Mesostructure Design Using Mixture of Nonionic Amphiphilic Block Copolymers

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Formation of mesoporous silica materials has been studied using mixtures of amphiphilic diblock copolymers (C\textsubscript{n}H\textsubscript{2n+1}(OCH\textsubscript{2}CH\textsubscript{2})\textsubscript{x}OH, C\textsubscript{n}EO\textsubscript{x}, n = 12 - 18 and x = 2 - 100) as the structure directing agents and sodium silicate as the silica source. Results obtained from X-ray diffraction patterns and transmission electron microscopy indicate that silica/polymer mesostructures are transformed from lamella to 2-d hexagonal (P6\textsubscript{mm}), 3-d hexagonal (P6\textsubscript{3}/mmc), cubic Pm\textsubscript{3}m and cubic Im\textsubscript{3}m, as the size (x) of hydrophilic head group increases. Optimum ratios between the hydrophilic EO groups and hydrophobic tail groups are investigated in order to obtain highly ordered mesoporous silica materials.

1. INTRODUCTION

Mesoporous materials have opened many new possibilities for applications in catalysis, separation and nanoscience due to their large, controllable pore sizes and high surface areas [1-4]. Pore structures of the mesoporous materials such as channel connectivity and pore size are one of the most important physical properties for practical applications depending on their uses. For example, two-dimensional (2-d) hexagonal channel structures are proper for the fabrication of metal [5,6] or semiconductor nanowires [7], and three-dimensional (3-d) channel or cage structures are more useful for catalyst in terms of diffusion and deactivation [3,4].
In general, two different approaches have been suggested in order to control the mesostructures [1,8,9]. First, different mesostructures can be obtained by varying concentrations, reaction temperature and composition of reaction mixtures [1]. Second, the mesostructures can be controlled from lamellar to bicontinuous, hexagonal and discontinuous cubic, as the hydrophilic effective head group size increases relative to the total volume of the surfactant chain and the kinetic surfactant tail length, suggested by Stucky and coworkers [8,9]. The second is believed to be much easier than the first because it is not necessary to vary the reaction conditions. However, it is difficult to control the effective head group size precisely by using single surfactants due to the limitation of commercially available products and synthetic difficulties. In view of the fact that the cooperative assembly of the composite mesostructures a kinetically determined process, it is reasonable that a mixture of two surfactants with different head group sizes can be a solution for this limitation. The average kinetic size and shape of a mixture of small and large surfactants should be equivalent to those of a medium surfactant. In this way, the surfactant effective head group size can be controlled by varying the molar ratio between the surfactants with small and large head group sizes [10-12].

Here, we present a facile synthetic approach for high-quality mesoporous silica materials that include 2-d hexagonal, 3-d hexagonal and 3-d cubic using mixture of nonionic amphiphilic block copolymers as the structure-directing agents. We have explored the possibility that the efficient head group size of a block copolymer is closely related to the size of block fraction (EO) that is hydrophilic, which can be controlled by varying mixing ratios of the nonionic amphiphilic block copolymers with different hydrophilic head group sizes.

2. EXPERIMENTAL

Mixtures of amphiphilic block copolymers such as diblock copolymers (C_nH_{2n+1}(OCH_2CH_2)_xOH, C_nEO_x, n = 12 - 18 and x = 2 - 100) were used as the structure-directing agents and sodium metasilicate as the silica source in the present work. Mesoporous silica materials were obtained following the synthesis procedure reported elsewhere [13], except for the use of the polymer mixtures as the structure-directing agents instead of a single polymer. Typically, molar ratios of C_{12}EO_x polymers to obtain a suitable EO group number (x) are listed in Table 1. Other polymer mixtures such as C_{16}EO_x, C_{18}EO_x and EO_xPO_{70}EO_x were obtained by a similar calculation method with C_{12}EO_x polymer.
mixture.

X-ray diffraction (XRD) patterns were obtained with a Cu Kα X-ray source using a Sintag X̄ instrument at room temperature. Transmission electron microscopic (TEM) images were taken from thin edges of the sample particles with a 2000 FX JEOL transmission electron microscope operating at 200 keV. Scanning electron microscopic (SEM) images were collected with a JEOL 630-F microscope operating at 5 kV. N₂ adsorption-desorption isotherms were obtained using a Micromeritics ASAP 2040 apparatus at liquid N₂ temperature after degassing the samples for 12 hours at 550 K.

