

# Synthesis of Mesoporous Silica from Commercial Poly(ethylene oxide)/Poly(butylene oxide) Copolymers: Toward the Rational Design of Ordered Mesoporous Materials

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Five commercial poly(ethylene oxide)/poly(butylene oxide) (PEO/PBO) triblock copolymer surfactants were utilized as structure-directing agents to synthesize mesoporous silica under acidic conditions. The structures of these materials were characterized by using powder X-ray diffraction (XRD), nitrogen adsorption analysis, and transmission electron micrographs (TEM). The relationship between the pore sizes of silica mesostructures and hydrophobic block weight as well as block architecture of their block copolymer templates was discussed. From the comparison of the critical micelle concentration (CMC) values of these PEO–PBO copolymers and the resultant silica mesostructures, it is proposed that the CMC of block copolymers correlates to the final silica mesostructures and can be used as an important criterion for the rational design of ordered mesoporous materials especially when they are synthesized as precipitates from solutions. Such conclusions are useful to fabricate ordered and large pore mesoporous materials.

## Introduction

In 1992, Mobil scientists reported the synthesis of a new family of mesoporous aluminosilicates (M41S) by the use of self-assembled organic aggregates as supramolecular structure-directing agents.<sup>1,2</sup> This discovery and subsequent investigations in this field opened up a new methodology for novel material synthesis and attracted considerable attention in the areas such as catalysis,<sup>3</sup> inclusion chemistry,<sup>4</sup> dye lasers,<sup>5</sup> separation of large molecules,<sup>6,7</sup> fabrication of nano-objects,<sup>8</sup> and ordered mesoporous carbon.<sup>9</sup> Recent advance in this research area has led to mesoporous materials with new compositions and hierarchical structures.<sup>10</sup>

Surfactants play an important role in the synthesis of mesoporous materials. Originally, long-chain quaternary ammonium surfactants were employed as templates.<sup>2</sup> Later, other surfactants, such as anionic,<sup>11</sup> neutral,<sup>12</sup> PEO-type nonionic surfactants,<sup>13–17</sup> were examined. The use of Pluronic block copolymers with poly(propylene oxide) (PPO) hydrophobic moieties under strong acidic conditions gave rise to highly ordered, large pore mesoporous materials SBA-15 and SBA-16 with improved hydrothermal stability and rich structural property compared to M41S materials.<sup>18,19</sup> Block copolymers with PBO as hydrophobic part are another big family of extensively studied surfactants in polymer science in addition to commonly used PEO–PPO type copolymers.<sup>20</sup> Several di- and triblock PEO/PBO copolymers have been employed as templates in the synthesis of mesoporous silica materials.<sup>21–30</sup> The family of commercial PEO/PBO surfactants (Dow Chemical Co.) has not been studied extensively.

Normally, mesostructured silica is synthesized in dilute aqueous solutions in the form of fine powders, where the concentration of surfactant is far below the concentration needed

to form a real liquid crystal phase and the cooperative self-assembly dominates the formation of inorganic/organic composites array at the mesoscopic level.<sup>11,31</sup> Other synthesis pathways include evaporation-induced self-assembly (EISA) which is carried out in nonaqueous solvent systems<sup>32</sup> and a lyotropic liquid crystal phase pathway to generate organized materials.<sup>33</sup> Compared to the large number of available block copolymers, only a fraction of these surfactants can be utilized to produce highly ordered mesostructures. Considering the fact that the cooperative assembly of the composite mesostructures is a complicated kinetically and thermodynamically determined process, the synthesis of ordered mesoporous materials is usually a trial and error process. It will be of great interest to find a way to choose which surfactant is suitable to give high-quality mesostructures as well as how to modify the synthesis strategies.

The present contribution concerns a systematic study of commercial triblock PEO–PBO–PEO copolymers as templates in the synthesis of mesoporous silica structures. The pore sizes of resultant mesostructured silica materials are correlated to the structural parameters of block copolymer templates. Moreover, it is evident from current study that the CMC of block copolymer surfactant is a powerful criterion for the experimental design of the synthesis of ordered mesoporous materials.

## Experimental Sections

**Chemicals.** All chemicals were used as received without further purification unless specially clarified. Commercial triblock PEO–PBO–PEO surfactants EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> (B70-4600, where “70” represents the weight percentage of BO part and “4600” represents the number-averaged molecular weight of block copolymer); EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> (B40-2500); EO<sub>45</sub>BO<sub>14</sub>EO<sub>45</sub> (B20-5000); EO<sub>34</sub>BO<sub>11</sub>EO<sub>34</sub> (B20-3800), and EO<sub>13</sub>BO<sub>11</sub>EO<sub>13</sub> (B40-1900) were obtained as gifts from Dow Chemical Co., Midland, MI.

**Syntheses.** Generally, the syntheses of mesoporous silica materials in this study were carried out in acidic solutions by

