

## Supporting Information

### Design of Amphiphilic ABC Triblock Copolymer for Templating Synthesis of Large-Pore Ordered Mesoporous Carbons with Tunable Pore Wall Thickness

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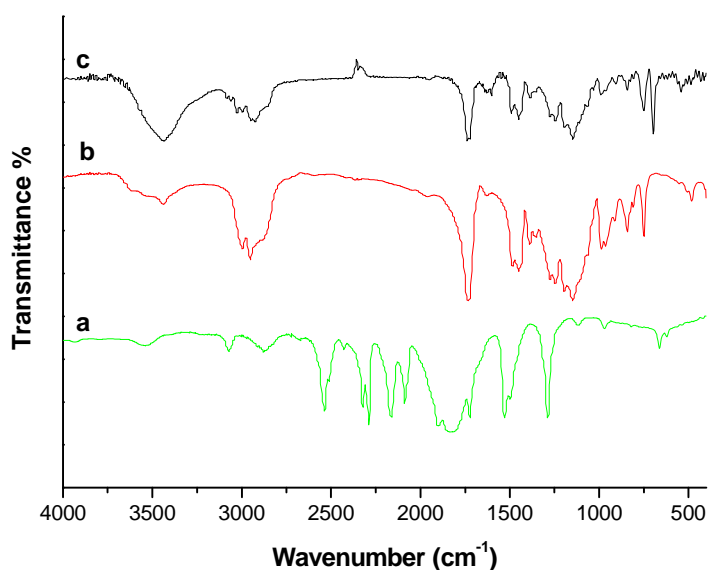
#### Preparation procedure of PEO-*b*-PMMA-*b*-PS triblock copolymer

Monomethoxy PEO 5000 (20.0 g) was dissolved in THF (60 mL), and 40 mL of pyridine was then added to obtain a homogeneous solution. The solution was placed in an ice-water bath, and to it, 3.00 g of 2-bromoisobutyrylbromide (13.0 mmol) was added dropwise under stirring for 30 min. The resultant solution was further stirred at 30 °C overnight. After cooling to room temperature, cold ether (200 mL) was added to the solution. The white product of PEO-Br was precipitated from the reaction solution. It was washed with cold ether and further dried in vacuum. Then, a glass tube was filled with 2.0 g of PEO-Br (0.40 mmol) macroinitiator, 5.0 g of MMA (50 mmol), 0.04 g of CuCl (0.4 mmol), 0.0692 g of PMDETA (0.40 mmol) and 10 g of THF. After degassed with three freeze-pump-thaw cycles, the tube was sealed under vacuum and then immersed in a thermostated oil bath at 50 °C. The reaction was continued for 8 h, the tube was withdrawn and cooled to room temperature. The reaction mixture was diluted with THF, and then added certain amount of activated Al<sub>2</sub>O<sub>3</sub> into the tube, filtrated the mixture through a column after stirring for 1 h to remove the catalyst, and precipitating into ether, PEO-*b*-PMMA diblock copolymer

