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Structural Design of Mesoporous Silica by Micelle-Packing Control Using Blends of Amphiphilic Block Copolymers

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The formation of mesoporous silica materials has been studied using blends of diblock ($C_nH_{2n+1}(OCH_2CH_2)_x-OH$, C_nEO_x , $n = 12 - 18$ and $x = 2-100$) and Pluronic triblock ($EO_xPO_{70}EO_x$, $x = 5-100$) amphiphilic block copolymers as the structure-directing agents and sodium silicate as the silica source. The mesostructure of the silica materials thus obtained, as determined by X-ray diffraction and transmission electron microscopy, changes as the volume of the hydrophilic EO group of the surfactant increases, from lamellar to two-dimensional hexagonal ($p6mm$), three-dimensional hexagonal, a cubic phase, and another cubic phase with $Im\bar{3}m$ symmetry. Particle morphologies of the mesoporous silica materials are correspondingly changed from sheetlike to irregular, faceted cubic shapes depending on the periodic mesoscale symmetry of the structure. It is reasonable that the structural transformations are due to the changes in hydrophobic surface curvatures, which can be controlled readily and precisely by using polymer blends with different hydrophilic headgroup sizes of the individual components. The hydrophilic–hydrophobic ratios between the EO headgroups and carbon tail groups were optimized in order to obtain highly ordered mesoporous silica materials. Mesoporous silica materials with the same structures but different unit cell sizes, which strongly suggests different pore sizes, can be readily obtained through the present synthetic approach.

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.^{1–7} The pore structure, such as channel connectivity and pore size, of the mesoporous materials is one of the most important physical parameters of these materials for practical applications, and must be designed depending on their uses. For example, MCM-41,^{1,2} FSM-16,^{3,4} SBA-3,^{8–10} and SBA-15^{11,12} with two-dimensional (2-d) hexagonal channel structures find applications in the fabrication of metal nanowires,^{13–15} semiconductor nanowires,¹⁶ and crystalline linear polymer nanofibers.¹⁷ MCM-48 (cubic $Ia\bar{3}d$),^{1,2,18} SBA-1 (cubic $Pm\bar{3}n$),^{8–10,19} SBA-16 (cubic $Im\bar{3}m$),^{11,12,19} KIT-1 (disordered),^{20,21} and MSU-X (disordered)²² with three-dimensional (3-d) channel or cage structures are more useful as catalysts in terms of diffusion and catalytic performance.^{5–7}

Generally, there are two methods to control the 3-d organization of the mesostructures. First, different silica/surfactant mesostructures can be obtained by using varying concentrations,

reaction temperatures, and compositions of reaction mixtures as demonstrated for SBA-3 and MCM-41¹⁰ or for MCM-41 and MCM-48 from hexadecyltrimethylammonium bromide (HTMABr, $C_{16}H_{33}N(CH_3)_3Br$).^{1,2} Alternatively, we have previously suggested that to a first approximation, using similar reaction parameters, the silica/surfactant mesophase can be explained and predicted by the effective hydrophilic–hydrophobic volume balance in the context of the classical micellar packing parameter, $g = V/a_0l$, where V is the total volume of the hydrophobic surfactant chain, a_0 is the effective hydrophilic headgroup size at the aqueous-micellar surface, and l is the kinetic surfactant tail length.^{10,23}

According to this model, lamellar mesostructures are transformed to bicontinuous, hexagonal, and discontinuous cubic phases, as the hydrophilic headgroup size increases relative to the total volume of the surfactant chain and the corresponding kinetic surfactant tail length. Thus, SBA-1 can be synthesized from hexadecyltriethylammonium bromide (HTEABr, $C_{16}H_{33}N-(C_2H_5)_3Br$), SBA-3 from HTMABr,^{8–10} SBA-15 from Pluronic P123 ($EO_{20}PO_{70}EO_{20}$), and SBA-16 from F127 ($EO_{100}PO_{70}EO_{100}$)^{11,12} under similar conditions. The second approach has advantages over the first because it does not necessarily require significant changes in reaction conditions, but it does require the additional surfactant or block copolymer synthesis. For block copolymers, the χ parameter phase space²⁴ as a function of solvent and temperature can be used to help define the packing parameter and hydrophobic and hydrophilic volume fractions of the block copolymer.

