Systematic phase control of periodic mesoporous organosilicas using Gemini surfactants†

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Highly ordered periodic mesoporous organosilica (PMO) materials with various mesostructures, including lamellar, bicontinuous cubic $Ia3d$, 2D hexagonal ($P6_3/mmc$), 3D hexagonal ($P6_3/mmc$) and cubic $Pm3n$, have been synthesized using Gemini surfactants with general formulas of $[\text{C}_n\text{H}_{2n+1}][\text{NH}($CH$_3$)$_2$(CH$_2$)$_s$N ($\text{CH}_3$)$_2\text{C}_n\text{H}_{2n+1}]\text{Br}_2$ ($n=6–18$ and $s=3–12$, C$_{n,0,s}$). The nature of the Gemini surfactant such as alkyl chain length ($n$) and spacer length ($s$), and the synthetic conditions such as reaction temperatures and molar compositions are controlling parameters for desired mesostructures. The PMO materials, synthesized at room temperature from C$_{n,0,s}$ exhibit phase transition from lamellar to bicontinuous cubic $Ia3d$, 2D hexagonal, 3D hexagonal and cubic $Pm3n$ as the chain length decreases, whereas only the lamellar and 2D hexagonal PMO materials with different lattice parameters depending on the chain length are obtained at high reaction temperature (373 K). The C$_{n,8,0}$ and C$_{n,10,0}$ surfactants also yield 2D hexagonal PMO material in a very wide range of synthetic condition at 373 K. The PMO materials with various mesostructures thus obtained exhibit high BET surface areas in the range of 900–1500 m$^2$ g$^{-1}$ and total pore volumes of about 0.5–1.4 cm$^3$ g$^{-1}$.

1. Introduction

Since the first report of M41S family by the Mobil company in the early 1990s, ordered mesoporous silicas have attracted a lot of interests in the fields of catalysis, adsorption, separation, and nanoscience due to their high surface areas and controllable pore sizes in the range of 2–30 nm.$^{1–9}$ Recently, the synthesis of a new type of mesoporous materials containing bridging organic groups within the framework, named periodic mesoporous organosilica (PMO) materials, has been reported.$^{10–14}$ The organic group which is dispersed in the framework in molecular scale give intense potentials for various applications such as catalyst$^{15,16}$ and template for nanomaterials.$^{17}$ Furthermore, the framework properties can be varied by the use of suitable organosilanes.$^{18–20}$

So far, a lot of research on the structural control of the mesoporous materials$^{21–26}$ has been carried out in order to satisfy overloading and various needs for the applications such as support, catalyst, adsorbant and template for the materials with new type of mesostructures. The researchers at Mobil company firstly suggested that the molar ratios of surfactant and silicate are the most important factor for the mesostructure formation.$^{1,2,27}$ Alternative approaches for the control of mesostructure were suggested using additives such as alcohol, anionic surfactant and non ionic surfactant.$^{13,23,28,29}$ Further potential studies via the micelle packing parameter ($g$ value) control were reported,$^{20,24,25}$ and the importance of the $g$ value for the formation of mesostructure is suggested by Stucky and co-workers.$^{20–26}$ According to this suggestion, mesostructures are transformed from lamellar to bicontinuous cubic, hexagonal and discontinuous cubic as the volume of hydrophilic head group increases comparing to the volume of hydrophobic tail group, which means the $g$ value decreases.

Gemini surfactant is a new class of amphiphilic dimeric molecules, which has numerous potentials for applications in solubilization process, phase studies, skin care and so on. It is well known that the Gemini surfactant has very low critical micelle concentration and remarkable ability to decrease the surface tension of water.$^{30–32}$ Moreover, the $g$ value of Gemini surfactant, which consists of hydrophilic head, hydrophobic tail and spacer groups, can be easily controlled, compared with those of the general monovalent surfactants. Thus, one can obtain several types of mesostructured materials from the Gemini surfactants with controlled packing parameters.