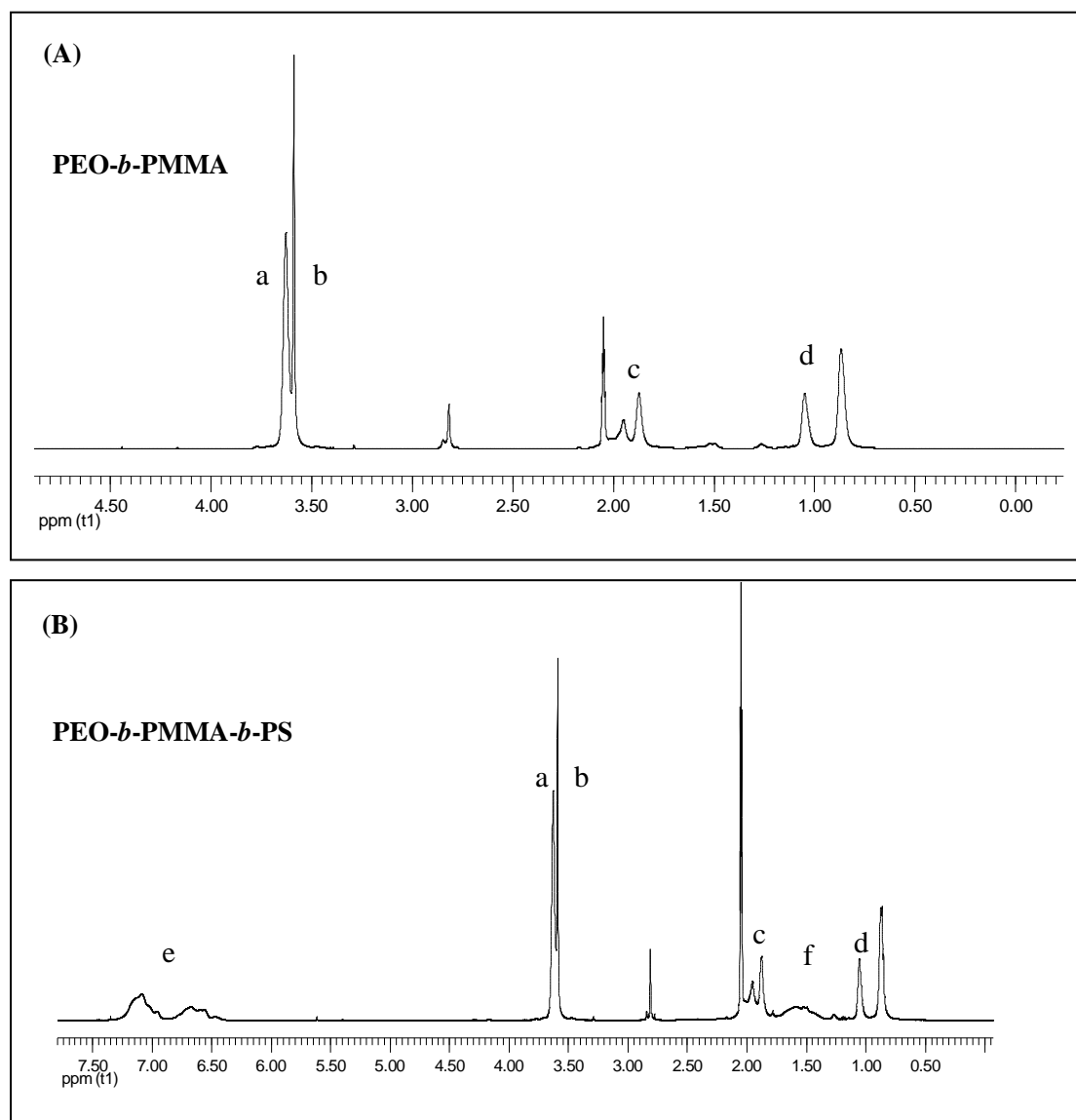
was obtained and dried in a vacuum oven overnight at room temperature. Then, 1.8 g of PEO-*b*-PMMA (0.10 mmol), 0.01 g of CuCl (0.10 mmol), 0.0173 g of PMDETA (0.10 mmol), and 15.0 g of styrene (144 mmol) were added to an ampoule bottle. The bottle containing reactants was fully degassed with three freeze pump thaw cycles and sealed under vacuum. It was subsequently immersed in a Thermostated oil bath at 110 °C under stirring to allow polymerization of styrene. The reaction was continued for 4 h, after which the system was cooled down to room temperature. The product was dissolved by 50 mL of THF and filtered through Al<sub>2</sub>O<sub>3</sub> Column to remove the catalyst. Petroleum ether (200 mL) was poured into the solution to precipitate PEO-*b*-PMMA-*b*-PS triblock copolymer. The copolymer was then dried in vacuum.

