

Syntheses of High-Quality Mesoporous Materials Directed by Blends of Nonionic Amphiphiles under Nonaqueous Conditions

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WE SINCERELY DEDICATE THIS ARTICLE TO PROF. GALEN D. STUCKY FOR HIS 65TH BIRTHDAY

A rapid solvent evaporation approach combined with the blends of nonionic amphiphiles as the structure-directing agents (SDA) has been demonstrated to direct the formation of high-quality mesoporous silica materials with two-dimensional (2D) hexagonal or 3D cubic mesostructures. By using oligometric alkyl-ethylene oxide surfactant Brij 35 ($C_{12}H_{25}EO_{23}$) as a co-template, high-quality hexagonal ($p6m$) mesoporous silica can be prepared by using triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) co-polymer Pluronic P123, $EO_{20}PO_{70}EO_{20}$, as a template in ethanol media. A highly ordered cubic (space group $Im\bar{3}m$) mesoporous silica is obtained by using poly(ethylene oxide)-*b*-poly(butylene oxide)-*b*-poly(ethylene oxide) co-polymer polyglycol B50-6600, $EO_{39}BO_{47}EO_{39}$, as a template and Brij 35 as a co-template. The SDA composed of triblock co-polymer and a small amount of nonionic surfactant can increase the efficiency of assembly of organic and inorganic hybrid species and result in the quality improvement of the silica mesostructure. Interestingly, by using B50-6600 mixed with a large amount of Brij 35 as the SDA, a limited mesophase transition from cubic (space group $Im\bar{3}m$) to 2D hexagonal ($p6m$) is first observed. Generally, the amphiphile blend approach can increase the total pore volumes, BET surface areas of the mesoporous materials, and reduce their microporosities.

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Key Words: mesoporous materials; synthesis; surfactant; nonaqueous condition.

1. INTRODUCTION

The synthesis of designed porous materials using organic molecules as the structure-directing agents (SDA) or the templates (1–4) is an area of expeditious growth. Block co-polymers consisting of at least two blocks with different affinities can be regarded as macromolecular analogs of low molecular weight surfactants (5, 6). Use of block co-poly-

mers has been recently shown to extend the pore sizes of ordered mesoporous silica to hundreds of Angstroms (3, 7).

“Nonaqueous” synthesis strategy has been proved to be a really versatile approach to rapidly produce patterned porous or nanocomposite materials with morphologies of films, membranes, fibres and monoliths (8–16) which offer a large scope of potential applications such as sensors, separation, supports for heterogeneous catalysis and optoelectric devices. However, the mesoporous materials synthesized under “nonaqueous” media always contain less ordered or more distorted domains than that from conventional aqueous synthesis. Besides the topological defects induced by the stress or epitaxial mismatch (17), the solvent may be another important factor to cause the less-ordered domains in mesostructured materials. For the mesoporous materials prepared from “nonaqueous” media, the solvents (C_2H_5OH , THF, etc.) with less polarity compared with common H_2O will increase the solubility of hydrophobes or namely diminish the hydrophilic (solvophilic) and hydrophobic (solvophobic) contrast. Thus, the inorganic–organic hybrid mesostructures resulted from self-assembly of inorganic silica species and organic amphiphiles under “nonaqueous” conditions may be less ordered.

Mixed surfactants system with unique aggregation behavior shares many superiorities over single surfactant system (18–24) and has already been employed in the synthesis of highly ordered mesoporous materials (25–30). Huo *et al.* (25) used the mixtures of gemini surfactant C_{n-3-1} , C_{n-s-n} and single head group cationic surfactant C_nTMA^+ to successfully synthesize high-quality MCM-41 and MCM-48 mesoporous materials. Khushalani *et al.* (26) synthesized ordered and pore size tunable mesoporous silica MCM-41 by using a mixture of cetylpyridinium chloride and cetyltrimethylammonium chloride. Using a mixture of cetyltrimethylammonium bromide and carboxylate anionic surfactant as the template, siliceous MCM-48 was synthesized with low surfactants to silica ratio by Chen *et al.* (27). Ryoo and co-workers (28, 29) obtained highly ordered MCM-41 employing the mixture of cationic surfactants as

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TABLE 1
Physicochemical Properties of the Mesoporous Silica Materials Prepared with the Blends of Nonionic Amphiphiles by Rapid Solvent Evaporation Method

