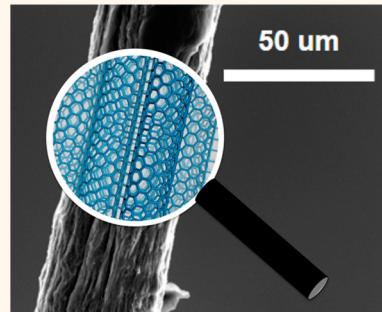


Macroscopic Nanotube Fibers Spun from Single-Walled Carbon Nanotube Polyelectrolytes

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ABSTRACT In this work, single-walled carbon nanotube (SWCNT) fibers were produced from SWCNT polyelectrolyte dispersions stabilized by crown ether in dimethyl sulfoxide and coagulated into aqueous solutions. The SWCNT polyelectrolyte dispersions had concentrations up to 52 mg/mL and showed liquid crystalline behavior under polarized optical microscopy. The produced SWCNT fibers are neat (*i.e.*, not forming composites with polymers) and showed a tensile strength up to 124 MPa and a Young's modulus of 14 GPa. This tensile strength is comparable to those of SWCNT fibers spun from strong acids. Conductivities on the order of 10^4 S/m were obtained by doping the fibers with iodine.



KEYWORDS: SWCNTs · fibers · liquid crystals · crown ethers · polyelectrolytes

Single-walled carbon nanotubes (SWCNTs) are the ultimate building block for the construction of novel devices due to their unique combination of properties. Processing bulk SWCNTs into functional materials requires their individualization in solution, which has been previously achieved by techniques such as dissolution in acids,^{1–3} organic solvents,^{4–6} surfactants,^{7,8} and biopolymers.^{9,10} The use of SWCNT polyelectrolytes has recently drawn considerable attention for dispersing SWCNTs.¹¹ In this class of methods, negatively charged SWCNTs form spontaneous dispersions in a series of aprotic organic solvents, such as dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and sulfolane,^{11–15} and have the potential to serve as an intermediate for covalent functionalization.^{12,16,17} However, the application of SWCNT polyelectrolytes to manufacture macroscopic materials such as neat SWCNT fibers¹⁸ has been only marginally explored. SWCNT fibers with good conductivity have the potential to replace metals for numerous applications including manufacturing robust and light electricity transmission cables,^{19,20} efficient field emission sources,^{21,22} and

electronic textile applications.²³ SWCNT fibers could also be used to fabricate more complex architectures due to their ultrastrong mechanical properties.²⁴

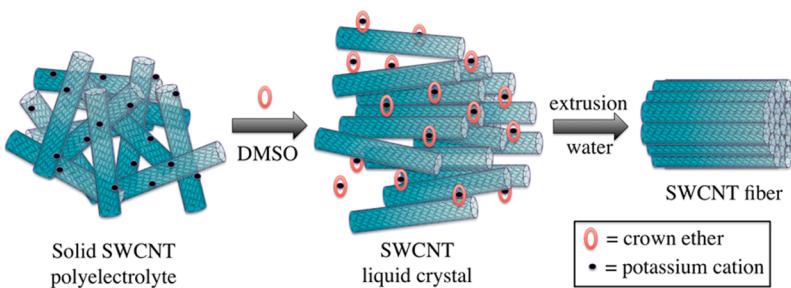
Some preliminary work in this area has been made by using composite materials where the fibers result as a mixture of the carbon nanotubes with other materials such as polymers.^{25,26} The main obstacle to generate good-quality neat SWCNT polyelectrolyte fibers has been the relatively low concentration of the dispersions,¹⁴ limited to 0.4 mg/mL for HiPco SWCNT polyelectrolytes¹¹ and to 4–5 mg/mL for electric arc SWCNT polyelectrolytes.^{11,13} The limited solubility of these SWCNT polyelectrolytes is likely due to the condensation of counterions on the surface of negatively charged SWCNTs, which shield the repulsive negative charges that promote SWCNT dispersion. Weaker repulsive interactions between SWCNTs cannot overcome van der Waals interactions and attain dispersion.¹³ A recent report has highlighted the advantages of crown ethers when used in SWCNT polyelectrolyte solutions, with a modest carbon nanotube concentration in solution.²⁷

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Scheme 1. Idealized schematic representation of the SWCNT polyelectrolyte solid, the crown-ether-assisted dispersion of SWCNT polyelectrolyte forming a liquid crystalline phase, and the formation of the fiber.