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It is of practical interest to find a way to change the effective head- and tail-group sizes systematically and continuously in order to more efficiently use this latter method. With this modification, combining the two approaches would lead to a powerful strategy for the synthesis of mesostructured materials. Such control of the hydrophilic–hydrophobic balance is often impractical because surfactant molecules with various chain sizes that cover the range to be studied are not easily available.

In view of the fact that the cooperative assembly of the composite mesostructures is both a kinetically and thermodynamically determined process, a blend of two surfactants with different headgroup sizes might be a solution for this limitation, as long as the average kinetic size and shape of a blend of surfactants is close to that of a single surfactant with the same structural kinetic dimensions. In this way, the surfactant effective headgroup size could be controlled by varying the molar ratio between the surfactants with small- and large-size head groups. This idea seems to work well in charged surfactants as demonstrated by Huo et al.,²³ who showed, in the context of generating a simple average of two surfactant packing parameters, that highly ordered mesostructures could be synthesized by mixing unlike surfactants. Chen et al., subsequently reported the synthesis of MCM-48 by using a mixture of cationic–anionic surfactants.²⁵ Ryoo and co-workers have reported the use of mixtures of cationic–cationic²⁶ and cationic–nonionic surfactants²⁷ in order to optimize the packing parameters for MCM-41 and MCM-48 structures. Recently, Cheng et al. have also reported that channel size and morphology of MCM-41 can be controlled by using mixtures of cationic–cationic surfactants.²⁸ However, there is no report of phase or structure control using mixed nonionic surfactant systems (blends), probably because they are poorly defined in terms of the classical micellar packing parameter and the corresponding definitions of headgroup size and the other associated surfactant parameters.

Here, we present the synthesis of high-quality mesoporous silica materials that include 2-d hexagonal ($p6mm$), 3-d hexagonal ($P6_3/mmc$), and cubic structures using mixtures of nonionic amphiphilic block copolymers as the structure-directing agents and sodium silicate as the silica source under acidic conditions. We have explored the possibility that the effective headgroup volume of a block copolymer is closely related to the size of the EO block fraction that is hydrophilic. Using this concept, we demonstrate the assembly and controllability of silica/polymer mesostructures depending on the headgroup sizes as defined by varying mixing ratios of nonionic amphiphilic block copolymers that have different hydrophilic headgroup sizes.

2. Experimental Section

Triblock copolymers such as Pluronic L121 ($\text{EO}_5\text{PO}_{70}\text{EO}_5$, $M_{\text{av}} = 4400$), P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}} = 5800$) and F127 ($\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, $M_{\text{av}} = 12600$), and diblock copolymer, $\text{C}_n\text{H}_{2n+1}(\text{OCH}_2\text{CH}_2)_x\text{OH}$ (C_nEO_x , $n = 12–18$, $x = 0–100$) were used as received from BASF, Aldrich and Sigma. Sodium metasilicate nonahydrate ($\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$) and hydrochloric acid (c-HCl, 37.6%) were obtained from Fisher Scientific.

Blends of amphiphilic block copolymers with various headgroup sizes were prepared by mixing two polymers with the same tail-group size but with different EO headgroup sizes. For example, in the C_{12}EO_x polymer system, we have chosen two adjacent polymers out of the four commercially available chemicals, C_{12}EO_0 (dodecanol), C_{12}EO_4 , $\text{C}_{12}\text{EO}_{10}$, and $\text{C}_{12}\text{EO}_{23}$, and mixed in varying ratios to get the desired average EO group

TABLE 1. Molar Ratios between Dodecanol (C_{12}EO_0), C_{12}EO_4 , $\text{C}_{12}\text{EO}_{10}$, and $\text{C}_{12}\text{EO}_{23}$ for C_{12}EO_x System and Mesostructures of the Mesoporous Silica Materials Thus Obtained^a

x	molar ratio			observed structure ^b	x	molar ratio		observed structure ^b
	EO_0	EO_4	EO_{10}			EO_{10}	EO_{23}	
3	0.25	0.75		L	11	0.92	0.08	3H
4		1.00		L	12	0.85	0.15	D
5		0.83	0.17	L + 2H	13	0.77	0.23	D
6		0.67	0.33	2H	14	0.69	0.31	CI
7		0.50	0.50	2H	16	0.54	0.46	CI
8		0.33	0.67	2H	18	0.38	0.62	CI
9		0.17	0.83	2H	20	0.23	0.77	CI
10			1.00	3H	23		1.00	CI

