Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Solvent-Induced Reconstruction in Confined Space: One-Dimensional Mesoporous Block Copolymer Structures in Cylindrical Nanopores

*Chun-Wei Chang, Mu-Huan Chi, Hao-Wen Ko, Chien-Wei Chu, Zhi-Xuan Fang, Yi-Hsuan Tu, and Jiun-Tai Chen**

Department of Applied Chemistry, National Chiao Tung University, Hsinchu, Taiwan 30010

EXPERIMENTAL SECTION

Materials

Polystyrene-*block*-poly(methyl methacrylate) (PS-*b*-PMMA) polymers with number-average molecular weights of 38-*b*-36.8 (PDI: 1.08) and 53-*b*-20.5 (PDI: 1.08) kg/mol were purchased from Polymer Source. Dimethylformamide (DMF), sodium hydroxide (NaOH), and toluene were obtained from Tedia. Acetic acid (AA) was obtained from Sigma Aldrich. Ruthenium tetroxide (RuO_4) was purchased from Acros. Anodic aluminum oxide (AAO) templates with pore diameters of ~230 nm and thicknesses of ~60 μm were purchased from Whatman. Polycarbonate filters (VCTP, pore size ~0.1 μm) were acquired from Millipore. Deionized (DI) water was obtained from Milli-Q system. Wipers (Kimwipes) were acquired from Kimberly-Clark.

Fabrication of the Synthesized AAO Templates

A two-step anodization process was used to fabricate the synthesized AAO templates. An aluminum foil (~99.9997%) was cleaned by isopropyl alcohol (IPA) under ultrasonication for 10 min. The aluminum foil was then electropolished by a mixed solution of ethanol/perchloric acid with a volume ratio of 80:20 at a voltage of 20 V under 4 °C for 2 min. The first anodization process was conducted using a 0.3 M oxalic acid solution at 16 °C for 1 h at a voltage of 40 V. Subsequently, the foil was immersed in a mixed solution of 6 wt % phosphoric acid (H_3PO_4) and 1.8 wt % potassium dichromate ($K_2Cr_2O_7$) for 1 h to etch the aluminum oxide layer. The second anodization process was conducted by a 0.3 M oxalic acid solution at 16 °C for 12 h at a voltage of 40 V. Finally, the foil was dipped in 5 wt % phosphoric acid for 35 min to widen the nanopores and porous aluminum oxide templates with pore diameters of ~60 nm were obtained.

Fabrication of PS-*b*-PMMA Nanotubes and Mesoporous Structures

To prepare PS-*b*-PMMA nanotubes, an AAO template was first immersed in a 5 wt % PS-*b*-PMMA/DMF solution for 10 s. The sample was then taken out, and the residual polymer solution outside the AAO surfaces was removed by Kimwipes. After the solution was dried by a vacuum pump and polymers are solidified, PS-*b*-PMMA nanotubes were released by selectively dissolving the AAO template using 5 wt % NaOH(aq).

To prepare mesoporous PS-*b*-PMMA structures, an AAO template was first immersed in a 5 wt % PS-*b*-PMMA/DMF solution for 10 s. Subsequently, the sample was taken out by a tweezer and the residual polymer solution outside the AAO surfaces was removed by Kimwipes. The sample was then immersed in acetic acid (AA) for 10 s. After the sample was taken out, the residual polymer solution outside the AAO surfaces was removed again by Kimwipes. Later, the sample was dried by a vacuum pump, followed

by selectively dissolving the AAO template using 5 wt % NaOH(aq), resulting in the formation of mesoporous PS-*b*-PMMA structures.

Structure Analysis and Characterization

The surface morphologies of the PS-*b*-PMMA nanotubes and mesoporous structures were observed by a field emission scanning electron microscope (FESEM, JEOL-7401F) with an accelerating voltage of 5 kV. Before SEM measurements, the samples were dried by a vacuum pump and coated with 4 nm of platinum. The interior morphologies of the PS-*b*-PMMA nanotubes and mesoporous structures were characterized by a bright-field transmission electron microscope (TEM, JEM-2100) with an accelerating voltage of 200 kV. Before TEM measurements, the samples were deposited onto copper grids coated with carbon and stained by RuO_4 vapor for 3 min.

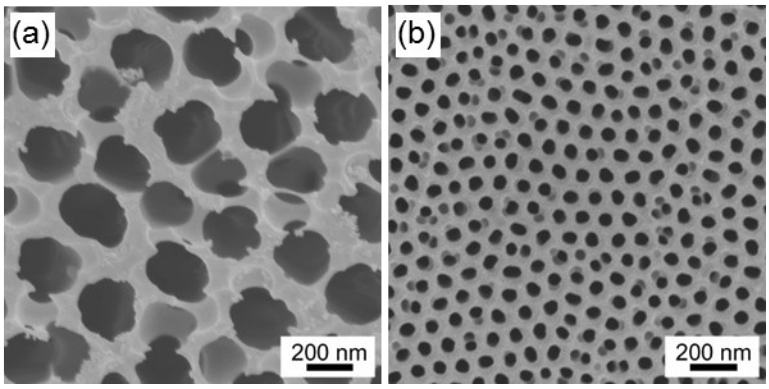

Figure S1. (a and b) SEM images of commercial and synthesized AAO templates with the average pore diameter ~230 nm and ~60 nm, respectively.