### **Characterization**

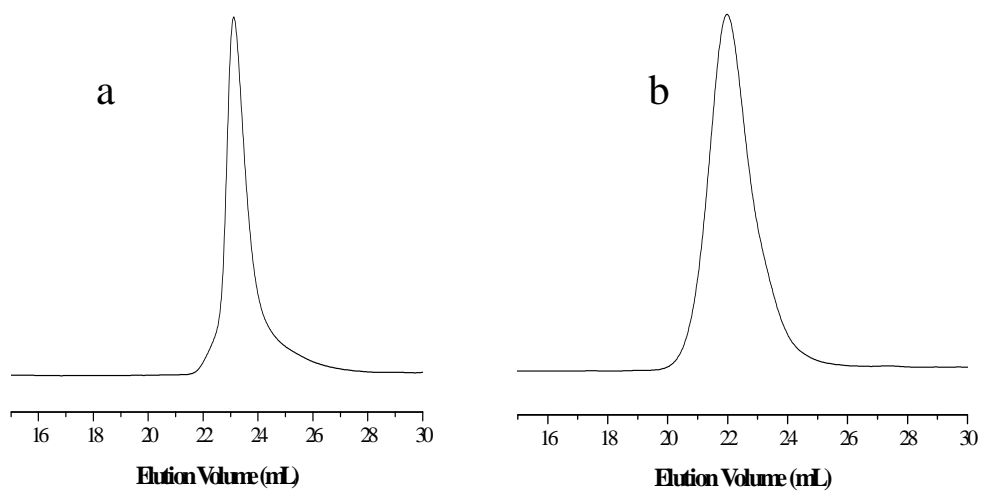
<sup>1</sup>H-NMR spectra were recorded at 25 °C on a DMX 500-MHz spectrometer (Bruker, Germany) with tetramethylsilane as an internal standard and CDCl<sub>3</sub> as a solvent. Gel permeation chromatography (GPC) was performed on an Agilent 1100 gel permeation chromatographer with refractive index detector and UV-vis detector (wavelength 190 – 950 nm, USA) by the use of THF as an eluent (1.0 mL/min). GPC was calibrated with mono-dispersed polystyrene standards. Fourier-transform infrared (FT-IR) spectra were collected on Nicolet Fourier spectrophotometer (USA) using KBr pellets.