^a A 3.0 g aliquot of the 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. ^b L, 2H, 3H, D, and CI denote lamella, 2-d hexagonal, 3-d hexagonal, disordered, and cubic $Im\bar{3}m$, respectively.

numbers (x) as listed in Table 1. Other polymer blends such as C_{16}EO_x , C_{18}EO_x , and $\text{EO}_x\text{PO}_{70}\text{EO}_x$ systems were obtained by the same procedure. Silica/polymer mesostructures were obtained following the synthesis procedure reported elsewhere,²⁹ except for the use of the polymer blends as the structure-directing agents instead of a single polymer. In a typical synthesis batch, 3.0 g of C_{12}EO_x polymer blend were dissolved in 57.4 g of distilled water and then 8.8 g of sodium metasilicate were added at room temperature with magnetic stirring, giving a clear solution. To this reaction mixture, 17.7 g of c-HCl were quickly added with vigorous magnetic stirring. The resulting gel mixture was stirred for 1 day at room temperature and subsequently heated for 1 day at 373 K in an oven to increase the degree of silanol group condensation. In the case of Pluronic triblock polymers, 3 g of a polymer mixture were dissolved in 75.0 g of distilled water and the reaction temperature was 313 K before heating to 373 K for 1 day. The solid product was filtered and dried at 373 K overnight. The product was then slurried in ethanol/HCl mixture, filtered, washed with ethanol, dried in an oven, and calcined in air under static conditions at 823 K. The product yield in a typical synthesis batch was above 95% on the basis of the silica recovery.

X-ray diffraction (XRD) patterns were obtained with a Cu $\text{K}\alpha$ X-ray source using a Scintag X₂ instrument at room temperature. Transmission electron microscopy (TEM) images were recorded by films and slow-scan CCD camera using a JEM-3010 instrument (JEOL), operating at 300 keV. Scanning electron microscopy (SEM) images were collected with a JEOL 630-F microscope operating at 5 kV. N_2 adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2040 apparatus at liquid N_2 temperature and pore size distributions were calculated by the BdB (Broekhoff and de Boer) method.^{30,31} Before the measurements, samples were degassed for 12 h at 550 K.

3. Results and Discussion

Figure 1 shows representative XRD patterns of the silica/amphiphilic block copolymer mesostructured materials obtained from C_nEO_x ($n = 12, 16$, and 18 , $x = 3–100$) polymer systems before calcination. The average EO group number (x) for each polymer system can be readily controlled by mixing nonionic amphiphilic block copolymers, which are commercially available and have the same hydrophobic tail groups (C_n) and different hydrophilic headgroup sizes (EO_x). For example, by mixing two surfactants from dodecanol (C_{12}EO_0), C_{12}EO_4 , $\text{C}_{12}\text{EO}_{10}$, and $\text{C}_{12}\text{EO}_{23}$,

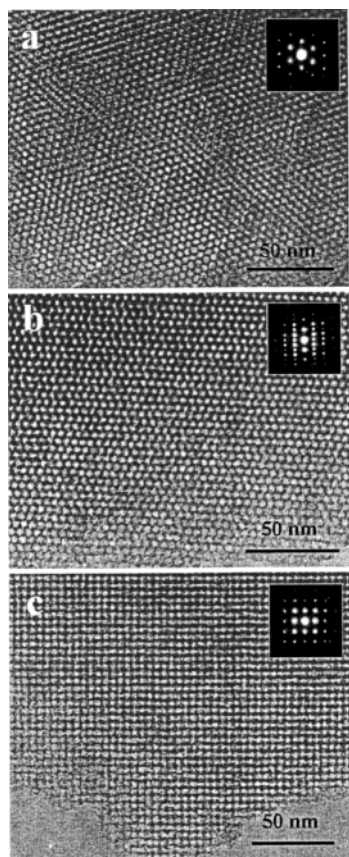


Figure 3. Transmission electron microscopic images for the calcined mesoporous silica materials obtained from the $C_{12}EO_x$ system: (a) $x = 7$, (b) $x = 10$, and (c) $x = 18$.