Sample	Surfactant ^a	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Micropore volume (cm ³ /g)	Mesopore size (nm)	Mesostructure	α (nm)
S11	P123	533	0.76	0.041	7.6	2D hexagonal	8.9
S12	P12: Brij 35 = 5:1	589	0.95	0.024	7.4	2D hexagonal	8.5
S13	P12:Brij 35 = 3:1	605	1.02	0.016	7.4	2D hexagonal	8.2
S21	B50-6600	290	0.44	0.046	9.0	3D cubic	15.6
S22	B50-6600:Brij 35 = 5:1	455	0.63	0.037	7.8	3D cubic	14.9
S23	B50-6600:Brij 35 = 5:2	602	0.83	0.028	7.6	3D cubic	14.2
S24	B50-6600:Brij 35 = 3:2	730	1.01	0.020	7.0	less ordered	—
S25	B50-6600:Brij 35 = 1:1	689	1.19	0.004	7.0	2D hexagonal	9.7

^aThe data listed below are mass ratio.

the SDA, and prepared highly ordered MCM-48 by using the mixture of cationic surfactant and polyoxyethylene alkyl ether nonionic surfactant. To our knowledge, however, no reports related to the mixed nonionic amphiphiles in the synthesis of mesoporous materials under “nonaqueous” condition have been published yet. In this paper, we report for the first time, the synthesis of high-quality mesoporous silica materials with 2D and 3D pore channels through a rapid solvent evaporation approach by using the blends of amphiphilic triblock co-polymers and nonionic surfactants as SDAs under “nonaqueous” synthesis media. The results show that the co-templates can increase the efficiency of co-operative assembly of organic and inorganic species and result in the formation of highly ordered silica mesostructure and even cause mesophase transition as the component of the amphiphile blends changes.

2. EXPERIMENTAL SECTION

2.1. Chemicals

Triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) co-polymer Pluronic P123 (Mw = 5800, EO₂₀PO₇₀EO₂₀) was obtained from BASF company, triblock poly(ethylene oxide)-*b*-poly(butylene oxide)-*b*-poly(ethylene oxide) co-polymer Polyglycol B50-6600 (Mw = 6800, EO₃₉BO₄₇EO₃₉) was obtained from Dow Company and oligomeric alkyl-ethylene oxide surfactants Brij 35 (C₁₂H₂₅EO₂₃), Brij 56 (C₁₆H₃₃EO₁₀), Brij 58 (C₁₆H₃₃EO₂₀), Brij 76 (C₁₈H₃₇EO₁₀) and Brij 78 (C₁₈H₃₇EO₂₀) were purchased from Aldrich. All these reagents were used without further purifications.

2.2. Synthesis

The mesoporous silica materials were prepared through a rapid solvent evaporation process under “nonaqueous” media by using a mixture of amphiphilic triblock co-polymers and nonionic surfactants as the SDA. The inorganic

sol-gels were prepared by stirring the mixture of a calculated amount tetraethyl orthosilicate (TEOS), ethanol, water and HCl at 20–30°C for 2 h. Then the ethanolic solution of the amphiphiles was added to the inorganic sol-gels and the mixture was further stirred for another 2 h followed by transferring to petri dishes and solvent evaporation. The final reaction mass composition was 0.6–1.5 g amphiphile blends: 2.08 g TEOS:0.1 g 2 M HCl:0.9 g H₂O:15 g C₂H₅OH (a typical starting mixture for the preparation of highly ordered 3D cubic mesoporous silica, for example, the composition is 0.60 g B50-6600, 0.24 g Brij 35, 2.08 g TEOS, 0.1 g 2 M HCl, 0.9 g H₂O and 15 g C₂H₅OH). The amounts of block co-polymer P123 and B50-6600 were kept constant for all starting mixtures, and the component of the amphiphile blends varied by the extra addition of nonionic surfactant Brij 35 (see Table 1 for detailed blends composition). The resulted thick membrane products were hydrothermally treated at 100°C in deionized water overnight. The calcination was carried out in an oven at 550°C for 5 h in air.