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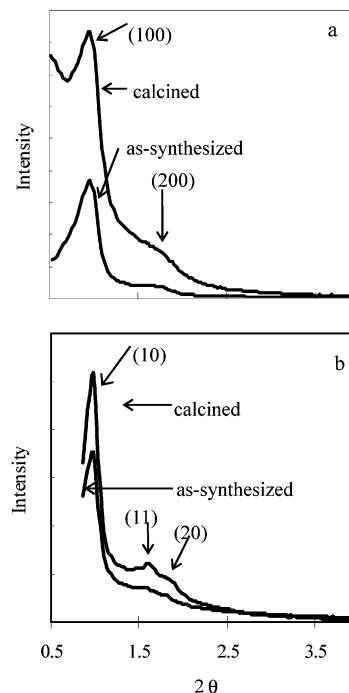
using block copolymers as templates and the tetraethyl orthosilicate (TEOS) as silica source. The products were collected in the form of fine powders.<sup>18,22</sup> The optimal synthesis condition was different for each block copolymer templates. In a typical preparation, 0.6 g of EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> was dissolved in 45 g 6 M HCl at 0 °C. To this opalescent clear solution, 1.5 g of TEOS was added under stirring. The final reactant molar composition is EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/HCl/H<sub>2</sub>O/TEOS = 0.044/38/347/1. White precipitates were observed within 5 min and the mixtures were stirred for 24 h. The optimal synthesis condition for EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> template was carried out at 40 °C with the reactants weight ratio of EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub>/KCl/2M HCl/TEOS = 1.5/3.36/30/2.08 (molar ratio: 0.06/4.5/6/1). For EO<sub>45</sub>BO<sub>14</sub>EO<sub>45</sub> template, the synthesis was carried out at 40 °C and the optimal reactants weight ratio was EO<sub>45</sub>BO<sub>14</sub>EO<sub>45</sub>/KCl/0.5 M HCl/TEOS = 0.5/2.24/30/2.08 (molar ratio: 0.01/3/1.5/1). In the EO<sub>34</sub>BO<sub>11</sub>EO<sub>34</sub> copolymer, the optimal synthesis condition was carried out at 38 °C and the reactant weight ratio was EO<sub>34</sub>BO<sub>11</sub>EO<sub>34</sub>/KCl/0.5M HCl/TEOS = 0.8/2.24/30/2.08 (molar ratio: 0.021/3/1.5/1). The optimal synthesis condition for EO<sub>13</sub>BO<sub>11</sub>EO<sub>13</sub> template was carried out at 40 °C and the reactants weight ratio was EO<sub>13</sub>BO<sub>11</sub>EO<sub>13</sub>/KCl/0.5 M HCl/TEOS = 0.8/2.24/30/2.08 (molar ratio: 0.042/3/1.5/1). Hydrothermal treatment of the reactant mixture at 100 °C for 24 h was employed for all samples. The solid products were collected by filtration and dried at room temperature in air. When the inorganic salts were used during synthesis, the products were washed with water for at least three times to remove such additives. The resulting powders were calcined at 550 °C for 4 h in air to obtain mesoporous silica materials.

**Analyses.** X-ray diffraction (XRD) patterns were recorded with a Scintag PADX diffractometer using Cu K $\alpha$  radiation. The nitrogen adsorption measurements were performed at 77 K using a Micromeritics ASAP 2010 analyzer utilizing Barrett–Emmett–Teller (BET) calculations of surface area and Barrett–Joyner–Halenda (BJH) calculations of pore volume and pore size (diameter) distributions from the adsorption branch of the isotherm. In some cases, the Broekhoff–de Boer (BdB) model was also used to calculate the pore size distributions.<sup>34</sup> Transmission electron micrographs (TEM) were obtained with a JEOL 2000 operating at 200 KV.

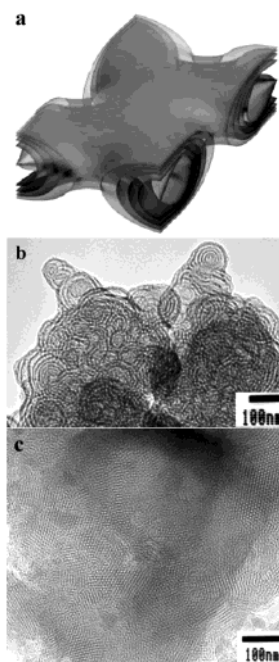
## Results

**EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>.** Block copolymer EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> exhibits very low water solubility at room temperature because of its unusual large hydrophobic/hydrophilic volume ratio; as a consequence, this copolymer has not been reported as a template in the synthesis of mesoporous materials. In our experiments at strong acidic conditions such as 6 M HCl and at low-temperature such as 0 °C, EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> shows a certain degree of solubility that is necessary for a successful synthesis of mesoporous powder materials.

Both as-synthesized and calcined mesoporous silica structures synthesized by using EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> as a template at the reactant molar composition of 0.044 EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/38 HCl/347 H<sub>2</sub>O/1 TEOS show two relatively broad XRD diffraction peaks in the region of  $2\theta = 0.9$ – $1.8^\circ$  (Figure 1a), the ratio of the corresponding  $d$ -spacing of two peaks is approximately 2:1 for both samples. The intensity of the diffraction peaks for the calcined sample is much stronger than that for the as-synthesized sample. Combined with TEM results, these two peaks may be mostly attributed to the (100) and (200) diffractions of a multilayer vesicle (MLV) structure (Figure 2a).<sup>16</sup> The  $d$ -spacing of the as-synthesized and calcined silica vesicles is 9.37 and 9.19 nm,

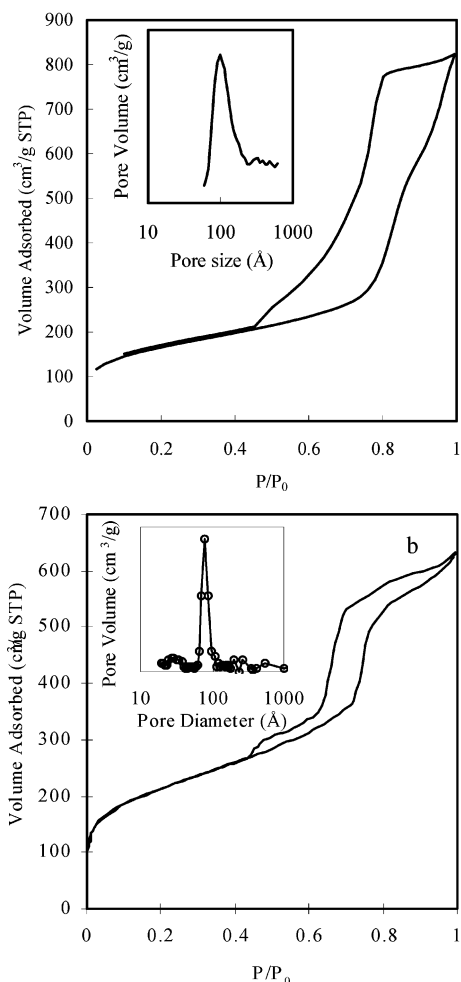


**Figure 1.** Powder XRD patterns of as-synthesized and calcined silica mesostructures prepared by using EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> triblock copolymer as a template. (a) Vesicle structure synthesized with reactant weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 1.5/0.60/45. (b) Hexagonal silica mesostructure synthesized with reactants weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 3.2/0.60/45.



