Supporting Information

Dynamic Cylindrical Assembly of Triblock Copolymers by a Hierarchical Process of Covalent and Supramolecular Interactions

Zhou Li,[†] Jun Ma,[†] Nam S. Lee,[†, ‡] and Karen L. Wooley[†, ‡, *]

[†]*Department of Chemistry, Washington University in St. Louis, St. Louis, MO 63130.*

[‡]*Department of Chemistry and Department of Chemical Engineering, Texas A&M University, College Station, Texas 77842.*

[*]To whom correspondence should be addressed. Email: wooley@chem.tamu.edu.

Experimental Section

Measurements

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded at 300 MHz on a Varian Mercury 300 spectrometer with solvent proton resonance as reference. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded at 75 MHz on a Varian Mercury 300 spectrometer with solvent carbon resonance as reference. Infrared spectra were obtained on a Perkin-Elmer Spectrum BX FT-IR system using diffuse reflectance sampling accessories.

Gel permeation chromatograph (GPC) was conducted on a Waters 1515 HPLC (Waters Chromatography, Inc.) equipped with a Waters 2414 differential refractometer and a Model PD2040 dual-angle (15^o and 90^o) light scattering detector (Precision Detectors, Inc.), and a three-column series PL gel 5μm Mixed C, 500 Å, and 104 Å, 300 × 7.5 mm columns (Polymer Laboratories Inc.). The system was equilibrated at 35 °C in THF, which served as the polymer solvent and eluent with a flow rate of 1.0 mL/min. Polymer solutions were prepared at a known

concentration (*ca.* 3 mg/mL) and an injection volume of 200 μL was used. Data collection and analysis were performed, respectively, with Precision Acquire software and Discovery 32 software (Precision Detectors, Inc.). The system was calibrated using polystyrene standards.

Differential scanning calorimetry (DSC) was conducted on a DSC822^e instrument (Mettler-Toledo, Inc.) at temperature range of −50 - 200 °C with a heating rate of 10 °C/min under nitrogen. The data were acquired and analyzed with STAR^e software (Mettler-Toledo, Inc.). The Glass transition temperature (T_g) values were taken at the midpoint of the inflection tangent, upon the third heating scans.

Dynamic light scattering (DLS) measurements were conducted using Delsa Nano C (Beckman Coulter, Inc., Fullerton, CA) equipped with a laser diode operating at 658 nm. Size measurements were made in *N*,*N*-dimethylformamide (DMF) (n = 1.4282, η = 0.794 cP at 25 ± 1 °C) or water (n = 1.3329, η = 0.890 cP at 25 ± 1 °C; n = 1.3293, η = 0.547 cP at 50 ± 1 °C; n = 1.3255, η = 0.404 cP at 70 ± 1 °C). Scattered light was detected at 15° angle and analyzed using a log correlator over 70 accumulations for a 0.5 mL of sample in a glass size cell (0.9 mL capacity). The samples in the glass size cell were equilibrated at the desired temperature for 60 minutes before measurements were made. The photomultiplier aperture and the attenuator were automatically adjusted to obtain a photon counting rate of *ca*. 10 kcps. The calculation of the particle size distribution and distribution averages was performed using CONTIN particle size distribution

analysis routines. The peak average of histograms from intensity, volume or number distributions out of 70 accumulations was reported as the average diameter of the particles.

Atomic force microscopy (AFM) was conducted on a MFP-3D-BIO system (Asylum Research, Santa Barbara, CA), operated in a tapping mode in air with high resolution probes (DP14/HI'RES/Al BS, from μmash: L, 125 μm; normal spring constant, 5.0 N/m; resonance frequency, 160 kHz). The average height and diameter values were determined by section analysis, using the IGOR Pro software package. Transmission electron microscopy (TEM) imaging was performed in high-contrast mode with a Hitachi H-7500 at 80 kV accelerating voltage.

Materials

Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized from methanol before use. *Tert*-butyl acrylate (*t*BA, 98%, Aldrich), methyl acrylate (MA, 99%, Aldrich), styrene (St, 99%, Aldrich), were passed through neutral alumina column before polymerizations. Iodotrimethylsilane (TMSI, 97%, Aldrich) and sodium thiosulfate ($Na_2S_2O_3$, 98.0%, Sigma-Aldrich) were used as received. The Grubbs' catalyst and the norbornenyl-functionalized RAFT chain transfer agent (NB-CTA) were prepared by the methods reported.[1,2] Spectr/Por® membranes (MWCO 3500 Da, Spectrum Medical Industries, Inc., Laguna Hills, CA) were used for dialysis.

