolved in toluene (a good solvent for both PEO and PDMS). We found (Figure 1F and Supporting Information) that SWNT could not be dispersed in these solutions (at polymer concentrations ranging from 1 to 10 wt %). The solutions underwent phase separation, and the tubes coagulated at the bottom of the vial. Note that solutions of the very same polymer in heptane, a selective solvent for the triblock (at similar concentration and temperature), resulted in the formation of a stable dispersion of SWNT (Figure 1C). In a second set of control experiments, we tested the behavior of SWNT in good solvents for homopolymers comprising the blocks: PEO (in water and toluene), PDMS (in heptane and toluene), and PS (in toluene). We found that in these solutions the polymers could not serve as dispersing agents for SWNT. Thus, we conclude that selective interaction of the different blocks with the solvent is essential for stabilization of dispersed SWNT.

Review of a few specific examples where block copolymers lead to dispersion of either bundles or individual tubes implies that they fit well into the framework presented here. For example, we observed a similar behavior to that reported by Moore et al.,<sup>15</sup> where Pluronic triblock copolymers in water, which is a selective solvent for them, lead to dispersion of SWNT (details and additional examples are given in Supporting Information).

The generic method presented here is simple and may be utilized for preparation of stable dispersions of well-separated SWNT in aqueous and organic solvents, at low and high concentrations. The approach is summarized in Figure 4: SWNT held by strong, short-range intertube attraction (Figure 4A) form ropes and bundles (Figure 4B). Gentle sonication causes exfoliation of ropes into individual tubes (Figure 4C). The exfoliated tubes may be stabilized in the liquid media and aggregation may be prevented by introduction of a relatively weak repulsion (of the order of a few kT) at a large distance between the tubes (some tens of nanometers), such as the osmotic (steric) repulsion among the tails of tethered block copolymers in good solvent conditions. The stable dispersions are macroscopically homogeneous (Figure 4D), and

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(25) We note here that the tendency of block B to adsorb onto SWNT is determined by the balance of SWNT–solvent, SWNT–monomer, and polymer–solvent interactions. Issues of polymers adsorption are discussed thoroughly in ref 23, chapter 3.



**Figure 4.** Schematic representation of the concept. (A) Total interaction energy  $W(r)$  versus the separation distance  $r$ , for two nanotubes, assuming a Lennard-Jones potential [ $W(r) = (C_{12}/r^{12}) - (C_6/r^6)$ ].<sup>4</sup> The attractive part of the potential leads to crystallization of SWNT in bundles, rendering the material indispersible (A, B). While sonication leads to temporary exfoliation (C),<sup>19</sup> adsorption of block copolymers in a selective solvent stabilizes the exfoliated tubes (D) and prevents re-aggregation. Macroscopic and microscopic imaging of SWNT dispersions indicate that the inklike dispersion is composed of individual tubes and small bundles: (E) cryo-TEM image (scale bar = 100 nm) and (F) HRTEM image (scale bar = 10 nm).<sup>26</sup>

electron microscopy imaging reveals (Figure 4E,F) that they are composed of individual tubes and small bundles. While steric stabilization has long been known as an efficient method for stabilization of colloidal solutions, its applicability to SWNT, where the adhesion forces among the particles are on the order of a few thousands of kT, is somewhat surprising. We suggest that end-tethered polymers may form a barrier and prevent SWNT from approaching the highly attractive (though short-ranged) region of the intertube potential.

The dispersing approach presented here is expected to be highly useful in the preparation of polymer–SWNT composites: because it offers the possibility of selecting a nonadsorbing block that is either identical or compatible with a target polymeric matrix, the dispersing agent may simultaneously act as a compatibilizing agent and adhesion promoter leading to marked strengthening of the SWNT–matrix interface, thus, improving the properties

of the resulting nanocomposites. As was discussed before,<sup>27</sup> the typical adhesive fracture energy of a polymer-straightened interface is on the order of 102–103 J/m<sup>2</sup>, about 100 times higher than the fracture energy of a carbon–carbon plane.

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**Supporting Information Available:** Description of additional materials and control experiments. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(26) A dispersion of 1 wt % SWNT in an aqueous 2.5 wt % solution of a block-copolymer PE10,500 (Figure 4E) was imaged using cryo-TEM, and a dispersion of 1 wt % SWNT in 1 wt % PS-tbuAC solution in ethanol (Figure 4F) was imaged by HRTEM.

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