2.3. Characterization

Powder X-ray diffraction patterns (PXRD) were recorded with a Rigaku DIMAX-IIA diffractometer using CuK α radiation. N₂ sorption measurements were performed at 77 K using a Micromeritics Tristar-3000 analyzer after the samples were pre-heated at 100°C for 1 h and then at 200°C for 3 h under N₂ flow. The surface areas were calculated from Brunauer–Emmett–Teller (BET) equation and mesopore size distributions were calculated by using Barrett–Joyner–Halanda (BJH) model from the adsorption branch of the isotherms. The micropore volumes were calculated from α_s plot curves. Transmission electron micrographs (TEM) images were obtained with a TEM-1200EX microscope operating at 80 kV. For TEM measurements, the ground samples embedded in epoxy resin were cut into 50–80 nm ultrathin sections.

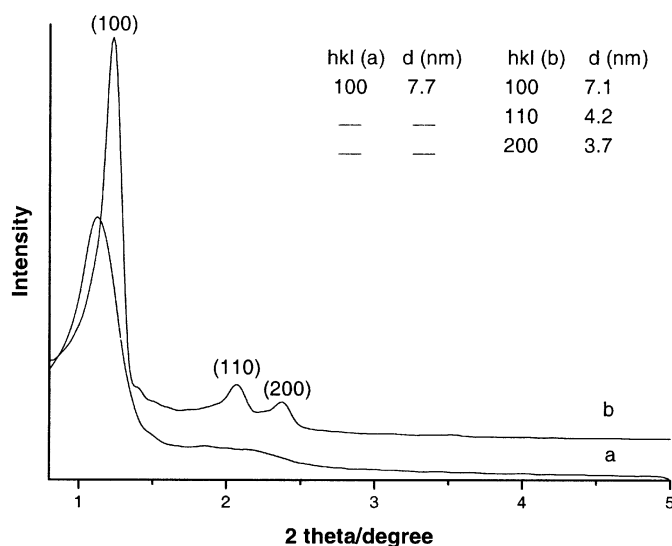


FIG. 1. PXRD patterns of calcined mesoporous silica samples synthesized by using triblock co-polymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) (a), without and (b), with the addition of nonionic surfactant Brij 35 ($\text{C}_{12}\text{EO}_{23}$) (mass ratio, P123:Brij 35 = 3:1) as the structure directing agents.

3. RESULTS AND DISCUSSION

“Nonaqueous” synthesis strategy combined with nonionic amphiphile blends offers an easy and rapid route to synthesize bulk mesoporous silica materials in our work. PXRD pattern (Fig. 1a) of calcined sample prepared with single block co-polymer P123 as an SDA by the “nonaqueous” synthesis route shows a diffraction peak with d spacing of 7.7 nm and two poorly resolved peaks at 2θ of 1.5–2.5° suggesting that a less-ordered 2D hexagonal ($p6m$) mesoporous silica material is formed. Figure 1b shows the representative PXRD pattern of calcined mesoporous silica templated by the amphiphile blends with the composition of P123:Brij 35 = 3:1 (mass ratio). Three well-resolved Bragg diffraction peaks indexed as [100], [110], [200] with high intensities are observed, indicating that a high-quality 2D hexagonal ($p6m$) mesoporous silica is obtained. These results suggest that with blends of amphiphiles as the SDA, the structure regularities of the final products can be very much improved. Moreover, the d value decreases with the addition of Brij 35 as shown in Fig. 1, which may be caused by the incorporation of shorter molecular chains of Brij 35 compared with those of triblock co-polymer P123.

N_2 adsorption–desorption measurements also indicate the high-quality 2D hexagonal mesostructure formation in the presence of amphiphile blends. The sorption curves for the calcined mesoporous silica products prepared by triblock co-polymer P123 under “nonaqueous” condition are typical IV isotherm with H1 hysteresis loop (Fig. 2). Compared with that for the mesoporous material templated by single P123, the product prepared from the amphiphile

