270 *Chem. Mater.* **2004,** *16,* 270−275

Macromolecular Templating Approach for the Synthesis of Hydrothermally Stable Mesoporous Organosilicas with High Periodicity and Thick Framework Walls

Eun-Bum Cho and Kookheon Char*

School of Chemical Engineering and Institute of Chemical Processes,
Seoul National University, Seoul 151-744, Korea

Received July 22, 2003. Revised Manuscript Received November 13, 2003

Hydrothermally stable mesoporous ethanesilica with a long-range hexagonal order (*p*6*mm*) and a relatively thick and micropore-free framework wall was synthesized by the core−shell approach using a nonionic PEO−PLGA−PEO triblock copolymer template and a 1,2-bis(triethoxysilyl)ethane (BTESE) organosilica precursor. The pore structure and morphology were characterized by SAXS, TEM, BET, and solid-state NMR measurement. The key parameters in the synthesis of mesoporous ethanesilica with a stable thick wall are the strong contrast between the hydrophilic PEO block and the hydrophobic PLGA block and the compatibility of PEO with the BTESE organosilicate precursor at an optimum reaction temperature of 323 K. The enhanced hydrothermal stability (i.e., the structural integrity was maintained for up to 25 days in boiling water of 373 K) is believed to be due to the thick pore wall (4.2 nm), the high degree of condensation and hydrophobicity of organosilica precursor used, and the significant reduction of micropores.

Introduction

Organic modification inside the mesoporous silica framework is regarded as an important technique because it changes the physical and chemical properties of porous materials as needed for various applications. Several periodic mesoporous organosilicas (PMOs) with heterogeneous organic−inorganic silica frameworks have been synthesized through the sol−gel condensation of bifunctional organo-bridged silsesquioxanes templated with low-molecular-weight surfactants.[1−9] However, the weak hydrothermal stability of these mesoporous silica and organosilica materials prepared with conventional surfactants limits practical and potential applications. Several efforts to increase the stability and the pore size have been reported through the core−shell approach using high-molecular-weight block copolymers,[10−26] and, particularly, the modification of the surface and framework also have been investigated through several methods and materials.[26−33] Nonionic and high-molecular-weight triblock copolymers such as poly(ethylene

---

* To whom correspondence should be addressed. Phone: (+82) 2-880-7431. Fax: (+82) 2-873-1548. E-mail: khchar@plaza.snu.ac.kr.

(1) Inagaki, S.; Guan, S.; Fukushima, Y.; Ohsuna, T.; Terasaki, O. *J. Am. Chem. Soc.* **1999**, *121*, 9611−9614.

(2) Inagaki, S.; Guan, S.; Ohsuna, T.; Terasaki, O. *Nature* **2002**, *416*, 304−307.

(3) Asefa, T.; MacLachlan, M. J.; Coombs, N.; Ozin, G. A. *Nature* **1999**, *402*, 867−871.

(4) Yoshina-Ishii, C.; Asefa, T.; Coombs, N.; MacLachlan, M. J.; Ozin, G. A. *Chem. Commun.* **1999**, 2539−2540.

(5) Melde, B. J.; Holland, B. T.; Blanford, C. F.; Stein, A. *Chem. Mater.* **1999**, *11*, 3302−3308.

(6) Kruk, M.; Jaroniec, M.; Guan, S.; Inagaki, S. *J. Phys. Chem. B* **2001**, *105*, 681−689.

(7) Stein, A.; Melde, B. J.; Schroden R, R. C. *Adv. Mater.* **2000**, *12*, 1403−1419.

(8) Lu, Y.; Fan, H.; Doke, N.; Loy, D. A.; Assink, R. A.; LaVan, D. A.; Brinker, C. J. *J. Am. Chem. Soc.* **2000**, *122*, 5258−5261.

(9) Kuroki, M.; Asefa, T.; Whitnal, W.; Kruk, M.; Yoshina-Ishii, C.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2002**, *124*, 13886−13895.

(10) Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024−6036.

(11) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548−552.

(12) Yu, C.; Yu, Y.; Zhao, D. *Chem. Commun.* **2000**, 575−576.

(13) Chang, L.-Q.; Wang, J. H.; Shin, Y.; Jeong, B.; Birnbaum, J. C.; Exarhos, G. J. *Adv. Mater.* **2002**, *14*, 378−382.

(14) Matos, J. R.; Mercuri, L. P.; Kruk, M.; Jaroniec, M. *Langmuir* **2002**, *18*, 884−890.

(15) Yu, K.; Hurd, A. J.; Eisenberg, A.; Brinker, C. J. *Langmuir* **2001**, *17*, 7961−7965.

(16) Simon, P. F. W.; Ulrich, R.; Spiess, H. W.; Wiesner, U. *Chem. Mater.* **2001**, *13*, 3464−3486.

(17) Zhu, H.; Jones, D. J.; Zajac, J.; Rozière, J.; Dutartre, R. *Chem. Commun.* **2001**, 2568−2569.

(18) Muth, O.; Schellbach, C.; Fröba, M. *Chem. Commun.* **2001**, 2032−2033.

(19) Cho, E.-B.; Kwon, K.-W.; Char, K. *Chem. Mater.* **2001**, *13*, 3837−3839.

