Mesoporous Organosilicas Prepared with PEO-Containing Triblock Copolymers with Different Hydrophobic Moieties

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Surfactant-templated mesoporous silica materials have attracted great interest since the discovery of hexagonally ordered mesoporous silica material (M41S) by Mobil Corporation.[1] Structures and pore sizes of the mesoporous silica materials have been varied by several surfactants and polymeric templates. Particularly, nonionic poly(ethylene oxide) surfactants or triblock poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) copolymers as structure-directing templates have been widely used for preparing mesoporous silicas such as SBA-15,[2−4] SBA-16,[3] and MSU-X.[5,6] The synthetic route of employing nonionic block copolymers has advantages for forming thicker walls, nontoxicity, and easy removal of the polymer during calcination. The block copolymer templates obviously yield larger structural features compared with the structural size obtained with low molecular weight surfactants.

Recently, a new class of mesoporous materials have been reported such as the periodic mesoporous organosilicas (PMOs).[7−11] These materials are unique in containing organic functional groups inside the channel wall. The organic modification of the silica framework provides diverse variation of optical, electrical, and mechanical properties. However, the organosilicas prepared by block copolymer templates have not yet been reported extensively in the literature.

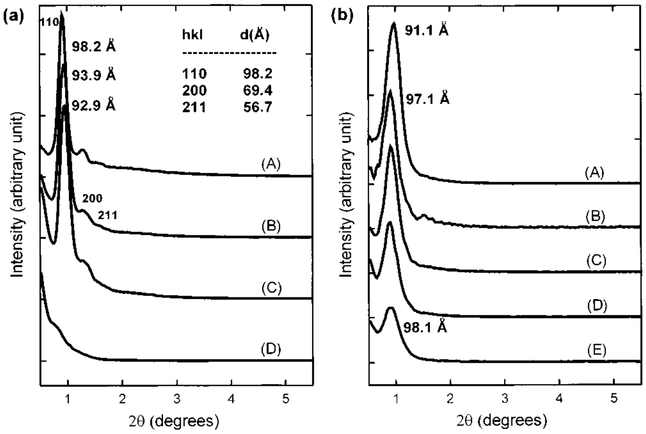

Figure 1. Powder small-angle X-ray scattering patterns of mesoporous ethanesilicas containing different weight proportions of TEOS and BTMSE. (a) Calcined samples of SBA-16 (trace A), S16-B5 (B), S16-B10 (C), and S16-B15 (D). (b) Calcined ethanesilicas prepared with LGE76 ($EO_{43}(L_{23}G_6)$-EO_{43}) template of LGE-B0 (trace A), LGE-B10 (B), LGE-B30 (C), LGE-B50 (D), and LGE-B60 (E). Numbers represent *d*-spacing values. Scattering patterns were obtained with a Bruker 2D-GADDS diffractometer using Cu Kα radiation with $\lambda = 1.5418$ Å.

In the present study, we describe the synthesis of mesoporous organosilicas from the co-condensation of TEOS and 1,2-bis(trimethoxysilyl)ethane (BTMSE) by using PEO-containing triblock copolymer templates such as F127 ($EO_{106}PO_{70}EO_{106}$; BASF) and poly(ethylene oxide)−poly(DL-lactic acid-*co*-glycolic acid)−poly(ethylene oxide) (PEO−PLGA−PEO). More hydrophobic PLGA block, compared with the PPO block in the PEO−PPO−PEO block templates, is chosen to provide more contrast between hydrophilicity and hydrophobicity of a block template such that the organosilicate is confined in the aqueous matrix phase.[12]

As the first step, we have studied the morphologies of mesoporous organosilicas using a commercial Pluronic F127 and a $EO_{43}(L_{23}G_6)EO_{43}$ ($\overline{M}_n = 7550$ gmol^{-1}; LGE76) triblock copolymer prepared in our laboratory through the ring-opening polymerization of a mixture of lactide and glycolide onto mono-methoxypoly(ethylene oxide).[13] In a typical synthesis of mesoporous organosilicas, a mixture (3.75 g) of BTMSE and TEOS was added to a 1.5 M HCl aqueous solution (160 g) containing LGE76 (1 g; 0.6 wt %) maintained at 30 °C. The mixture was stirred vigorously for about 0.5 h and then the solid products were aged for 24 h at 100 °C. The products were isolated, washed, and filtered off. Solvent extraction of the polymeric surfactants was carried out by a solution of 10 g of HCl (37 wt %) and 70 g of methanol (or ethanol) and dried at room temperature. Calcination was carried out in a furnace by employing a stepwise temperature increase from 30 to 450 °C for 10 h under N_2 flow. The synthetic method of organically modified SBA-16 with F127 was similar to the procedures described above and the quantities of reactants are reported elsewhere.[3] Mesoporous organosilica materials obtained with the F127 template were prepared with BTMSE:TEOS weight ratios of 0:100 (SBA-16),