Compared with the mesoporous silica materials, there have been few reports on the mesostructural control for the PMO materials,$^{33}$ regardless of the potential of PMO materials. Especially, the sufficient synthetic routes and systematic approaches for various mesostructured PMO materials have not yet been discovered. The difficulties in the synthesis of PMO materials are associated with the following three things due to the hydrophobic moieties in the organosilane precursor; firstly, the amphiphilic organosilane has different charge
density compared to normal inorganic materials, which is important for the coulombic interaction and consequent self-assembly. Secondly, the hydrophobic interaction between hydrophobic moieties of surfactants and organosilanes. Finally, the micelle packing parameter should be controlled to synthesize this new class mesoporous material with various mesostructures. In order to guide the self-assembly perfectly, all these competing factors should be balanced altogether. Inagaki et al. reported a systematic route for the PMO materials via the control of micelle packing parameter and charge density using nonionic amphiphilic surfactant as an additive.

Here, we report a systematic phase control of PMO materials with various kinds of mesostructures such as lamellar, bicontinuous cubic \(\text{Ia3d}^2\), 2D hexagonal, 3D hexagonal and cubic \(\text{Pm3n}\) via balanced self-assembly using the Gemini surfactants, which can generate controllable charge density, hydrophobic interaction and \(g\) value. Additionally, the synthetic conditions for mesostructures of PMO materials are also discussed.

## 2. Experimental

### 2.1 Surfactants

Gemini surfactants \([\text{C}_n\text{H}_{2n+1}\text{N(CH}_3\text{)}_2\text{CH}_2\text{N(CH}_3\text{)}_2\text{C}_n\text{H}_{2n+1}]\text{Br}_2\) \((s = 3–6, \text{ and } n = 12–22)\) were obtained by reaction between stoichiometric amounts of 1-bromoalkane (Aldrich) and \(N,N',N''\)-tetramethyl diaminoalkane (Aldrich and TCI) in acetonitrile (Aldrich). For the \([\text{C}_n\text{H}_{2n+1}\text{N(CH}_3\text{)}_2\text{CH}_2\text{N(CH}_3\text{)}_2\text{C}_n\text{H}_{2n+1}]\text{Br}_2\) \((s = 8–12, \text{ and } n = 12–22)\) type surfactants, dibromoalkane (Aldrich) and \(N,N\text{-dimethylalkylamine (TCI)}\) were used. All the chemicals were used as received. After solvent evaporation, the products were then dissolved in chloroform and re-crystallized by adding ethyl acetate (Aldrich) and cooling to 273 K. The Gemini surfactants thus obtained were gained by filtrating and drying at RT under vacuum. The Gemini surfactants thus obtained were designated with \(\text{C}_{n\sigma-n\sigma}\).

### 2.2 Synthesis

The PMO materials were synthesized following the procedure reported elsewhere, using bis(triethoxysilyl)ethane (BTEE, Aldrich) as the framework sources, except for the use of the Gemini surfactants, whose micelle packing parameters can be easily controlled. A typical molar composition of the synthetic mixture was BTEE : surfactant : \(\text{NaOH} : \text{H}_2\text{O} = 1 : 0.005–0.35 : 1.0–3.0 : 250–400\). The Gemini surfactant and \(\text{NaOH}\) were dissolved completely in distilled water and the BTEE was added into the solution. After stirring the reaction solution for 24 h at RT, the misty solution was kept at 373 K for 24 h (HT method, \(\text{OH}^-/\text{Si} = 2.6\)). The other set of samples with less amount of \(\text{NaOH}\) were obtained without heating at room temperature, 293 K (RT method, \(\text{OH}^-/\text{Si} = 1.1\)). Then the products were filtrated and dried at 373 K overnight. Finally, the surfactant was removed using 100 ml of ethanol solution containing 2 g of \(c\)-HCl (35%) for 1 g of the as-synthesized sample. This extraction procedure was repeated twice more in order for the complete removal of surfactant. The details of synthetic conditions the PMO materials and their physical properties are listed in Table 1.