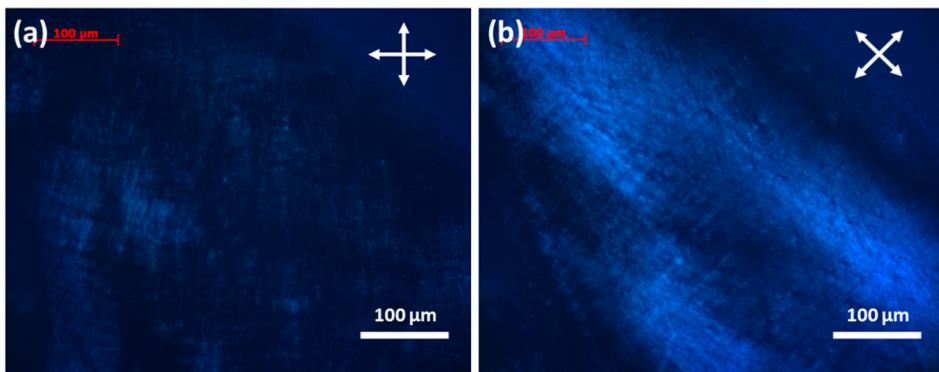


Figure 1. Cross-polarized optical microscopy images of SWCNT HiPco polyelectrolyte dispersions in DMSO with crown ether: (a) 16 mg/mL HiPco SWCNT polyelectrolytes with 4% (m/V) crown ether, 0°; (b) 16 mg/mL HiPco SWCNT polyelectrolytes with 4% (m/V) crown ether, 45°. The liquid crystal domains can be seen by changes of brightness in the sample when the cross-polarizers are rotated.

Recently, our group used crown ethers to trap the counterions and prevent their condensation onto SWCNTs, increasing the solubility in DMSO to 9.4 mg/mL.²⁸ However, fibers spun from 9.4 mg/mL concentrations are brittle and cannot be properly analyzed. In this article we report how to obtain SWCNT polyelectrolyte dispersions up to 52 mg/mL using speed mixing. These solutions are viscous, display liquid crystalline behavior, and when spun into a coagulating solvent form fibers presenting superior tensile strength. To the best of our knowledge, these are the first examples of neat SWCNT fibers made from SWCNT polyelectrolyte solutions, without any polymer or additive.

Compared with other established solution-based methods for fiber manufacture, our methods have some advantages. The surfactant-based method produces SWCNT fibers with diminished properties in comparison with other procedures,^{29,30} probably due to shortening of the nanotubes by the sonication step. For the acid-based spinning method, SWCNTs are dispersed in strong acids such as fuming sulfuric acid or chlorosulfonic acid,^{31,32} which requires careful handling and acid-resistant equipment. This new approach involves generating SWCNT fibers in conditions similar to those used for Birch reductions, yet resulting in mechanical and electrical properties comparable to properties obtained by other methods with HiPco SWCNTs (see below). Moreover, the reagents used for

this procedure are common and relatively economically feasible.

RESULTS AND DISCUSSION

In a typical experiment, 400 mg of HiPco SWCNT polyelectrolytes (made by a method reported before³³) was mixed with 10 mL of an 8% (m/V) 18-crown-6 solution in DMSO, to give an initial mixing concentration of 40 mg/mL (similar procedures were used for 20 and 60 mg/mL). The mixture was sealed in a dry glass vial and stirred for 1 h at a speed of 1000 rpm. Then the mixture was further mixed in a speed mixer (DAC 400.1 FVZ) at 2350 rpm.²² To remove undispersed large aggregates, the dispersions were filtered through a 20 μm mesh. The resulting dispersions showed birefringence in some parts under the cross-polarized optical microscope, which indicates a biphasic behavior in which the isotropic phase is in equilibrium with the liquid crystalline phase (Figure 1). Liquid crystallinity provides a great advantage for making SWCNT fibers because the SWCNTs are already aligned in the liquid crystalline domains. This preorientation makes it easier to obtain fibers with well-aligned SWCNTs when injected through a narrow needle into a coagulation solution.^{22,32,33} To determine the final concentrations of the dispersions, the liquid phase was diluted 2000 times and analyzed by UV-vis spectroscopy using a proportionality constant of 0.323 mL/mg mm⁻¹ (see

