Supplementary Material (ESI) for Soft Matter

Supplemental Materials for

Helix Self-assembly through the Coiling of Cylindrical Micelles

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Synthesis and methods:

Synthesis and characterization of PAA_{94}-*b*-PMA_{103}-*b*-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 follow: a white solid was obtained, (yield: 96.4 %). M_n = 25000 g/mol, M_w/M_n = 1.09. ^{1}H-NMR (DMSO-d_6, 500 MHz): chemical shift, δ 1.00-2.00 (br, meso and racemo C***H***$_2$ of the polymer backbone), 2.00-2.42 (br, C***H*** of the polymer backbone), 3.45-3.95 (br, OC***H***$_3$), 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): δ 34.0-36.3, 41.5, 52.2, 126, 127.0-129.3, 175.0, 176.4 ppm. IR (cm^{-1}): 541, 698, 759, 827, 1166, 1244, 1453, 1494, 1602, 1738, 2800-3600.

Atomic Force Microscopy: 5-10 μL 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 μL of polymer solution onto a carbon-coated copper TEM grid and allowing the solution to dry in room temperature. Then 5 μL 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 μL) 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 virtrification 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 ℃ to prevent sublimation of vitreous water and THF. The digital images were recorded by a Gatan low-dose CCD camera.

Results:

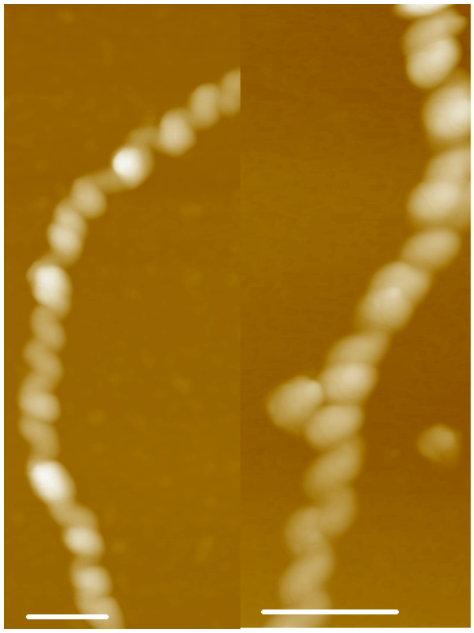

Figure S1 Atomic force microscope for left-handed helix (left) and right-handed helix (right). The helix is collapsed due to the evaporation of solvent. Amine = triethylenetetramine, amine group: acid group molar ratio = 10 : 1, H_2O% (v) = 67% in THF and after 20 day aging; scale bar is 20 nm.

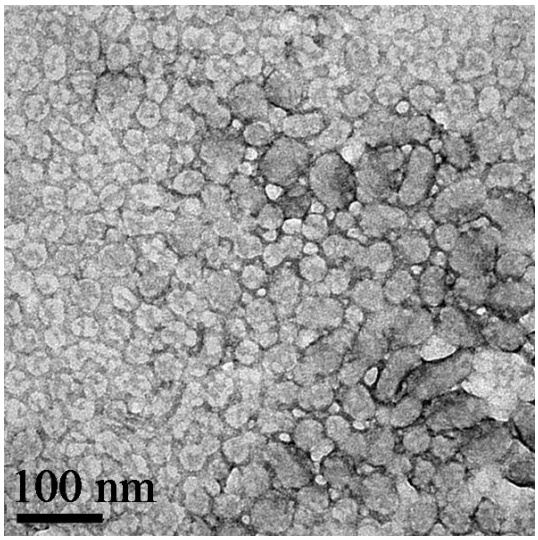

Figure S2 TEM image for amine = ethylenediamine, amine group: acid group molar ratio = 10 : 1; H_2O% (v) = 67% in THF and after 20 day aging.

References:

S1. Q. G. Ma, K. L. Wooley, *Journal of Polyme Science Part a-Polymer Chemistry*, 2000, 38, 4805-4820.

S2. D. J. Pochan, Z. Y. Chen, H. G. Cui, K. Hales, K. Qi and K. L. Wooley, *Science*, 2004, 306, 94-97