### 2.3 Characterization

X-Ray diffraction (XRD) patterns were obtained with a Cu \(K\alpha\) X-ray source using Rigaku X-ray diffractometer. Transmission electron microscopy (TEM) images were received using JEOL-high resolution transmittance electron microscopy. Scanning electron microscopy (SEM) images were collected by JSM-890 field emission scanning electron microscopy after Pt coating. Nitrogen sorption analysis performed using Autosorb-1 apparatus (Quantachrome) at liquid N\(_2\) temperature after degassing the sample at 473 K for 10 h, and pore size distributions were calculated by BJH (Barrett, Joyner and Halenda) method.

## 3. Results and discussion

### 3.1 Effect of tail length: RT method

Fig. 1 shows XRD patterns for the PMO materials obtained from the \(\text{C}_{n\sigma-n\sigma}\) surfactants \((n = 12–22)\) at room temperature (RT method). The XRD patterns clearly indicate the systematic phase transition of PMO materials from lamellar to cubic \(\text{Pm3n}\) via 2D hexagonal and 3D hexagonal phases as the tail length \(n\) of \(\text{C}_{n\sigma-n\sigma}\) decreases. The material obtained

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<th>Table 1: Synthetic conditions for PMO materials and their physical properties</th>
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<td><strong>Surfactant</strong></td>
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* The mesophases of PMO materials were determined from XRD patterns. *\(^a\) BET specific surface areas calculated from the nitrogen adsorption. *\(^b\) Total pore volume measured at \(p/p_0 = 0.99\). *\(^c\) Calculated by BJH method from nitrogen adsorption branches. *\(^d\) The sample with cubic \(\text{Ia3d}\) mesophase in Fig. 2.
from the C_{22-6-22} surfactant shows typical three peaks which can be denoted to (100), (200) and (300) of lamellar structure, and the mesostructure is collapsed after the removal of surfactants by solvent extraction. In case of the C_{20-6-20} surfactant, the materials exhibit three relatively broad XRD peaks which are the characteristics of 2D hexagonal symmetry (P6\text{mm}). The broad peaks indicate that the hexagonal mesostructure is somewhat disordered in the present synthetic condition. When the tail length is shortened to 18, five XRD peaks are observed, which cannot be easily indexed to any phases each other. Three peaks can be indexed to the 2D hexagonal mesophase, but the other peaks that are marked with a star in Fig. 1 cannot be precisely indexed to any mesophase. These are probably due to the mixed mesophases being converted from 2D hexagonal phase to some mesophases through the intermediate mixture phase. The C_{16-6-16} surfactant results in the XRD patterns with intense three peaks and relatively weak three peaks. All the peaks can be indexed to (100), (002), (101), (110), (103) and (200) of 3D hexagonal (P6_3/mmc) mesophase with c/a = 1.63, which is very close to the value of 1.633 for the hexagonal close-packed (hcp) structure of hard spheres. 26 Both the C_{14-6-14} and C_{12-6-12} surfactants give discontinuous cubic Pm3n mesophases as shown in Fig. 1. In the case of the C_{14-6-14} surfactant, the XRD patterns exhibit well resolved peaks, attributed to (200), (210), (211), (222), (320) and (321), respectively, whereas more broad lines are observed from the C_{12-6-12} surfactant. All the PMO materials after solvent extraction gives the nitrogen adsorption–desorption isotherms with type IV, which are characteristics of mesoporous materials (see electronic supplementary information (ESI)). The PMO materials with various mesostructures thus obtained exhibit high BET surface areas and total pore volumes as shown in Table 1.