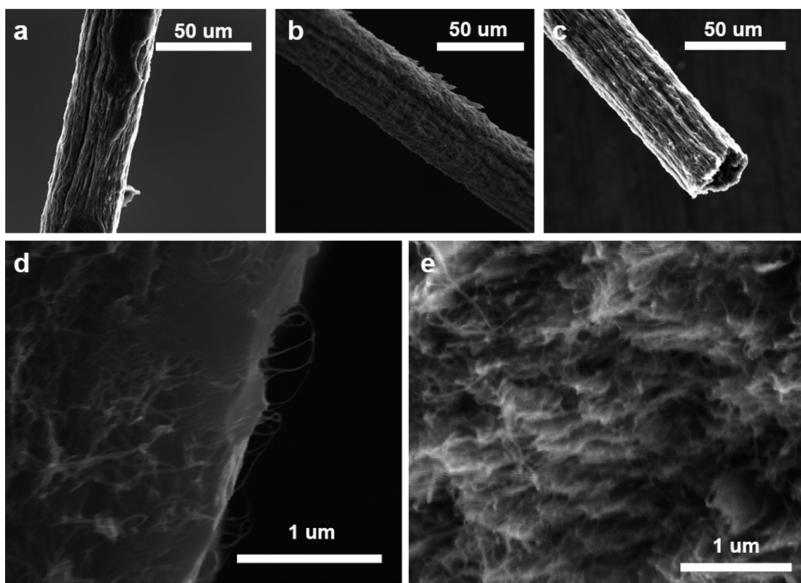


Figure 2. SEM images of fibers spun from a 35 mg/mL SWCNT solution: (a) fiber spun into water; (b) fiber spun into a 0.1 M HCl solution; (c) fiber spun into a 0.001 M NaI_3 solution; (d) enlarged side-wall view of a fiber; (e) enlarged cross-section of a fiber.

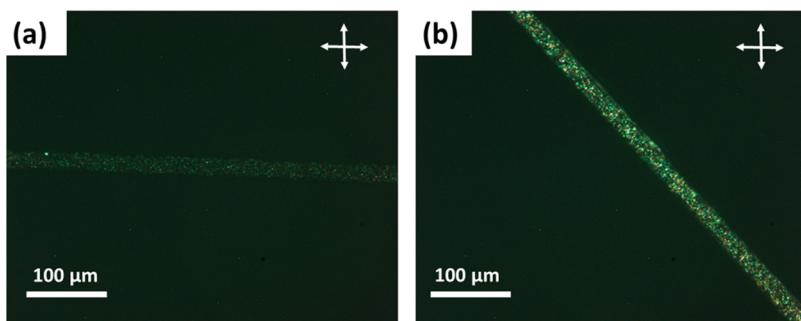


Figure 3. Cross-polarized optical microscopy images of a representative SWCNT HiPco fiber made from polyelectrolyte dispersions in DMSO with crown ether. The images were taken under polarized reflected mode. (a) When the fiber axis is parallel to the illumination polarizer, the fiber displays minimal birefringence. (b) When the fiber is rotated at a 45° angle with respect to the illumination and analyzer polarizer, the fiber displays bright birefringence, indicating SWCNT alignment along the axis of the fiber.

Figure S2, Supporting Information).³³ UV-vis experiments showed that about 80% of the initial amount of material remained dispersed after filtration, which demonstrates the high efficiency of this method to obtain concentrated SWCNT polyelectrolyte dispersions.

SWCNT fibers were made by injecting different concentrations of polyelectrolyte dispersions into aqueous solutions (water, aqueous hydrochloric acid, and iodide solutions) through a 125 μm size spinneret. The flow through the spinneret produces shear that helps align the liquid crystal domains during the injection. When the forming SWCNT liquid fiber enters in contact with the aqueous solution, the SWCNTs are stripped of the extra electrons and hence destabilized, causing their collapse into a dense fiber due to van der Waals interactions. The resulting SWCNT fibers were collected on a rotating Teflon drum (see Figure S1, Supporting Information), immersed in water overnight, and thereafter dried at 100 $^\circ\text{C}$ for 24 h.

