

Supporting Information

Functionalization of Single-Walled Carbon Nanotubes With Well-Defined Polystyrene by “Click” Coupling

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Experimental

General

Single-walled carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc. (Houston, TX). Styrene was purified by passing through basic alumina and was stored in the refrigerator. All other reagents and solvents were purchased from commercial suppliers and used as received. Laser Raman spectroscopy was performed on a Bruker RFS 100 instrument equipped with a YAG laser and a Ge high-sensitivity detector. FTIR was performed on a Bio-Rad FTS-40 instrument. All IR samples were prepared as pellets using spectroscopic grade KBr in a Carver press at 15,000

psi. Atomic force microscopy was done using a Digital Instruments NanoScope IIIa Multimode AFM, with samples prepared by spin-coating sample solutions onto freshly cleaved mica substrates at 2500 rpm. The images were recorded with standard tips in tapping mode at a scan rate of 1.0 Hz. TEM analysis was performed using a Philips CM12 operating at 120 keV. NMR was performed on a Bruker 200 MHz instrument in CDCl_3 or CD_2Cl_2 . Thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under Argon. Ultrasonication was done in a Branson Ultrasonics B1510 bath sonicator. Filtration was done through Teflon membranes (Millipore) having pore sizes of either 200 or 450 nm. Polymer molecular weight and polydispersity index (PDI) were estimated by gel permeation chromatography (GPC) using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive index detector, a Waters 2475 Fluorescence detector, and four Polymer Labs PLgel individual pore size columns. Polystyrene standards were used for calibration, and tetrahydrofuran (THF) was used as the eluent at a flow rate of 1.0 mL/min. The concentrations of the soluble polymer-functionalized SWNTs were calculated from UV/vis absorption spectra measured using a Cary 50 UV-visible spectrophotometer

Preparation of *p*-nitrophenyl propargyl ether. A solution of propargyl bromide (50.00 g, 420 mmol) in toluene (200 mL) was added dropwise to a solution of *p*-nitrophenol (55.65 g, 400 mmol) and tetrabutylammonium bromide (12.89 g, 40 mmol) in 0.8 N NaOH (500 mL) at 60 °C. After complete addition, the reaction mixture was allowed to stir for 24 h at 60°C. A yellowish white precipitate was obtained by cooling the mixture to room temperature. The organic layer was washed with distilled water (3×100 mL) and the

solvent was removed *in vacuo*, yielding pale yellow crystals. The combined crude product was dissolved in dioxane (ca. 300 mL) and precipitated in ca. 1000 mL of distilled water. The precipitate was filtered and washed with distilled water until a white powder remained (66.06 g, 96%). ^1H NMR (200 MHz, CDCl_3): δ = 2.58 (t, 1 H, J = 2.4 Hz), 4.79 (d, 2 H, J = 2.4 Hz), 7.05 (d, 2 H, J = 9.3 Hz), 8.22 (d, 2 H, J = 9.3 Hz).

Preparation of *p*-aminophenyl propargyl ether. A cooled solution of stannous chloride dihydrate (203.00 g, 900 mmol) in concentrated HCl (500 mL) was added dropwise to a solution of *p*-nitrophenyl propargyl ether (31.90 g, 180 mmol) in dioxane (700 mL) at 10 °C. After complete addition, the reaction mixture was allowed to stir for 48 h at room temperature, slowly becoming more yellow in color. After neutralizing with aqueous sodium hydroxide, the solution was extracted with dichloromethane (4×250 mL). The organic layer was then dried with anhydrous sodium sulfate and the solvent was evaporated *in vacuo*, yielding a yellowish brown viscous oil. The crude product was purified by distillation under reduced pressure (bp 95 °C, 10 mmHg) to afford a colorless and highly viscous oil, which crystallized into white platelet crystals upon standing (23.16 g, 87%). ^1H NMR (200 MHz, CDCl_3) δ = 2.49 (t, 1 H, J = 2.3 Hz), 3.42 (br, 2 H), 4.60 (d, 2 H, J = 2.3 Hz), 6.63 (d, 2 H, J = 8.9 Hz), 6.82 (d, 2 H, J = 8.7).

Preparation of alkyne functionalized SWNTs. In a typical experiment, SWNTs (160 mg, 13.33 mmol of carbon) and *p*-aminophenyl propargyl ether (7.85 g, 53.32 mmol, 4 equiv/mol of carbon) were added to a flask equipped with a reflux condenser and a

magnetic stir bar. The flask was evacuated and backfilled with nitrogen three times and then left under nitrogen. Subsequently, isoamyl nitrite (7.81 g, 66.65 mmol, 5 equiv/mol of carbon) was added slowly via syringe. The mixture was then placed in an oil bath and stirred vigorously at 60 °C for 5 h. The resulting paste was diluted with DMF (250 mL) and filtered through a PTFE (450 nm pore size) membrane. The collected solid was washed with DMF until the filtrate became colorless. Dispersing the solid in DMF by sonication followed by filtration afforded purified functionalized SWNTs. DMF was removed by washing with diethyl ether, and the product was dried in a vacuum oven (55 °C) for 72 h.