The decrease in the tail length of the Gemini surfactants with same spacer length corresponds to an increase in the curvature of the surfactant layer toward water. While the hydrophilic group tends to dissolve into water, the hydrophobic moieties gather together to form a hydrophobic core. The shapes of the mesostructure thus obtained may be determined by the balance of the attractive and the repulsive forces acting at the hydrophobic interfaces of the aggregates. The mesophases are known to be transformed from lamellar to bicontinuous, hexagonal and discontinuous cubic as the hydrophilic–hydrophobic balance number increases. Similar to mesophases found in surfactants, the formation of PMO materials with different mesostructures in Fig. 1 can be explained by the hydrophilic–hydrophobic balance of the structure-directing agents.

Synthesis conditions for the PMO materials in Fig. 1 do not result in formation of a bicontinuous cubic mesostructure (Ia\text{3}d) even though the C_{21-6-21} (mixture of C_{22-6-22} and C_{20-6-20}), of which the tail length may lie between the lamellar and 2D hexagonal structures, is utilized. Fig. 2 shows the XRD patterns for the PMO materials from the C_{20-6-20} surfactant with different concentration in the reaction mixture. It is well known that the molar ratio of surfactant/silica in the reaction mixture is one of the controllable factors for the desired mesostructures. For example, as the surfactant/silica molar ratio (cetyltrimethylammonium chloride, under basic condition) was varied, the products thus formed could be grouped into four main categories: ratio < 1, MCM-41 (2D hexagonal); ratio = 1–1.5, MCM-48 (cubic Ia\text{3}d); ratio = 1.2–2, MCM-50 (lamellar); ratio = 2, cubic octamer. 1,2 Similarly, the mesostructures in the PMO system are also affected by surfactant concentration as shown in Fig. 2. When the surfactant concentration is low (surfactant/BTEE = 0.006), the 2D hexagonal (P6\text{mm}) mesostructure with three relatively broad XRD peaks is obtained. As the surfactant concentration becomes higher (surfactant/BTEE = 0.01 and 0.025), the XRD pattern thus obtained exhibits several peaks that can be indexed to bicontinuous cubic Ia\text{3}d mesophase. The C_{18-6-18} surfactant also gives a formation of cubic Ia\text{3}d mesophase at high concentration of surfactant (surfactant/BTEE = 0.025).

The various kinds of mesostructures obtained from the C_{n-6-6} surfactants can also be confirmed by TEM images. As shown in Fig. 3a, the PMO material from C_{20-6-20} surfactant at

Fig. 1 XRD patterns of PMO materials obtained from C_{n-6-6} surfactants under RT method after solvent extraction, except of the material from C_{22-6-22} (lamellar structure). The materials were obtained from a molar composition of BTEE : surfactant : NaOH : H\text{2}O = 1 : 0.05 : 1.1 : 260.
low concentration (surfactant/BTEE = 0.006) gives hexagonal arrays of rod-type pores (2D hexagonal), which is very similar with that of MCM41 material. Fig. 3b shows the 3D hexagonal mesostructure (C_{16-6-16}), matching with the XRD data (Fig. 1). In case of C_{14-6-14} surfactant, the TEM image (Fig. 3c) represents well ordered cubic Pm\textbar 3n mesophase, which is very similar with the mesostructure of SBA-1 and SBA-6.\textsuperscript{20,34,35} The TEM image of Fig. 3d shows a well-ordered cubic mesostructure viewed along the (111) direction, indicating that the PMO material obtained from C_{20-6-20} surfactant at low concentration (surfactant/BTEE = 0.01) has highly ordered cubic Ia\textbar 3d structures. Particle morphologies of the PMO materials in Fig. 1 are dependent on the mesostructures, as shown in Fig. 4. The morphologies are changed from sheet-like (C_{22-6-22}, Fig. 4a, lamellar) to irregular (C_{20-6-20}, Fig. 4b, 2D hexagonal), and to spherical or somewhat faceted morphologies (C_{16-6-16}, Fig. 4c, 3D hexagonal; C_{14-6-14}, Fig. 4d, cubic Pm\textbar 3n). These morphological changes of PMO materials depending on the mesostructures are similar to those of mesoporous silica materials.\textsuperscript{35}