Table 1

<table>
<thead>
<tr>
<th>x</th>
<th>Molar ratio</th>
<th>mesostructure⁹</th>
<th></th>
<th>Molar ratio</th>
<th>mesostructure⁹</th>
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<tr>
<td>3</td>
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<td>0.75</td>
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<td>11</td>
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<tr>
<td>4</td>
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<td></td>
<td>L</td>
<td>12</td>
<td>0.85</td>
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<td>5</td>
<td>0.83</td>
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<td>L₂H</td>
<td>13</td>
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<td>6</td>
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<td>0.33</td>
<td>2H</td>
<td>14</td>
<td>0.69</td>
</tr>
<tr>
<td>7</td>
<td>0.50</td>
<td>0.50</td>
<td>2H</td>
<td>16</td>
<td>0.54</td>
</tr>
<tr>
<td>8</td>
<td>0.33</td>
<td>0.67</td>
<td>2H</td>
<td>18</td>
<td>0.38</td>
</tr>
<tr>
<td>9</td>
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<td>0.83</td>
<td>2H</td>
<td>20</td>
<td>0.23</td>
</tr>
<tr>
<td>10</td>
<td>1.00</td>
<td></td>
<td>3H</td>
<td>23</td>
<td>1.00</td>
</tr>
</tbody>
</table>

³³.0 g of polymer mixture was dissolved in 57.4 g of distilled water and then 8.8 g of sodium metasilicate was added at room temperature with magnetic stirring, giving a clear solution. To this reaction mixture, 17.7 g of c-HCl was quickly added with vigorous magnetic stirring.

⁹ L, 2H, 3H, D and CI denote lamella, 2-d hexagonal, 3-d hexagonal, disordered and cubic \( Im3m \), respectively, which are determined by XRD patterns.
3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of silica/polymer mesostructures, obtained from $C_{12}EO_x$ polymer system, before calcinations. EO group number ($x$) can be readily controlled by varying mixing ratios of dodecanol ($C_{12}EO_0$), $C_{12}EO_4$, $C_{12}EO_{10}$ and $C_{12}EO_{23}$ as listed in Table 1. The XRD results indicate that silica/polymer mesostructures are very sensitive to the EO group number ($x$). Silica/$C_{12}EO_3$ mesostructure corresponds to the lamellar structure. As $x$ increases, the mesostructures are transformed from lamella to 2-d hexagonal ($P6mm$), 3-d hexagonal ($P6_3/mmc$) and cubic $I3m$. Optimum EO group numbers ($x$) for lamella, 2-d hexagonal, 3-d hexagonal and cubic $I3m$ mesostructure are 3, 7, 10 and 18, respectively. Unfortunately, the present synthesis conditions using $C_{12}EO_x$ systems does not result in the formation of a bicontinuous cubic mesostructure ($Ia3d$) but gives a mixture of lamellar and 2-d hexagonal structure (Figure 1), even though $x = 5$, which is between the ratios for lamellar and 2-d hexagonal structures, is used. Particle morphologies of the silica/$C_{12}EO_x$ mesostructured materials are also changed from sheet-like to irregular and to faceted cubic depending on the mesostructures.
Fig. 2. Transmission electron microscopic images for the mesoporous silica materials obtained from C$_{12}$EO$_x$ system: (a) $x = 7$, (b) $x = 10$, and (c) $x = 18$. 
Figure 2 shows TEM images for calcined mesoporous silica materials obtained from C\textsubscript{12}EO\textsubscript{x} system. Figure 2a indicates that the material from C\textsubscript{12}EO\textsubscript{7} has a highly ordered 2-d hexagonal structure, similar to those of SBA-3 and MCM-41, which are well-known mesoporous materials having 2-d hexagonal channel structures. The mesoporous silica materials from C\textsubscript{12}EO\textsubscript{10} and C\textsubscript{12}EO\textsubscript{18} give TEM images (Figure 2b and 2c) for 3-d hexagonal and cubic Im\textit{3m} mesostructures, which are coincided with the XRD patterns in Figure 1. Trends of mesostructural transformation for the C\textsubscript{16}EO\textsubscript{x} and C\textsubscript{18}EO\textsubscript{x} systems are similar to those of C\textsubscript{12}EO\textsubscript{x} system. XRD patterns and TEM images for the mesostructured materials indicate that lamellar (\(x = 6\)), 2-d hexagonal (\(x = 8\)), disordered (\(x = 10\)) and cubic \textit{Pm\textit{3m}} (\(x = 20\)) mesostructures are obtained from the C\textsubscript{16}EO\textsubscript{x} system in the present conditions and lamellar (\(x = 7\)), 3-d hexagonal (\(x = 10\)), cubic \textit{Pm\textit{3m}} (\(x = 20\)), disordered (\(x = 40\)) and cubic \textit{Im\textit{3m}} (\(x = 60\)) structures from the C\textsubscript{18}EO\textsubscript{x} system. According to the results from C\textsubscript{n}EO\textsubscript{x} systems, silica mesostructures are transformed from lamella to 2d hexagonal (\textit{P6\textit{mm}}), 3-d hexagonal (\textit{P6\textit{3/mmc}}), cubic \textit{Pm\textit{3m}} and cubic \textit{Im\textit{3m}}, as the size of EO head group increases. It is noteworthy that mixtures of amphiphilic block copolymers can be used for structure directing of silica/polymer mesostructures and the average size and shape of a mixture of polymers with small and large head groups are similar to those of polymer with medium head group.