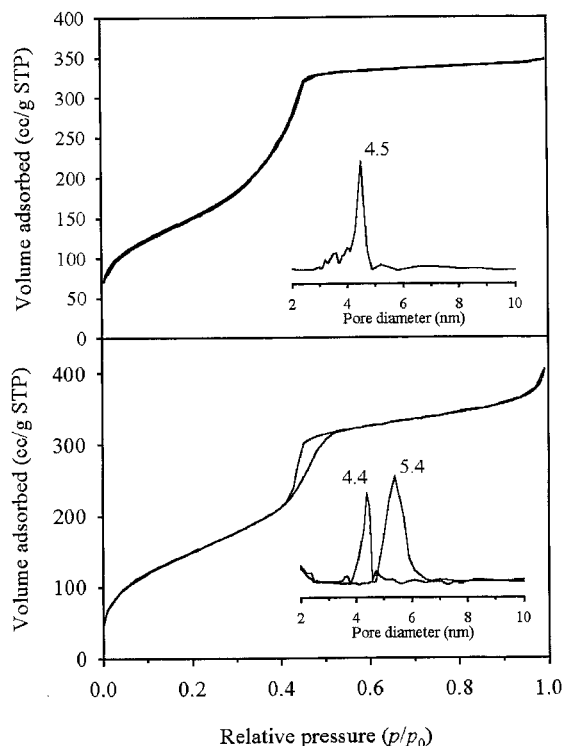


Figure 4. N_2 adsorption-desorption isotherms and corresponding pore size distribution curves for the calcined mesoporous silica materials obtained from the $C_{12}EO_x$ system: (a) $x = 7$ and (b) $x = 18$.

indicates that the material has well-defined uniform pore dimensions. BET surface area and pore volume for the material are $552 \text{ m}^2 \text{ g}^{-1}$ and $0.54 \text{ cm}^3 \text{ g}^{-1}$, respectively. The cubic $Im\bar{3}m$

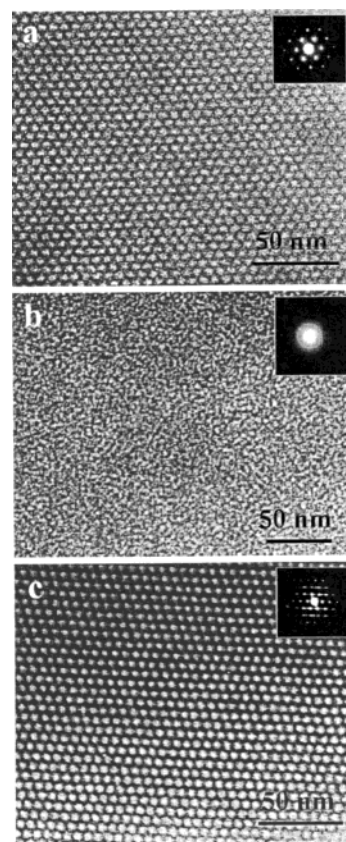


Figure 5. Transmission electron microscopic images for the calcined mesoporous silica materials obtained from (a) $C_{16}EO_8$, (b) $C_{16}EO_{10}$, and (c) $C_{16}EO_{20}$.

mesostructured material from $C_{12}EO_{18}$ gives type-IV isotherms with an H2 hysteresis loop as shown in Figure 4, part b. The pore size distribution curves indicate that the material has bottle-shaped pores,¹⁹ with a pore opening size of 4.4 nm and a larger cage diameter of 5.4 nm. The analysis results give a BET surface area of $572 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.61 \text{ cm}^3 \text{ g}^{-1}$.

Results from the $C_{16}EO_x$ and $C_{18}EO_x$ systems are similar to those of the $C_{12}EO_x$ system. XRD patterns for the $C_{16}EO_x$ system (Figure 1) can be indexed as lamellar ($x = 6$), 2-d slightly distorted hexagonal ($c2mm$ symmetry like SBA-8) ($x = 8$), disordered ($x = 10$), and cubic ($x = 20$) mesostructures. Figure 5 shows TEM images obtained from the calcined materials, which coincide with the XRD results. In the $C_{18}EO_x$ system, lamellar ($x = 7$), 3-d hexagonal ($x = 10$), cubic ($x = 20$), disordered ($x = 40$), and cubic $Im\bar{3}m$ ($x = 60$) mesostructures are obtained, as determined by the XRD patterns in Figure 1 and the TEM images in Figure 6. Particle morphologies of the silica/ $C_{16}EO_x$ and silica/ $C_{18}EO_x$ mesostructures are similar to those of the silica/ $C_{12}EO_x$ mesostructures.