**Figure 2.** Schematic drawing of an MLV structure (a) and TEM images (b), (c), of calcined silica mesostructures prepared by using EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> triblock copolymer as a template. (b) Vesicle structure synthesized with reactant weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 1.5/0.60/45. (c) Hexagonal structure synthesized with reactant weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 3.2/0.60/45.

respectively. TEM analysis results of the calcined sample confirm that the silica material synthesized by using EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> as a template has a typical MLV structure (Figure 2b). The layer-to-layer distance estimated from the TEM image is



**Figure 3.** Nitrogen adsorption–desorption isotherm plots and pore size distribution curves (inset) of calcined silica mesostructures prepared by using EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> triblock copolymer as a template. (a) Multilayer vesicle structure synthesized with reactant weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 1.5/0.60/45. (b) Hexagonal structure synthesized with reactant weight ratio TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 3.2/0.60/45.

in the range of 9–11 nm, in accordance with the broad peak distribution as shown in XRD results.

When the component weight ratio of silica source (TEOS) to block copolymer is increased (TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub>/6 M HCl = 3.2/0.60/45), the XRD pattern of resulting silica mesostructure is shown in Figure 1b. Compared to the XRD pattern of silica MLV structures (Figure 1a), the diffraction peaks for both as-synthesized and calcined silica structures synthesized at this increased TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> ratio are much narrower and more diffraction peaks can be found at high angles. Combined with TEM results, these peaks can be well indexed to the (10), (11), and (20) diffractions of a two-dimensional (2-D) hexagonal structure (*p6m*). The cell parameter is 10.8 and 10.6 nm for the as-synthesized and calcined samples, respectively. TEM analyses confirm the hexagonal mesopore array in the calcined samples (Figure 2c). Obviously, by simply changing the reactant ratio of silica source to structure-directing agents, a structure transition from MLV to hexagonal structures is observed in the presence of EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> block copolymer template.

Both calcined MLV and hexagonal silica structures templated by EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> at a different TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> ratio yield type IV N<sub>2</sub> adsorption–desorption isotherms with type H<sub>1</sub> hysteresis loops (Figure 3); however, the difference between two structures is clear since the pore size distribution for calcined

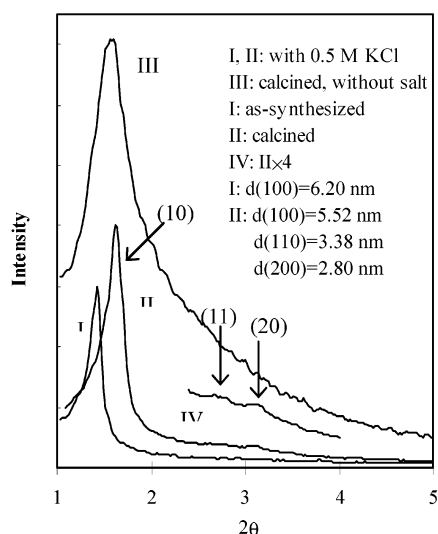
hexagonal structure (inset of Figure 3b) is much narrower than that of MLV structure (inset of Figure 3a). This is also in agreement with XRD and TEM results, further suggesting that the uniformity for hexagonal structures is much better than that for MLV structures. MLV silica structure has a surface area of 599 m<sup>2</sup>/g, a pore volume of 1.28 cm<sup>3</sup>/g, and a BJH mean pore size at 10.2 nm. Calcined hexagonal silica structure has a BET surface area of 761 cm<sup>2</sup>/g, a pore volume of 0.97 cm<sup>3</sup>/g, and a BJH mean pore size at 5.8 nm. When using a BdB model,<sup>34</sup> the pore size for hexagonal silica structure is 7.6 and 7.5 nm calculated from the adsorption and desorption branch, respectively, suggesting the existence of 1-D mesoporous channel within such structures.<sup>34</sup>

It is quite unusual to note that in calcined silica samples with MLV structures, the pore size (10.2 nm) is larger than the *d*-spacing (9.19 nm) calculated from the first diffraction peak. In addition, a small extent of structure shrinkage (~2%) during calcination is also observed. A bicontinuous intermediate state in the transition from *L*<sub>α</sub> to *L*<sub>3</sub> proposed by Pinnavaia and co-workers might be responsible for the formation of mesostructured silica vesicles.<sup>16</sup> It is suggested that the linkages between the undulated bilayers are not uniformly distributed, resulting in the broad XRD peaks and pore size distributions observed in MLV silica structures.