Synthesis of α-norbornenyl polystyrene (NB-PS).

The polymer was prepared from the polymerization mixture of St (18.20 g, 175 mmol), NB-CTA (541 mg, 0.862 mmol), AIBN (1.6 mg, 1.0×10^{-2} mmol) at 50 °C. The polymerization was quenched after 40 h when the monomer conversion was measured to be 10% by ^{1}H NMR spectroscopy (the conversion was calculated by the integration ratio of aromatic protons and one alkenyl proton (6.32-7.40 ppm) to the other two alkenyl protons (5.7 ppm and 5.2 ppm)). The isolated yield was 1.60 g (74 %, based on the conversion of St). M_n^{calc} = 2740 Da, M_n^{GPC} = 3340 Da, PDI = 1.14. T_g: 93 °C. IR (cm^{-1}): 3150-2850 (strong), 1943 (medium-weak), 1869 (medium-weak), 1802 (medium-weak), 1725 (medium-strong), 1601 (medium-strong), 1583 (medium), 1541 (weak), 1493 (strong), 1452 (strong), 1371 (medium), 1266 (medium), 1181 (medium), 1154 (medium), 1110 (medium), 1068 (medium-strong), 1028 (medium-strong), 906 (medium), 757 (strong). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 0.80-0.90 (-C***H***$_3$ of the RAFT chain end and backbone protons), 1.10-2.50 (alkyl protons of RAFT agent and polystyrene backbone protons), 2.74-2.79 (>C***H***-CH=CH-C***H***<), 3.23-3.50 (-C***H*****$_2$**SC(S)S-), 6.03-6.16 (-C***H***=C***H***-), 6.32-7.40 (aromatic protons). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 40.0-41.8, 42.5-46.0, 126, 128, 145.

Synthesis of *α*-norbornenyl polystyrene-*b*-poly(methyl acrylate) (NB-PS-*b*-PMA).

The polymer was prepared from the polymerization mixture of MA (8.60 g, 100 mmol), NB-PS as the macro-CTA (993 mg, 0.297 mmol) and AIBN (0.9 mg, 5.5×10^{-3} mmol) at 50 °C. The polymerization was quenched after 20 h when the monomer conversion was measured to be 8% by ^{1}H NMR spectroscopy. Yield: 1.18 g (70 %, based on the conversion of MA). M_n^{calc} = 5560 Da, M_n^{GPC} = 5580 Da, PDI = 1.15. T_g: 93 °C, 11 °C. IR (cm^{-1}): 3100-2850 (medium-strong,

multiple peaks), 1802 (weak), 1733 (strong), 1600 (medium-weak), 1541 (weak), 1493 (medium), 1452 (medium-strong), 1388 (medium-weak), 1253 (medium-weak), 1195 (medium), 1164 (medium-strong), 1110 (medium weak), 988 (weak), 906 (weak), 827 (medium-weak), 752 (medium). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 0.80-0.90 (-C***H***$_3$ of the RAFT chain end and backbone protons), 1.10-2.50 (alkyl protons of RAFT agent and polymer backbone), 2.74-2.79 (>C***H***-CH=CH-C***H***<), 3.23-3.30 (-C***H*****$_2$**SC(S)S-), 3.55-3.75 (-OC***H***$_3$ of MA units), 6.03-6.15 (-C***H***=C***H***-), 6.30-7.40 (aromatic protons). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 35.7-37.2, 40.5-46.5, 51.6, 126, 128, 145, 175.

Synthesis of α-norbornenyl polystyrene-*b*-poly(methyl acrylate)-*b*-poly(*t*-butyl acrylate) (NB-PS-*b*-PMA-*b*-P*t*BA).