Various self-organizing structures such as micelles, vesicles, microemulsions, and liquid crystals are formed in amphiphilic block copolymer/water and amphiphilic block copolymer/water/oil systems with change in the EO group size.^{34–39} The increase in the number of EO units in the poly(ethylene oxide)-type block copolymer 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 mesophase thus obtained may be determined by the balance of the attractive and the repulsive forces acting at the hydrophobic interfaces of the aggregates. Liquid crystalline mesophases are known to be transformed from lamellar to bicontinuous, hexagonal and

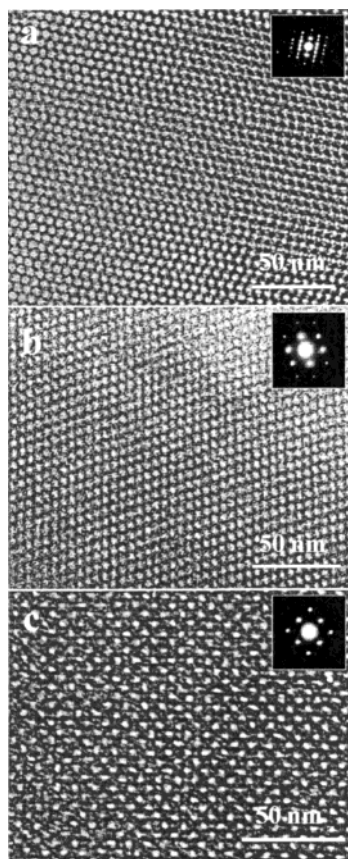


Figure 6. Transmission electron microscopic images for the calcined mesoporous silica materials obtained from (a) $C_{18}EO_{10}$, (b) $C_{18}EO_{20}$, and (c) $C_{18}EO_{60}$.

discontinuous cubic as the hydrophilic–hydrophobic balance number increases. Similar to mesophases found in surfactants and amphiphilic block copolymers, the formation of mesoporous silica materials with different mesostructures can be explained by the hydrophilic–hydrophobic balance of the structure-directing agents, as suggested for cationic surfactants^{10,23} and for amphiphilic block copolymers such as the Pluronic triblock copolymer ($EO_xPO_yEO_x$). The poly(ethylene oxide) in the polymer acts as the hydrophilic headgroup below the cloud point because EO groups are more hydrophilic than the poly(propylene oxide) moiety. The EO/PO ratio, i.e., hydrophilic–hydrophobic balance, has a large effect on the formation of the mesostructured silica.¹² Ratios of EO/PO = 0.07–1.5 favor the formation of hexagonal mesoporous silica structures. Lower ratios (<0.07) form lamellar mesostructured silica, whereas higher EO/PO ratios (>1.5) yield cubic mesoporous silica phases.

It is noteworthy that a blend of amphiphilic block copolymers can be used to selectively determine the silica/polymer mesostructure as effectively as a single block copolymer. No mixture of separated mesostructured materials is obtained. Furthermore, the $C_{12}E_9$ mixture polymer system, which is obtained by mixing $C_{12}EO_{10}$ with $C_{12}EO_4$ as shown in Table 1, yields a mesostructured silica material with a structure of the same symmetry as that obtained from a single diblock copolymer, $C_{12}EO_9$. In view of the fact that the cooperative assembly of the composite mesostructures is largely a kinetically determined process, it is reasonable that the polymer blend can be used as the structure-directing agent and the average kinetic size and shape of a mixture of small and large surfactants is essentially equivalent to the average kinetic size and shape of a single medium-sized surfactant. The hydrophilic–hydrophobic balance of the structure-

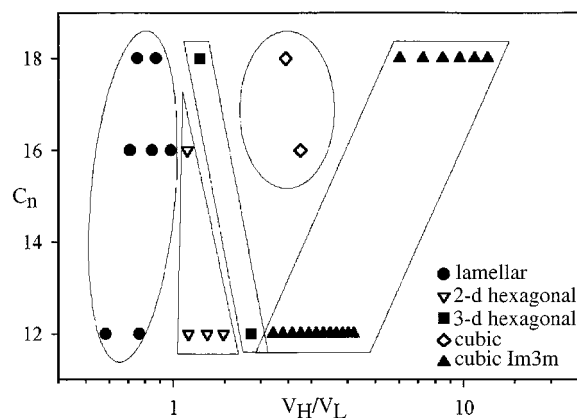


Figure 7. Relationship between hydrophilic–hydrophobic ratios in the polymer blends and the resulting silica/amphiphilic polymer mesostructures. A probable space-group assignment for the $m3m$ cubic phase (diamonds) is $Fm\bar{3}m$.