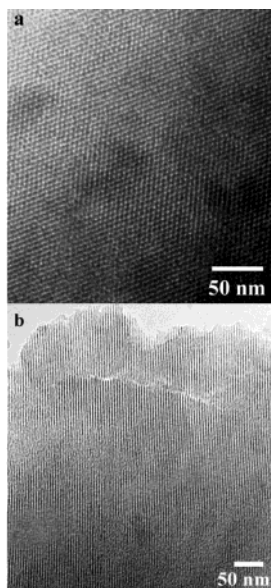
When the reactant ratio of TEOS/EO<sub>15</sub>BO<sub>45</sub>EO<sub>15</sub> is further increased (>4.2/0.60), amorphous silica was obtained as evidenced by XRD and TEM results (data not shown). This may be explained by the fact that when the concentration of TEOS in the starting reactants is increased to a certain degree, the condensation of inorganic silica species overrides the cooperative self-assembly of organic/inorganic composites that is necessary to give ordered mesostructures.<sup>11</sup>

**EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub>.** Block copolymer EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> has not been reported before as a template in the synthesis of ordered mesoporous materials. The CMC of this surfactant is 35 mg/L at room temperature according to the handbook of Dow Chemical Co. In our syntheses procedures, “salting-out” inorganic salts such as KCl were employed as additives to increase the quality of mesoporous materials.<sup>26,35</sup> The XRD patterns of as-synthesized and calcined mesoporous materials prepared by using EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> as a template and 1.5 mol/L KCl as additives at 40 °C are given in Figure 4 (reactant molar ratio: EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub>/KCl/2M HCl/TEOS = 0.06/4.5/6/1). As-synthesized sample shows a sharp diffraction peak at  $2\theta = 1.42^\circ$ . After calcination, the first peak appears at  $2\theta = 1.60^\circ$  and the intensity is increased; two additional peaks are also observed at relatively high angles. The ratio of the reciprocal *d*-spacing values (5.52, 3.38, 2.80 nm) of these peaks is similar to 1:√3:2. Combined with the TEM analysis result, these peaks can be indexed to the (10), (11), and (20) diffractions of a 2-D hexagonal structure (Figure 4). The cell parameters of as-synthesized and calcined samples are 7.16 and 6.37 nm, respectively. The shrinkage of cell parameter after calcinations is ~11%. Typical TEM images along [001] and [100] directions of a hexagonal structure are also observed (Figure 5), in accordance with the XRD analysis results. The cell parameter of the calcined sample estimated from TEM images is 5.8 nm, a little smaller than that calculated from XRD results. Calcined samples give rise to type IV N<sub>2</sub> adsorption–desorption isotherms with type H<sub>1</sub> hysteresis loops typical of mesoporous materials (Figure 6). Calcined mesoporous material synthesized from EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> and 1.5 mol/L KCl has a surface area of 721 m<sup>2</sup>/g, a pore volume of 0.65 cm<sup>3</sup>/g, and a BJH mean pore size of 3.4 nm. When the BdB model is employed to calculate the





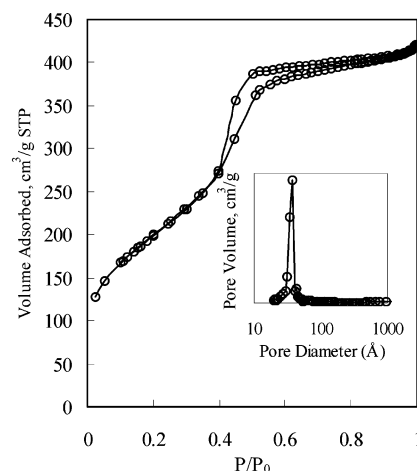
**Figure 4.** Powder XRD patterns of as-synthesized and calcined silica mesostructures prepared by using  $\text{EO}_{17}\text{BO}_{14}\text{EO}_{17}$  triblock copolymer as a template at 40 °C with 1.5 mol/L KCl (curve I, II) and without salt (curve III).



**Figure 5.** TEM images of calcined hexagonal silica mesostructures prepared by using  $\text{EO}_{17}\text{BO}_{14}\text{EO}_{17}$  triblock copolymer as a template at 40 °C with 1.5 mol/L KCl, (a) along [001] direction and (b) along [100] direction.

pore size distributions, the pore size calculated from the adsorption branch (3.8 nm) is similar to that calculated from the desorption branch (4.3 nm), further confirming the existence of 1-D mesoporous channel within such structures.<sup>34</sup> In both BJH and BdB methods, the pore size distributions are very narrow (inset of Figure 6), suggesting the high quality of the resulting hexagonal mesostructure.

The use of inorganic salts is essential to the synthesis of high-quality mesoporous materials. When the inorganic salts were not used while keeping the other reacting condition unchanged (reactants ratio, temperature, hydrothermal treatment, etc.), disordered mesoporous materials were obtained. Compared with the XRD patterns synthesized with 1.5 M HCl, the XRD curve obtained in the absence of inorganic salts gives rise to one much broader diffraction peak (Figure 4, curve III), and no additional diffraction at high angle is observed. Such results are in accordance with our former reports.<sup>26</sup> The CMC and critical

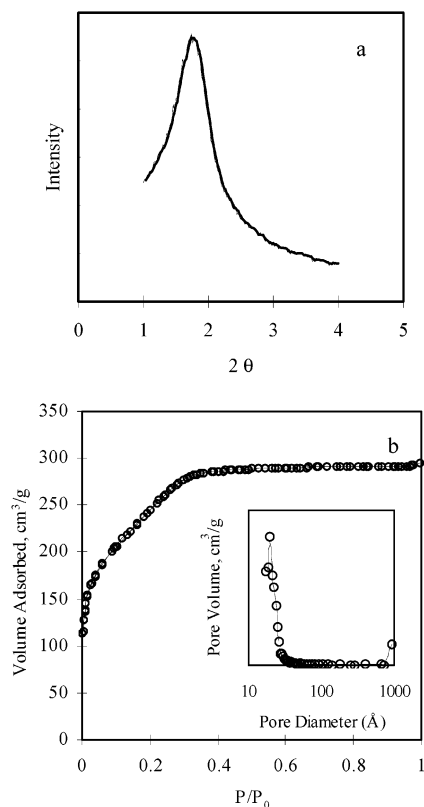


**Figure 6.** Nitrogen adsorption-desorption isotherm plots and pore size distribution curves (inset) of calcined hexagonal silica mesostructures prepared by using  $\text{EO}_{17}\text{BO}_{14}\text{EO}_{17}$  triblock copolymer as a template at 40 °C with 1.5 mol/L KCl.

micelle temperature (CMT) can be decreased in the presence of “salting-out” inorganic salts such as sodium chlorides and potassium chlorides;<sup>20,36,37</sup> thus, the self-assembling ability of block copolymer templating systems can be greatly improved. The use of “salting-out” inorganic salts can dramatically widen the syntheses domain (in temperature, surfactant concentration, etc.) and broaden the range of block copolymer surfactants that can be utilized to produce high-quality mesostructures (see also Results and Discussion below).