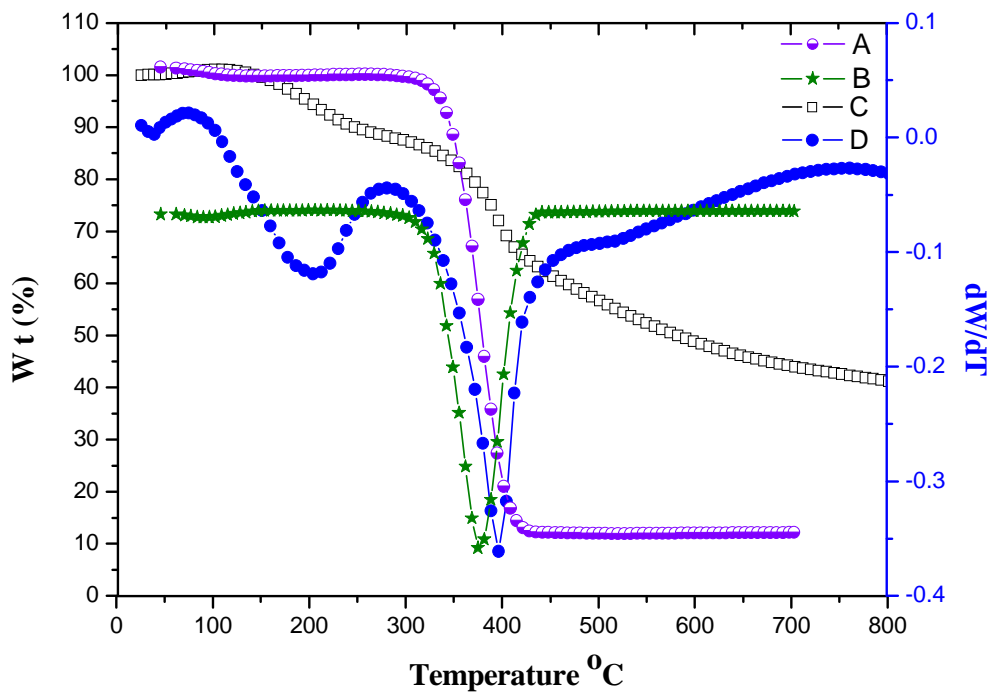
**Figure S1.** FT-IR spectra of (a) PEO5000-Br, (b) diblock copolymer PEO-*b*-PMMA and (c) triblock copolymer PEO-*b*-PMMA-*b*-PS. For curve (a), the strong and broad band at 2880 cm<sup>-1</sup> is associated with the C-H vibrating peaks, the weak peak at 1730 cm<sup>-1</sup> is assigned to the carbonyl (-C=O) stretch group from the acetylation reaction. In curve (b), the band at 1730 cm<sup>-1</sup> with high relative intensity is attributed to the MMA block units, indicating the polymerization of MMA initiated by the PEO-Br. In curve (c), the bands at 3100 – 3000, 1602 and 700 cm<sup>-1</sup> indicates the presence of styrene units in the PEO-*b*-PMMA-*b*-PS triblock copolymer after the polymerization of styrene.