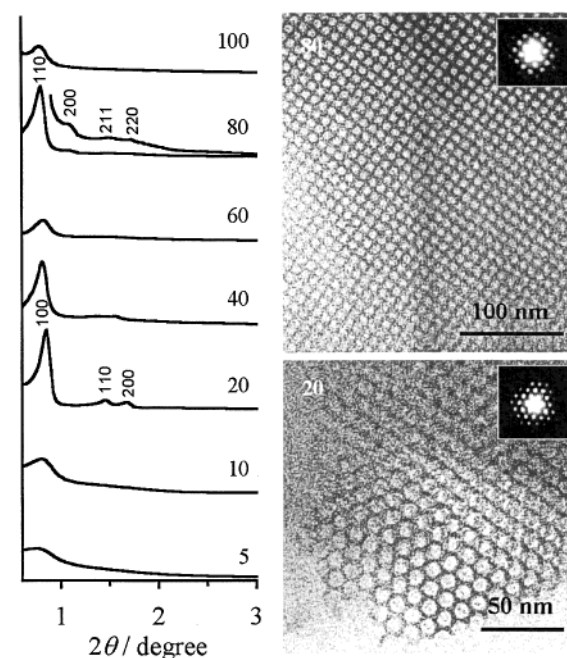


Figure 8. X-ray diffraction patterns and transmission electron microscopic images for the mesostructured silica materials obtained from Pluronic triblock copolymer, $EO_xP_{70}EO_x$ systems. The numbers denote the average EO group numbers (x) in the polymer mixtures.

directing agents can be precisely controlled in the formation of silica/polymer mesostructures by varying the molar ratio between the surfactants with small and large head-group sizes, even though amphiphilic block copolymers are more poorly defined in terms of the classical micellar packing parameter and the corresponding definitions of headgroup area and the other associated surfactant parameters.

Figure 7 shows the relationship between hydrophilic–hydrophobic balance in the blends of the amphiphilic block copolymers and silica/polymer mesostructures obtained. The molar volume of hydrophilic headgroups can be calculated by the sum of molar volumes of poly(ethylene oxide) and hydroxide: $V_H = xV_{EO} + V_{OH}$, where V_H , V_{EO} , and V_{OH} are the molar volumes of the hydrophilic part, the ethylene oxide (EO) group, and the hydroxyl group, respectively, and x is the number of EO units. It has been reported that V_{EO} is 38.8 cm³/mol and V_{OH} is 8.8 cm³/mol according to the experimental data on $C_{12}EO_x$.^{34,40} The molar volume of hydrophobic part, V_L , can be obtained by $V_L = nV_C$, where n is the number of carbon units

