Supporting Information for Manuscript on Grafting and Patterned Grafting of Block Copolymer Nanotubes onto Inorganic Substrates

Materials and Reagents. Methanol (99.8 %, MeOH) and tetrahydrofuran (99.9%, THF) were purchased from Fisher Scientific. THF was freed of moisture by passing it through a filtration unit purchased from Innovative technology Inc. *N*,*N*'-dimethylformamide (99%, DMF), ethylene glycol (99%), 1-hydroxybenzotriazole (95%, HBT), *N*-(3-dimethylaminopropyl)-*N*-ethylcarbodiimide hydrochloride (commercial grade, EDCl), *N*,*N*'-dicyclohexylcarbodiimide (99%, DCC), *N*,*N*-diisopropylethylamine (99.5%, DPEA), and 3-aminopropyltrimethoxysilane (97 %, APTMS) were purchased from Aldrich and used without further purification. PS-PCEMA-PtBA,[1] PAES-PS-PAES,[1] and PCEA[2] were prepared as previously described. PAA used was derived from the hydrolysis of a PtBA homopolymer. The PtBA sample was prepared by ATRP[3] and possessed a size exclusion chromatography (SEC) weight-average molecular weight M_w of 1.2×10^4 and polydispersity M_w/M_n of 1.15.

Measurements and Techniques. Size exclusion chromatographic analysis was carried out at 22 ^oC on a Waters 515 system equipped with two columns (Waters Styragel HT4 and μStyragel 500 Å) and a differential refractometer (Water 2410). The eluant used was THF and the calibration standards used were monodisperse PS samples. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained on a Bruker Avance 300 MHz spectrometer using deuterated chloroform ($CDCl_3$) as the solvent. For static contact angle measurements, pictures of liquid droplets sized at 2 μL were taken under ambient conditions using a digital camera (CoolPix 4500, Nikon). Water and ethylene glycol were used as the probe liquids and their contact angles were measured at five different positions for each sample and averaged.

Tapping-mode atomic force microscopy (AFM) analysis was carried out on a Veeco Nanoscope IIIa instrument. The force constant and oscillation frequency for the cantilever used were ca. 40 N/m and

ca. 300 kHz, respectively. Transmission electron microscopy (TEM) measurements were performed on Hitachi H-7000 instrument operated at 75 kV. The specimens for TEM observation were prepared by aspirating the sample solution in THF on carbon-coated copper grids using a home-built device. Before TEM observations, the samples were stained with OsO_4 vapor for 1 h. Fluorescence microscopic measurements were performed on a Nikon Elipse TE 2000-U instrument.

Nanotubes. PS-PCEMA-PAA nanotubes were derived from PS-PCEMA-PtBA nanofibers. The preparation of such nanofibers has been reported before[4, 5] and the procedure is thus not repeated here. To expose the PtBA core chains at nanofiber ends, we shortened the fibers by ultrasonication. A typical run involved ultrasonicating, in Branson-1200 ultrasound bath, 5-mL of a 0.3 wt-% PS-PCEMA-PtBA nanofiber solution in THF for 4 h. After ultrasonication, the nanofibers were fractionated by ultracentrifugation using a Jouan-KR25I instrument. To separate the fibers from low-molar mass debris, the sample was centrifuged at 17000 rpm for 30 min to settle the nanofibers. The precipitate was then redispersed in 25 mL of THF. This process was repeated thrice to yield a nanofiber solution in THF. The high-molar mass component in the resultant sample was separated as a precipitate by centrifugation at 5000 rpm for 30 min. This process was repeated also thrice. THF in the final solution was evaporated by N_2 flow to a final volume of 5 mL before 20 mL of methanol was added to precipitate the nanofibers. The precipitates were collected by centrifugation at 5000 rpm for 30 min. The precipitate was dried by N_2 blowing.

For hydrolysis, 20 mg of the dried nanofibers was dissolved in 10 mL of CH_2Cl_2. To it was added 2.0 mL of trifluroacetic acid. The mixture was stirred magnetically for 4 h before 10 mL of MeOH was added and the mixture was centrifuged at 10000 rpm for 30 min to settle the nanotubes. The precipitate was redispersed in 3 mL of THF. To it was added 20 mL of MeOH and the resultant mixture was centrifuged again at 10000 rpm for 30 min to settle the nanotubes. This process was repeated thrice before the precipitate was redispersed in 3.0 mL of DMF for storage and future use.

Nanotube End Functionalization by PAES-PS-PAES. HBT, 4.0 mg or 0.030 mmole, and EDCI, 6.0 mg or 0.031 mmole, were added into a 25-mL round-bottom flask in a glove bag filled by nitrogen. Transferred to it by a cannula was 2.8 g of a 0.5 wt-% nanotube solution in DMF. After the mixture was bubbled by N_2 for 15 min, 45 mg of PAES-PS-PAES was added, which was followed by further N_2 bubbling for 15 min. The mixture was stirred magnetically for 24 h under ambient conditions. Then another batch HBT, 4.0 mg, and EDCI, 6.0 mg, dissolved in 1.0 mL of N_2-bubbled DMF was added. The mixture was stirred magnetically for another 24 h before 20 mL of N_2-bubbled DMF was added. The dilute mixture was centrifuged at 17000 rpm for 30 min to settle the nanotubes. The precipitate was redispersed in 25 mL of N_2-bubbled DMF and the dispersion was centrifuged at 17000 rpm again for 30 min. This was repeated thrice. Finally, the nanotubes were dispersed in 3.0 mL of N_2-bubbled DMF for further use.