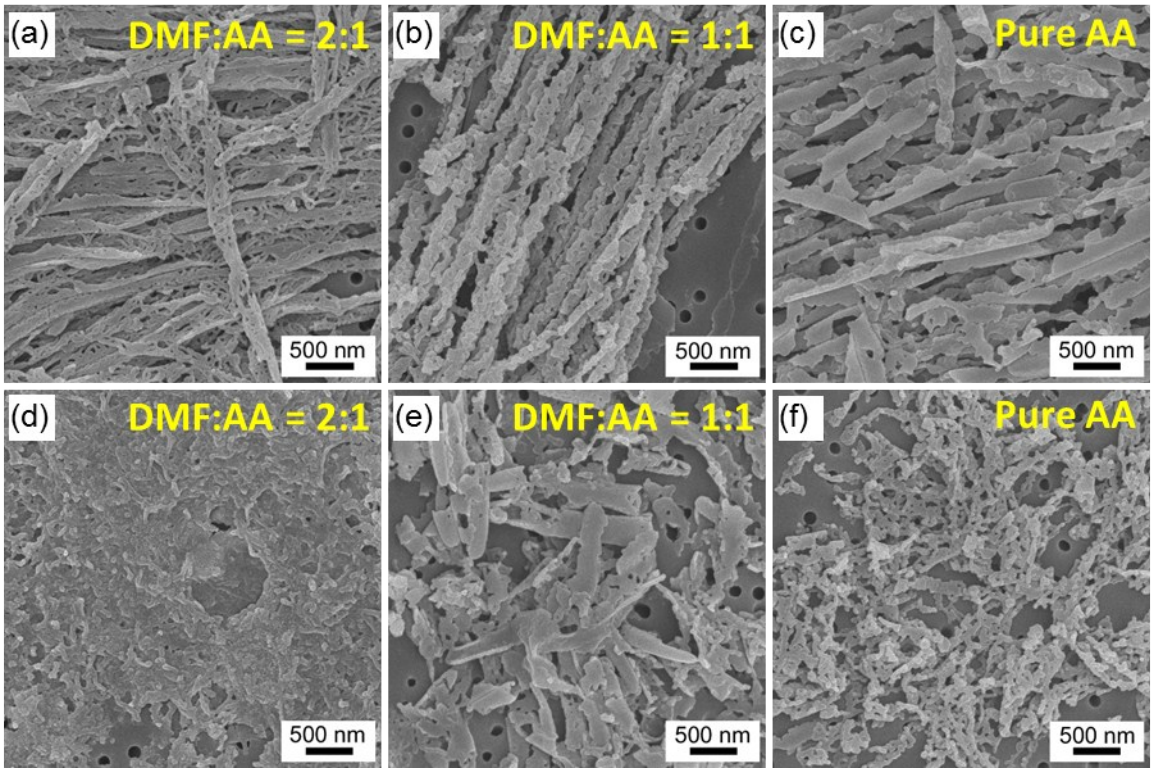

Figure S2. (a and b) SEM images of PS_{53k}-*b*-$PMMA_{20.5k}$ nanostructures prepared by immersing PS-*b*-PMMA nanotubes in different DMF-to-AA ratios at differnt times: (a-c) 10 s and (d-f) 12 h.

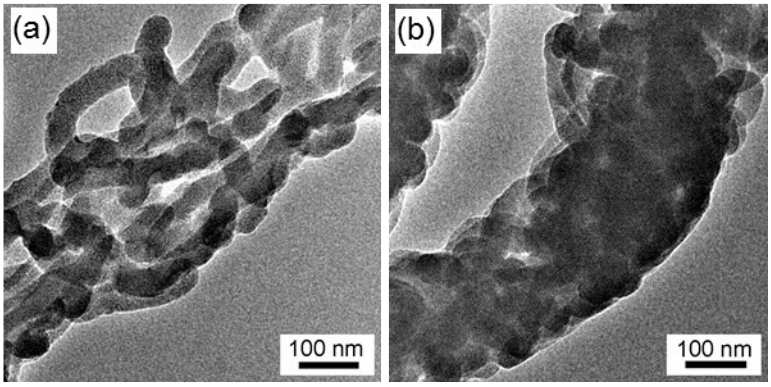

Figure S3. (a and b) TEM images of PS_{53k}-*b*-$PMMA_{20.5k}$ mesoporous structures fabricated by the selective solvent-induced reconstruction method using PS-*b*-PMMA/DMF solution with concentration of 10 wt % and 20 wt %, respectively. Before the TEM measurements, the mesoporous structures are stained by RuO_4 vapors, which selectively stain the PS blocks.