(20) Matos, J. R.; Kruk, M.; Mercuri, L. P.; Jaroniec, M.; Asefa, T.; Coombs, N.; Ozin, G. A.; Kamiyama, T.; Terasaki, O. *Chem. Mater.* **2002**, *14*, 1903−1905.

(21) Burleigh, M. C.; Markowitz, M. A.; Wong, E. M.; Lin, J.-S.; Gaber, B. P. *Chem. Mater.* **2001**, *13*, 4411−4412.

(22) Yang, S.; Mirau, P. A.; Pai, C.-S.; Nalamasu, O.; Reichmanis, E.; Lin, E. K.; Lee, H.-J.; Gidley, D. W.; Sun, J. *Chem. Mater.* **2001**, *13*, 2762−2764.

(23) Yang, S.; Mirau, P. A.; Pai, C.-S.; Nalamasu, O.; Reichmanis, E.; Pai, J. C.; Obeng, Y. S.; Seputro, J.; Lin, E. K.; Lee, H.-J.; Sun, J.; Gidley, D. W. *Chem. Mater.* **2002**, *14*, 369−374.

(24) Yang, S.; Horibe, Y.; Chen, C.-H.; Mirau, P.; Tatry, T.; Evans, P.; Grazul, J.; Dufresne, E. M. *Chem. Mater.* **2002**, *14*, 5173−5178.

(25) Goto, Y.; Inagaki, S. *Chem. Commun.* **2002**, 2410−2411.

(26) Guo, W.; Park, J.-Y.; Oh, M.-O.; Jeong, H.-W.; Cho, W.-J.; Kim, I.; Ha, C.-S. *Chem. Mater.* **2003**, 15, 2295−2298.

(27) Han, Y.; Wu, S.; Sun, Y.; Li, D.; Xiao, F.-S. *Chem. Mater.* **2002**, *14*, 1144−1148.

(28) On, D. T.; Kaliaguine, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 3248−3251.

(29) On, D. T.; Kaliaguine, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 1036−1040.

(30) Zhang, Z.; Han, Y.; Zhu, L.; Wang, R.; Yu, Y.; Qiu, S.; Zhao, D.; Xiao, F.-S. *Angew. Chem., Int. Ed.* **2001**, *40*, 1258−1262.

(31) Liu, Y.; Zhang, W.; Pinnavaia, T. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 1255−1258.

10.1021/cm0346733 CCC: $27.50

oxide)−poly(propylene oxide)−poly(ethylene oxide) (PEO−PPO−PEO) which form supramolecular structures in aqueous solution have the advantage of realizing large mesopores with thicker framework.[10,11] However, the synthesis of highly periodic mesoporous organosilicas with hydrothermally stable and thick framework walls has proven to be somewhat difficult with the PEO−PPO−PEO block templates under typical experimental conditions because the difference in the hydrophilicity of a PEO block and the hydrophobicity of a PPO block is not so large as to confine organosilica precursors in the aqueous continuous phase,[19] although a long-range ordering of the organosilica monolith is achieved through the direct liquid crystal templating approach at relatively high block copolymer concentration[17] or with the aid of an inorganic salt (NaCl)[26] and the phenylene-bridged mesoporous materials at high reaction temperature as reported elsewhere.[25]

In the present study, we describe an approach for synthesizing 2D-hexagonal mesoporous ethanesilicas using several poly(ethylene oxide)−poly(DL-lactic acid-*co*-glycolic acid)−poly(ethylene oxide) (PEO−PLGA−PEO) structure-directing agents in low concentrations and a moderate temperature condition, and we also report remarkably enhanced hydrothermal stability of the mesoporous ethanesilicas based on the improved framework wall properties. The main issue of the present study is to address several factors to control the interaction between each block of the block copolymer templates and an organosilicate precursor for forming mesoporous organosilica with long-range order and a framework that is thick-walled and chemically robust.

Experimental Section

Synthesis of Block Copolymer Templates. We have synthesized $EO_{16}(L_{23}G_6)EO_{16}$, $EO_{16}(L_{28}G_3)EO_{16}$, and $EO_{16}(L_{32}G_8)EO_{16}$ triblock copolymers (denoted as LGE54, LGE53, and LGE63, respectively) through the ring opening polymerization from mixtures of distilled 3,6-dimethyl-1,4-dioxane-2,5-dione (DL-lactide) (Aldrich) and glycolide (Polyscience) with mono-methoxypoly(ethylene oxide) (Aldrich) and hexamethylene diisocyanate (Sigma) as a coupling agent. Final block copolymer products were obtained by successive filtration and drying in a vacuum after precipitating the block copolymer in diethyl ether. Molecular weights (5390, 5300, and 5700) and polydispersity indices (1.19, 1.19, and 1.22) were determined by GPC and their functional compositions were quantified by ^{1}H NMR analysis. GPC data of the triblock copolymer templates were obtained by using a Waters LC system coupled with a Waters 410 differential refractometer. The flow rate of THF used as a mobile phase was 1 mL/min. ^{1}H NMR (300 MHz) spectra used to determine the chemical structure of the block templates were obtained with a JEOL JNM-LA 300 WB FT-NMR system at room temperature. The weight fractions of PEO blocks (f_{PEO}) for the three block copolymers prepared in the present study were found to be 0.40, 0.38, and 0.33, respectively, as shown in Table 1.