Atom transfer radical polymerization of styrene. In a typical polymerization, a dry flask containing 2,2'-bipyridine (416 mg, 2.66 mmol) was evacuated and refilled with nitrogen three times. Deoxygenated styrene (10.40 g, 0.10 mol, 75 equiv) and DMF (2 mL) were added via syringes (previously purged with nitrogen). After stirring for 1 h at room temperature, CuBr (191 mg, 1.33 mmol) was added and the reaction mixture was degassed by three freeze-pump-thaw cycles. Then the flask was placed in a thermostated oil bath at 110 °C. After 3 min ethyl 2-bromoisobutyrate (260 mg, 1.33 mmol) was injected. The polymerization was conducted for 4 to 6 h and stopped at approximately 60% conversion by cooling to room temperature and opening the flask to air. The mixture was dissolved in THF (150 mL), passed through a column of neutral alumina, concentrated to ca. 75 mL, and precipitated into methanol (ca. 1000 mL). ^1H NMR (200 MHz, CDCl_3): δ = 0.80-1.04 (br), 1.20-2.30 (br), 3.66 (br), 4.40 (br), 6.38-7.36 (br). GPC: M_n = 4.83 kg/mol. M_w/M_n = 1.09. Polystyrenes with molecular weight of approximately 2.00 and 8.60 kg/mol were

prepared using the same procedure except the ratios of monomer to initiator were 50:1 and 150:1, respectively.

Preparation of azide-terminated polystyrene. In a typical experiment, bromide-terminated polystyrene prepared by ATRP (5.00 g, 1.04 mmol) was dissolved in DMF (50 mL). Subsequently, NaN₃ (676 mg, 10.40 mmol, 10.00 equiv) was added. The reaction mixture was stirred overnight at room temperature and the polymer was precipitated in water. The solid was washed with distilled water five times (200 mL each) and finally with methanol (200 mL) to remove NaBr and unreacted NaN₃. The white powder was dried under vacuum at room temperature overnight and then stored in a freezer. ¹H NMR (200 MHz, CDCl₃): δ = 0.80-1.04 (br), 1.20-2.30 (br), 3.66 (br), 3.95 (br), 6.30-7.36 (br). GPC: M_n = 4.86 kg/mol, M_w/M_n = 1.08.

Coupling of PS-N₃ to alkyne-functionalized SWNTs by Huisgen cycloaddition. In a typical experiment, a 50 mL flask was charged with alkyne functionalized SWNTs (10 mg) and DMF (15 mL). After sonicating for 5 min at room temperature until a black suspension is achieved, azide-functionalized polystyrene (483 mg, 0.10 mmol) and (PPh₃)₃CuBr (65 mg, 0.070 mmol) were added. The reaction mixture was evacuated and refilled with nitrogen three times followed by stirring under argon at temperatures between 20 and 100°C for reaction times spanning 24 to 65 h. After cooling to room temperature, the mixture was diluted with 200 mL of THF, bath sonicated for 5 min, and filtered through a 200 nm PTFE membrane. The product was washed thoroughly with THF (5 × 100 mL),

methanol, aqueous ammonium hydroxide solution (28%), water, methanol, and CH_2Cl_2 (1×100 mL of each), and then dried under vacuum overnight. The typical procedure for the click coupling reaction catalyzed by CuI/DBU is similar to the procedure described above. The final composition of a typical reaction mixture was as follows: alkyne functionalized SWNTs (10 mg), azide functionalized polystyrene (483 mg, 0.10 mmol), CuI (38 mg, 0.20 mmol), DBU (1.52 g, 10.00 mmol), and DMF (15 mL).

Measurement of SWNT-PS conjugate solubility. A vial charged with polystyrene-functionalized SWNTs (10 mg) and THF (10 mL) was sonicated for 3 min. Then the vial was centrifuged at 5000 rpm for 20 min and subsequently allowed to stand undisturbed overnight. The supernatant was carefully separated and diluted with THF to appropriate concentrations for UV/vis absorption measurement. The specific extinction coefficient for shortened SWNTs ($0.0103 \text{ L mg}^{-1} \text{ cm}^{-1}$) was used to calculate the concentration of the functionalized full-length SWNTs.

Appended video clip. The clip shows two vials, one containing a THF solution of 4,800 g/mol PS-functionalized SWNTs (on left), and the other containing a THF suspension of the less soluble 8,600 g/mol PS-functionalized SWNTs that have been allowed to settle for 24 h. The video shows that simply shaking the vial containing the insoluble material causes it to re-dissolve, forming a completely homogeneous solution.