The polymer was prepared from the polymerization mixture of *t*BA (1.94 g, 15.1 mmol), NB-PS-*b*-PMA as the macro-CTA (385 mg, 0.0689 mmol), AIBN (0.6 mg, 3.7×10^{-3} mmol) and 2-butanone (2.0 mL) at 50 °C. The polymerization was quenched after 20 h when the monomer conversion was measured to be 35% by ^{1}H NMR spectroscopy. Yield: 882 mg (83 %, based on the 35% conversion of *t*BA). M_n^{calc} = 15400 Da, M_n^{GPC} = 15900 Da, PDI = 1.20. T_g: 93 ^{o}C, 43 ^{o}C, 11 ^{o}C. IR (cm^{-1}): 3100-2800 (medium-strong, multiple peaks), 1943 (medium-weak), 1738 (strong), 1601 (medium-weak), 1448 (medium-strong), 1371 (strong), 1256 (medium-strong, broad), 1164 (strong), 845 (medium), 757 (medium-weak). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 0.80-0.90 (-C***H*****$_3$** of the RAFT chain end), 1.10-2.50 (alkyl protons of RAFT agent and polymer backbone, -(C***H*****$_3$**$)_3$C of *t*BA units), 2.74-2.79 (>C***H***-CH=CH-C***H***<), 3.23-3.50 (m, -C***H*****$_2$**SC(S)S-),

3.65 (-OC***H₃*** of MA units), 6.03-6.15 (-C***H***=C***H***-), 6.30-7.40 (aromatic protons). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 28.0-29.0, 35.5-38.5, 40.5-47.5, 51.8, 80.4, 126, 128, 145, 174, 176.

ROMP-based synthesis of molecular brushes with triblock side chains (PNB-*g*-(PS-*b*-PMA-*b*-P*t*BA)).

To a solution of Grubbs' catalyst in CH_2Cl_2 (4.2 mg/mL, 100 μL, 1 equiv.) under argon in a scintillation vial capped with a septum was added the NB-PS-*b*-PMA-*b*-P*t*BA solution in CH_2Cl_2 (73.1 mg/mL, 1000 μL, 100 equiv.) *via* a syringe. The reaction was allowed to stir at room temperature for 1 h and the molecular brush product was obtained after quenching the reaction by ethyl vinyl ether (EVE) and precipitating the reaction mixture in methanol. Yield: 69.2 mg (95%). M_n^{calc} = 1.59×10^6 Da, M_n^{GPC} = 1.51 ×10^6 Da, PDI=1.15. T_g: 93 ^{o}C, 43 ^{o}C, 11 ^{o}C. IR (cm^{-1}): 3100-2800 (medium-strong, broad), 1943 (medium-weak), 1738 (very strong, broad), 1601 (medium-weak), 1448 (medium-strong), 1371 (strong), 1256 (medium-strong), 1164 (strong, broad), 845 (medium), 757 (medium-weak). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 1.20-2.05 (polymer backbone protons), 1.25-1.60 (-C(C***H₃***)$_3$ of *t*BA), 2.10-2.58 (grafted side chain backbone protons), 3.50-3.66 (-OC***H₃*** of MA), 6.36-7.30 (aromatic protons). ^{13}C NMR (75 MHz, CD_2Cl_2, ppm): δ 28.0-29.0, 35.5-38.5, 40.5-47.5, 51.7, 80.4, 126, 128, 145, 174, 176.

Hydrolysis of NB-PS-*b*-PMA-*b*-P*t*BA to NB-PS-*b*-PMA-*b*-PAA.

NB-PS-*b*-PMA-*b*-PAA (27.8 mg) was loaded into a vial and dissolved in CH_2Cl_2 (5.0 mL). A solution of TMSI (5.0 mL, 2.5 mL TMSI diluted by 15.0 mL CH_2Cl_2) was added. After 90 min, the excess solvent and reagent were removed *in vacuo*. The residue was then redissolved in THF (7 mL) and decolorized by addition of an aqueous solution of $Na_2S_2O_3$ to afford a colorless

solution. Dialysis of the solution against nanopure water for 5 days cleaved the silyl ester bonds and gave the final amphiphilic NB-PS-*b*-PMA-*b*-PAA, which was collected after removal of water by lyophilization. Yield: 17.8 mg (89%). T_g = 93 °C, 11 °C. (T_g for PAA was not observed or overlapped with that of PS.) IR (cm^{-1}): 3500-2750 (very strong, very broad), 1723 (medium), 1601 (medium-strong), 1492 (medium-strong), 1452 (medium-strong), 1368 (medium-weak), 1168 (medium), 1026 (weak), 825 (medium), 698 (medium). ^{1}H NMR (300 MHz, THF-d_8, ppm): δ 1.20-2.58 (polymer backbone protons), 3.50-3.66 (-OC$\boldsymbol{H_3}$ of MA), 6.36-7.40 (aromatic protons), 10.80-11.60 (-COO$\boldsymbol{H}$). ^{13}C NMR (75 MHz, THF-d_8, ppm): δ 33.4-37.5, 40.5-47.5, 51.3, 126, 128, 144, 172, 174.