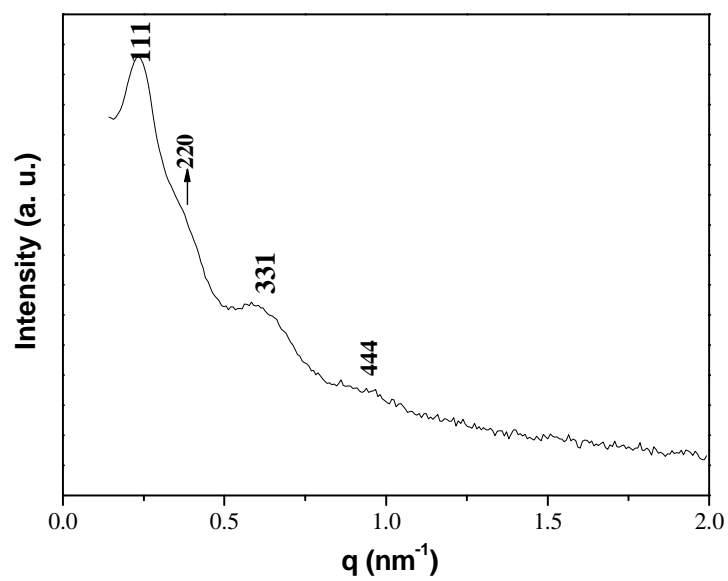
**Figure S2.**  $^1\text{H}$  NMR spectra of PEO-*b*-PMMA diblock copolymer (A) and triblock copolymer PEO-*b*-PMMA-*b*-PS (B). The signal (a) at 3.63 ppm is assigned to  $-\text{CH}_2-\text{CH}_2-$  in PEO block. The signals (b, c and d) at 3.59, 1.88 – 1.96, 0.85 – 1.05 ppm, respectively, are ascribed to  $-\text{OCH}_3$ ,  $-\text{CH}_2-$ ,  $-\text{CH}_3$  in the repeated MMA unit. Signals (e, f) at 6.57 – 7.13, 1.50 – 1.61 ppm are indexed to benzene ring and  $-\text{CH}_2-$  in PS units.



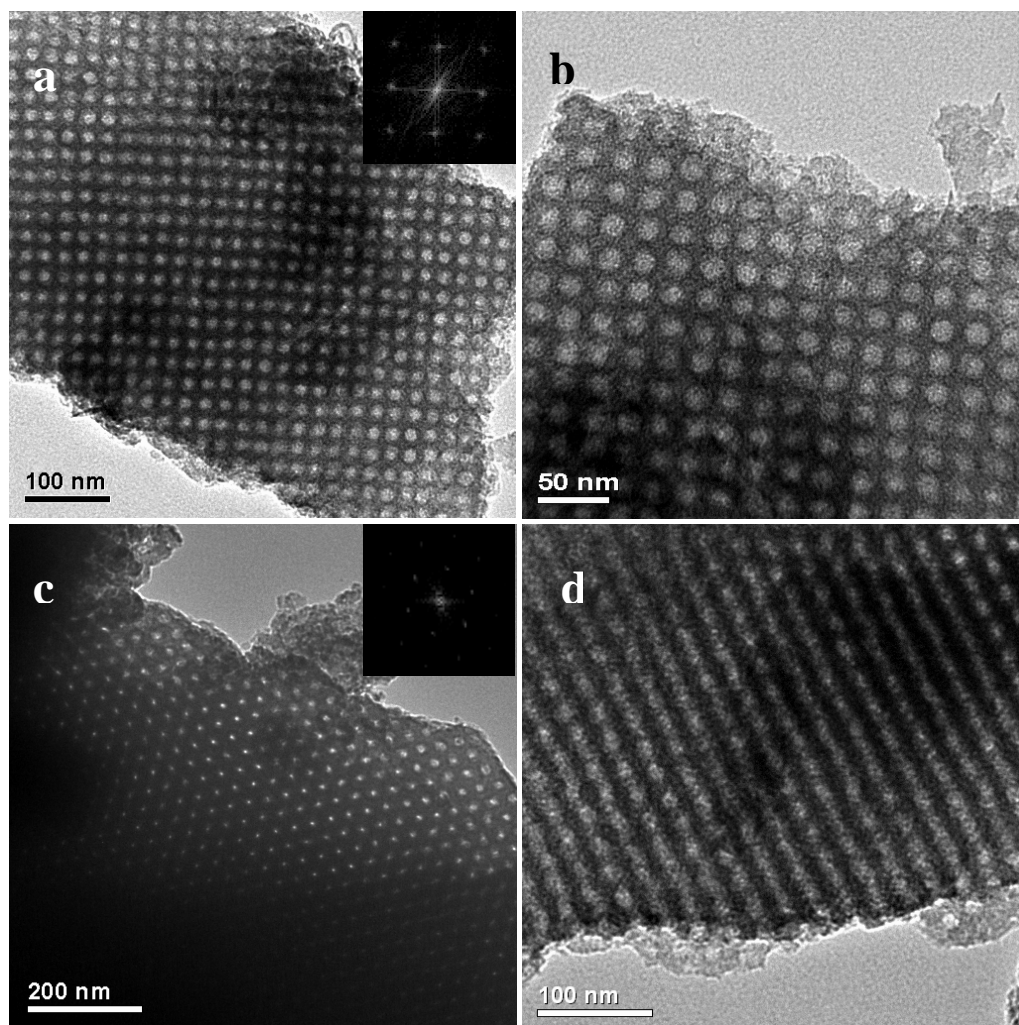
**Figure S3.** GPC traces of (a) PEO-*b*-PMMA diblock copolymer and (b) PEO-*b*-PMMA-*b*-PS triblock copolymer using THF as the eluent.