Preparation of Periodic Mesoporous Silica and Organosilica. In a synthesis of mesoporous silica, tetraethyl orthosilicate (TEOS) was used as silica source and the molar composition of the final mixture was LGE54/TEOS/HCl/ethanol/H_2O = 0.014:1.0:6.5:5.07:163.9. After the mixture was stirred for about 0.5 h at 298 K, the solid products were aged for 24 h at 373 K. Calcination was carried out in a furnace by employing a stepwise temperature increase from 303 to 773 K for 10 h under N_2 flow. In the case of preparing mesoporous ethanesilica, 1,2-bis(triethoxysilyl)ethane (BTESE) (Aldrich) and 1,2-bis(trimethoxysilyl)ethane (BTMSE) (Aldrich) were used as organosilica precusors. The molar composition of the final mixture in the synthesis of mesoporous organosilica was LGE53/BTESE/HCl/ethanol/H_2O = 0.03:1.0:7.0:10.1:348.7. White precipitates were obtained after the mixture was stirred for about 0.5 h at either 313 or 323 K and the solid products were then successively aged for 24 h at 373 K. Extraction of the block template was carried out by successive treatment with distilled water, ethanol, and acetone, and then dried at room temperature. The reason the solvent extraction method is employed to remove the block templates for organosilica precursors used in the present study is that there is a chance of converting the bridged carbons in the organosilica precursor into siloxane bonds, as confirmed with Si NMR, under a calcination environment containing a small amount of oxygen.

Table 1. Characterization of PEO−PLGA−PEO Triblock Copolymer Templates Used in Present Study

sample	$\overline{M}_n$[a] (g/mol)	PI[a]	ω_{PEO}[b]	f_{LA}[b]
LGE54 ($EO_{16}(L_{23}G_6)EO_{16}$)	5390	1.19	0.40	0.80
LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$)	5300	1.19	0.38	0.90
LGE63 ($EO_{16}(L_{32}G_8)EO_{16}$)	5700	1.22	0.33	0.80

[a] Molecular weight and polydispersity index were determined by GPC. [b] Weight and mole fractions of each block were quantified by ^{1}H NMR. $\overline{M}_n$, number average molecular weight; PI, polydispersity index; ω_{PEO}, weight fraction of PEO block; and f_{LA}, mole fraction of lactic acid in the PLGA block.

Characterization and Calculation. Powder SAXS experiments were performed under 2D SAXS at the 4C1 line of Pohang Accelerator Laboratory in POSTECH using a synchrotron radiation with $\lambda = 1.608$ Å and a Bruker 2D SAXS with a GADDS diffractometer using Cu Kα radiation with $\lambda = 1.54$ Å. Data obtained by a 2D detector using the synchrotron radiation were processed by a 2D data processing software. TEM images were obtained with a Philips TECHNAI F30 operated at an accelerating voltage of 300 kV. Samples were sonicated for 1 h in an adequate quantity of ethanol and the solution was dropped and dried onto a carbon film on a copper grid. N_2 adsorption−desorption isotherms were measured with a Micromeritics ASAP 2010 analyzer. Samples were pre-degassed at 423 K and 30 μmHg for 6 h, and the pore size distributions were calculated from the adsorption branches of isotherms by the BJH method. The BET specific area was calculated from data in the relative pressure range from 0.06 to 0.2. The total pore volume was evaluated from the amount adsorbed at a relative pressure of 0.98 and the sum of micropore volume was obtained using the α_s plot method.[34,35] The solid-state NMR spectra were obtained with a Bruker DSX400 spectrometer. All samples were spun at a rate of 6.5 kHz and chemical shifts were obtained with respect to the tetramethylsilane reference peak. ^{13}C CP-MAS NMR spectra were measured in experimental conditions of 5-ms contact time, 3-s recycle delay, and 4600 scans, and the ^{29}Si CP-MAS NMR were obtained with 5-ms contact time, 4-s recycle delay, and 15 000 scans, respectively.

Results and Discussion

PEO−PLGA−PEO (LGE) triblock copolymers were designed and synthesized for use as a hexagonally ordered structure-directing agent to prepare a well-defined and hydrothermally stable mesoporous organosilica with large pores and thick framework walls. The hydrophobic PLGA block was chosen to increase the repulsive interaction between the hydrophobic PLGA

---

(32) Kruk, M.; Asefa, T.; Jaroniec, M.; Ozin, G. A. *J. Am. Chem. Soc.* **2002**, *124*, 6383−6392.

(33) Anwander, R. *Chem. Mater.* **2001**, *13*, 4419−4438.

(34) Jaroniec, M.; Kruk, M.; Olivier, J. P. *Langmuir* **1999**, *15*, 5410−5413.