**$\text{EO}_{45}\text{BO}_{14}\text{EO}_{45}$ .** The CMC of block copolymer  $\text{EO}_{45}\text{BO}_{14}\text{EO}_{45}$  is 280 mg/L. This surfactant has been studied before by Budd and co-workers<sup>21</sup> as a template in the synthesis of mesoporous materials; while inorganic salts were not used in their studies, only disordered silica mesostructures were prepared and no meaningful pore size distribution analyses were obtained according to the authors. By using the inorganic salt synthesis approach described above, a well-ordered cubic silica mesostructure has been prepared at 40 °C with  $\text{EO}_{45}\text{BO}_{14}\text{EO}_{45}$  as a template (reactant molar ratio:  $\text{EO}_{45}\text{BO}_{14}\text{EO}_{45}/\text{KCl}/0.5 \text{ M HCl}/\text{TEOS} = 0.01/3/1.5/1$ ).<sup>26</sup> XRD patterns of as-synthesized material show the first peak at  $2\theta = 1.36^\circ$ ; after calcination at least two peaks ( $2\theta = 1.51, 2.09^\circ$ ) are observed. Combined with TEM results, these peaks can be indexed to the (110), (200) of an I type cubic structure (Im-3m). The cell parameters are 9.2 and 8.3 nm for the as-synthesized and calcined samples, respectively. As in  $\text{EO}_{17}\text{BO}_{14}\text{EO}_{17}$ , it is also noted that these diffraction peaks of mesoporous materials synthesized in the presence of 1.0 M KCl are much narrower than that obtained without using inorganic salts. TEM analysis also confirms this cubic structure; the cell parameter of the calcined sample measured from TEM is 8.0 nm, in good accordance with XRD results. The nitrogen sorption isotherm of the calcined sample is type IV with a slight hysteresis. The calcined cubic silica structure synthesized by  $\text{EO}_{45}\text{BO}_{14}\text{EO}_{45}$  at 40 °C with 1.0 mol/L KCl has a small pore size of 2.4 nm (calculated by BJH model), a BET surface area of 485  $\text{m}^2/\text{g}$ , and a pore volume of 0.28  $\text{cm}^3/\text{g}$ .

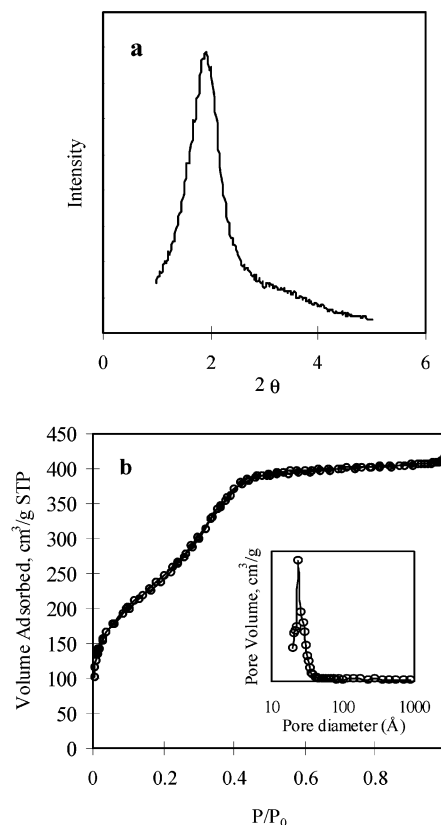
**$\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$ .** Block copolymer  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  has also been studied before; the resulting mesoporous silicas showed very broad XRD diffraction peaks and no meaningful pore size distribution was obtained.<sup>21</sup> The block copolymer has a large CMC value of 4300 mg/L. In our experiments, the synthesis procedure was modified by using the inorganic salt approach. The XRD pattern of calcined samples synthesized at 38 °C with



**Figure 7.** (a) XRD pattern; (b) nitrogen adsorption–desorption isotherm plots and pore size distribution curves (inset) of calcined silica mesostructures prepared by using  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  triblock copolymer as a template at 38 °C with 1.0 mol/L KCl.

reactant molar ratio of  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}/\text{KCl}/\text{HCl}/\text{TEOS} = 0.021/3/1.5/1$  shows a relatively broad diffraction peak at  $2\theta = 1.78^\circ$ , and no additional diffraction peak at high angles is observed, suggesting that the resulting materials have no long-range order at mesoscale (Figure 7a). However, compared to the XRD pattern of silica materials synthesized without inorganic salts,<sup>21</sup> the quality of silica structures obtained by the inorganic salt approach is greatly improved since the broadness of diffraction peak in our experiments is still much narrower than that in the former case. This conclusion is also confirmed by the gas sorption analysis results. Calcined mesoporous materials synthesized at 38 °C by using  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  in the presence of 1.0 M KCl yield type IV  $\text{N}_2$  adsorption–desorption isotherm with no hysteresis loops (Figure 7b). Calcined materials have a BET surface area of 884  $\text{m}^2/\text{g}$ , a pore volume of 0.46  $\text{cm}^3/\text{g}$ , and a mean pore size distribution (BJH model) at 2.0 nm. Although the resulting silica mesostructure is disordered, the pore size distribution is quite uniform (inset of Figure 7b), similar to MSU-X type mesoporous materials reported by Pinnavaia et al.<sup>15</sup>