Stucky and coworkers \[8,9\] have suggested that to a first approximation the surfactant-silica mesophase can be explained and predicted by the classical micellar packing parameter, \(g = V/a_0 l\), where \(V\) is the total volume of the surfactant chain, \(a_0\) is the effective head group size at the micellar surface and \(l\) is the kinetic surfactant tail length. According to this, mesostructures are transformed from lamellar to bicontinuous, hexagonal and discontinuous cubic, as the hydrophilic effective head group size increases relative to the total volume of the surfactant chain and he kinetic surfactant tail length. The present results are very coincident with their prediction with the packing parameter, which can be controlled readily and precisely by mixing polymers with different hydrophilic head group sizes (\(a_0\)). It is reasonable that the structural transformations are due to the changes in micellar surface curvatures. Optimum EO group numbers (\(x\)) for the formation of highly ordered mesoporous silica materials can be precisely determined from the present works. N\textsubscript{2} adsorption-desorption isotherms and pore size distribution curve for the hexagonal material from C\textsubscript{12}EO\textsubscript{7} are essentially the same as those of SBA-3 and MCM-41. The cubic \textit{Im\textit{3m}} mesostructured material (C\textsubscript{12}EO\textsubscript{18}) gives
type IV isotherms with H2 hysteresis loop, indicating the material have bottle shaped pores [14].

Mesoporous silica materials with the same structures but different pore sizes can be readily obtained through the present synthetic approach. Figure 3 shows XRD patterns for the materials obtained from C_{12}EO_7, C_{16}EO_8 and C_{18}H_{35}EO_{10}, respectively. The XRD patterns indicate that 2-d hexagonal mesoporous materials can be obtained in a highly ordered form with different pore sizes by using mixtures of polymers with optimum head group sizes. Schematic models in Figure 3 indicate that large head group (x = 10) is necessary for formation of the 2-d hexagonal mesostructures when a polymer mixture with long chain hydrophobic tail group (C_{18}) is used, while small head group (x = 7) is needed for the polymer with short tail group (C_{12}). Similarly, cubic Im3m mesostructure is obtained when EO group number (x) is 60 for C_{18}EO_x system, whereas x = 18 is suitable for the same structure in case of C_{12}EO_x system.

![Fig. 3. XRD patterns for the mesoporous materials with 2-d hexagonal channel structures, obtained from (a) C_{12}EO_7, (b) C_{16}EO_8 and (c) C_{18}H_{35}EO_{10} and schematic models of correlation between head group size and chain length for surfactant micelles.](image)

In conclusion, use of mixtures of amphiphilic block copolymers as the structure-directing agents makes it possible to design and control the silica/polymer mesostructures precisely and the present synthetic approach may be useful for synthesis of mesoporous materials with new structures.

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