(35) Kruk, M.; Jaroniec, M.; Ko, C. H.; Ryoo, R. *Chem. Mater.* **2000**, *12*, 1961−1968.

block and the organosilica precursors as well as between the PLGA block and the hydrophilic PEO block in a selective aqueous solution, and its degree of hydrophobicity can also be controlled by the relative ratio of DL-lactide and glycolide in the PLGA block. Moreover, the PLGA block also is biodegradable and biocompatible for facile and clean removal of the block to obtain pores inside the organosilica matrix.

Key controlling factors in the synthesis of ordered mesoporous organosilica are the compatibility between hydrophilic PEO blocks and organosilica precursors and the reaction kinetics of organosilica precursors based on the volume fractions of natural block copolymer templates and silica sources coexisting with hydrophilic PEO phase in aqueous system. From this point of view we have tried to find the optimal point of the compatibility and reaction kinetics among silica sources and block copolymer templates. As shown in Table 1, we have used three kinds of LGE block copolymers with weight ratios of the PEO block in the range of 0.3−0.4 to achieve the hexagonal mesophase. In the case of employing the LGE63 block template, we were unable to obtain a highly ordered mesophase using TEOS or BTESE as silica or organosilica sources. However, we found that silica and organosilica materials show highly ordered 2D-hexagonal (*p*6*mm*) mesophase when LGE54 and, especially LGE53, block copolymer templates were used as structure-directing agents for TEOS, BTESE, and BTMSE precursors. These results clearly demonstrate that the volume fraction of hydrophobic block in LGE triblock copolymers is an important factor to realize the ordered hexagonal mesophase in the hybridization between block copolymer templates and (organo)silicates, and also the stiff hydrophobic blocks seem to require relatively long hydrophilic chains.

Scattering patterns of a mesoporous silica material synthesized with the LGE54 polymer template using TEOS as a silica source are shown in Figure 1(a). The as-synthesized sample of Figure 1(a, trace A) represents three well-resolved peaks indexed as (100), (110), and (200) reflections indicating *p*6*mm* hexagonal symmetry. The intense (100) peak shows the large lattice spacing of $d = 94.0$ Å corresponding to the 2D-hexagonal unit cell parameter $a = 108.5$ Å. After calcination at 773 K for 10 h under N_2 flow, the *p*6*mm* hexagonal mesoscopic order is preserved as shown in Figure 1(a, trace B) and the (100) peak is slightly shifted to a *d*-spacing value of 89.2 Å and a unit cell parameter of 103.0 Å. The BET surface area calculated at relative low pressures in the adsorption isotherm is 770 m^2/g and pore volume, pore diameter, and wall thickness are estimated as 1.236 cm^3/g, 63 Å, and 40 Å, respectively, by the Barrett−Joyner−Halenda (BJH) method as shown Figure 3(a).

In the case of employing BTESE as a silica precursor source, we found that the mesoporous ethanesilicas prepared with LGE block copolymers show the cylindrical mesostructure at normal temperature conditions below 313 K. However, we also found the 2D-hexagonal mesostructure appears at the reaction temperature in the range of 313−323 K when a LGE53 block copolymer template was used. The intense (100) peak of Figure 1(b, trace B) shows the large lattice spacing of $d = 104.5$ Å corresponding to the 2D-hexagonal unit cell parameter $a = 120.7$ Å, which is synthesized with a LGE53 template and a BTESE organosilica precursor at 323 K. Figure 1(b) shows that the long-range order in hexagonal mesostructures sensitively depends on the reaction temperature, which is believed to affect the degree of compatibility between the PEO blocks and the organosilica precursors. Temperature in the range of 313−323 K is found to be the optimum for such a highly ordered mesophase in the LGE block copolymer and ethane bridged organosilica precursor system. The enhanced compatibility between the PEO block and the organosilica precursor upon temperature increase is believed to originate from the fact that the slight increase in the hydrophobicity of PEO block by increase in temperature nearly matches the hydrophobicity of BTESE precursors compared with fully hydrophilic TEOS. We also note that the change in the Bragg spacing, as well as the integrity of long-range order of the mesoporous organosilica, depends more on the reaction conditions such as temperature and solution property than on the length of hydrophobic blocks in LGE templates. The well-defined 2D-hexagonal (*p*6*mm*) mesophases are also verified by TEM images in Figure 2(a−c). The Brunauer−Emmet−Teller (BET) surface area of a solvent-extracted sample synthesized at 323 K is estimated to be about 854 m^2/g from the nitrogen adsorption isotherm as shown in Figure 3(b) and Table 2. The pore volume, micropore volume, pore diameter, and wall thickness are calculated as 1.171 cm^3/g, 0.0067 cm^3/g, 79 Å, and 42 Å, respectively, by the BJH method. An ultralow microporosity of 0.57 vol % as well as a thick framework wall of 42 Å are the key achievements of mesoporous ethanesilica with large pores and high periodicity.