**$\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}$ .** Block copolymer  $\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}$  has a relatively large CMC value of 700 mg/L. The XRD pattern of calcined samples synthesized at 40 °C and the reactant molar ratio of  $\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}/\text{KCl}/0.5\text{M HCl}/\text{TEOS} = 0.042/3/1.5/1$  give a relatively broad diffraction peak at  $2\theta = 1.96^\circ$  (Figure 8a), and no additional diffraction peak at high angles is observed. Calcined mesoporous materials synthesized at 40 °C by using  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  as a template in the presence of 1.0 M KCl yield type IV  $\text{N}_2$  adsorption–desorption isotherm with no hysteresis loops (Figure 8b). Calcined materials have a BET surface area of 904  $\text{m}^2/\text{g}$ , a pore volume of 0.64  $\text{cm}^3/\text{g}$ , and a mean pore size distribution (BJH model) at 2.4 nm. The resulting disordered



**Figure 8.** (a) XRD pattern; (b) nitrogen adsorption–desorption isotherm plots and pore size distribution curves (inset) of calcined silica mesostructures prepared by using  $\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}$  triblock copolymer as a template at 40 °C with 1.0 mol/L KCl.

silica materials possess uniform pore size distribution (inset of Figure 8b), similar to that observed in the  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  templating systems.

For block copolymers  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  and  $\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}$ , different syntheses conditions have been tested to prepare ordered mesostructures, for example, the syntheses temperature (0–50 °C); the reactant ratio [including the concentration of surfactants (0.2–5 g/30 g HCl); the concentration of HCl (0.1–6 M), TEOS/surfactants]; different inorganic salts (KCl,  $\text{K}_2\text{SO}_4$ , NaCl,  $\text{Na}_2\text{SO}_4$ ) and concentration (0.1–2 M); and other postsynthesis methods such as with or without hydrothermal treatment, the hydrothermal treatment temperature and time, and so forth. Considering that the molecular weight distribution and some homopolymers coexisting within the commercial block copolymers may affect the uniformity and structure of resulting mesoporous materials, we also tried to purify those commercial block copolymers according to literature before using them as templates in the synthesis of mesoporous materials.<sup>38</sup> However, all these attempts resulted in disordered mesoporous materials. It can be concluded that under our syntheses conditions, ordered silica mesoporous materials cannot be prepared by using block copolymers  $\text{EO}_{34}\text{BO}_{11}\text{EO}_{34}$  and  $\text{EO}_{13}\text{BO}_{11}\text{EO}_{13}$  as templates. Such phenomena will be discussed in the following section.

## Discussion

Some physical parameters of PEO/PBO block copolymers and their templated silica mesostructures are listed in Table 1. For comparison, physical data obtained from one triblock<sup>24</sup> and one diblock PEO/PBO<sup>23</sup> copolymer templating systems that we

**TABLE 1: Physical Parameters of Block Copolymers and Their Templated Mesostructures**

A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>e</sup>	F <sup>f</sup>	G <sup>g</sup>
EO <sub>36</sub> BO <sub>47</sub> EO <sub>39</sub>	6800	3500	<i>h</i>	cubic	12.1	12.0
EO <sub>15</sub> BO <sub>45</sub> EO <sub>15</sub>	4700	3300	<i>h</i>	vesicle	9.19	10.2
EO <sub>17</sub> BO <sub>10</sub>	1500	750	22	hexagonal	8.75	6.0
EO <sub>17</sub> BO <sub>14</sub> EO <sub>17</sub>	2500	1000	35	hexagonal	5.52	3.4
EO <sub>45</sub> BO <sub>14</sub> EO <sub>45</sub>	5000	1000	280	cubic	5.87	2.4
EO <sub>13</sub> BO <sub>11</sub> EO <sub>13</sub>	1900	760	700	disordered	4.50	2.4
EO <sub>34</sub> BO <sub>11</sub> EO <sub>34</sub>	3800	760	4300	disordered	4.96	2.0

<sup>a</sup> Structures of block copolymers. <sup>b</sup> Average molecular weight. <sup>c</sup> Average hydrophobe molecular weight. <sup>d</sup> CMC of block copolymers (mg/L) at room temperature according to the handbook of Dow Chemical Co. <sup>e</sup> Determined silica structures synthesized by corresponding block copolymer templates. <sup>f</sup> The *d* spacing calculated from the first diffraction peak for each mesoporous material (nm). <sup>g</sup> Pore size of silica materials (nm). <sup>h</sup> Not reported because of very low solubility in water.

reported before are also listed in this table. Several useful conclusions may be drawn from these studies.

**(1) Correlation between CMC of Surfactants and the Structures of Resulting Mesostructures.** It can be inferred from Table 1 that block copolymer surfactants that have small CMC values (<20 mg/L, in the PEO/PBO block copolymer series) will template ordered silica mesoporous materials with certain structures (hexagonal, cubic, vesicle, etc.); on the contrary, surfactants that have large CMC values (>300 mg/L) will give rise to disordered mesostructures. For block copolymers with CMC values in the middle range (20–300 mg/L) that normally produce disordered mesostructures, syntheses methods that decrease the CMC of surfactants will improve the quality of final mesostructure (disordered → ordered structure, broad → uniform pore size distribution, etc.). In this context, the first conclusion that we may draw is that the CMC of surfactants can be used as an important criterion to choose suitable templates for the synthesis of ordered mesoporous materials.