Hydrolysis of PNB-*g*-(PS-*b*-PMA-*b*-P*t*BA) to PNB-*g*-(PS-*b*-PMA-*b*-PAA).

PNB-*g*-(PS-*b*-PMA-*b*-P*t*BA) (27.4 mg) was loaded into a vial and dissolved in CH_2Cl_2 (5.0 mL). A solution of TMSI (5.0 mL, 2.5mL TMSI diluted by 15.0 mL CH_2Cl_2) was added. After 90 min, the excess solvent and reagent were removed *in vacuo*. The residue was then redissolved in THF (7 mL) and decolorized by addition of an aqueous solution of $Na_2S_2O_3$ to afford a colorless solution. Dialysis of the solution against nanopure water for 5 days cleaved the silyl ester bonds and gave the final amphiphilic PNB-*g*-(PS-*b*-PMA-*b*-PAA), which was collected after removal of water by lyophilization. Yield: 17.2 mg (88%). T_g= 93 °C, 10 °C. IR: 3500-2750 (very strong, very broad), 1723 (medium), 1600 (medium-strong), 1492 (medium-strong), 1452 (medium-strong), 1366 (medium-weak), 1168 (medium), 1026 (weak), 845 (medium), 698 (medium). ^{1}H NMR (300 MHz, THF-d_8, ppm): δ 1.20-2.58 (polymer backbone protons),

3.50-3.66 (-OC***H₃*** of MA), 6.36-7.38 (aromatic protons), 10.60-11.40 (-COO***H***). ^{13}C NMR (75 MHz, THF-d_8, ppm): δ 33.0-37.5, 40.5-46.8, 51.2, 126, 128, 144, 172, 174.

Self assembly of amphiphilic macromolecules to nanostrcutres.

The general procedure was: PNB-*g*-(PS-*b*-PMA-*b*-PAA) or NB-PS-*b*-PMA-*b*-PAA (10.0 mg) was dissolved in DMF (2.0 mL) to afford a clear solution, which was then dialyzed against nanopure water for 5 days to afford the self assembled nanostructures. Water was changed 3 times a day.

General protocol for sample preparation for AFM imaging.

A drop of the nanostructure solution (2 μL) was deposited directly onto a freshly cleaved mica and allowed to incubate under ambient conditions for 5 min. After the extra solution was blotted off, the mica was dried at room temperature.

General protocol for sample preparation for TEM imaging.

A drop of the nanostructure solution (5 μL) was deposited directly onto a carbon-coated copper TEM grid and allowed to incubate under ambient conditions for 5 min. After the extra solution was blotted off, the grid was dried at room temperature and stained by either 1.0% PTA solution or RuO_4 vapor.

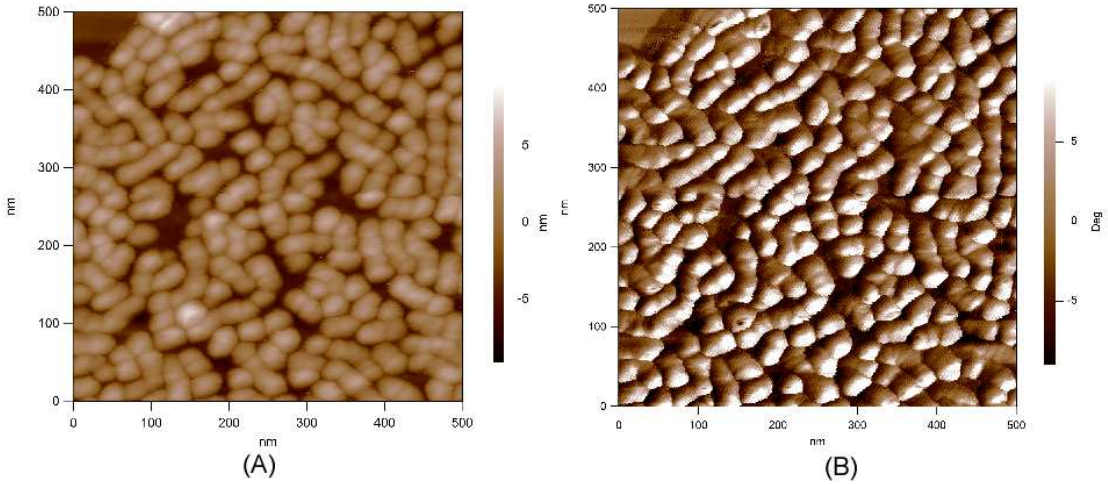

Fig. S1. AFM images of the hierarchical cylindrical nanostructures from PNB-*g*-(PS-*b*-PMA-*b*-PAA) self-assembled in aqueous solution. (A) Height image. (B) Phase image.