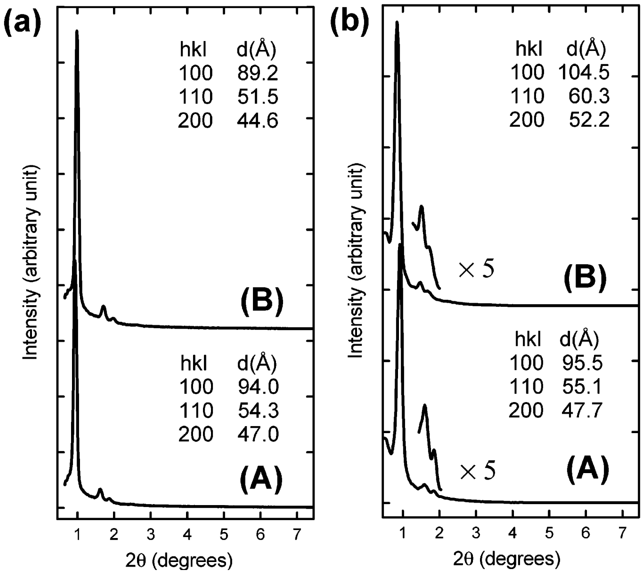

Figure 1. Small-angle X-ray scattering patterns of as-synthesized (a, trace A) and calcined (a, trace B) mesoporous silica (a) prepared with a LGE54 ($EO_{16}(L_{23}G_6)EO_{16}$) triblock copolymer template; and solvent-extracted ethanesilicas (b, trace A, B) with a LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$) block template using BTESE as an organosilica source. Reaction temperatures for the scattering pattern (b, trace A, B) are 313 and 323 K, respectively.

Particularly, mesoporous ethanesilica (Figures 1(b, trace A), 2(d and e), and 3(c)) synthesized at 313 K shows the hexagonal structure containing both open and blocked cylindrical mesopores with uniform diameter

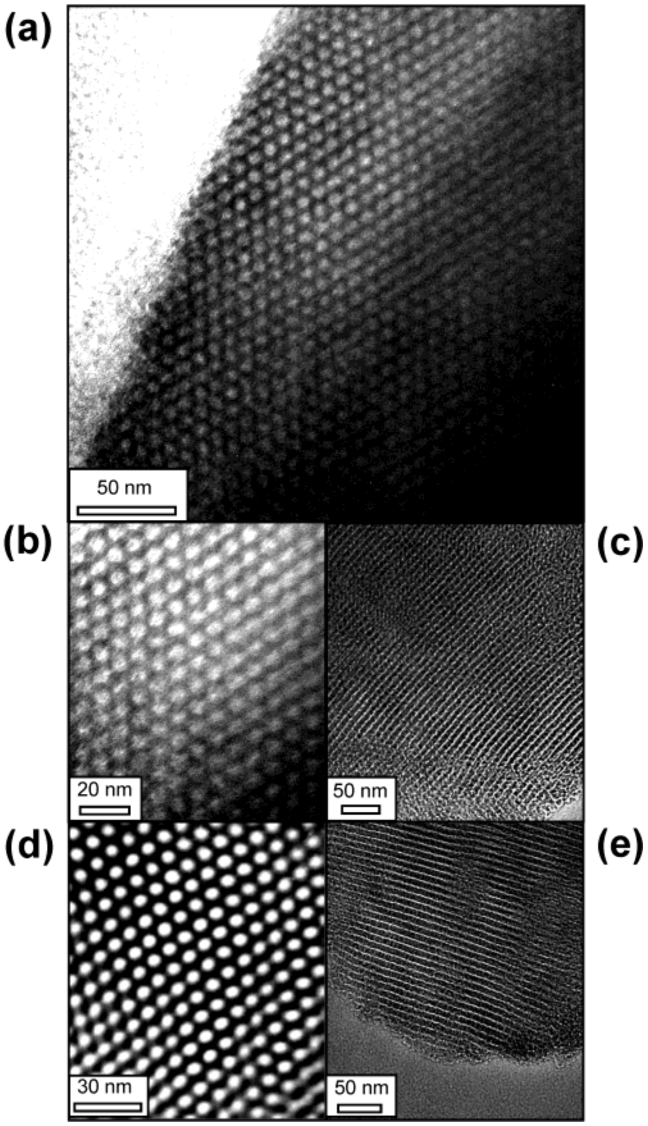

Figure 2. TEM images of solvent-extracted mesoporous ethanesilica synthesized with a LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$) block copolymer template: (a), (b), and (c) are images of sample prepared at 323 K, and (d) and (e) are synthesized at 313 K.

(see also Table 2). The lower-pressure step during the two-step desorption branch shown in Figure 3(c) indicates that the adsorbed nitrogen gas remains trapped inside the pores until the relative vapor pressure is reduced to 0.45 providing a clue for the existence of *blocked* cylindrical mesopores. The two-step isotherm, which is believed to be close to the equilibrium state by adjusting the dwell time at each relative pressure, is quite reversible and reproducible. It has been reported that this new type of mesoporous silica (*p*lugged *h*exagonal *t*emplated *s*ilica; PHTS) has excellent thermal, hydrothermal, and mechanical stability.[33] We denote this unique mesoporous organosilica material prepared with the LGE53 template as a *p*lugged *h*exagonal *t*emplated *o*rganosilica (PHTO). Because we note that the subtle structural change from a regular hexagonal order to blocked mesopores occurs within a narrow range of temperature (i.e., 10 °C), no further detailed study on the structural change was performed.