The fibers were characterized by using different techniques. Scanning electron microscopy (SEM) and

polarized optical microscopy (POM) were used to study the morphology of the fibers (Figure 2, Figure 3, and Supporting Information). The fiber diameter for the 16, 35, and 52 mg/mL solutions ranged from 20 to 35 μm . The SEM images qualitatively illustrate large-scale alignment of the SWCNT along the fibers' axis, which is expected to lead to robust mechanical properties, although the fibers do not display the same level of fine-scale alignment as those spun from acid solutions.³¹ Carbon nanotube alignment in the fibers is also confirmed by cross-polarized microscopy. Figure 3 shows the birefringence of a carbon nanotube fiber under cross-polarizers with intense birefringence when the fiber forms a 45° angle with the polarizer, indicating predominant axial alignments of the SWCNTs in the solid fiber.

The mechanical properties were analyzed in a static testing mode using a dynamic mechanical analysis system (TA Instruments model Q800) with the assistance of a 20 mm long paper frame to mount the fiber into an aligned position.³² The result for a typical

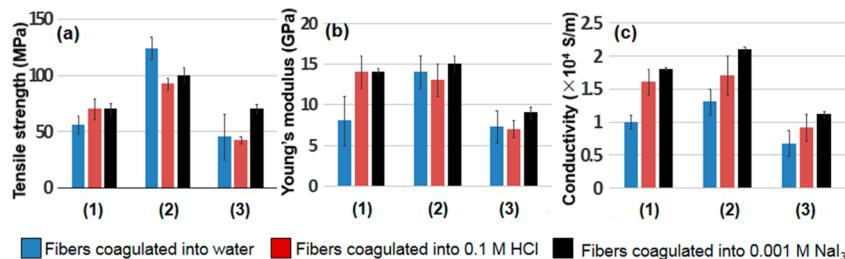


Figure 4. Summary of the properties of fibers manufactured under different conditions: (a) tensile strength, (b) Young's modulus, and (c) conductivity of fibers coagulated into different solutions. The materials used for fiber spinning, from left to right, are (1) 16 mg/mL SWCNT polyelectrolyte with 4% (m/V) 18-crown-6 in DMSO; (2) 35 mg/mL SWCNT polyelectrolytes with 8% (m/V) 18-crown-6 in DMSO; (3) 52 mg/mL SWCNT polyelectrolytes with 12% (m/V) 18-crown-6 in DMSO.

TABLE 1. Properties of HiPco Fibers Obtained under Different Conditions^a

	initial concentration								
	20 mg/mL HiPco SWCNT polyelectrolytes with 40 mg/mL crown ether in DMSO			40 mg/mL HiPco SWCNT polyelectrolytes with 80 mg/mL crown ether in DMSO			60 mg/mL HiPco SWCNT polyelectrolytes with 80 mg/mL crown ether in DMSO		
	16 mg/mL	35 mg/mL	52 mg/mL	water	0.1 M HCl	0.001 M NaI ₃	water	0.1 M HCl	0.001 M NaI ₃
final concentration	16 mg/mL								
coagulation solution	water	0.1 M HCl	0.001 M NaI ₃	water	0.1 M HCl	0.001 M NaI ₃	water	0.1 M HCl	0.001 M NaI ₃
diameter (μm)	25 (5)	22 (2)	22 (5)	32 (1)	31(6)	32 (6)	25(2)	24(5)	22(1)
tensile strength (MPa)	56(8)	71(13)	68(16)	124(9)	92(5)	100(3)	45(5)	42(7)	70(4)
Young's modulus (GPa)	8(3)	14(2)	14(2)	14(2)	13(2)	15(1)	7.3(0.4)	7(1)	9.0(0.7)
elongation (%)	1.1(0.5)	0.4(0.1)	0.4(0.2)	1.9(0.2)	1.0(0.2)	0.9(0.1)	0.43(0.08)	0.5(0.2)	0.9(0.3)
conductivity (×10 ⁴ S/m)	1.0(0.1)	1.6(0.2)	1.8(0.2)	1.3(0.2)	1.7(0.3)	2.1(0.2)	0.67(0.02)	0.91(0.04)	1.11(0.04)

^a Numbers in parentheses represent the uncertainty of the value.