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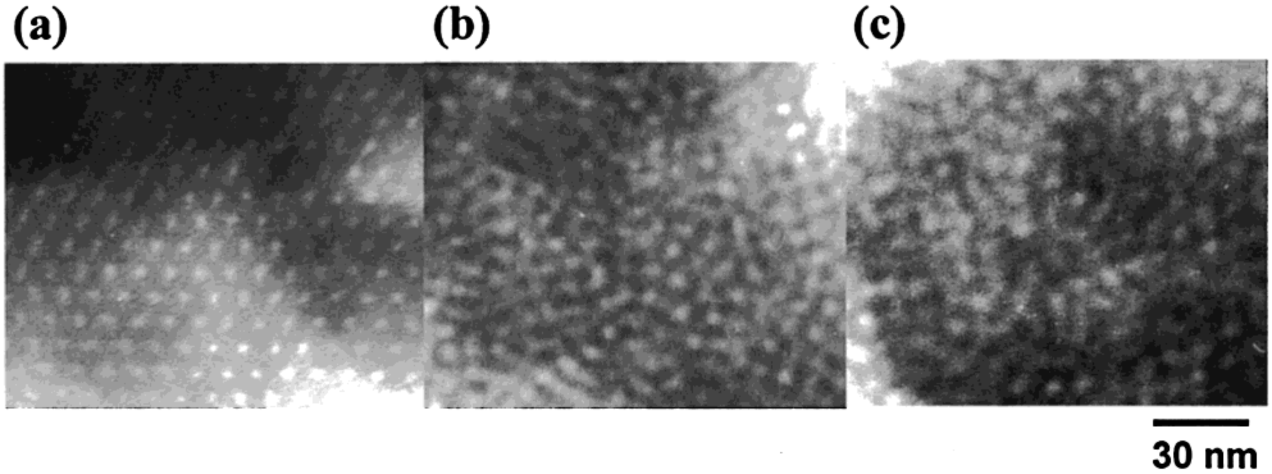

Figure 2. TEM images of calcined mesoporous ethanesilicas: (a) is for S16-B5 prepared with F127 ($EO_{106}PO_{70}EO_{106}$) and (b) and (c) are for the LGE-B30 and LGE-B50 obtained from LGE76 ($EO_{43}(L_{23}G_6)EO_{43}$), respectively. TEM images were obtained with a JEOL JEM-200CX operated at an accelerating voltage of 120 kV.

Table 1. Physicochemical Properties of Mesoporous Ethanesilicas[a]

sample code	block copolymer	BET surface area ($m^2\,g^{-1}$)	pore volume[b] ($cm^3\,g^{-1}$)	pore diameter[b,c] (nm)
S16-B5	$EO_{106}PO_{70}EO_{106}$	933	0.54	4.9
S16-B10	$EO_{106}PO_{70}EO_{106}$	640	0.38	4.2
S16-B15	$EO_{106}PO_{70}EO_{106}$	432	0.45	58.5
LGE-B10	$EO_{43}(L_{23}G_6)EO_{43}$	666	0.39	6.4
LGE-B30	$EO_{43}(L_{23}G_6)EO_{43}$	595	0.33	5.8
LGE-B50	$EO_{43}(L_{23}G_6)EO_{43}$	572	0.37	5.8
LGE-B60	$EO_{43}(L_{23}G_6)EO_{43}$	470	0.34	5.7

[a] N_2 adsorption−desorption isotherm data were measured on a Micromeritics ASAP 2010 analyzer. Samples were pre-degassed at 200 °C and 30 μm Hg for 6 h. [b] Pore volumes and sizes reported here were calculated from the adsorption branches of the isotherms by the BJH method. [c] Pore diameter represents the one at the maximum of pore volume in a pore sizes distribution.

5:95 (S16-B5), 10:90 (S16-B10), and 15:85 (S16-B15). Also, the organosilicas prepared with the LGE76 template were 0:100 (LGE-B0), 10:90 (LGE-B10), 30:70 (LGE-B30), 50:50 (LGE-B50), and 60:40 (LGE-B60).

Figure 1 shows the SAXS data for mesoporous organosilicas containing different amounts of BTMSE in TEOS templated with two different types of block copolymers. Note that the SAXS data reported here are for calcined samples to show the structural variation as a function of BTMSE amount for each block template. We also note, however, from the comparison of the SAXS data for samples before and after calcinations that there was no significant structural difference except the slight decrease in *d* spacing value after calcination.

In the case of employing the F127 triblock template, we found that the cubic morphology is maintained until 10 wt % of BTMSE is incorporated into the silica source, as shown in Figure 1a (traces A to C). The analysis of higher order peaks in traces A−C of Figure 1a confirms the formation of cubic ($Im\bar{3}m$) morphology as previously verified by Zhao and co-workers.[3] The high periodicity, surface area, and pore volume of the mesoporous organosilicas containing BTMSE of <10 wt % are also verified with transmission electron micrograph (Figure 2a) and N_2 adsorption data (Table 1).