Table 2 shows the physicochemical properties of two different kinds of hexagonally mesostructured materials. Mesoporous ethanesilica and PHTO prepared in this study clearly contain smaller amounts of micropores than other mesoporous materials as reported to date. The micropores have more frequently been observed in nonionic or Pluronic (PEO−PPO−PEO) block copolymer templating systems such as MSU-X and SBA-X. The origin of micropores inside the silica framework in the block templating system suggests that the poly(ethylene oxide) chains in the Pluronic triblock copolymers can have a chance to penetrate into the silica wall, as commercial Pluronic triblock copolymers with high polydispersity sometimes contain free PEO and PPO chains which can move more freely into the relevant

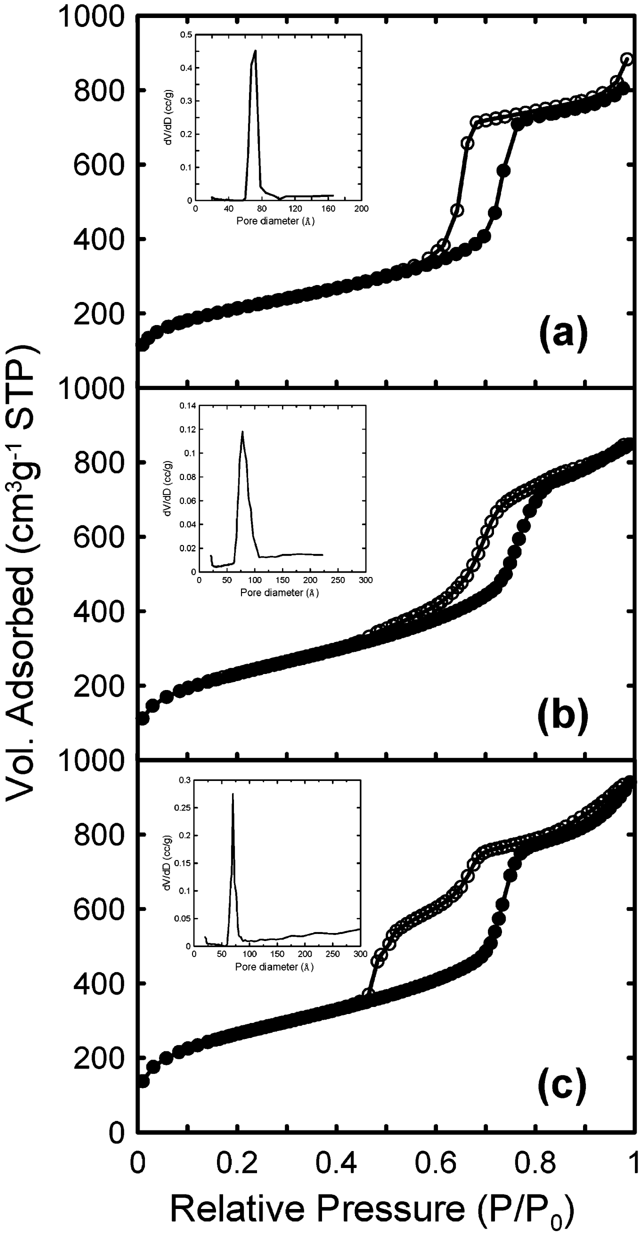

Figure 3. N_2 adsorption−desorption isotherm of mesoporous silica and ethanesilica. Trace (a) is the isotherm of calcined mesoporous silica prepared with a LGE54 ($EO_{16}(L_{23}G_6)EO_{16}$) triblock copolymer template, and traces (b) and (c) are isotherms of solvent-extracted mesoporous ethanesilicas prepared with a LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$) block copolymer template. Reaction temperatures of (b) and (c) are 323 and 313 K, respectively. Pore distributions and pore diameters are calculated by the BJH method.

Table 2. Physicochemical Properties of Mesoporous Ethanesilicas Prepared with a LGE53 Triblock Copolymer Template[a]

sample	T_{HTT} (h)	S_{BET} (m^2/g)	V (cm^3/g)	D_p (nm)	W (nm)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	$V_{meso,blocked}$ (cm^3/g)	Φ_{micro} (%)
ethanesilica[b]	0	854	1.171	7.9	4.2	0.0067	1.164	0	0.57
	360	740	1.326	8.2	3.9	0.0121	1.313	0	0.92
	600	711	1.347	8.3	3.7	0.0162	1.330	0	1.20
PHTO	0	960	1.294	7.0	4.0	0.0478	1.246	0.335 (27%)	3.69
	360	448	0.979	7.6	3.4	0.0191	0.959	0	1.95
	600	403	0.840	7.3	3.7	0.0184	0.821	0	2.19

[a] Pore volumes and diameters were calculated from the adsorption branches of isotherms by the BJH method. [b] Ethanesilica is the highly ordered hexagonal mesoporous material. T_{HTT}, hydrothermal treatment time in boiling water; S_{BET}, BET surface area; V, pore volume; D_p, pore diameter; W, wall thickness; V_{micro}, micropore volume; V_{meso}, mesopore volume; $V_{meso,blocked}$, volume of blocked mesopores; and Φ_{micro}, fraction of micropore volume to total pore volume.