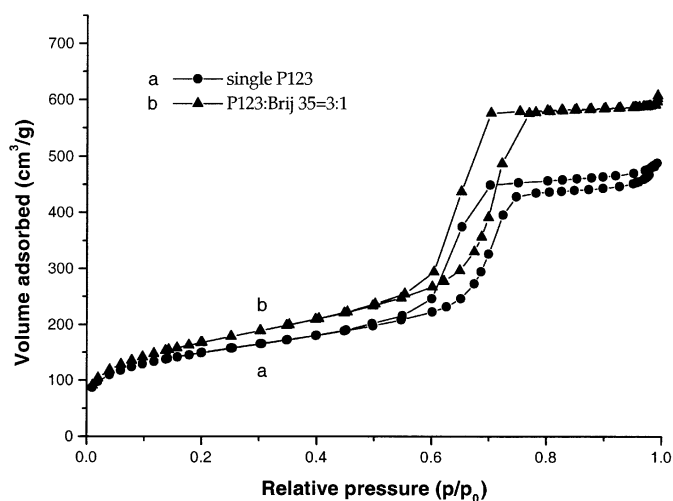


FIG. 2. Nitrogen adsorption–desorption isotherm plots of calcined samples synthesized by using triblock co-polymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) (a), without and (b) with the addition of nonionic surfactant Brij 35 ($\text{C}_{12}\text{EO}_{23}$) (mass ratio, P123:Brij 35 = 3:1) as the SDA.

blends shows a more regular hysteresis loop, suggesting highly ordered mesopore channels with narrow size distribution. The BET surface areas and total pore volumes for the calcined mesoporous products templated by the mixed amphiphiles (P123:Brij 35 = 3:1) are $605 \text{ m}^2/\text{g}$ and $1.02 \text{ cm}^3/\text{g}$, respectively, which are larger than those for calcined mesoporous silica products prepared by single block co-polymer P123. The micropore volume declines from 0.041 to $0.016 \text{ cm}^3/\text{g}$ as the extra addition of Brij 35 increases. Moreover, the BJH pore size distribution also declines from 7.6 to 7.4 nm with the addition of Brij 35, in accordance with the d value changes shown in PXRD patterns.

The case for 3D cubic mesoporous silica is similar. Block co-polymer B50-6600 has proved to be able to direct caged siliceous mesostructure formation in acidic aqueous media in previous literature (31). PXRD pattern (Fig. 3a) for 3D cubic mesoporous silica materials templated by single block co-polymer B50-6600 under “nonaqueous” synthesis condition shows only one resolved diffraction peak that may be indexed as [110]. With mixing of a small amount of nonionic surfactant Brij 35 (B50-6600:Brij 35 = 5:2), PXRD pattern (Fig. 3b) for calcined mesoporous silica shows four well-resolved diffraction peaks which may be indexed as [110], [200], [211] and [220] (space group $Im\bar{3}m$), indicating that amphiphile blends system can also improve the quality of 3D cubic mesoporous silica materials.

From TEM observations, more ordered domains with cubic caged mesostructures can easily be found. Figure 4a shows the representative [100] plane and its electron diffraction pattern. These results confirm that the mesoporous products prepared by triblock co-polymer B50-6600

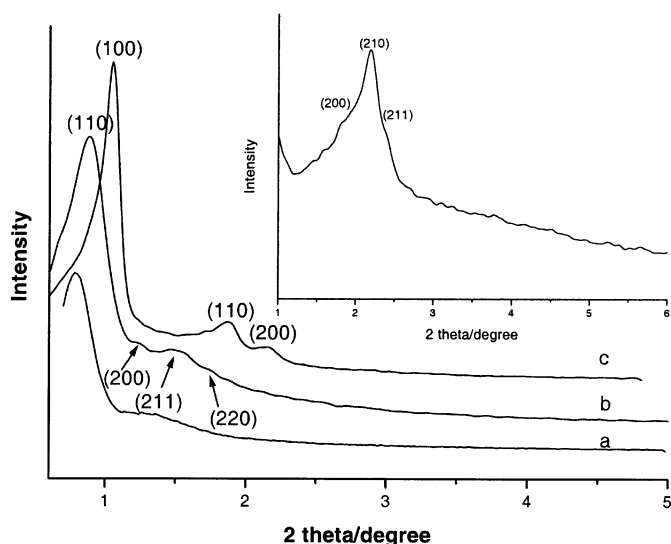


FIG. 3. PXRD patterns of calcined mesoporous silica samples templated by (a), single block co-polymer B50-6600; (b, c), mixture of block co-polymer B50-6600 and nonionic surfactant Brij 35 with the mass ratio of (b), 5:2; (c), 1:1. Inset, PXRD pattern of calcined mesoporous silica material templated by single nonionic surfactant Brij 35 under nonaqueous condition.

mixed with a small amount of nonionic surfactant Brij 35 have highly ordered 3D cubic mesostructure ($Im\bar{3}m$ space group). N_2 adsorption–desorption measurements for calcined products templated by amphiphile blends (B50-6600:Brij 35 = 5:2) show type-IV isotherm with larger regular type-H2 hysteresis loop than that for calcined mesoporous materials prepared from single block co-polymer B50-6600 (Fig. 5), suggesting that mixed amphiphiles such as the SDA can improve the caged structure regularity of the 3D cubic mesoporous materials. Like 2D hexagonal mesoporous materials, the microporosity for the calcined 3D mesoporous silica products prepared from mixed amphiphiles decreases with the increase in the amount of nonionic surfactant Brij 35.