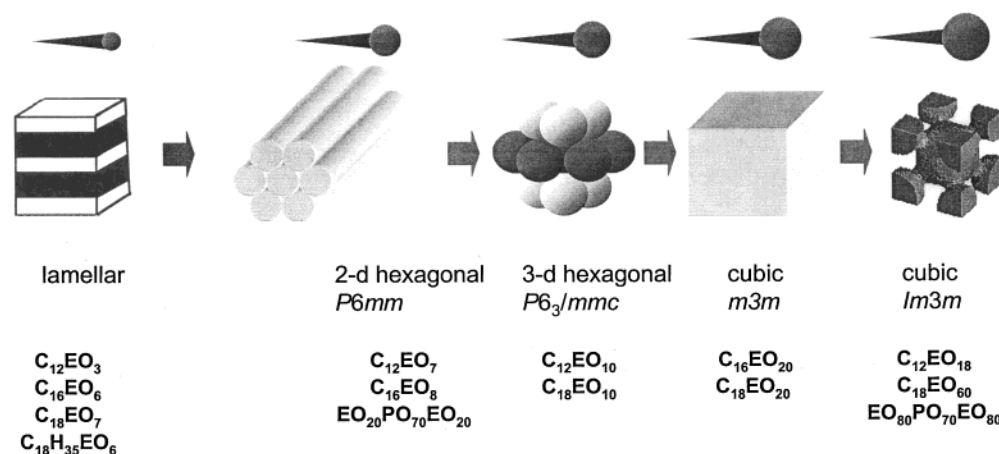


Figure 9. Suggested mesostructures as a function of the hydrophilic-hydrophobic balance in amphiphilic block copolymer blends. On the basis of preliminary TEM and X-ray results, a probable space-group assignment for the cubic $m\bar{3}m$ phase preceding the $Im\bar{3}m$ phase is $Fm\bar{3}m$.

and V_C is the molar volume of a carbon unit ($17.9 \text{ cm}^3/\text{mol}$).^{34,40} These values can be used to calculate the hydrophilic-hydrophobic ratio (V_H/V_L). Figure 7 indicates that the hydrophilic-hydrophobic ratio of 0.5–1.0 results in the formation of lamellar mesostructures and the ratio of 1.0–1.7 yields 2-d hexagonal mesostructures. Three-dimensional hexagonal, cubic (possibly $Fm\bar{3}m$), and cubic $Im\bar{3}m$ mesostructures are obtained in the range of 1.2–2.0, 2.0–3.0, and 2.0–12.0, respectively. The nature of the amphiphilic block copolymers also affects the formation of mesostructures. The present results did not reveal a cubic mesostructure other than the $Im\bar{3}m$ structure in the $C_{12}EO_x$ system nor was 2-d hexagonal symmetry found in the $C_{18}EO_x$ system. It is likely, however, that the cubic $Fm\bar{3}m$ structure is closely related to the HCP structure, so that it might be accessible by further fine-tuning of the synthesis conditions.

Mesoporous silica materials with the same mesostructures but with different unit cell sizes can be readily obtained through the present synthetic approach,³² as they can in mixed-cationic surfactant systems.²⁶ Two-dimensional hexagonal silica mesostructures are obtained by using $C_{12}EO_7$, $C_{16}EO_8$, and $C_{18}H_{35}EO_{10}$ as the structure-directing agents. The XRD patterns indicate that the materials have highly ordered 2-d hexagonal mesostructures with different lattice parameters (a_0).³² The values of a_0 are 5.5, 6.6, and 7.1 nm for $C_{12}EO_7$, $C_{16}EO_8$, and $C_{18}H_{35}EO_{10}$, respectively. The experimental data show that a_0 is proportional to n for various C_nEO_x . A large headgroup ($x = 10$) is necessary for the formation of the 2-d hexagonal mesostructures when a polymer blend with long chain hydrophobic tail group ($C_{18}H_{35}$) is used, while a small headgroup ($x = 7$) is needed for a polymer with a short tail group (C_{12}). Similarly, the cubic $Im\bar{3}m$ mesostructure is obtained when the EO group number (x) is 60 for $C_{18}EO_x$ system, whereas $x = 18$ is optimum length for the same structure in case of the $C_{12}EO_x$ system.

The present approach to control the hydrophilic-hydrophobic balance of the structure-directing agents can also be applied to the Pluronic triblock copolymers. Figure 8 shows the XRD patterns and TEM images for the silica/polymer mesostructures obtained by using mixtures of Pluronic L121, P123, and F127. 2-d hexagonal mesostructure are obtained in the range of $x = 12$ –40 in the $EO_xPO_{70}EO_x$ systems, whereas $x = 70$ –90 results in the formation of cubic $Im\bar{3}m$ mesostructures.

4. Conclusions

High-quality mesoporous silica materials that include 2-d hexagonal, 3-d hexagonal and cubic structures have been

synthesized by using blends of nonionic amphiphilic block copolymers as structure-directing agents and sodium silicate as the silica source under acidic conditions. Figure 9 summarizes the transition of silica/amphiphilic block copolymer mesostructures depending on the hydrophilic-hydrophobic balance of the structure-directing agents. The mesostructures are transformed from lamellar to 2-d hexagonal, 3-d hexagonal, cubic, and another cubic phase with $Im\bar{3}m$ symmetry, as the size of hydrophilic EO headgroup increases. The use of amphiphilic block copolymer blends as structure-directing agents makes it possible to design and control mesostructure phase and domain dimensions precisely and easily.

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