Fig. 5 shows the relationship between the tail length (n) in the Gemini surfactants (C_{n-6-n}) and the PMO mesostructures obtained from RT method. The effect of surfactant concentration in the reaction mixture on the mesostructures is also shown in Fig. 5. The phase diagram indicates that the mesostructures are highly dependent on the shape and concentration of surfactants. Fig. 5 indicates that the tail length of C_{22-6-22} is long enough to generate lamellar mesostructure in the relatively wide range of surfactant concentration. The Ia\textbar 3d mesostructures are obtained at high concentration of the C_{20-6-20} and C_{18-6-18} surfactants. The 2D hexagonal mesostructure is obtained under the narrow range, only at the low concentration of the C_{20-6-20} surfactant. The C_{16-6-16} surfactant gives formation of only 3D hexagonal

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**Fig. 2** XRD patterns of PMO materials obtained from the different concentration of C_{20-6-20} surfactant under RT method after solvent extraction. Numbers denote the molar ratios of surfactant/BTEE. The materials were obtained from molar compositions of BTEE : C_{20-6-20} surfactant : NaOH : H_{2}O = 1 : 0.06–0.025 : 1.1 : 260.

**Fig. 3** TEM images of as-synthesized PMO materials synthesized from (a) C_{20-6-20} (surfactant/BTEE = 0.006, 2D hexagonal), (b) C_{16-6-16} (3D hexagonal), (c) C_{14-6-14} (cubic Pm\textbar 3n), and (d) C_{20-6-20} (surfactant/BTEE = 0.01, cubic Ia\textbar 3d) under RT method. The images are viewed along the (a) [001], (b) [011], (c) [110] and (d) [111] axes, respectively.

**Fig. 4** SEM images of PMO materials synthesized from C_{n-6-n} surfactants under RT method.

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mesostructure at various surfactant concentration. It is noteworthy that the cubic $Pm\text{3}n$ mesostructure from $C_{14-6-14}$ and $C_{12-6-12}$ are obtained in the very wide range of surfactant concentration. The present results in Fig. 5 indicate that the decrease of the tail length leads phase transformation from lamellar to bicontinuous cubic $Ia\text{3}d$, 2D hexagonal, 3D hexagonal, and finally to cubic $Pm\text{3}n$ under the RT method.

3.2 The effect of tail length: HT method

When the reaction mixtures are heated to 373 K after the reaction at room temperature for 24 h, the PMO materials thus obtained do not show the phase transformation depending on the tail length of $C_{n-6-n}$ surfactants, but only 2D hexagonal structures with different lattice parameters ($a_0$) as shown in Fig. 6. All the materials exhibit XRD patterns with a very intense diffraction peak and two or more weak peaks, which are characteristic of 2D hexagonal ($P\text{6}mm$) structure. The lattice parameters obtained from the XRD patterns are 5.0, 5.3, 5.6 and 5.9 nm when the tail lengths ($n$) are 14, 16, 18 and 22, respectively. Fig. 7 shows $N_2$ adsorption-desorption isotherms obtained at liquid $N_2$ temperature for the PMO materials after surfactant extraction and the corresponding pore size distribution curves determined by the BJH method. The isotherms are type IV without hysteresis which is characteristics of 2D hexagonal mesoporous materials. A well defined step in the adsorption and desorption curve appears between partial pressures $p/p_0$ of 0.2–0.5. Physical properties of the materials are listed in Table 1. The pore sizes were 2.3, 2.7, 3.0, and 3.4 nm when $n = 14$, 16, 18 and 22, respectively. The wall thicknesses which were calculated from the lattice parameters and pore sizes are about 2.6 ± 0.1 nm.