**Figure S4.** TGA/DTG curves (A, B) of the PEO-*b*-PMMA-*b*-PS triblock polymer conducted in N<sub>2</sub>, suggesting that triblock copolymer can be fully decomposed in N<sub>2</sub> at ~ 430 °C, and TGA/DTG curves (C, D) of the PEO-*b*-PMMA-*b*-PS/resols composites (as-made FDU-18-8) conducted in N<sub>2</sub>, indicating that the EO unit can be decomposed at ~ 200 °C and most of the polymer templates can be decomposed at ~ 400 °C in N<sub>2</sub>.

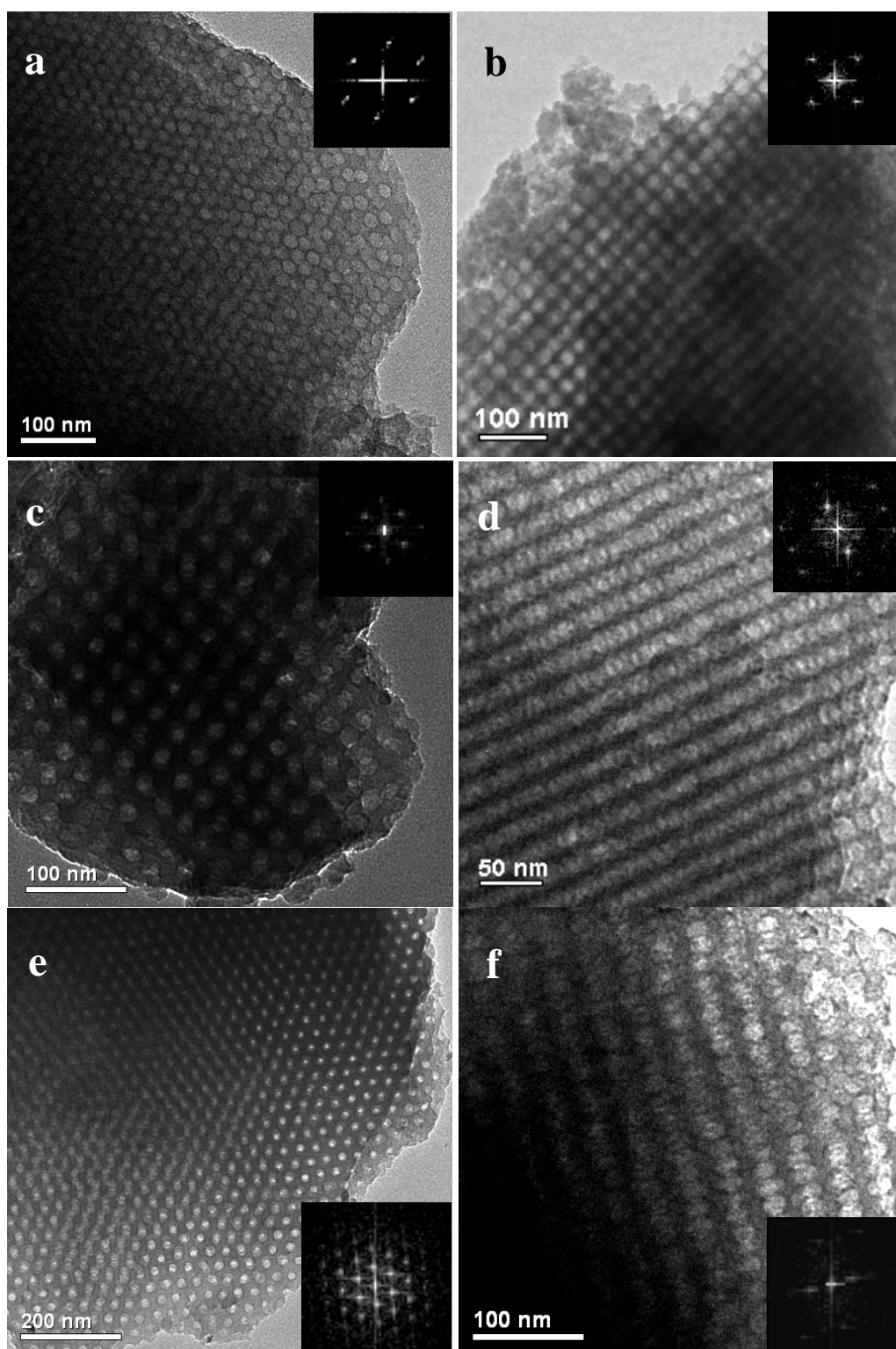


**Figure S5.** The SAXS pattern of the mesoporous carbon FDU-18-8-1200 sample obtained by further pyrolyzing FDU-18-8-800 sample at 1200 °C in N<sub>2</sub>.

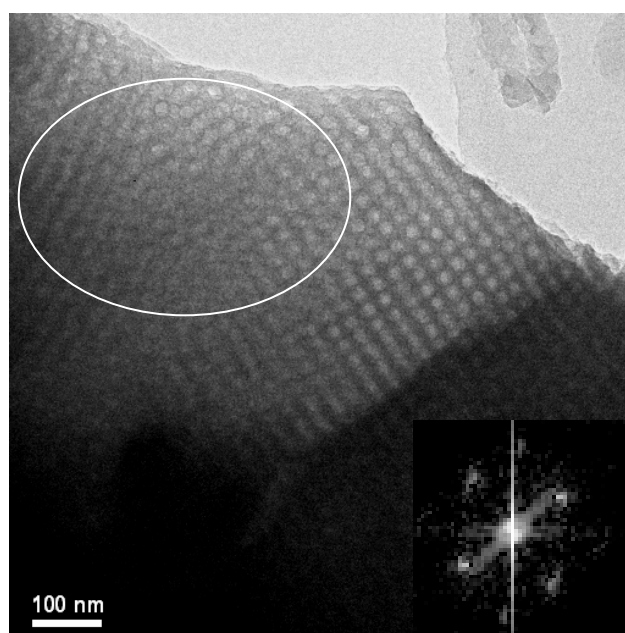


**Figure S6.** TEM images of the mesoporous carbon FDU-18-8-1200 pyrolyzed at 1200 °C in N<sub>2</sub> viewed from (a, b) [100], (c) [110], and (d) [211] directions, respectively. Insets are corresponding FFT diffractograms.