Interestingly, as shown in Fig. 3c, PXRD pattern for mesoporous silica product prepared by using mixed amphiphiles with blends composition B50-6600:Brij 35 = 1:1 shows three well-resolved [100], [110] and [200] Bragg diffraction peaks, indicating the formation of well-ordered 2D hexagonal ($p6m$) mesoporous silica materials. These results suggest that a clear mesophase transition emerges herein. N_2 adsorption–desorption measurements show that the calcined mesoporous silica materials prepared from B50-6600 and Brij 35 blends indeed have a typical IV isotherm with well-parallel H1 hysteresis loop, confirming the structural changes. TEM image (Fig. 4b) for this sample shows strut-like channels typical of [100] plane of 2D hexagonal mesostructure, further indicating the structural change from cage-like cubic mesostructure ($Im\bar{3}m$) to uniform 1D pore channel 2D hexagonal mesostructure

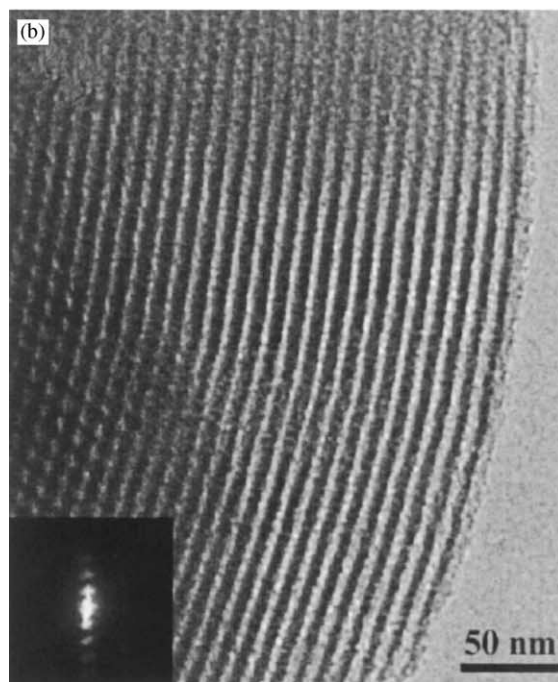
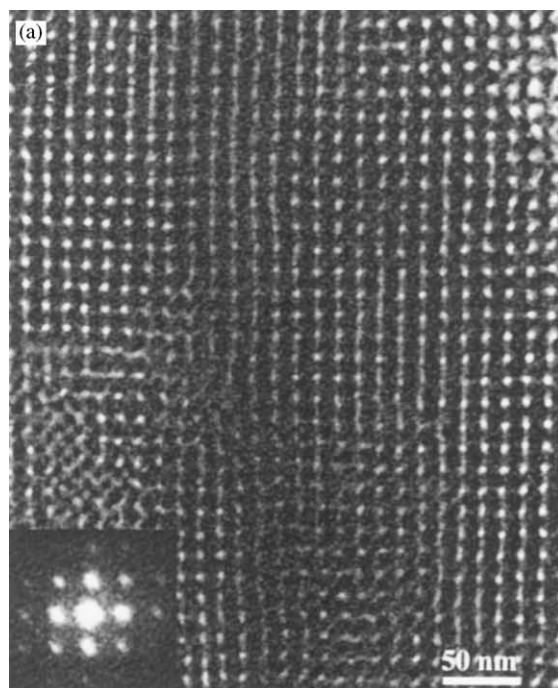


FIG. 4. TEM images of the calcined mesoporous silica samples prepared by using the blends of B50-6600 and Brij 35 with different mass ratio of (a), 5:2; (b), 1:1 as the templates. The image (a), showing the (100) plane of the cubic lattice with the $Im\bar{3}m$ space group; the image (b), showing the (100) plane of the typical 2D hexagonal mesostructure. Insets are representative ED patterns.