Encapsulation of Fluoresceinamine. HBT, 26 mg or 0.19 mmole, EDCI, 31 mg or 0.16 mmole, and fluoresceinamine, 15.6 mg or 0.045 mmole, were added into a 25-mL round-bottom flask. To it was added 2.8 g of N_2-bubbled DMF. After the mixture was bubbled by N_2 for 15 min, 2.7 g of a 0.5 wt-% nanotubes solution in DMF was added by a cannula. The mixture was bubbled by N_2 for 15 min before wrapping by aluminum foil and left stirring magnetically for 48 h. After this, 20 mL of N_2-bubbled MeOH was added and the mixture was centrifuged at 10000 rpm for 30 min to settle the nanotubes. The nanotubes were re-dispersed in 3 mL of N_2-bubbled THF and precipitated out again by adding in 20 mL of N_2-bubbled MeOH and centrifugation at 10000 rpm for 30 min. This process was repeated thrice. The final precipitate was redispersed in 3 mL of N_2-bubbled DMF for storage and further use.

Surface Modification of Mica or Glass Substrate. A literature method was adopted for surface modification of mica or glass plates by APTMS.[6 7, 8] First, placed inside a polyethylene container with a screw-on lid were several mica or glass plates sized at ~1×1 cm^2. The container was capped and

purged with N_2 for 10 min. With N_2 flowing, 0.3 mL of APTMS and 0.1 mL of DPEA in separate vials were placed in the container. The system was equilibrated for 3 h before the APTMS modified plates were removed and placed in N_2-purged vials for storage.

APTMS-patterned Surfaces. PCEA, 0.050 g, was dissolved in 1.0 g of DMF. Several drops of this solution were then dispensed on either a microscope cover slip or a freshly cleaved mica plate. The sample was spun at 3000 rpm for 50 s to yield a thin film. The spin-coated film was dried in the dark at 25 ^{o}C for 12 h before a copper grid (400 mesh size, Electron Microscopy Sciences) was fixed on its top using scotch tape placed at the peripheral of the grid. The masked film was irradiated with a focused UV beam from a 500-W Hg lamp (Newport, 6285 500W Hg lamp) passed through a 270-nm cut-off filter for 20 min. This was followed by pattern development in chloroform under ultrasonication for 2.5 h to remove the non cross-linked part of the film. The PCEMA-patterned glass or mica plates were then modified by APTMS following procedures described above. Crosslinked PCEA regions could be mostly removed by subjecting the APTMS-treated substrates to ultrasonication in chloroform for another 3 h.

Reaction of APTMS-modified Substrate with Succinic Anhydride. APTMS-modified mica or glass plates were placed in a vial and the vial was sealed by a septum. After N_2 bubbling for 15 minutes, 1.0 mL of succinic anhydride solution in dry pyridine at 0.10 g/mL was added. The system was heated to 50 ^{o}C and left at the temperature for 2.5 h. After this, the mica or glass plates were removed and rinsed by methanol thrice and THF thrice. The plates were then placed in 2 mL of 0.1-M HCl for 1 h before they were washed by distilled water and dried by air blow.

Reaction of APTMS-modified Substrate with PAA. PAA, 40 mg, was dissolved in 2 mL of DMF. To it were then added HBT (7 mg or 0.052 mmole) and DCC (10 mg or 0.048 mmole).[9, 10] After N_2 bubbling for 15 min, the solution mixture was added to a vial containing APTMS-modified mica or glass plates. The vial was shaken by a vortexer for 24 h. After the reaction, the plates were

rinsed by methanol, at 2 mL each time, for five times. The cleaned plates were dried by placing them in an oven at 110 ^{o}C for 30 s.

Grafting of Nanotubes onto Succinic Anhydride- or PAA-Modified Mica or Glass Surfaces. HBT (6.6 mg or 0.049 mmole) and DCC (10 mg or 0.048 mmole) were dissolved in 10 mL of DMF before the mixture was bubbled by N_2 for 15 min. One milliliter of this solution was mixed with 1.0 mL of 0.4 wt% nanotube solution in DMF. Under N_2 bubbling, 0.5 mL of the mixture was added to a vial containing carboxyl-modified mica or glass plates. The vial was shaken by a vortexer for 24 h before the reaction liquid was removed and 2 mL DMF was added to rinse the plates. After removing the DMF, another 2 mL was added. To ensure complete removal of nanotubes that were not chemically grafted, the plates and DMF were shaken by a vortexer for 24 h. Nanotube grafting onto PAA-modified surfaces was achieved similarly.

Grafting of Nanotubes onto APTMS-Modified Mica or Glass Surfaces. Nanotubes could be grafted directly to APTMS-modified mica or glass surfaces using suberic acid as the bridging molecule. To do this an example run involved first dissolving 6.6 mg (0.049 mmole) of HBT and 10 mg (0.048 mmole) of DCC in 10 mL of a 1 wt % suberic acid solution in DMF. The mixture was bubbled by N_2 or 15 min before its addition to a vial containing APTMS-modified mica or glass plates. The procedures after this were same as what was described above for nanotube grafting on to substrates modified by succinic anhydride.

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