experiment is shown in Supporting Information Figure S6. The best fiber tensile strength of HiPco SWCNTs was obtained from 35 mg/mL dispersions in water, which gave a tensile strength of 124 MPa and a Young's modulus of 14 GPa (Figure 4a and b). This tensile strength obtained for this solution spinning technique is comparable to typical results of HiPco from acid-based methods (116 MPa for fuming sulfuric acid³¹ and 50–150 MPa for chlorosulfonic acid³²) and better than that for as-spun bare fibers from the surfactant-based method (65 MPa, assuming a density of the fiber of 1 g/cm³).³⁰ For the Young's modulus, our result of 14 GPa is almost 1 order of magnitude lower than the typical results from the acid-based method (120 GPa for both fuming sulfuric acid³¹ and chlorosulfonic acid³²), but still better than the as-spun bare fibers from the surfactant-based method (12 GPa, assuming a density of the fiber of 1 g/cm³).³⁰ However, recently, solution-spinning of long, low-defect, few-walled carbon nanotubes dissolved in chlorosulfonic acid has yielded fibers with a tensile strength of up to 1.3 GPa.²² Note that other techniques have also been used to produce high-quality fibers with outstanding properties including direct spinning of fibers from a chemical vapor deposition reactor³⁴ and drawing carbon nanotubes from carbon nanotube forests.³⁵ However, in this paper we focus on bare fibers made with wet spinning methods. Experiments where fibers are generated using carbon nanotube polyelectrolyte solutions with

carbon nanotubes other than HiPco are currently under study.

Apart from the mechanical properties, we also studied how to produce doped SWCNT fibers by changing the coagulating solution. The best results were obtained for fibers coagulated into a 0.001 M NaI₃ aqueous solution. The resulting fibers maintain similar mechanical properties, while achieving better conductivities than fibers coagulated into water and slightly higher than HCl solutions (Figure 4c). This indicates that, during its formation, the fiber incorporated some dopants from the coagulation bath, which was further supported by the EDAX results (Figure S9). Electrical conductivities up to $(2.1 \pm 0.2) \times 10^4$ S/m were obtained, which is 1 order of magnitude lower than the best HiPco fibers spun from superacids (5×10^5 S/m for fuming sulfuric acid³¹ and 8.3×10^5 S/m for chlorosulfonic acid³²), but still higher than most surfactant-based fibers (1.7×10^4 S/m with DNA as surfactant,²⁹ 1.4×10^4 S/m with lithium dodecyl sulfate as surfactant,³⁰ and 6.7×10^2 S/m with sodium dodecyl sulfate as surfactant³⁶). In a previous work we found that small-diameter HiPco nanotubes are slightly functionalized in DMSO, which may affect the properties of the produced fibers.³³ We are currently investigating other sources of SWCNTs for the production of fibers that do not contain small-diameter tubes. Furthermore, functionalization can arise from the coagulating phase, similar to a Birch reaction, where hydrogen

atoms can be added to the carbon nanotube walls, disrupting electron percolation. Raman spectra of the fibers (Supporting Information, Figures S10–S12) show increased D peaks in comparison with HiPco, which is indicative of chemical functionalization. Still, the properties observed for these fibers are very promising, in some cases comparable with the best fibers of HiPco SWCNTs. Table 1 summarizes all the fiber properties obtained under different conditions. Our results indicate that a concentration around 35 mg/mL is optimal to achieve the best fiber properties.

CONCLUSIONS

In summary, we have demonstrated that high concentration HiPco SWCNT polyelectrolyte dispersions in DMSO could be achieved with the assistance of crown ether and speed-mixing (from 9 mg/mL in our previous report up to 52 mg/mL) and hence could be used in the manufacture of SWCNT fibers. Also, the HiPco SWCNT polyelectrolyte dispersions show well-defined liquid crystalline behavior, which is advantageous for spinning

well-aligned SWCNT fibers. SWCNT fibers were obtained with tensile strengths similar to fibers made from strong acids. Good electrical conductivities were achieved after a simple one-step iodide doping during coagulation. The methodology presented here provides an easy and convenient way of producing SWCNT fibers from polyelectrolyte SWCNT dispersions, with outstanding mechanical and electrical properties. This solution processing method can be potentially used not only with HiPco but also with different SWCNTs produced by other techniques. We envision that SWCNT fibers from polyelectrolytes can be further improved by using longer SWCNTs, increasing the orientation of SWCNTs in the direction of the fiber, refining the removal of large aggregates, removal of crown ether incorporated within the fiber, and using SWCNTs with larger diameters less prone to functionalization. The use of SWCNT polyelectrolytes for making fibers is of importance due to the well-known chemistry of these solutions, which can allow *in situ* functionalization of SWCNT fibers and potentially cross-linked fibers with superior mechanical properties.