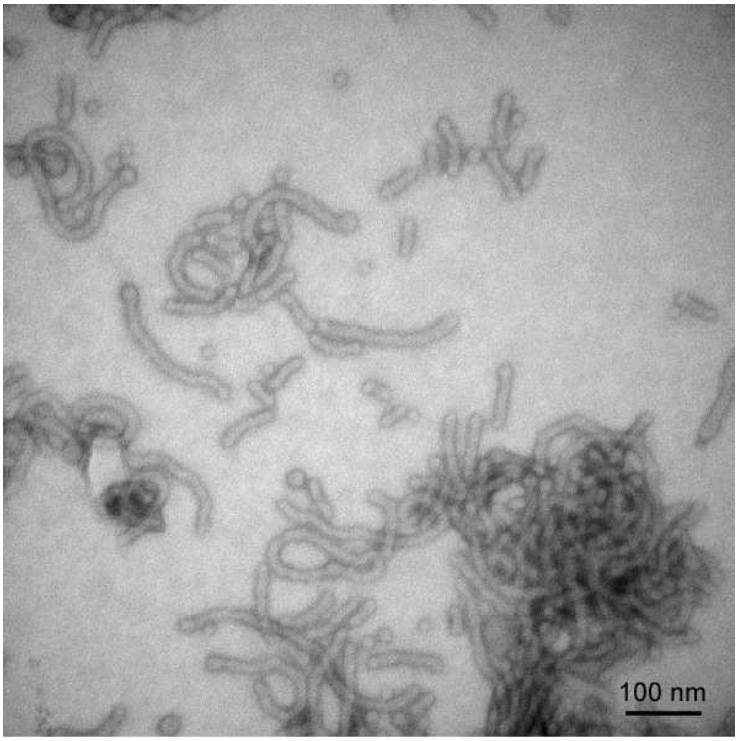

Fig. S2. TEM image of the re-assembled cylindrical nanostructures. The sample solution was prepared from the disassembled PNB-*g*-(PS-*b*-PMA-*b*-PAA), which was collected by lyophilization

and redissolved in DMF, and then dialyzed against water. The sample was stained with 1.0% PTA solution.

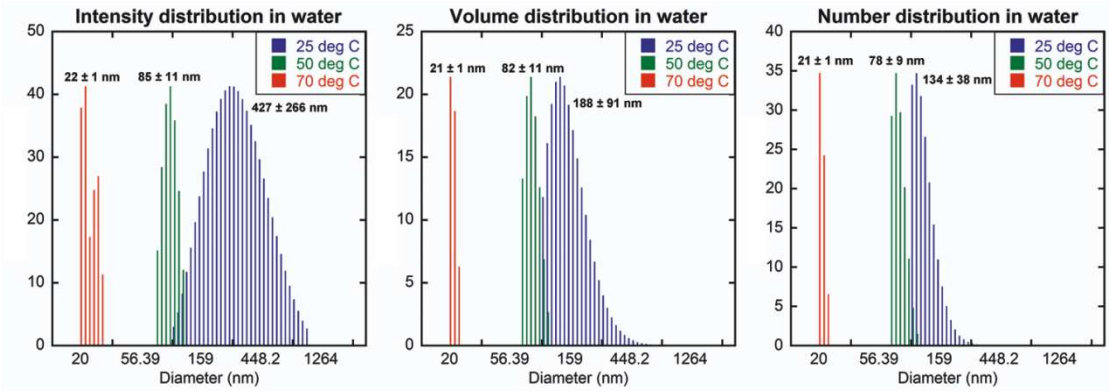

Fig. S3. DLS histograms of the dynamic hierarchical nanostructures of PNB-*g*-(PS-*b*-PMA-*b*-PAA) in aqueous solutions at different temperatures (blue: 25 °C, green: 50 °C, and red: 70 °C).