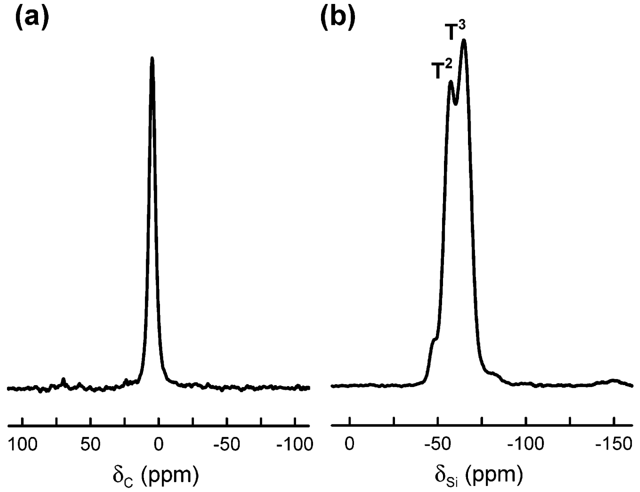

Figure 4. Solid-state ^{13}C (a) and ^{29}Si CP-MAS NMR (b) spectra of solvent-extracted mesoporous ethanesilica prepared with a LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$) triblock copolymer template.

phases. PEO−PLGA−PEO triblock copolymers synthesized and purified carefully in this study have a relatively low polydispersity index (i.e., ~1.2), which explains why mesoporous ethanesilica prepared in this study has a low volume fraction of micropores. Table 2 also shows that the percentage of blocked pores relative to the total mesopores is approximately 27 vol % for the case of PHTO.

To verify that the BTESE is incorporated into the ethanesilica matrix framework, solid-state ^{13}C- and ^{29}Si CP-MAS NMR experiments on the solvent-extracted samples were performed. The ^{13}C CP-MAS NMR spectrum in Figure 4a represents a single resonance peak assigned to ethane carbon at δ −4 indicating the complete removal of the LGE template by the solvent extraction. The ^{29}Si CP-MAS NMR spectrum in Figure 4b also shows the characteristic signals assigned to $CSi(OSi)_3$ (T^3, δ −65) and $CSi(OSi)_2(OH)$ (T^2, δ −57) confirming the presence of ethane moieties inside the ethanesilica framework and the high degree of condensation of the silanol groups. The elemental analysis for the solvent-extracted mesoporous ethanesilica also reveals the complete removal of the polymeric template and the successful incorporation of the BTESE silica precursors. The results of the elemental analysis (wt %) are 18.32% C, 3.25% H, 0.00% N, and 0.00% S. In the case of mesoporous silica, little carbon is detected after either the calcination or the solvent extraction, as confirmed by solid-state ^{13}C NMR and elemental analysis.

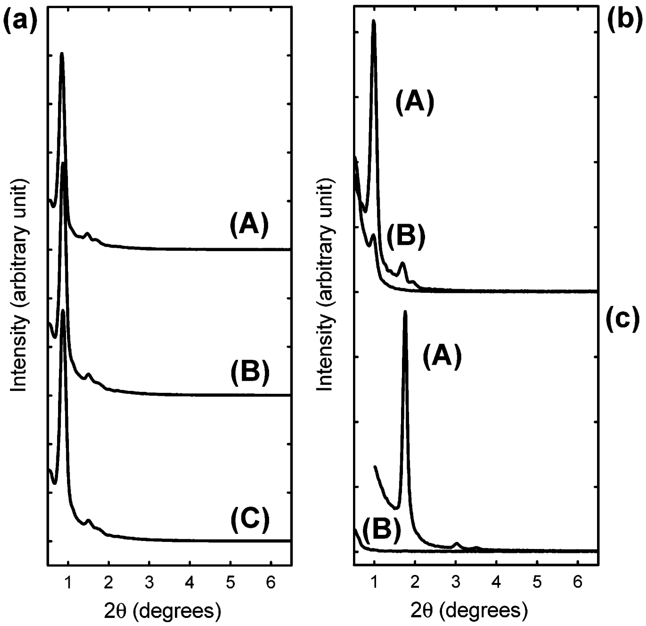

Figure 5. Small-angle X-ray scattering patterns of mesoporous silica and organosilica materials prepared with different templates after different hydrothermal treatment times. (a) Mesoporous ethanesilica synthesized in this study: (A) is solvent-extracted and (B) and (C) are samples obtained after heating in boiling water for 360 and 600 h, respectively. (b) Mesoporous silica synthesized in this study: (A) and (B) are patterns after 48 and 96 h in boiling water, respectively. (c) Mesoporous ethanesilica synthesized with ODTMA surfactant using BTMSE organosilica source: (A) is solvent-extracted and (B) is after the treatment of 24 h.