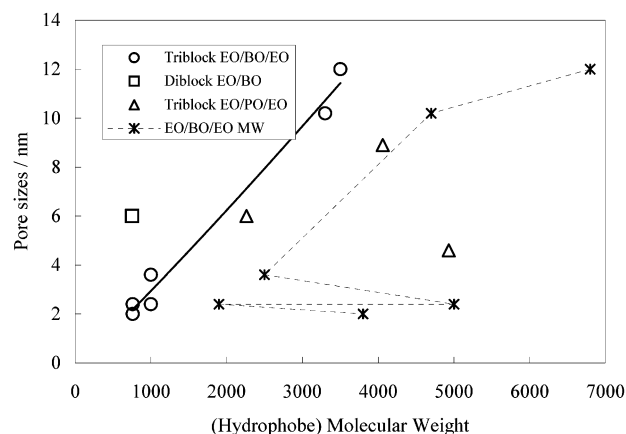
This conclusion has been drawn on the basis of solution syntheses of mesoporous precipitates where the cooperative self-assembly is the dominant process. It is generally accepted that the preformation of micelles is crucial to the successful synthesis of mesoporous materials from dilute solutions and the cooperative self-assembly of composite micelles leads to ordered mesostructures.<sup>1,2,39</sup> For example, at 17 °C the CMC of block copolymer EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> is 4.5 wt %<sup>40</sup> while in a typical synthesis condition of SBA-15 the concentration of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> in starting reactants is ~3.0 wt %; thus, SBA-15 cannot be synthesized at low temperatures unless increasing the temperature<sup>18</sup> or using inorganic salts<sup>26</sup> to decrease the CMC of EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>. Moreover, the decreasing ability to obtain ordered mesostructures for block copolymers with increasing CMC values as revealed in this study further suggests that CMC may correlate to the self-assembly ability of surfactants in the synthesis of mesoporous materials.

Evidences for the correlation between CMC of surfactants and the final mesostructures appear earlier in the literature especially in block copolymer templating systems, such as the temperature dependence of successful synthesis of highly ordered SBA-15<sup>18</sup> and the ionic strength dependence of successful synthesis of highly ordered SBA-15 at low temperature with inorganic salts.<sup>26</sup> However, current results provide a systematic study of a series of block copolymers with different CMC by correlating these physical parameters with their templated mesostructures; the conclusion is more direct that

**TABLE 2: Correlation of CMC of PBO-Type Block Copolymers and Their Templated Mesostructures**

CMC (mg/L)	0	20	300
formation of mesostructure	I <sup>a</sup>	II <sup>b</sup>	III <sup>c</sup>

<sup>a</sup> Region I: ready to synthesize ordered mesostructures. <sup>b</sup> Region II: where strategies can be used to decrease the CMC to give ordered mesostructures. <sup>c</sup> Region III: difficult to make ordered mesostructures.



**Figure 9.** Correlation between pore sizes of mesoporous materials and the molecular weights of the hydrophobic blocks of their copolymer templates. Data points “Δ” have been selected from ref 19. Data points “\*” are plotted against the overall molecular weight of the PEO/PBO triblock copolymers (dotted line).

block copolymers with decreasing CMC will lead to mesoporous materials with increasing quality.

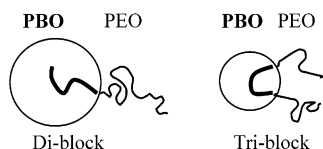
We are also concerned quantitatively about the CMC of block copolymers and the final mesostructures. On the basis of the results obtained in PEO–PBO type block copolymer templating systems (Table 1), the synthetic region of mesostructures may be divided into approximately three parts according to the CMC of their templates (Table 2). In region I where the CMC of block copolymer is below 20 mg/L at room temperature, these templates are ready to synthesize ordered mesostructures. In region II where the CMC is approximately between 20 and 300 mg/L, strategies can be used to decrease the CMC to give ordered mesostructures such as increasing the temperature or ionic strength. When the CMC is further increased (Region III), it will be difficult to make ordered mesostructures.

A more delicate correlation between CMC of surfactants and their templated mesostructures needs extensive study of various surfactant templating systems. Although such a conclusion has been drawn on the basis of PEO/PBO block copolymers, we believe that the general trend is also true for other surfactant templating systems but the synthesis region listed in Table 2 may be slightly different for other series of block copolymer surfactants (PEO/PPO).

**(2) Correlation between Pore Size and Structure of Surfactants.** The pore size control is one of the most important subjects in the study of mesoporous materials. For clarity, the data listed in Table 1 is plotted in Figure 9 to correlate the pore size to the structural parameter of block copolymer templates. Since the pore sizes of mesoporous materials depend on the calculation model, we use BJH model for all samples to compare the pore sizes.

(i) When the other syntheses conditions are similar (acidic solution syntheses, 100 °C hydrothermal treatment, etc.), the pore sizes of mesoporous materials templated by triblock PEO–PBO–PEO copolymers correlate directly to the molecular weight of hydrophobes of templates, but are not related to the molecular weight of block copolymer templates.





**Figure 10.** Schematic drawing showing possible conformations of diblock and triblock PEO/PBO copolymers in their micelles. The copolymers are drawn with approximately the same numbers of BO and EO units.

(ii) When the block copolymers possess similar hydrophobe molecular weight but different block architecture (di- or triblock), the pore sizes of mesoporous materials templated by diblock copolymers are much larger than that templated by triblock copolymers. Although only one data is listed because of the limitation of commercial diblock copolymers, we believe that this conclusion is reasonable and may be applied to other available templates. Similar observations have been extensively studied in block copolymer studies.<sup>20,41,42</sup> As schematically shown in Figure 10, triblock copolymers may give rise to micelles of approximately half the radius of the micelles formed by diblock copolymers with the same composition, because both ends of the hydrophilic blocks must emerge from the micelle core into the corona. Consequently, the BO blocks within the hydrophobic cores are more stretched for diblock copolymers than that for triblock copolymers; therefore, for block copolymers with approximately the same BO units, the hydrophobic core of micelles are much larger for diblock copolymers than for triblock copolymers; thus, the former templates will give rise to larger pore size of mesoporous materials since the pore sizes are determined by the hydrophobic volume of templates.