We further noticed that the cubic morphology is no longer maintained when BTMSE quantity exceeds 15 wt % as shown in the scattering pattern (trace D) of Figure 1a. The N_2 adsorption−desorption isotherm on the S16-B15 sample containing 15 wt % of BTMSE in total silica source exhibits a mixed form of type I and II, the characteristics of microporosity and nonporosity (see Supporting Information).[14] From several experiments, we conclude that the PEO−PPO−PEO structure-directing template with a small difference between the hydrophilicity of the PEO block and hydrophobicity of the PPO block are not so effective for forming mesoporous organosilicas with a large amount of BTMSE incorporated.

Figure 1b illustrates the powder small-angle X-ray scattering patterns of calcined ethanesilicas obtained with the LGE76 triblock template as a function of BTMSE content in the total silica. Scattering patterns show a single intense reflection with *d* spacing values from 91 ($2\theta = 0.97$) to 98 Å ($2\theta = 0.91$). TEM (Figures 2b and 2c) and N_2 adsorption data (Table 1) also verify that a large amount of mesopore is still maintained, even after the addition of 60 wt % BTMSE in the silica, although the samples are found to be less ordered in the long range. These results imply that the LGE76 triblock template is quite effective for forming mesoporous organosilica materials containing a large amount of BTMSE. We also found that the yield of solid content is almost 100%. We, however, noticed that the LGE76 triblock copolymer in dilute aqueous solution is not homogeneously dissolved, as evidenced in the dynamic light scattering data (i.e., a small amount of micelle cluster is observed) and thus does not form monodisperse micelles, which is necessary for forming the ordered cubic morphology. The decrease in the main peak intensity with increasing BTMSE content in the scattering data shown in Figure 1b agrees with the decrease in the BET surface area data shown in Table 1.

Table 1 shows the physicochemical properties of mesoporous ethanesilicas characterized by the BJH method. The N_2 adsorption−desorption isotherms of the mesoporous ethanesilica materials prepared with the LGE76 template exhibit typical type IV behavior, which

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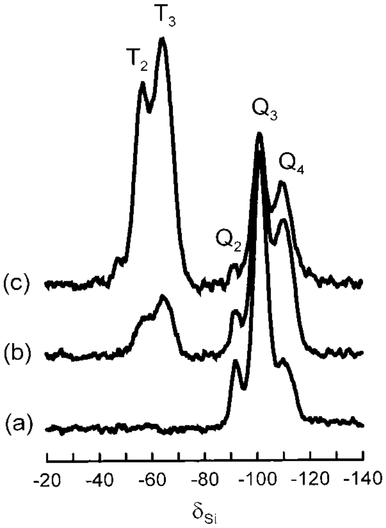

Figure 3. Solid-state ^{29}Si CP-MAS NMR spectra of mesoporous ethanesilicas prepared with a LGE76 triblock copolymer. The spectra are for (a) LGE-B0, (b) LGE-B10, and (c) LGE-B50, respectively, and obtained with a Bruker DSX400 spectrometer.

is characteristic of mesoporous materials with a sharp inflection at $P/P_0 \approx 0.42$ (i.e., H$_2$ hysteresis) (see Supporting Information).

To verify BTMSE incorporated into the silica solids prepared with the LGE76 template, solid-state ^{13}C and ^{29}Si CP-MAS NMR experiments on the solvent-extracted samples were performed. The ^{13}C CP-MAS NMR spectra represent a resonance assigned to the carbon in the ethane bridge of organosilica at δ of -4 and a resonance at δ of -70 corresponding to the carbon originating from polymeric surfactants (see Supporting Information). The ^{29}Si CP-MAS NMR of the LGE-B0 sample shows the characteristic signals assigned to $Si(OSi)_4$ (Q$_4$ δ -110), $(HO)Si(OSi)_3$ (Q$_3$ δ -101), and $(HO)_2Si(OSi)_2$ (Q$_2$ δ -92), respectively (Figure 3a). In contrast, the ethanesilicas obtained from the BTMSE precursor represent another characteristic signal assigned to $CSi(OSi)_3$ (T$_3$ δ -65) and $CSi(OSi)_2(OH)$ (T$_2$ δ -57) as shown in Figures 3b and 3c, confirming the presence of the ethane moieties inside the silica framework. Integration of ^{29}Si MAS NMR signals also confirms the successful quantitative incorporation of the BTMSE into the mesoporous silica materials. Normalized relative peak areas of Q and T peaks were calculated for the LGE-B10, LGE-B30, and LGE-B50 samples, respectively. From these normalized peak areas, we obtain the ratios of $T/(T + Q)$ as 0.10, 0.36, and 0.60, respectively, and these values are well compared with the BTMSE content in the total silica. We note that the ethane group in the organosilica is almost intact during the calcination at 450 °C as verified with ^{29}Si NMR and the block copolymer LGE76 is entirely degraded at 450 °C as verified with TGA measurement.

In summary, we can conclude that more hydrophobic PEO−PLGA−PEO triblock copolymer is more effective in incorporating organosilicate precursors into the mesoporous silica materials than the PEO−PPO−PEO triblock copolymer template. We believe that this result presents a case showing the importance of proper choice or design of block copolymer templates suitable for mesoporous organosilica materials tailored to specific needs.

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Supporting Information Available: Figures of N$_2$ adsorption−desorption isotherms and solid-state ^{13}C CP-MAS NMR spectra (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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