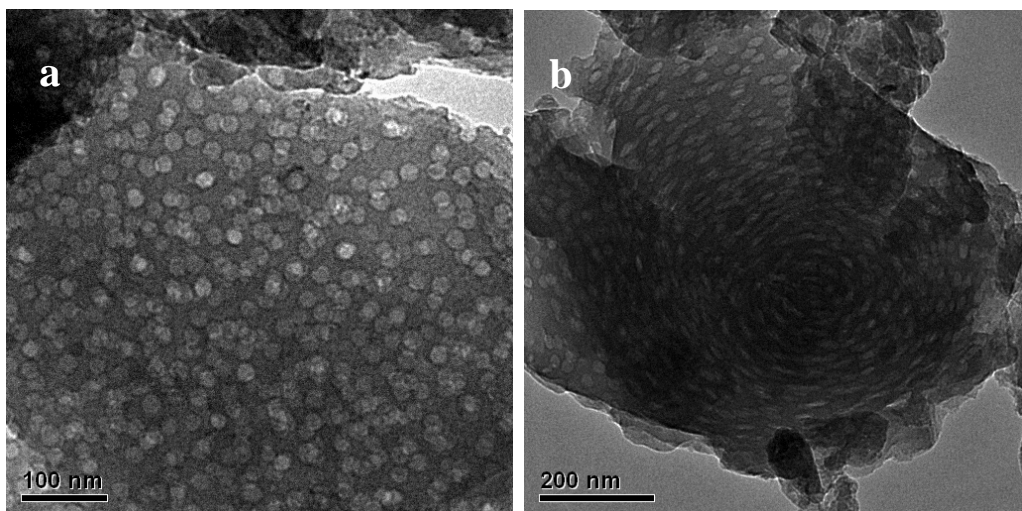




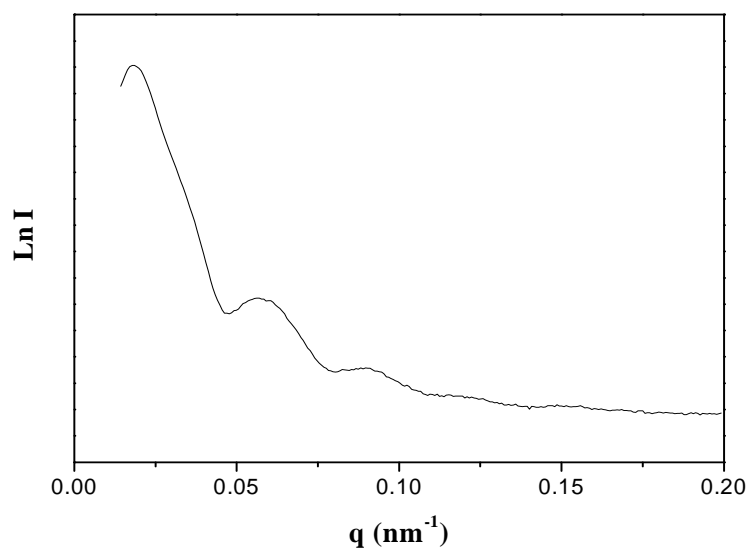
**Figure S7.** TEM images of mesoporous carbon with different resols/PEO-PMMA-PS ratio after pyrolyzed at 800 °C in N<sub>2</sub>. (a, b) FDU-18-6-800 viewed from the (a) [110] and (b) [100] directions; (c, d) FDU-18-10-800 viewed from (c) [100] and (d) [211] directions, and (e, f) of FDU-18-14-800 viewed from the (e) [110] and (f) [211] directions. Insets are corresponding FFT diffractograms.



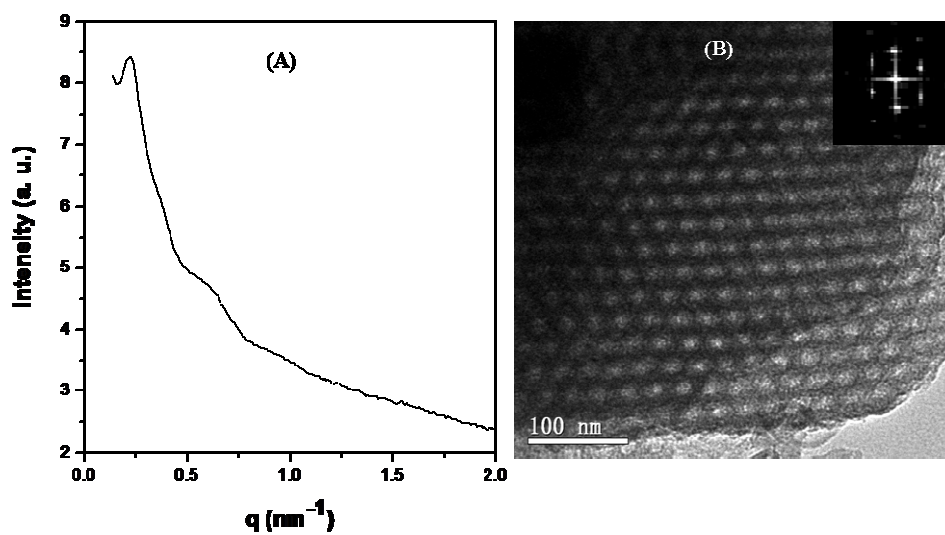
**Figure S8.** The TEM image of mesoporous carbon FDU-18-14-800 templated by the ABC-type triblock copolymer  $\text{PEO}_{125}\text{-}b\text{-PMMA}_{100}\text{-}b\text{-PS}_{138}$  after pyrolyzed at 800 °C in  $\text{N}_2$ . The image was taken along the [110] direction, in which some domain with defects can be visible. Insets are corresponding FFT diffractograms.



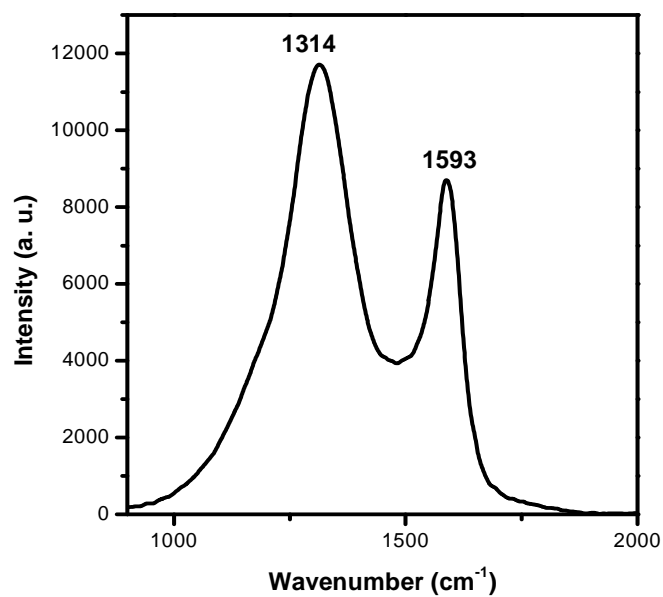
**Figure S9.** TEM images of mesoporous carbon FDU-18-16-800 sample prepared with a high resol/PEO-PMMA-PS ratio of 16 after pyrolyzed at 800 °C in N<sub>2</sub>, showing disordered mesostructure.



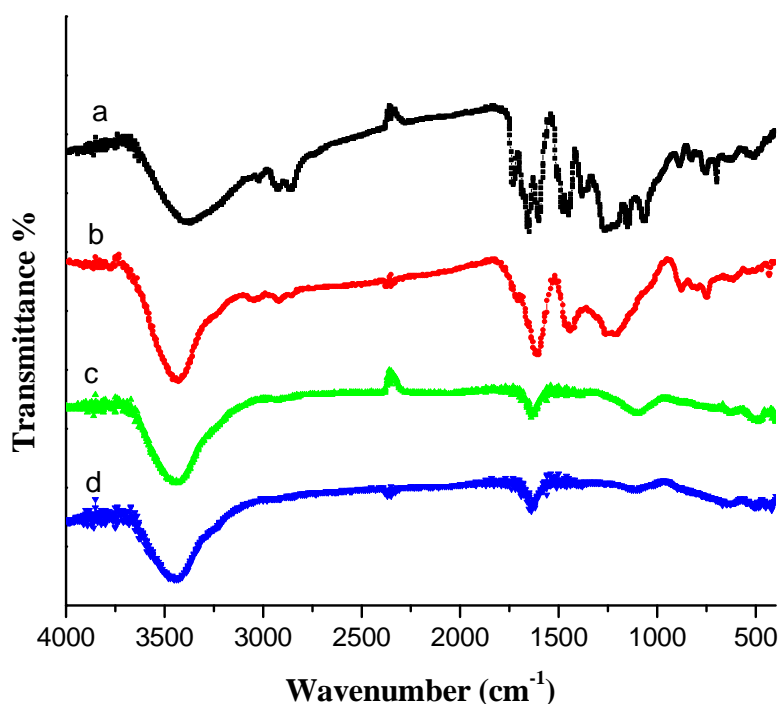
**Figure S10.** The SAXS pattern of the mesoporous carbon FDU-18-16-800 obtained with a high resol/PEO-PMMA-PS weight ratio of 16 after pyrolysis at 800 °C in N<sub>2</sub>.



**Figure S11.** The SAXS pattern (A) and TEM image (B) of the mesoporous carbon FDU-18-8-1200 product after treatment in KOH solution (4.2 M) at 140 °C for 20 h. Insets are corresponding FFT diffractograms.



**Figure S12.** The Raman spectrum of the ordered mesoporous carbon FDU-18-8-800 templated by ABC-type triblock copolymer PEO<sub>125</sub>-*b*-PMMA<sub>100</sub>-*b*-PS<sub>138</sub> after pyrolysis at 800 °C in N<sub>2</sub>.



**Figure S13.** FT-IR spectra of (a) as-made FDU-18-8, (b) FDU-18-8-450, (c) FDU-18-8-800 and (d) FDU-18-8-1200. In curve (a), the strong and broad band at 3400 cm<sup>-1</sup> is associated with the phenolic –OH groups, and the bands at 1100, 1730 and 2800 cm<sup>-1</sup> are assigned to PEO-*b*-PMMA-*b*-PS. In curve (b), the disappearance of peaks at 1109, 1730 and 2850 – 2930 cm<sup>-1</sup> associated with PEO, PMMA and PS blocks, respectively, suggesting the removal of PEO-*b*-PMMA-*b*-PS template by pyrolysis in N<sub>2</sub>. In curve (c, d), almost no C-H adsorption was observed, suggesting almost complete removal of H and O by pyrolysis at the high temperature.