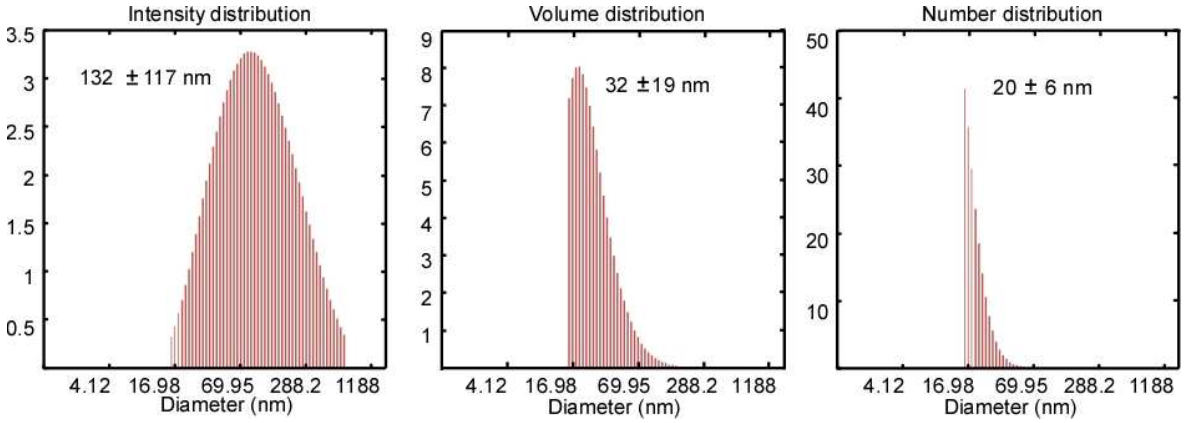

Fig. S4. DLS histograms of PNB-*g*-(PS-*b*-PMA-*b*-PAA) in DMF solution before dialysis.

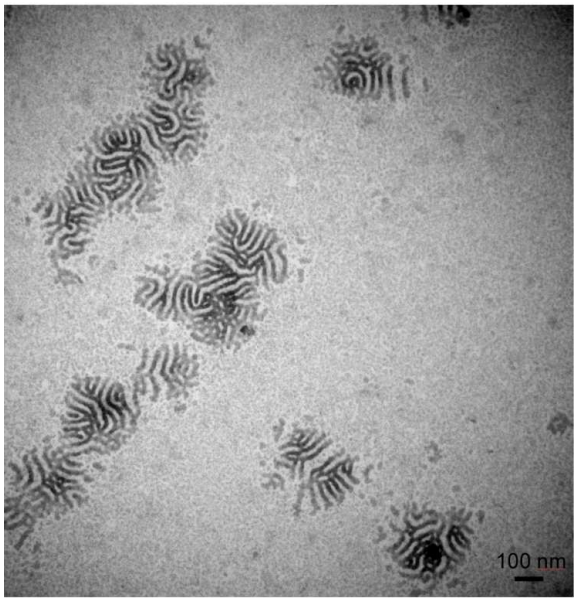

Fig. S5. TEM image of the patterns dried from the DMF solution of PNB-*g*-(PS-*b*-PMA-*b*-PAA). The sample was stained with RuO_4 vapor.

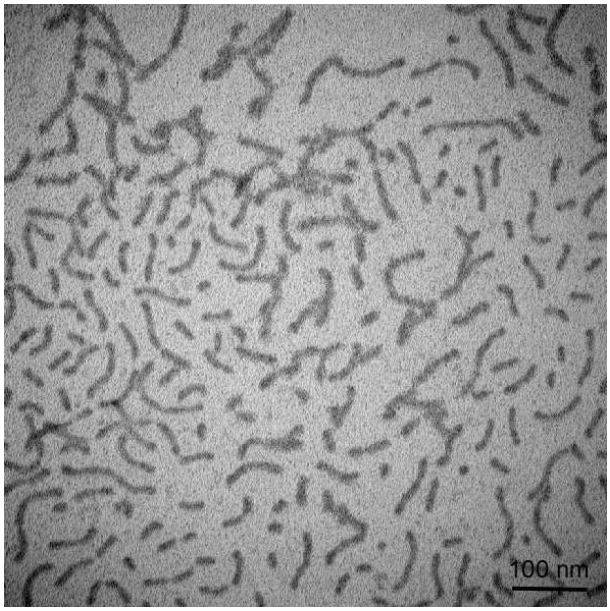

Fig. S6. TEM image of the hierarchical structures self-assembled from PNB-*g*-(PS-*b*-PMA-*b*-PAA) in aqueous solution. The sample was stained with RuO_4 vapor.

1. Choi, T. L.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2003**, *42*, 1743-1746.
2. Li, Z.; Zhang, K.; Ma, J.; Cheng, C.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, *47*, 5557-5563.

Complete list of authors and the full citation of Reference 10:

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