EXPERIMENTAL SECTION

Materials. The HiPco SWCNTs (product code: 195.1) used in the work were obtained from Rice University and purified by a previously reported procedure.³⁰ Potassium block and DMSO were purchased from Sigma-Aldrich, and naphthalene was purchased from Alfa Aesar. All of the reagents above were used as received without further treatment. 18-Crown-6 was purchased from TCI and purified by recrystallization in dry acetonitrile. Freshly distilled tetrahydrofuran (THF) was used for making the SWCNT polyelectrolytes.

General Procedure for the Synthesis of SWCNT Polyelectrolytes. The synthesis of SWCNT polyelectrolytes was performed using a modification of Voiry *et al.*^{12,13} In a typical procedure, 100 mg of metallic potassium (2.56 mmol), 234 mg of naphthalene (1.83 mmol), and 80 mL of distilled THF were added to a 100 mL round-bottom flask and stirred for 3 days at room temperature until no obvious solid is present. The resulting dark green solution served as the stock solution and was used within 24 h of preparation. Then, 300 mg of purified HiPco SWCNTs and 48 mL of the potassium stock solution were added to a 100 mL round-bottom flask and stirred for 2 days under room temperature. The crude product was filtrated using 0.45 μ m PTFE membranes and rinsed with distilled THF to get a black solid SWCNT polyelectrolyte material. The SWCNT polyelectrolyte was dried at room temperature in a vacuum overnight. All the work was done in the glovebox under a nitrogen atmosphere.

Dispersion of SWCNT Polyelectrolytes. For the preparation of a polyelectrolyte dispersion with an initial concentration of 40 mg/mL (final concentration 35 mg/mL), around 400 mg of dry SWCNT polyelectrolytes was ground with a mortar and mixed with 10 mL of DMSO containing 80 mg/mL 18-crown-6 in a 20 mL Wheaton glass vial. The mixture was shaken for 1 h at 1000 rpm. Then the sample was mixed for 1 h in a dual asymmetric centrifugation mixer (DAC 400.1 FVZ SpeedMixer) at 2350 rpm. The resulting dispersions were filtered through a 20 μ m mesh to remove large-size aggregates. After mixing and filtration, a mixture with a starting concentration of 40 mg/mL yielded a mixture with a final concentration of 35 mg/mL. To obtain high-quality POM images, the dispersions were further centrifuged at 16000g for 4–6 h and the dense bottom phases were checked by POM. A volume of 0.5 mL of the dispersions was diluted 2000 times to take the UV-vis spectrum, which was used to determine the exact solubility of SWCNT polyelectrolytes

based on a previously determined calibration curve.²⁷ Similar procedures were adopted for the dispersions of 20 and 60 mg/mL while maintaining the same ratio of SWCNT polyelectrolytes to crown ether.

Spinning of SWCNT Polyelectrolyte Fibers. The spinning of SWCNT polyelectrolyte fibers was processed using the setup illustrated in Figure S1. SWCNT polyelectrolyte dispersions were loaded into a stainless steel syringe, and the dispersions were extruded through a 125 μ m tubing into the coagulation solutions: water, 0.1 M HCl, and 0.001 M NaI₃ solutions. The resulting fibers were collected on a Teflon drum and immersed in water overnight to remove water-soluble impurities. Then the fibers were dried at 100 °C for 24 h.

Mechanical Properties Test of SWCNT Fibers. The test of the mechanical properties was done in a dynamic mechanical analysis system. The samples were tested with the assistance of 20 mm paper frames following a previous literature method.²⁸ The diameters of the fibers were determined by SEM images. For the fibers that do not have a perfectly round cross-section (such as in Figure S4c), the diameters of the fiber were estimated by a simple calculation of the average of the shortest distance and longest distance found around the cross section.

Conflict of Interest: The authors declare no competing financial interest.

Supporting Information Available: Scanning electron microscopy image of fibers from different conditions, polarized optical microscopic images of different concentrations of SWCNT polyelectrolytes, UV-vis spectra of 2000 times diluted 20, 40, and 60 mg/mL SWCNT polyelectrolytes, mechanical test results for a conventional fiber, EDAX results of fibers from different conditions from 40 mg/mL, Raman spectra of fibers obtained from different conditions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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