The difference between the RT method and the HT method is an additional hydrothermal treatment at 373 K. However, the phase diagram under the HT method in Fig. 8 is very different from the phase diagram under the RT method (Fig. 5). These results may indicate that low-temperature synthesis favors the formation of various structured PMO materials, especially cage-like mesostructures, as suggested previously in silica based periodic mesoporous materials. Generally, the degree of condensation of frameworks increases at higher temperature. The higher condensation degree may lead the decrease of surface curvature of surfactant-framework meso-composites, which results in the favorable formation of 2D hexagonal structure rather than the formation of 3D hexagonal or cubic $Pm\text{3}n$ mesostructures. However, 2D hexagonal structures were formed from the $C_{22-6-22}$ surfactant from the HT method, which gives the lamellar structure at the RT method. A possible explanation for this exception is that the 2D hexagonal structure is the most thermodynamically stable phase when the PMO materials are synthesized using the Gemini surfactants as the templates.

3.3 The effect of spacer length: HT method

The effect of spacer length ($s$) of the Gemini surfactants on the PMO mesostructures are investigated using $C_{18-s-18}$ surfactants ($s = 3–12$). When the spacer length is 12, a disordered structure is obtained as shown in Fig. 9. Except for $s = 12$, all the XRD patterns in Fig. 9 show typical 2D hexagonal mesostructures with different lattice parameters. The lattice parameters of

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**Fig. 5** Effects of the tail length ($n$) in the Gemini surfactants ($C_{n-6-n}$) and the surfactant concentration in the reaction mixture on the PMO mesostructures obtained from RT method.

**Fig. 6** XRD patterns of PMO materials from $C_{n-6-n}$ surfactants under HT method after solvent extraction. The materials were obtained from a molar composition of BTEE : surfactant : NaOH : $H_2O = 1 : 0.05 : 2.6 : 356$. 

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PMO materials obtained from C18-3-18, C18-6-18, C18-8-18, and C18-10-18 are 6.53, 5.63, 5.89, and 5.73 nm, respectively. However, there is no correlation between the spacer length and the lattice parameters of the PMO materials. The material from C18-3-18 surfactant shows the biggest lattice parameter which is about 1 nm bigger than the smallest one from the C18-6-18 surfactant. This is probably due to the interaction between the anionic framework sources and positively charged head groups of surfactants, and the nature of the surfactants.

The C18-6-18 surfactant, which is composed with 6-carbon spacer, keep the longest distance between two cationic head groups, therefore the two tail chains of the Gemini surfactant may be bent a bit in order to reach the hydrophobic core of micelle (Fig. 10). On the other hand, when the spacer is longer than 6, the lattice parameters somewhat increase again. Possible explanation for this result is the schematic diagrams in Fig. 10, where the carbon chain length of spacer groups (C8 and C10) may be flexible enough to move into the hydrophobic cores. This may lead the decrease in the distance between two cationic head groups, and then increases in the lattice parameter. These may also result in the formation of the 2D hexagonal mesostructures from C18-8-18 and C18-10-18 surfactants at very wide range of surfactant concentration, as shown in Fig. 11. The head groups with $x = 8$ and 10 have enough mobility to adjust the charge density between hydrolyzed organosilica species and the surfactant head groups. Therefore, the mobility can induce the suitable packing parameter of the Gemini surfactants for the formation of 2D hexagonal mesostructure.

4. Conclusion

Various kinds of PMO materials have been successfully synthesized by utilization of Gemini surfactants as the templates, and the effects of surfactant structures and reaction
The mesostructures obtained under the RT method indicate the phase transformation from lamellar, to bicontinuous cubic $Ia3d$, 2D hexagonal ($P6_{3}mm$), 3D hexagonal ($P6_{3}mmc$), and finally to cubic $Pm3n$ mesostructures with the decreases in the tail length of $C_{n-6}O$ surfactants. The HT method results in the formation of 2D hexagonal PMO materials with different pore sizes and lattice parameters. The use of Gemini surfactants depending on the spacer length ($C_{18-22}$) and the surfactant concentration in the reaction mixture on the PMO mesostructures obtained from HT method.

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