($p6m$) as a large amount of surfactant Brij 35 is added. Our results based on PXRD pattern (Fig. 3 inset) and TEM images (not shown here) show that single surfactant Brij 35

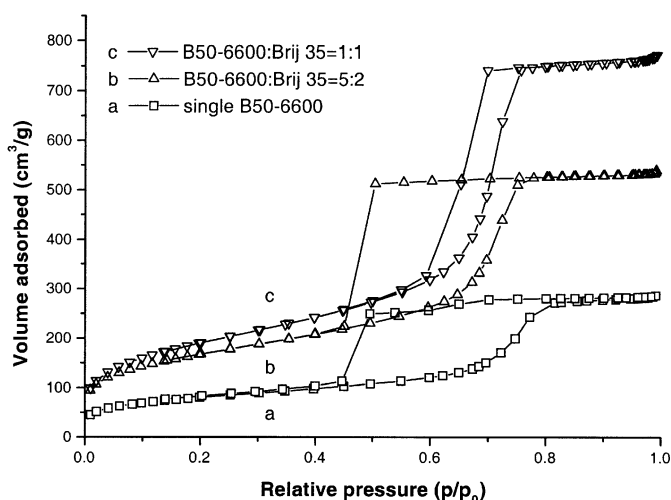


FIG. 5. N_2 adsorption-desorption isotherm curves of calcined mesoporous samples templated by (a), single block co-polymer B50-6600; (b, c), mixture of block co-polymer B50-6600 and nonionic surfactant Brij 35 with the mass ratio of (b), 5:2; (c), 1:1.

used as SDA only yields 3D caged cubic mesostructure ($Pm\bar{3}n$). Furthermore, using a larger amount of block co-polymer B50-6600 instead of addition of extra Brij 35, only disordered or lamellar mesostructured silica are formed under “nonaqueous” condition (not shown here). So the oligomeric alkyl-ethylene oxide surfactant Brij 35 used here plays an important role in the formation of regular mesostructure and causes mesophase transition.

Besides Brij 35, other oligomeric nonionic surfactants such as Brij 56, Brij 58, Brij 76 and Brij 78 can also be used as the co-templates to improve the quality of the mesoporous silica materials when triblock co-polymer P123 or B50-6600 are used as the SDA under “nonaqueous” conditions. Similar to the case of Brij 35, the BET surface areas and the total pore volumes of the mesoporous materials prepared by adding nonionic surfactants mentioned above as the co-templates increase compared with those of the products templated by single block co-polymers.

The improvement of the mesostructure may be caused by the synergism functions of the mixed surfactants system. The amphiphile blends may re-adjust the interplay of inorganic-organic and organic-organic species. In low polar organic solvents such as ethanol, the segregation force between the PPO (PBO) and the PEO blocks is weak, which may cause poor microseparation, and further result in poor ordering of the silica mesostructure. However, with the addition of oligomeric nonionic surfactant such as Brij 35, the hydrophobicity of the micellar core of the amphiphiles may be strengthened due to the introduction of more hydrophobic alkyl chains. Furthermore, the micellar packing may become tighter because of the interaction of different EO chains from two types of amphiphiles. Therefore, mixed

amphiphiles may result in the improvement of the mesostructure ordering. With the addition of a large amount of surfactant Brij 35 to the B50-6600 system, the micellar curvature limitedly changes, namely does not change dramatically from 3D cubic to lamellar, so a mesophase transition from 3D cubic to 2D hexagonal is observed.

In summary, employing the blends of tri-block co-polymers and oligomeric nonionic surfactants as the SDAs, the quality of 2D hexagonal and 3D cubic mesoporous materials can be very much improved under “nonaqueous” conditions. The addition of oligomeric nonionic surfactants can reduce the microporosities but increase the surface areas and pore volumes of the products. A limited mesophase transition from cubic $Im\bar{3}m$ to hexagonal $p6m$ is also observed as the component of the blends changes under “nonaqueous” synthesis condition.