(iii) We also compare current data with the pore size of mesoporous materials obtained from PEO/PPO block copolymers.<sup>19</sup> For triblock copolymers with the same hydrophobe molecular weight, BO type surfactants will template much larger pore mesostructures than PO type copolymers. It is estimated that the hydrophobicities per chain unit for BO are  $\sim 6$  times larger than that for PO unit.<sup>20</sup> Early studies also revealed that PEO/PBO copolymers pack more efficiently at the interface, as evidenced by a smaller area per molecule at the interface; CMC values were also lower than that for structural equivalent PEO/PPO copolymers.<sup>43</sup> Since the PO unit may exhibit a certain degree of hydrophilicity especially at low temperature, a portion of PO chain may be occluded in the silica matrix during the synthesis of copolymer/silica mesostructures.<sup>44</sup> It is expected that the degree of such occlusion of hydrophobic chains within silica should be much reduced for more hydrophobic BO blocks. Since the hydrophobic core of block copolymers corresponds to the final pore size of mesoporous materials, PEO/PBO copolymers with more hydrophobic moiety favor ordered larger pore mesoporous materials than PEO/PPO copolymers with less hydrophobic parts.

(iv) For triblock copolymers with the same BO units, the length of EO chain will affect the pore size of final mesostructures. From our experimental data, it is interesting to note that longer EO chains lead to smaller pore sizes of mesoporous materials, for example, EO<sub>45</sub>BO<sub>14</sub>EO<sub>45</sub> (2.4 nm) versus EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> (3.4 nm), EO<sub>13</sub>BO<sub>11</sub>EO<sub>13</sub> (2.4 nm) versus EO<sub>34</sub>BO<sub>11</sub>EO<sub>34</sub> (2.0 nm). From the XRD data of samples before and after calcination, the cell parameter shrinkage of mesoporous materials templated by EO<sub>45</sub>BO<sub>14</sub>EO<sub>45</sub> and EO<sub>17</sub>BO<sub>14</sub>EO<sub>17</sub> is 9.8% and 11%, respectively. Therefore, the significant pore size difference (2.4 and 3.4 nm, respectively) may not be attributed to the shrinkage during calcination even taking into account that different amounts of EO groups are buried in the inorganic

walls. This is also true in PEO/PPO triblock templating systems; the pore size of SBA-15 (8.9 nm) templated by EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub> is larger than that of SBA-16 (7.8 nm) templated by EO<sub>106</sub>PO<sub>70</sub>EO<sub>106</sub>.<sup>19</sup> Surfactants with large headgroups tend to form cubic mesostructures; we postulate that such effect may be related to the fact that the curvature of cubic structures is larger than that of other structures and the surfactant molecules with larger headgroups are packed less stretched to give smaller hydrophobic cores, resulting in smaller size of mesopores.

Another quantitative consideration is the correlation between the pore size of mesoporous materials and the association number  $N$  of spherical micelles since  $N$  is proportional to the core volume, that is, to the core radius cubed. To a first approximation, the core radius can be viewed as proportional to the pore size ( $D$ ) of the mesoporous material. For EO<sub>*m*</sub>BO<sub>*n*</sub> or EO<sub>*m*</sub>BO<sub>*n*</sub>EO<sub>*m*</sub> copolymers it has been determined both from theory<sup>45</sup> and experiments<sup>20,46</sup> that  $N$  scales approximately as  $n$  to power 1 and  $m$  to power  $-0.5$  for spherical micelles. This understanding can be expressed by the following equation:

$$D^{1/3} \propto n^1 m^{-0.5} \quad (1)$$

Equation 1 explains that for copolymers with the same BO block length, the use of surfactants with longer EO chains will lead to a smaller pore size of the final mesostructure. The  $m$  scaling fits quite well in the EO<sub>13</sub>BO<sub>11</sub>EO<sub>13</sub> and EO<sub>34</sub>BO<sub>11</sub>EO<sub>34</sub> triblock copolymers. Unfortunately, the correlation between core radius and block length is not known for cylindrical micelles. Also, because other syntheses parameters such as temperature and ionic strength will influence the core radius for an individual copolymer, it was not possible to explore an overall quantitative correlation between pore size and micelle core radius for all the block copolymers in this study.

**(3) How To Design Large Pore Ordered Mesoporous Materials.** The above conclusions are important to the rational design of ordered large pore mesoporous materials. It can be inferred that this goal can be reached by using diblock PEO–PBO block copolymers with large BO repeating units. For a successful synthesis of power samples, the CMC of this surfactant is also important. This can be easily done by adjusting the proper PEO/PBO weight ratio during sequential anionic polymerization of block copolymers.<sup>20</sup> It is also estimated that this surfactant approach may be applied to the synthesis of ordered large pore mesoporous films ( $> 10$  nm).

## Conclusions

Mesoporous silica materials with different structures (cubic, hexagonal, MLV, and disordered mesostructure with uniform pore sizes) and variable pore size (2–10 nm) have been synthesized by using a series of commercial triblock PEO–PBO–PEO copolymers as templates. It is revealed that the CMC of block copolymer surfactant is a powerful criterion for the experimental design of synthesis of ordered mesoporous materials. The pore sizes of resultant mesostructured silica materials are correlated to the structural parameters of block copolymer templates. (1) The pore size of mesoporous materials is dependent on the molecular weight of hydrophobes of block copolymer templates; (2) for different block architectures, the pore size of mesoporous materials templated by diblock copolymer is much larger than that templated by triblock copolymer; (3) for different hydrophobic block compositions with the same hydrophobic molecular weight, the pore size of mesoporous materials is much larger for PBO than that for PEO moieties; and (4) for triblock copolymers with the same

hydrophobic nature and repeating units, larger EO units favors smaller pore sizes of mesoporous materials. Such conclusions are important to rationally design ordered and large pore mesoporous powder and film materials.

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