To examine and compare the hydrothermal property of mesoporous silica and organosilica samples, the mesoporous silica, ethanesilica, and PTHO prepared with LGE block copolymer templates in this study and 2D-hexagonal mesoporous silica material[1] synthesized with a octadecyltrimethylammonium bromide (ODTMA, $C_{18}H_{37}N(CH_3)_3Br$) template and a 1,2-bis(trimethoxysilyl)ethane (BTMSE) organosilica precursor were heated in boiling water at 373 K for several days without additional treatments. In the case of the solvent-extracted ethanesilica samples prepared with the LGE53 block template, all the scattering patterns shown in Figure 5(a) (traces a−c) are retained after being treated in boiling water for approximately 600 h. However, as shown in Figure 5(b), the structural order of the calcined mesoporous silica material prepared with the LGE54 block template is maintained up to 48 h of treatment in boiling water, whereas the structural order disappears for further treatment, which is similar to the case

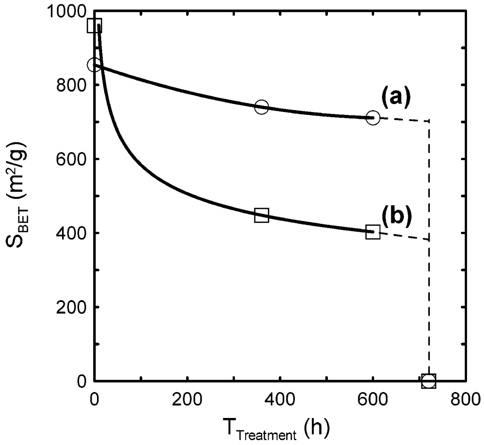

Figure 6. Change in the BET surface area of mesoporous ethanesilicas as a function of hydrothermal treatment time. Reaction temperatures of (a) and (b) are 323 and 313 K, respectively.

of the calcined SBA-15 reported elsewhere.[11] Mesoporous ethanesilica prepared with the ODTMA surfactant and the BTMSE organosilica precursor also show quite weak hydrothermal stability as shown in Figure 5(c) and previously reported.[1] As the scattering pattern of highly ordered hexagonal mesoporous ethanesilica prepared in this study is fully retained after 600 h, as shown in Figure 5, the surface area is also nearly maintained from 854 to 711 m^2/g as shown in Figure 6 and Table 2. The mesostrucure of the hexagonal PHTO is also maintained after 600 h treatment with significant decrease in surface area from 960 to 403 m^2/g, and the two-step desorption branch disappears after the treatment. The retention of scattering pattern and the reduction of surface area of the PHTO sample after the hydrothermal treatment are presumably related to the clogging of the pore mouths. Cylindrical and amorphous structured mesoporous ethanesilica prepared in this study show hydrothermal stability similar to that of the PHTO sample. These results demonstrate that the highly ordered mesoporous ethanesilica with a negligible amount of micropores inside the thick organosilica wall is more stable in boiling water than (ethane-)silica samples that are not fully ordered and that contain a somewhat larger amount of micropores. Cubic structured mesoporous silicas, such as FDU-1[12] prepared by PEO−PBO−PEO triblock copolymer and mesoporous ethanesilica[26] prepared with the aid of NaCl salt, show increased hydrothermal stability such as 9 and 6 d as reported, respectively, which also shows that the template materials and the thick framework wall play a very important role in increasing the hydrothermal stability of silica materials. Such extraordinary hydrothermal stability of the ethanesilica samples prepared in the present study is believed to be a synergistic effect due to its thick pore wall, the small amount of micropores, the high degree of condensation, and the hydrophobicity of the organosilica framework based on the ethane moieties of BTESE organosilica precursor. To address the exact mechanism for the enhanced hydrothermal stability of mesoporous organosilicas, it is suggested that various PEO−PLGA−PEO or other triblock templates with different compositions and molecular weights, as well as organosilica precursors with different chemical structures, should be thoroughly examined to compare wall thickness, wall density, and hydrophobicity of the framework of mesoporous organosilica.

In summary, we have obtained a highly ordered 2D-hexagonal (*p*6*mm*) mesoporous ethanesilica with remarkably enhanced hydrothermal stability. To prepare such a highly ordered mesophase with a thick organosilica framework wall and a small amount of micropores, we controlled the hydrophobicity of each block within the block copolymer template in aqueous solution through the direct synthesis of PEO−PLGA−PEO block copolymer templates and varied the reaction temperature to enhance the selective compatibility between the hydrophilic block of the block template and organosilica precursor. Among several block copolymer templates examined, we found that the LGE53 ($EO_{16}(L_{28}G_3)EO_{16}$) block copolymer is a good structure-directing agent for preparing hexagonally ordered and hydrothermally stable mesoporous ethanesilica. This suggests that the design and synthesis of block copolymer templates, apart from the reaction conditions, are important factors to realize mesoporous organosilicas with unique physicochemical properties.

Acknowledgment. This work was supported by the National Research Laboratory Fund (NRL 400-20010136) of the Ministry of Science and Technology (MOST) and the Brain Korea 21 Program at Seoul National University from the Ministry of Education. Small-angle X-ray scattering experiments performed at the Pohang Light Source (PLS) were supported in part by MOST and POSCO. We thank Ms. M. Kim at Samsung Advanced Institute of Technology for TEM evaluation and Ms. H.-R. Cho at Seoul National University for assistance in synthesis. We also thank Prof. J.-S. Lee and Mr. J.-H. Ahn at K-JIST for GPC evaluation.

Supporting Information Available: Small-angle X-ray scattering pattern and N_2 adsorption-desorption isotherm of mesoporous ethanesilica prepared with LGE63 block copolymer template (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

CM0346733