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REFERENCES

- (a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, *Nature* **354**, 710 (1992); (b) J. S. Beck, J. C. Vartuli, W. J. Roth, and M. E. Leonowicz, *J. Am. Chem. Soc.* **114**, 10,834 (1992).
- S. Mann and G. A. Ozin, *Nature* **382**, 313 (1996).
- (a) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, and G. D. Stucky, *Science* **279**, 548 (1998); (b) D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, and G. D. Stucky, *J. Am. Chem. Soc.* **120**, 6024 (1998).
- (a) A. Corma, *Chem. Rev.* **97**, 2373 (1997); (b) J. Y. Ying, C. P. Mehnert, and M. S. Wong, *Angew. Chem. Int. Ed.* **38**, 56 (1999).
- P. Alexandridis, J. F. Holzwarth, and T. A. Hatton, *Macromolecules* **27**, 2414 (1994).
- G. Wanka, H. Hoffmann, and W. Vlbriche, *Macromolecules* **27**, 4145 (1994).
- S. A. Bagshaw, E. Prouzet, and T. J. Pinnavaia, *Science* **269**, 1242 (1995).
- Y. Lu, R. Ganguli, C. A. Drewien, M. T. Anderson, J. C. Brinker, W. Gong, Y. Guo, H. Soyezy, B. Dunn, M. H. Huang, and J. I. Zink, *Nature* **389**, 364 (1997).
- (a) D. Zhao, P. Yang, N. Melosh, B. F. Chmelka, and G. D. Stucky, *Adv. Mater.* **10**, 1380 (1998); (b) D. Zhao, P. Yang, D. I. Margolese, B. F. Chmelka, and G. D. Stucky, *Chem. Commun.* 2499 (1998).
- P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, and G. D. Stucky, *Nature* **396**, 152 (1998).
- P. Yang, D. Zhao, B. F. Chmelka, and G. D. Stucky, *Chem. Mater.* **10**, 2033 (1998).
- (a) H. Yang, A. Kuperman, N. Coombs, S. Mamiche-Afara, and G. A. Ozin, *Nature* **379**, 703 (1996); (b) H. Yang, N. Coombs, I. Sokolov, and G. A. Ozin, *Nature* **381**, 589 (1996).
- H. Miyata and K. Kuroda, *J. Am. Chem. Soc.* **121**, 7618 (1999).
- P. Feng, X. Bu, G. D. Stucky, and D. J. Pine, *J. Am. Chem. Soc.* **122**, 994 (2000).
- N. A. Melosh, P. Davidson, and B. F. Chmelka, *J. Am. Chem. Soc.* **122**, 823 (2000).

16. N. A. Melosh, P. Lipic, F. S. Bates, F. Wudl, G. D. Stucky, G. H. Fredrickson, and B. F. Chmelka, *Macromolecules* **32**, 4332 (1999).
17. H. W. Hillhouse, J. W. van Egmond, M. Tsapatsis, J. C. Hanson, and J. Z. Larese, *Chem. Mater.* **12**, 2888 (2000).
18. M. Bergstrom, *Langmuir* **17**, 993 (2001).
19. A. Patist, S. Devi, and D. O. Shah, *Langmuir* **15**, 7403 (1999).
20. A. Khan and E. F. Marques, *Curr. Opin. Colloid. In.* **4**, 402 (1999).
21. R. Zana and B. Michels, *Langmuir* **14**, 6599 (1998).
22. K. Aramaki and H. Kunieda, *Colloid Polym. Sci.* **277**, 34 (1999).
23. A. Shiloach and D. Blankschtein, *Langmuir* **14**, 7166 (1998).
24. A. Shiloach and D. Blankschtein, *Langmuir* **14**, 1618 (1998).
25. Q. Huo, D. Margolese, and G. D. Stucky, *Chem. Mater.* **8**, 1147 (1996).
26. D. Khushalani, A. Kuperman, N. Coombs, and G. A. Ozin, *Chem. Mater.* **8**, 2188 (1996).
27. F. Chen, L. Huang, and Q. Li, *Chem. Mater.* **9**, 2685 (1997).
28. R. Ryoo, C. H. Ko, and I. S. Park, *Chem. Commun.* 1413 (1999).
29. R. Ryoo, S. H. Joo, and J. M. Kim, *J. Phys. Chem. B* **103**, 7435 (1999).
30. L. R. Dai, T. W. Wang, L. T. Bu, and G. Chen, *Colloid Surface A* **181**(1-3), 151 (2001).
31. C. Yu, Y. Yu, and D. Zhao, *Chem. Commun.* 575 (2000).