Supplementary Materials for

Helix Self-assembly through the Coiling of Cylindrical Micelles

Sheng Zhong, a Honggang Cui, a Zhiyun Chen, b,c Karen L. Wooley b and Darrin J. Pochan a

a Department of Materials Science and Engineering and Delaware Biotechnology Institute, University of Delaware, Newark, DE 19716, USA. Fax: +1 302 831 4545; Tel: +1 302 831 3569; E-mail: pochan@udel.edu
b Center for Materials Innovation, Department of Chemistry and Department of Radiology, Washington University in Saint Louis, Saint Louis, Missouri, 63130, USA.
c Current Address: Rhodia Inc. 350 George Patterson Drive, Bristol, PA 19007, USA.

Synthesis and methods:

Synthesis and characterization of \( \text{PAA}_{94}-b-\text{PMA}_{103}-b-\text{PS}_{88} \): The triblock copolymer was synthesized by an atom transfer radical polymerization (ATRP) procedure. The accurate description of the synthetic and characterization procedure can be found in the references [S1, S2]. The characterizations are presented as follows: a white solid was obtained, (yield: 96.4 %). \( M_a = 25000 \text{ g/mol}, M_w/M_n = 1.09 \). \(^1\)H-NMR (DMSO-\( d_6 \), 500 MHz): chemical shift, \( \delta \) 1.00-2.00 (br, meso and racemo \( CH_2 \) of the polymer backbone), 2.00-2.42 (br, \( CH \) of the polymer backbone), 3.45-3.95 (br, \( OC_3H_3 \)), 6.15-6.80 (br, ortho-\( H \) from the aromatic ring), 6.80-7.45 (br, meta- and para-\( H \) from the aromatic ring), 11.5-12.9 (br, \( COO \)H) ppm. \(^{13}\)C-NMR (DMSO-\( d_6 \), 125 MHz): \( \delta \) 34.0-36.3, 41.5, 52.2, 126, 127.0-129.3, 175.0, 174.6 ppm. IR (cm\(^{-1}\)): 541, 698, 759, 827, 1166, 1244, 1453, 1494, 1602, 1738, 2800-3600.

Atomic Force Microscopy: 5-10 \( \mu \)L solution was deposited onto a freshly prepared mica disk and allowed to dry. Then the sample was rinsed with 2 mL of deionized water to remove dried excess multivalent amines and unattached polymeric cylinders. Samples were imaged on a Digital Instruments Multi Mode Nanoscope IIIA atomic force microscope in tapping mode using silicon tips (300 MHz, 40 N/m) with a scan rate of 0.75 Hz.

Transmission Electron Microscopy (TEM): TEM experiments were carried out on a Tecnai G2 12 microscope at a voltage of 120 kV. TEM samples were prepared by casting 2-4 \( \mu \)L of polymer solution onto a carbon-coated copper TEM grid and allowing the solution to dry in room temperature. Then 5 \( \mu \)L freshly made 1.0 wt% uranyl acetate aqueous solution was applied onto the samples. The excess solution was wicked away by filter paper after 2 minutes. Afterwards, the sample was allowed to dry.

Cryogenic Transmission Electron Microscopy (Cryo-TEM): A Gatan cryo-holder system was used to examine the samples in a Tecnai G2 12 microscope at voltage 120 kV. A droplet of the suspension (5 \( \mu \)L) was dipped manually on a holey carbon film coated on copper TEM grid. The specimen was blotted and plunged into a liquid ethane container cooled by liquid nitrogen. This procedure proceeded in the Vitrobot vitrification system. The vitrified samples were transferred to a Gatan 626 cryo-holder and cryo-transfer stage cooled by liquid nitrogen. During TEM observation, the cryo-holder was maintained below -170 \( ^\circ \)C to prevent sublimation of vitreous water and THF. The digital images were recorded by a Gatan low-dose CCD camera.
Results:

Figure S1 Atomic force microscope for left-handed helix (left) and right-handed helix (right). The helix is collapsed due to the evaporation of solvent. Amine = triethylenetetramine, amine group: acid group molar ratio = 10:1, H$_2$O% (v) = 67% in THF and after 20 day aging; scale bar is 20 nm.

Figure S2 TEM image for amine = ethylenediamine, amine group: acid group molar ratio = 10:1; H$_2$O% (v) = 67% in THF and after 20 day aging.

References: