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

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In this paper, we demonstrate a successful synthesis of highly ordered mesoporous carbons with large pores and tunable pore walls by using a home-designed ABC amphiphilic triblock copolymer poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-polystyrene (PEO-*b*-PMMA-*b*-PS) with gradient hydrophilicity as a template and resol as a carbon source via the solvent evaporation induced self-assembly (EISA) strategy. SAXS, TEM, HRSEM, and N_2 sorption characterizations show that the obtained carbon products possess ordered face-centered cubic (fcc) close-packed ($Fm\overline{3}m$) mesostructure with large pores of about 20.0 nm. By simply adjusting the resol/template ratios, the wall thickness of products can easily be tuned in the range of 10−19 nm. For the first time, we observed numerous large micro/mesopores in the carbon pore walls, originating from the removal of PMMA segment during the pyrolysis. The obtained mesoporous carbons have an extra-large lattice constant of up to 55.0 nm, high surface areas of ~ 900 m^2/g, and pore volume of ~ 0.6 cm^3/g, as well as high stability even in concentrated KOH solution. The gradient hydrophilicity of the ABC triblock copolymer template facilitates the continuous invasion of resol precursor molecules along the PEO to PMMA segments of the spherical PEO-PMMA-PS micelles, tuning the pore wall thickness. The rationally designed ABC-type triblock copolymers make it possible to synthesize ordered mesoporous carbons with ultrathick pore walls as well as excellent chemical and thermal stability.

1. Introduction

In recent years, ordered mesoporous carbon materials have attracted increasing attention for their unique properties, including high specific surface areas, large pore volume, high thermal and mechanical stability, and chemical inertness. They have great potential for applications in various fields, such as adsorption and separation, catalysis, electrochemistry, and sensorics.[1−7] An approach based on the organic−organic assembly between poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymers and thermopolymerizable phenolic formaldehyde resin precursors (resols) was developed for the direct templating-synthesis of ordered mesoporous carbons with various pore structures.[8−14] This innovative method is relatively simple, reproducible, cost-efficient, and very suitable for mass production of mesoporous carbons with narrow pore-size distribution, and thus greatly surpasses

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the laborious and costly hard-templating approach.[15−23] The key feature is the formation of highly ordered organic−organic mesostructured composites consisting of thermosetting resin precursors and thermally decomposable PEO-PPO-PEO templates via a solution synthesis or solvent evaporation induced self-assembly (EISA) process. However, PEO-PPO-PEO templates usually lead to ordered mesoporous carbons with pore size smaller than 4.0 nm and wall thickness less than 7.0 nm because of the limitation of the chain length of the hydrophilic PEO and hydrophobic PPO segments. From the viewpoint of material synthesis and applications, the effective tuning of the pore parameters of ordered mesoporous carbons, such as pore size, pore wall thickness and pore symmetries is of great interest.[24,25] Because the pore structures of the mesoporous materials are predominantly determined by the parameters of the amphiphilic surfactant templates, including the total molecular weight of block copolymers, hydrophilicity/hydrophobicity ratio and volume fractions of each segment, rationally designing new block copolymers holds great promise in templating synthesis of diverse ordered mesoporous materials with tunable porosities.

Recently, we have used poly(ethylene oxide)-*block*-polystyrene (PEO_{125}-*b*-PS_{230}) diblock copolymer to template ordered mesoporous carbons with ultralarge pore size (∼22 nm) via the EISA approach.[26] Such a large pore size is attributed to the long length of the hydrophobic PS blocks. Similarly, by employing poly(ethylene oxide)-*block*-poly(methyl methacrylate) (PEO_{125}-*b*-PMMA_{144}) as a template, we have synthesized ordered mesoporous carbon with large pores (∼ 10.5 nm) and a very thick walls (∼ 12 nm).[27] The long PMMA segment not only provides the hydrophobicity for the generation of mesopores, but also partially interacts with the resol precursor molecules, resulting in the thick pore walls. The above-mentioned templates are exclusively two-component AB or ABA type block copolymers. Self-assembly of block copolymers is usually governed by three parameters including composition, interfacial tension, and sequencing.[28,29] For two-component block copolymers, there is one composition variable ($f_A = 1 - f_B$), one segment−segment interaction (SSI) parameter (χ_{AB}), and one (for AB) or two sequences (for ABA type). Differently, ABC-type triblock copolymers have two independent composition variables, three SSI parameters (χ_{ij}), and three distinct sequences, resulting in a much richer mesophase behavior. For example, the attractive rhombohedral mesophase (space group $R3\bar{c}$) with a bicontinuous network structure is rarely observed in AB or ABA block copolymers, but is easily achieved in a large domains for ABC triblock copolymers.[30] Therefore, compared with AB or ABA block copolymers, amphiphilic ABC triblock copolymers are more adaptive candidates as the templates for the creation of novel mesoporous materials with designable structures, compositions, and tunable pore/wall parameters. To the best of our knowledge, no work has been reported for the synthesis of ordered mesoporous carbons with adjustable pore parameters by using such templates.

We thus designed an amphiphilic ABC triblock copolymer poly(ethylene oxide)-*block*-poly(methyl methacrylate)-*block*-polystyrene (PEO_{125}-*b*-PMMA_{100}-*b*-PS_{138}) with gradient hydrophilicity prepared by the simple method of atom transfer radical polymerization (ATRP).[27] By using this ABC-type triblock copolymer as a template, we have successfully synthesized highly ordered mesoporous carbons with large pores (up to 20 nm) via an EISA method using tetrahydrofuran as the solvent. The obtained carbon products possess ordered face-centered cubic (fcc) close-packed ($Fm\bar{3}m$) mesostructure with superlarge lattice constant of up to 55.0 nm. By simply adjusting the resol/template ratios, the carbon wall thickness can easily be tuned in the range of 10−19 nm. A multitude of large micro/mesopores (around 2 nm) in the carbon walls is, for the first time, clearly observed by HRSEM images.

2. Experimental Section

2.1. Chemicals. Monomethoxy poly(ethylene oxide) (monomethoxy PEO5000), 2-bromoisobutyryl bromide and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) were purchased from Acros Corp. Tetrahydrofuran (THF), pyridine, styrene, ethylether, CuBr, petroleum ether (60−90 °C), phenol, formalin solution (37 wt %), NaOH, and HCl were purchased from Shanghai Chemical Corp. Methyl methacrylate (MMA) and styrene (St) were purified by filtrating through an $\mathrm{Al_2O_3}$ column. All other chemicals were used as received. Deionized water was used for all experiments. The resol precursors with low molecular weight ($M_w < 500$) were prepared according to a procedure reported previously.[9]

2.2. Preparation of PEO-*b*-PMMA-*b*-PS Triblock Copolymer. The amphiphilic PEO-*b*-PMMA-*b*-PS triblock copolymers were prepared through a simple ATRP method by sequential polymerization of methyl methacrylate (MMA) and styrene (St)

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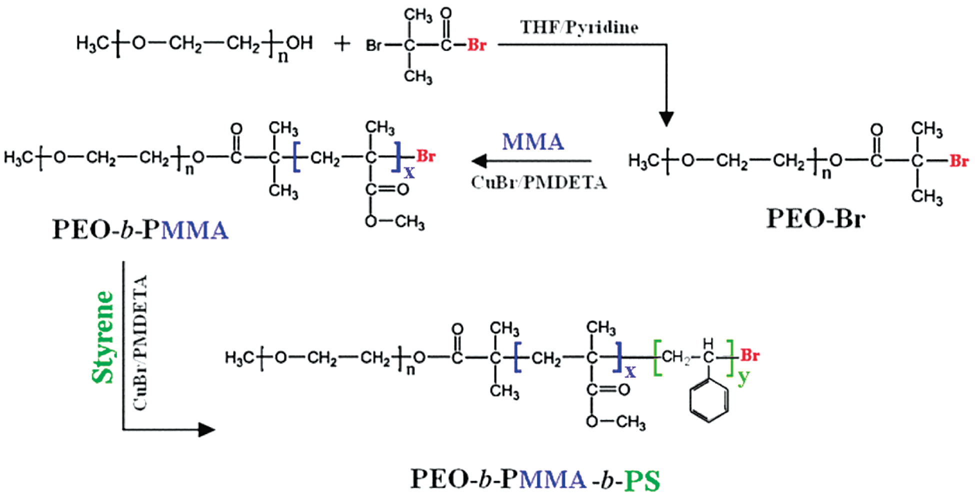

Figure 1. Synthetic route for the ABC type amphiphilic triblock copolymer PEO-*b*-PMMA-*b*-PS via ATRP technique.

using PEO-Br as an initiator, similar to the procedure reported previously.[27] The obtained PEO-*b*-PMMA-*b*-PS triblock copolymers have an average molecular weight of ~ 30 000 g/mol and a polydispersity index (PDI) of 1.198. Experimental details are described in the Supporting Information.

2.3. Synthesis of Mesoporous Carbons. An EISA approach was employed to prepare mesoporous carbon by using the triblock copolymer PEO-*b*-PMMA-*b*-PS as a template, THF as a solvent, and the resol as a carbon precursor. For a typical synthesis, PEO-*b*-PMMA-*b*-PS (0.05 g, 1.67×10^{-3} mmol) and resol (0.40 g, 0.80 mmol) were dissolved in THF (5.0 mL) with magnetic stirring. The obtained homogeneous solution was poured onto Petri dishes to evaporate the solvent at room temperature for 12 h, followed by heating in an oven at 100 °C for 24 h to cure the resol into phenolic formaldehyde (PF) resins. The as-made PEO-*b*-PMMA-*b*-PS/PF composite product was scraped and crushed into powders for pyrolysis under N_2 at different temperatures. Pyrolysis was carried out in a tubular furnace under N_2 at different temperature (450−1200 °C) for 3 h. The heating rate was 1 °C/min below 450 and 5 °C/min above 450 °C. The obtained samples were designated as FDU-18-X-Y, where X and Y refer to the weight ratio of the resol/template and pyrolysis temperature, respectively.

2.4. Characterization and Measurements. Thermogravimetric (TG) analysis was carried out using a Mettler Toledo TGA-SDTA851 analyzer (Switzerland) from 25 to 700 °C under nitrogen with a heating rate of 5 °C/min. Small angle X-ray scattering (SAXS) measurements were taken on a Nanostar U small-angle X-ray scattering system (Bruker, Germany) using Cu Kα radiation (40 kV, 35 mA). The *d*-spacing values were calculated by the formula d500 $= 2\pi/q$. The wall thickness was calculated from the formula[31] $W_t = \sqrt{2}a/2 - D$, where a represents the cell parameter and D is the pore diameter calculated from the N_2 sorption measurement. Transmission electron microscopy (TEM) experiments were conducted on a JEOL 2011 microscope (Japan) operated at 200 kV. High-resolution scanning electron microscopy (HRSEM) images were taken using a field emission Hitachi S-5500 (Japan) operated at 30 kV. Nitrogen sorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 analyzer (USA). Before measurements, the samples were degassed in a vacuum at 200 °C for at least 6 h. The Brunauer−Emmett−Teller (BET) method was utilized to calculate the specific surface areas. By using the Broekoff−de Boer (BdB) sphere model,[32] the pore volumes and pore size distributions were calculated from the adsorption branches of isotherms, and the total pore volumes (V_t) were estimated from the adsorbed amount at a relative pressure P/P_0 of 0.992. The micropore surface areas (S_m) were calculated from the $V-t$ plot method using the equation, $V_m/\text{cm}^3) = 0.001547I$, where I represents the y intercept in the $V-t$ plots. The t values were calculated as a function of the relative pressure using the de Bore equation, $t/\text{Å} = [13.99/(\log(P_0/P) + 0.0340)]^{1/2}$. Raman spectra were obtained with a Dilor LabRam-1B microscopic Raman spectrometer (France), using a He−Ne laser with an excitation wavelength of 632.8 nm. The C, H, and O contents were measured on a Vario EL III elemental analyzer (Germany).

3. Results and Discussion

3.1. The ABC Triblock Copolymer Template. The triblock copolymer PEO-*b*-PMMA-*b*-PS with high molecular weight (~30 000 g/mol) can easily be prepared via a simple ATRP method. The preparation mainly involves three steps, i.e., the synthesis of the macromolecular initiator PEO-Br via the reaction of monomethoxy PEO5000 with 2-bromoisobutyryl bromide and sequential polymerization of methyl methacrylate and styrene monomers (Figure 1). The detailed preparation procedure is shown in the Supporting Information. The chemical structures and compositions of PEO-Br, PEO-*b*-PMMA diblock copolymer and PEO-*b*-PMMA-*b*-PS triblock copolymer were confirmed by Fourier transform infrared spectra (FT-IR) (Figure S1 in the Supporting Information) and ^{1}HNMR spectroscopy (Figure S2 in the Supporting Information). The signals (a, b, c, and d) for the PEO-*b*-PMMA at 3.63, 3.59, 1.88−1.96, 0.85−1.05 ppm, respectively, are ascribed to $-CH_2-CH_2-$, $-OCH_3$, $-CH_2-$, and $-CH_3$ in the repeated EO and MMA units, respectively (Figure S2A in the Supporting Information). The new signals at 1.50−1.61 and 6.57−7.13 ppm for the triblock copolymer PEO-*b*-PMMA-*b*-PS are assigned to the styrene unit (Figure S2B). The molecular weight of PEO-Br and PEO-*b*-PMMA diblock copolymer and

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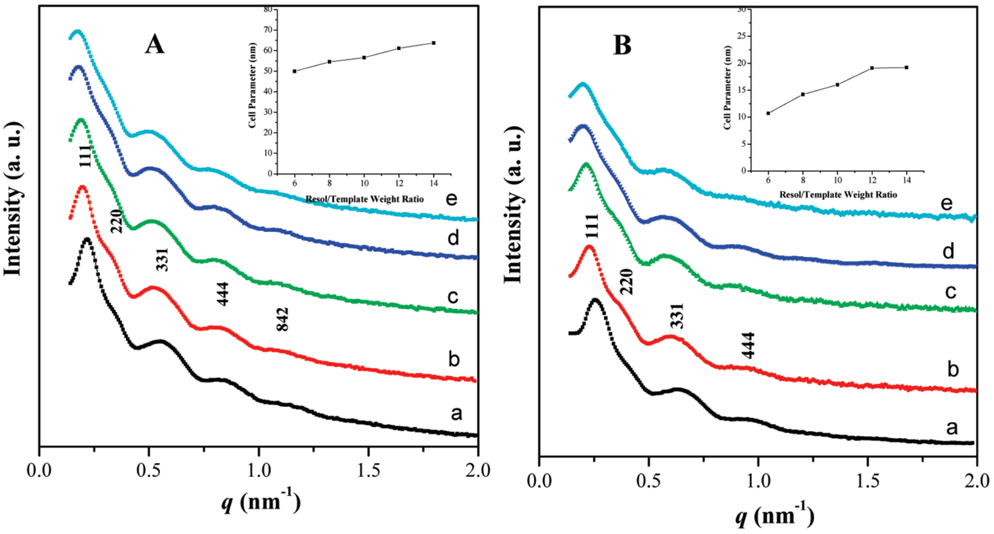

Figure 2. SAXS patterns of the ordered mesoporous carbonaceous samples (A) FDU-18-X-450 and (B) FDU-18-X-800 obtained with different resol/PEO-PMMA-PS ratios after pyrolysis at 450 and 800 °C: (a) FDU-18-6, (b) 12. FDU-18-8, (c) FDU-18-10, (d) FDU-18-12, and (e) FDU-18-14. The insets in A and B show the dependence of the cell parameter (*a*) on the resol/template ratio for FDU-18-X-450 and FDU-18-X-800, respectively.

Table 1. Textural Properties of the Ordered Mesoporous Carbonaceous Materials Templated by ABC Triblock Copolymer PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138} with Different Resol/Template Ratio after Pyrolysis at Different Temperatures (450, 800, 1200 °C)[a]

sample		*d* (nm)	a_0 (nm)	*D* (nm)	*W*t (nm)	S_{BET} (m^2/g)	V_t (cm^3/g)	V_M (cm^3/g)	S_b (m^2/g)
FDU-18-6-	450	28.8	49.9	23.4	11.9	548	0.38	0.18	387
	800	24.6	42.7	19.4	10.7	977	0.60	0.38	830
	1200	24.5	42.5	18.2	11.9	1270	0.79	0.39	868
FDU-18-8-	450	31.5	54.5	23.7	14.9	524	0.35	0.17	387
	800	27.6	47.8	19.6	14.2	808	0.53	0.31	682
	1200	26.5	46.0	19.0	13.7	1260	0.86	0.45	885
FDU-18-10-	450	32.7	56.6	23.0	17.0	520	0.33	0.14	350
	800	29.4	51.0	20.0	16.0	744	0.45	0.30	643
	1200	29.4	51.0	19.1	16.9	1240	0.81	0.43	812
FDU-18-12-	450	35.3	61.1	23.2	20.0	513	0.31	0.15	346
	800	31.6	54.6	19.5	19.1	722	0.40	0.28	618
	1200	30.6	52.8	19.7	17.6	1383	0.75	0.36	814
FDU-18-14-	450	36.8	63.7	23.5	21.5	464	0.28	0.13	329
	800	31.9	55.2	19.8	19.2	691	0.37	0.28	578

[a] The *d*-spacing values were calculated by the formula $d = 2\pi/q$, and the unit-cell parameters were calculated from the formula $a_0 = d_{111}*\sqrt{3}$. The wall thickness values were calculated from $W_t = \sqrt{2}a/2 - D$, where *a* represents the cell parameter and *D* is the pore diameter.[32] S_{BET} and S_M are the total BET surface area and micropore surface area calculated from the *t*-plots, respectively. V_t and V_M are the total pore volume and micropore volume, respectively.

PEO-*b*-PMMA-*b*-PS calculated from ^{1}H NMR data are about 5700, 15 700, and 30 000 g/mol, respectively, and therefore, the composition of the obtained ABC triblock copolymer can be approximately formulated as PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138}. Gel-permeation chromatography (GPC) shows a polydispersity index (PDI) of 1.098 and 1.198 for the PEO-*b*-PMMA diblock copolymer and the PEO-*b*-PMMA-*b*-PS triblock copolymer (Figure S3 in the Supporting Information), respectively, indicating narrow molecular-weight distributions. The TG analysis of the PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138} triblock copolymer shows a weight loss of about 97 wt % in the temperature range of 310−450 °C under N_2, implying that it can be removed by pyrolysis in N_2 (Figure S4A, B in the Supporting Information).

3.2. SAXS Patterns. The SAXS pattern of the mesoporous carbonaceous material (FDU-18-8-450) templated by the ABC-type triblock copolymer with a low resol/PEO-PMMA-PS ratio (0.8) after pyrolysis at 450 °C in a N_2 atmosphere shows five well-resolved scattering peaks at *q*-values of 0.199, 0.354, 0.550, 0.874, and 1.14 nm^{-1} (Figure 2Ab), which can be indexed to the 111, 220, 331, 444, and 842 reflections of a face-centered cubic (fcc) mesostructure with the space group $Fm\bar{3}m$. The cell parameter (*a*) is calculated to be 54.5 nm (Table 1), indicating an ultralarge unit. Highly ordered cubic fcc mesoporous carbonaceous structures can be obtained in a broad range of resol/PEO-PMMA-PS ratio (X = 6−14). Similar to the sample FDU-18-8-450, all of the obtained mesoporous carbonaceous samples FDU-18-X-450 (X = 6−14) show well-resolved SAXS patterns, suggesting ordered cubic fcc mesostructures (Figure 2A, a−e). With the increase in the resol/PEO-PMMA-PS ratio, the scattering peaks shift to lower *q*-value vectors, clearly indicating the increase of the mesostructure cells. Calculations based on the SAXS patterns show that the unit-cell parameter of the resultant FDU-18-X-450 samples increases from 49.9 to 63.7 nm (Figure 2A, inset). These results clearly indicate that the mesostructure unit templated from the ABC-type triblock copolymer can be

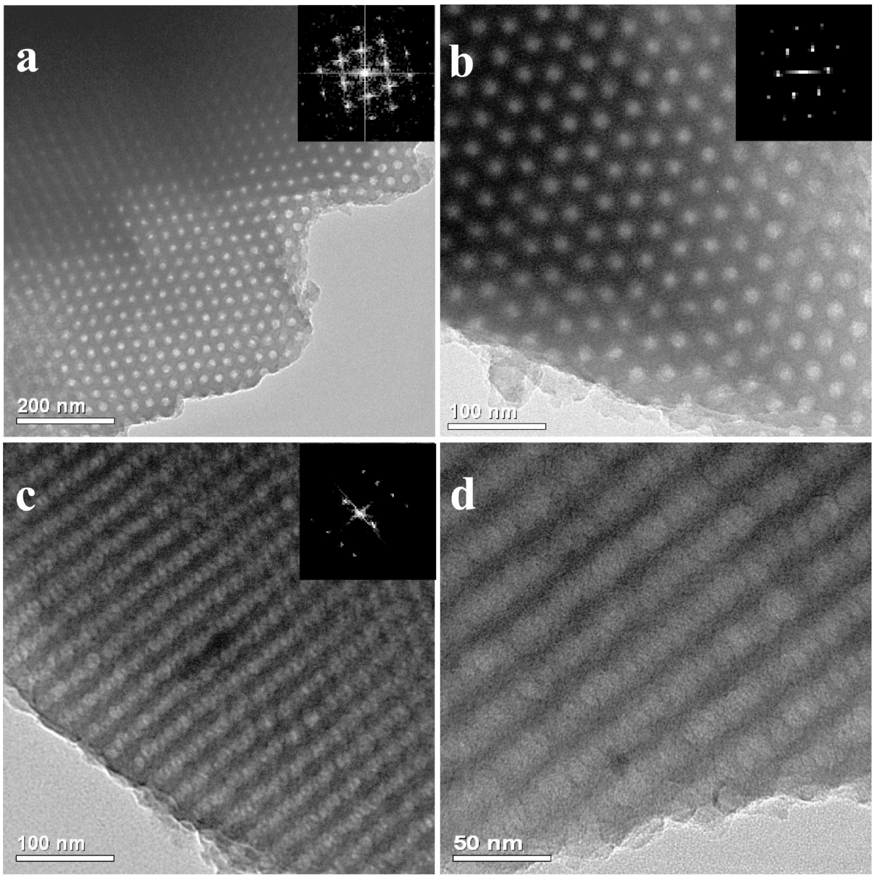

Figure 3. TEM images of the ordered mesoporous carbon FDU-18-8-800 templated by ABC-type amphiphilic triblock copolymer PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138} after pyrolysis at 800 °C in N_2 viewed from the (a) [100], (b) [110], and (c, d) [211] direction.

continuously tuned by simply adjusting the precursor/template weight ratio.

After further pyrolysis at 800 °C in N_2, all of the obtained FDU-18-X-800 samples with different resol/PEO-PMMA-PS ratios show four well-resolved scattering peaks in the SAXS patterns which can also be assigned to the cubic fcc mesostructure ($Fm\bar{3}m$) (Figure 2B), indicating good thermal stability. Compared with those after pyrolysis at 450 °C, the SAXS patterns of FDU-18-X-800 show broader peaks, which are shifted to higher q-value vectors, suggesting that the ordered mesostructure degenerates and further shrinks. On the basis of the calculation of cell parameters, the mesostructure shrinkage is small, in the range of 9.90−14.4%, implying that a rigid carbon framework is formed after pyrolysis at 800 °C. Similarly, with the increase in the resol/PEO-PMMA-PS ratio, the cell parameters (a) of the FDU-18-X-800 samples (X = 6−14) increase linearly up to 55.2 nm (Figure 2B, inset), suggesting a generation of an ultralarge mesoporous carbon structure. The corresponding structure shrinkage decreases as the resol/template ratio increases, implying an increase of the structural stability.

After further pyrolysis at even higher temperature of 1200 °C, the SAXS patterns of the samples FDU-18-X-1200 (X = 6−14) lose resolution, suggesting a further degeneration of the mesostructures. Despite of it, four scattering peaks are still resolved (Figure S5 in the Supporting Information), clearly indicating that the ordered cubic fcc mesostructures are retained. For example the FDU-18-8-1200 sample, synthesized with a low resol/PEO-PMMA-PS ratio of 8, only shows a further structural shrinkage of 3.7%, and the cell parameter remains as high as ∼46.0 nm after pyrolysis at the high temperature of 1200 °C. These results further suggest that the cubic carbon mesostructure is highly thermally stable.

3.3. TEM Images.

TEM images and corresponding Fourier diffractograms further confirm that the mesoporous carbonaceous materials have highly ordered fcc cubic mesostructure with ultralarge unit cells. As shown in Figure 3, the mesoporous carbon FDU-18-8-800 pyrolyzed at 800 °C shows a high degree of periodicity over large domains, viewed from the [100], [110], and [211] directions. It confirms that the carbon mesostructure templated by the ABC-type triblock copolymer has a highly ordered cubic (fcc) symmetry ($Fm\bar{3}m$). The uniform spherical large mesopores are clearly visible in the images, indicative of the spherical packing from monodispersed PEO-PMMA-PS globular micelles during the EISA process. The cell parameter of FDU-18-8-800 is estimated to be about 48.0 nm, consistent with that from the SAXS pattern.

TEM images reveal that the ordered cubic fcc mesostructure is well-retained for the carbon product after pyrolysis at 1200 °C (Figure S6 in the Supporting Information), further confirming the high thermal stability.

The TEM images of the FDU-18-6-800 sample obtained with lower resol/PEO-PMMA-PS (X = 6) ratio also show a high degree of periodicity over large domains, viewed from the [110] or [100] directions of an fcc ordered mesostructure (Figure S7a, b in the Supporting Information). Although the images show some small white spots around the primary mesopores, it could not be confirmed that they are caused by micropores. Compared with FDU-18-8-800, the pore walls, as evaluated from the TEM images, seem to be a little thinner. The cell parameter is approximately 42.5 nm, agreeing well with the value from the SAXS pattern.

Similarly, TEM images show that the FDU-18-X-800 (X = 10−14) samples obtained with higher resol/PEO-PMMA-PS ratios have large-domain regularity assigned to the ordered cubic fcc mesostructures (Figure S7 in the Supporting Information), and large cell parameters. The cell parameter measured from the TEM images increases with the increase of resol/PEO-PMMA-PS ratios. However, some structure defects can also be observed in some domains for the FDU-18-14-800 sample (Figure S8 in the Supporting Information), suggesting a degeneration of the mesostructure. Our TEM measurements show that the fraction of the defect domains increases with the resol/PEO-PMMA-PS ratio. When the resol/PEO-PMMA-PS ratio increases to 16, only a disordered mesostructure but with uniform spherical pores is observed (Figure S9 in the Supporting Information), suggesting a random packing of the ABC block copolymer micelles. The SAXS measurement also shows the low ordering of the mesostructure synthesized at a resol/PEO-PMMA-PS weight ratio of 16 (Figure S10 in the Supporting Information). These results indicate that the PEO-PMMA-PS templates easily form globular micelles, strongly dependent on the hydrophobic segment.

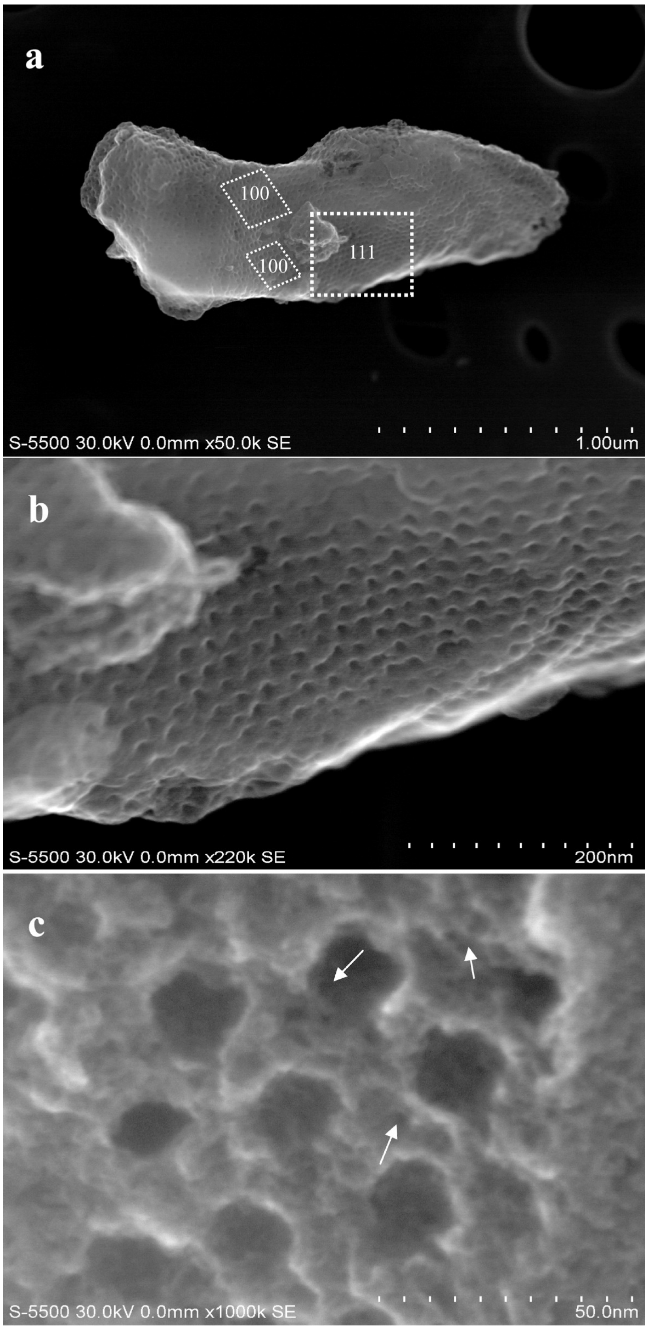

Figure 4. High-resolution SEM images of the mesoporous carbon FDU-18-8-1200 templated by ABC-type triblock copolymer PEO_{125}-$PMMA_{100}$-PS_{138} after pyrolysis at 1200 °C in N_2 with magnification of (a) × 50 K, (b) × 220 K, and (c) × 1000 K. The boxed areas in the part (a) show the (100) and (111) planes of the fcc mesostructure, and the arrows in the part (c) mark the mesopore voids in the carbon walls.

3.4. N_2 Sorption Isotherms. All the FDU-18-X-450 (X = 6−14) samples show N_2 sorption isotherms (Figure 5 A) of typical type IV curves with a sharp capillary condensation step in the relative pressure range of 0.85−0.92. It indicates the uniform mesopores with ultralarge pore size. The huge H_2-type hysteresis loops with delayed capillary evaporation steps are observed at relative pressure of ca. 0.5, indicative of caged mesopores with a small entrance sizes (< 5.0 nm).[30] Similar to previous reports,[9−11] the adsorption and desorption branches of the FDU-18-X-450 samples are not completely closed at the region of low relative pressure, which is ascribed to the organic polymer feature of the frameworks.[33] According to the BdB sphere model, the FDU-18-X-450 (X = 614) samples possess similar mean pore sizes ranging from 23.0 − 23.7 nm (Figure 5B), clearly suggesting that it is highly dependent on the hydrophobic volume of the ABC copolymer template and not related to the ratio of the resol/PEO-PMMA-PS. The wall thickness of the obtained FDU-18-X-450 samples calculated from the N_2 sorption and SAXS results is very high in the range from 11.9 to 21.5 nm, and increases upon the increase in resol/template ratios (Table 1), clearly indicating that the resol precursors are involved in the assembly and contribute the hydrophilic domain volumes. The BET surface areas are calculated to be 548−464 m^2/g and slightly decrease as the ratio increases (Table 1), related with the pore wall thickness. Meanwhile, the total pore volumes and the micropore pore volume decrease from 0.38 to 0.28 cm^3/g and from 0.18 to 0.13 cm^3/g, respectively, and the micropore surface area roughly

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(33) McKeown, N. B.; Budd, P. M.; Msayib, K. J.; Ghanem, B. S.; Kingston, H. J.; Tattershall, C. E.; Makhseed, S.; Reynolds, K. J.; Fritsch, D. *Chem.—Eur. J.* **2005**, *11*, 2610.

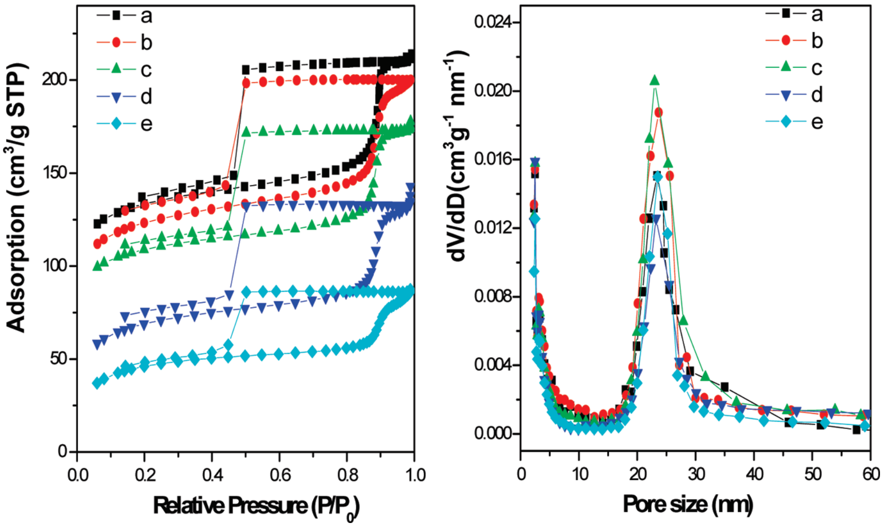


Figure 5. (A) N_2 adsorption/desorption isotherms and (B) pore size distribution curves of the mesoporous carbonaceous FDU-18-X-450 templated by the ABC-type triblock copolymer (PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138}) after pyrolysis at 450 °C in N_2. The resols/PEO-PMMA-PS ratio X = (a) 6, (b) 8, (c) 10, (d) 12, (e) 14. The N_2 adsorption/desorption isotherms of FDU-18-8-450, FDU-18-10-800, FDU-18-12-800, and FDU-18-14-800 are vertically offset by −10, −20, −50, and −70 cm^3/g, respectively. The pore distribution is calculated by the BdB sphere model.

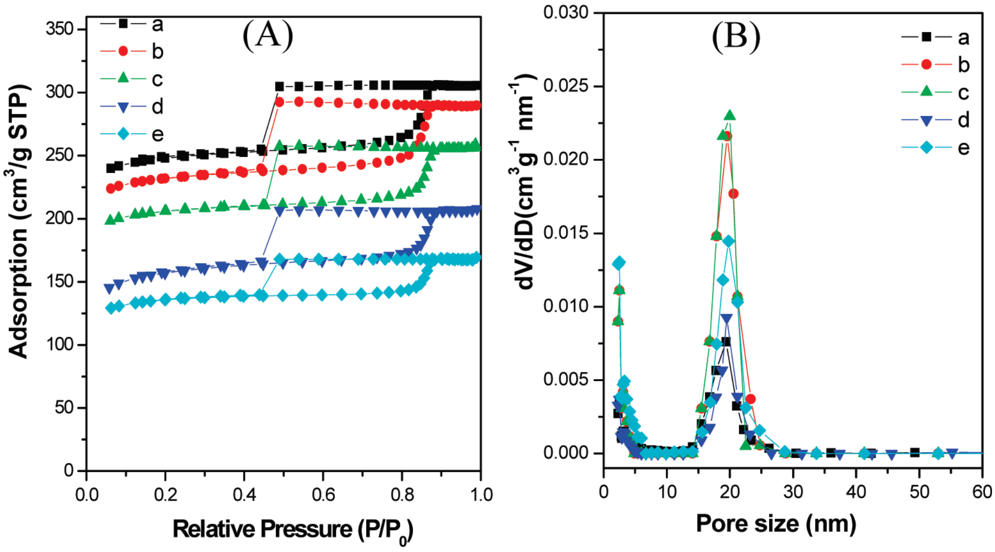


Figure 6. (A) N_2 adsorption/desorption isotherms and (B) pore size distribution curves of the mesoporous carbon FDU-18-X-800 templated by ABC-type triblock copolymer PEO-PMMA-PS after pyrolysis at 800 °C in N_2. The isotherms of FDU-18-10-800, FDU-18-12-800, and FDU-18-14-800 are vertically offset by −20, −50, −100 cm^3/g, respectively.

calculated from the *t*-plot curves also decreases from 387 to 319 m^2/g. These results suggest that the increase of the ratio can lead to a thick pore wall and reduce microporosity and surface area correspondingly. Notably, the samples FDU-18-X-450 also show a shoulder peak in the range of 10 and 15 nm (Figure 5B), implying the presence of the secondary pores. It may be related with the PMMA segment of the ABC-type triblock copolymer.

N_2 sorption isotherms of the mesoporous carbon FDU-18-X-800 samples obtained by further pyrolysis at 800 °C exhibit characteristic type IV curves with sharp capillary condensation at a relative pressure of 0.80−0.88, indicating that large and uniform spherical pores with small entrances are preserved (Figure 6A). The mean pore sizes (Figure 6B) with narrow distribution in the range of 19.4−20.0 nm are smaller than for samples pyrolyzed at 450 °C and not correlated with the ratio of the resol/ABC copolymers (Table 1). The pore wall thickness of FDU-18-X-800 samples are calculated to be in the range of 10.7−19.2 nm, less than that of the corresponding FDU-18-X-450 sample (Table 1), reflecting further structural shrinkages during high temperature pyrolysis. It should be noted that the thicknesses are much larger than those (9.9 nm) of the reported mesoporous carbon templated from diblock copolymer PEO_{125}-*b*-PS_{230} with identical PEO chain length. The result implies that the PMMA blocks in the PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138} triblock copolymer can interact with the resol precursors and contribute the carbonaceous pore walls. Meanwhile, the BET surface area significantly increases up to 977 m^2/g with the resol/PEO-PMMA-PS ratio (Table 1), much higher than that of the corresponding FDU-18-X-450 sample

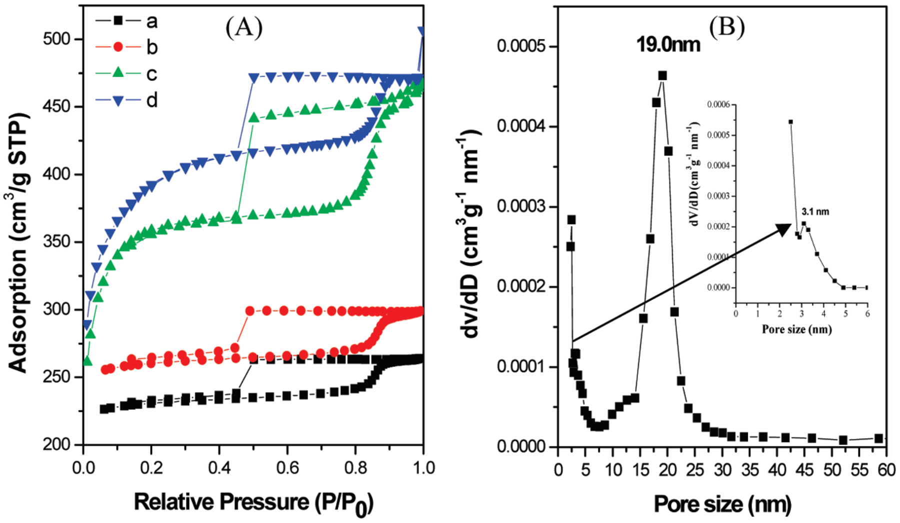


Figure 7. (A) N_2 adsorption/desorption isotherms of (a), FDU-18-8-1200, (b), FDU-18-10-1200, (c), FDU-18-6-1200, and (d), FDU-18-12-1200, samples pyrolyzed at 1200 °C for (a, b) 2 h and (c, d) 4 h in N_2, and (B) pore size distribution of the FDU-18-8-1200. The isotherms of FDU-18-8-1200 and FDU-18-10-1200 are vertically offset by 150 cm^3/g, respectively.

because of the continuous release of carbon, hydrogen, and oxygen species during pyrolysis. The *t*-plot calculations reveal that the micropore surface areas and pore volumes of the FDU-18-X-800 samples are much higher than those for the FDU-18-X-450 samples pyrolyzed at 450 °C, and decrease with the increase of the resol/PEO-PMMA-PS ratio (Table 1). It suggests that the high-temperature pyrolysis mainly brings about micropores, and thin pore walls favor the generation of microporosity.

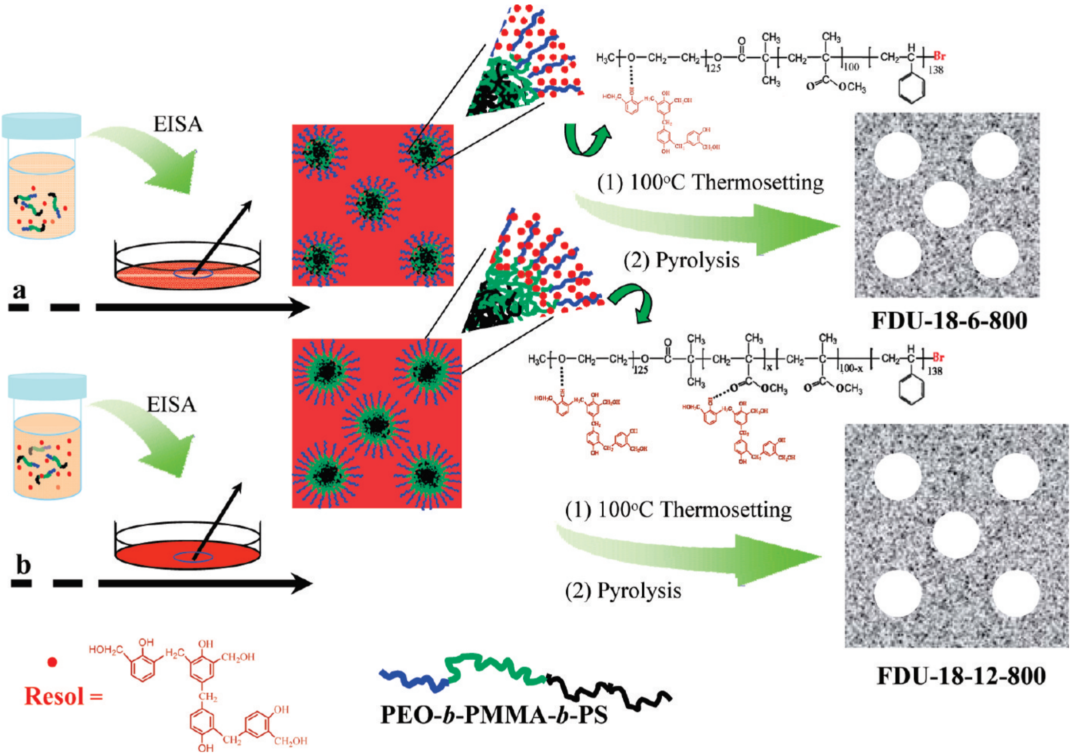
N_2 sorption isotherms of the FDU-18-8-1200 samples after further pyrolysis at high temperature of 1200 °C show a decrease of the nitrogen condensation step, suggesting a reduction in mesoporosity (Figure 7). Similarly, the sample FDU-18-8-1200 shows an obvious bimodal pore size distribution at 3.1 and 19.0 nm, respectively. The prime mesopore size of 19.0 nm is slightly smaller than that of the FDU-18-8-800, and the wall thickness decreases to 13.7 nm because of the structure shrinkage, consistent with the conclusions mentioned above. The small mesopores of about 3.1 nm may be attributed to tunnels in the carbon walls formed during the pyrolysis at 1200 °C. No secondary mesopores were observed in previous reports about mesoporous carbons such as FDU-16 templated from PEO-PPO-PEO block copolymers,[9-11] and FDU-18 from PEO-PS diblock copolymer[27] after being pyrolyzed at the same temperature of 1200 °C. Therefore, the formation of the small secondary mesopores for the FDU-18-8-1200 is probably related to the unique presence of the PMMA segment in PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138} templates. As a result of the further release of the carbon, hydrogen and oxygen containing small molecules, the BET surface area, pore volume and micropore surface area increase to values as high as 1260 m^2/g, 0.86 cm^3/g, and 1085 m^2/g, respectively.

Because of the thick pore walls, the FDU-18-X-1200 sample shows excellent stability even after treatment in a concentrated KOH solution (4.2 M) for 20 h at 140 °C. Both the SAXS and TEM characterizations reveal that the ordered mesostructure was well retained after the harsh treatment (Figure S11 in the Supporting Information).

3.5. Pore Walls. FE-SEM images of the FDU-18-8-1200 sample show uniform and regularly aligned mesopores throughout the whole particle, suggesting a highly ordered cubic mesostructure over a large domain (Figure 4a, b). Interestingly, from the HRSEM images (Figure 4c), numerous small pores with spherical morphology in the size of around 2−3 nm are obviously visible in the thick pore walls, in agreement with the observation of a bimodal mesopore size distribution from the N_2 sorption. Our HRSEM measurements show that some of the small mesopores on the carbon walls are isolated, but connected with each other by micropores. It is the first time that the mesoporous tunnels on the walls are directly observed by SEM. The results further confirm the disordered small micro/mesopores generated during the pyrolysis, implying that the PMMA segment is involved in the interaction with the resol precursors.

Elemental analysis indicates that the mesoporous carbonaceous FDU-18-8-450 framework contains C (77.5 wt %), H (4.60 wt %) and O (15.9 wt %) with C:H:O of 6.5:4.6:1.0 in molar ratio, which is close to the composition of phenolic resins. After pyrolysis at 800 °C, the FDU-18-800 sample possesses a molar ratio for C:H:O of 16.0:3.7:1.0, i.e., a strongly reduced hydrogen and oxygen content. It suggests that the carbon frameworks are obtained after treatment at 800 °C. The Raman spectrum of FDU-18-8-800 shows typical bands (G and D) of amorphous carbon from the phenolic resin with similar intensity. The former at 1593 cm^{-1} is ascribed to graphitic sp^2 carbons and the latter at 1314 cm^{-1} to sp^3 carbons in defects (Figure S12 in the Supporting Information). This reveals that the obtained carbon materials have a low degree of graphitization. FT-IR spectra (Figure S13) further identify the polymeric network of FDU-18-8-450 pyrolyzed at the low temperature and carbon framework feature of FDU-18-8-800 and FDU-18-8-1200 at the high temperature.

Scheme 1. Proposed Mechanism for the Formation of the Ordered Cubic fcc Mesoporous Carbonaceous Materials with Large Pores and Tunable Wall Thickness Synthesized by Organic−organic Assembly of the Resol Precursors and ABC-Type Triblock Copolymer PEO_{125}-*b*-$PMMA_{100}$-*b*-PS_{138}T[a]



[a] The gradient hydrophilicity of the ABC copolymer can lead to interaction with different amounts of resol molecules via hydrogen-bonding, resulting in different pore wall thickness.

3.6. Formation of Mesostructures. The ABC-type triblock copolymer PEO-PMMA-PS can interact with phenolic resol precursors and direct the assembly of the organic−organic mesostructure (Scheme 1). We speculate that the successful adjustment of the pore wall thickness of the ordered mesoporous carbonaceous frameworks by simply varying the resol/template ratios is attributed to the unique composition of the ABC-type PEO-PMMA-PS copolymer template. Along the ABC copolymer chain, the hydrophilicity is reduced gradually from the PEO to PMMA and PS segments. The gradient hydrophilicity makes the PEO-*b*-PMMA-*b*-PS copolymer different from previous templates such as PEO-PPO-PEO, PEO-*b*-PS, and PEO-*b*-PMMA.

The PMMA segment together with PS block in PEO-PMMA-PS triblock copolymer mainly contributes to the hydrophobic core during the organic−organic assembly of the mesostructures induced by the solvent evaporation, which results in a constant mesopore size around ~20 nm (after pyrolysis at 800 °C). When the ratio of the resol/PEO-PMMA-PS (such as X = 6, 8) is low, the resol molecules can preferentially interact with the PEO units of the ABC copolymer through the hydrogen bonding rather than with the PMMA blocks because of the strong stereohindrance effect. The PEO-*b*-PMMA-*b*-PS copolymers arrange the resol precursor assembly into globular micelles which further pack into an ordered cubic fcc mesostructure (Scheme 1a). Heating at 100 °C causes the thermopolymerization of resols and solidifies the mesostructure. The composite mesostructure can be converted into ordered mesoporous carbons by carbonization in N_2 at a high-temperature (such as 800 °C). When the PEO-PMMA-PS/resol ratio increases, the resol molecules can interact not only with the PEO segment but also partially with the PMMA segments by hydrogen bonding (Scheme 1b), and as a result, more resols can be accommodated, leading to an increase in the hydrophilic volume and wall thickness of carbonaceous frameworks. After heating at 450 °C, the PMMA blocks occluded in the resol networks can be pyrolyzed and removed, yielding the small secondary pores. Additionally, the pyrolysis of rich-oxygen PMMA segments can probably leave some oxygen species on the pore walls. The further carbonization at higher temperature (800−1200 °C) can release more carbon, hydrogen, and oxygen species, creating the random mesopore voids of 2−3 nm connected by small micropores on the carbon pore walls. Thus, the disordered mesopore voids are accessible and become visible. Our HRSEM measurements provided clear images of the small mesopore voids. Because of the weak interaction, adding too high amounts of the resols leads to inhomogeneous hydrophilic domains (in the case X > 14), and thus, disordered wormlike mesostructure is formed.

4. Conclusions

We demonstrate a successful synthesis of ordered large pore mesoporous carbons with controllable wall thickness by using a home-designed ABC-type triblock copolymer PEO-*b*-PMMA-*b*-PS as a template. The ABC copolymer can form spherical micelles to direct the formation of an ordered cubic fcc ($Fm\overline{3}m$) mesostructure during the organic–organic assembly via the EISA process. The unique gradient hydrophilicity of the PEO-*b*-PMMA-*b*-PS template facilitates the continuous incorporation of resol molecules along the PEO to PMMA segment of the micelles via hydrogen interaction, resulting in successful tuning of the pore wall thickness from 10 to 20 nm by simply varying the resol/ABC-type-template ratio. The obtained mesoporous carbonaceous products possess superlarge pores (up to 20 nm) and large unit-cell constants (up to 55.0 nm). For the first time, we observed numerous small spherical mesopores randomly dispersed in the carbon walls by using HRSEM. These pores are presumably left by the removal of the PMMA segments during the pyrolysis. The obtained mesoporous carbons have high surface areas of ~900 m^2/g and pore volume of ~0.6 cm^3/g. The thick pore-wall mesoporous carbons show excellent thermal (1200 °C) and chemical stability (in concentrated KOH solution at 140 °C).

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Supporting Information Available: Experimental details; FT-IR spectra of PEO-Br, PEO-*b*-PMMA, and PEO-*b*-PMMA-b-PS triblock copolymer; ^{1}H NMR spectra and GPC traces of PEO-*b*-PMMA diblock copolymer and triblock copolymer PEO-*b*-PMMA-*b*-PS; TG analysis of PEO-*b*-PMMA-*b*-PS; TEM images of FDU-18-6-800, FDU-18-8-1200, FDU-18-10-800, FDU-18-14-800, and FDU-18-16-800; FT-IR spectra of as-made FDU-18-8, FDU-18-8-450, FDU-18-8-800, and FDU-18-8-1200 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.