Synthesis of Ultra-Large-Pore SBA-15 Silica with Two-Dimensional Hexagonal Structure Using Triisopropylbenzene As Micelle Expander

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It is proposed herein that in order to obtain ultralarge-pore ordered mesoporous silicas using surfactant-templated synthesis with micelle expanders, one should select a micelle swelling agent with a moderate swelling ability to achieve an appreciable pore diameter enlargement while avoiding the formation of heterogeneous and/or poorly defined nanostructure. It is suggested to identify viable swelling agents based on the extent of solubilization of swelling agents in micellar solutions. On the basis of this reasoning, cyclohexane, 1,3,5-triethylbenzene and 1,3,5-triisopropylbenzene (TIPB) were selected for the synthesis of large-pore SBA-15 silicas with two-dimensional (2-D) hexagonal structures of cylindrical mesopores. SBA-15 with pore diameter tunable from 10 to 26 nm was obtained at initial synthesis temperature 12.25−20 °C using Pluronic P123 triblock copolymer as a micellar template and triisopropylbenzene as a micelle expander. Structures of the materials were characterized using small-angle X-ray scattering, TEM, and gas adsorption. The lowering of the initial synthesis temperature with adjustment of the amount of TIPB afforded pore diameters up to 26 nm (BJH pore diameters up to 34 nm) and (100) interplanar spacings up to 26 nm for 2-D hexagonal structure. As the initial synthesis temperature was lowered further, the pore diameter increased further (to ~50 nm) with appreciable retention of cylindrical pore shape, but the pore structure became heterogeneous. The present approach makes silicas with 2D hexagonally ordered cylindrical pores of diameter up to 26 nm readily available and opens new opportunities in the synthesis of materials with other pore geometries and framework types.

Introduction

Over the last seventeen years, ordered mesoporous materials (OMMs) templated by surfactant micelles have attracted much attention because of the elegant, predictive synthesis approach and their many potential applications.[1−13] From the beginning, the issue of the pore size tailoring captured the attention of scientists and engineers working in this field of research, because the use of the surfactant micelles as templates opened an opportunity to adjust the pore size through well-known approaches for the adjustment of the size of the micelles.[14,15] In particular, the increase in the chain length of the surfactant or the addition of a micelle expander (swelling agent) were found to be effective in the pore size control in OMMs,[14−19] including silicas with two-dimensional (2-D) hexagonal arrays of cylindrical pores: MCM-41[14,15] and FSM-16[20] templated by alkylammonium surfactants, and SBA-15 silica templated by Pluronic block copolymers.[17,18,21,22] The use of micelle expanders is particularly convenient, as in an ideal case, one can continuously increase the pore diameter by increasing the amount of the swelling agent used. In the case of MCM-41[14,15] and SBA-15,[17,18] transmission

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electron microscopy (TEM) images indicated that the use of a micelle expander, 1,3,5-trimethylbenzene (TMB, mesitylene), allows one to adjust pore diameters up to 10 and 30 nm, respectively. However, in both cases, subsequent work involving the syntheses outlined in the aforementioned studies did not provide confirmation of the formation of homogeneous, well-ordered silicas with cylindrical mesopores of such large sizes. In particular, further studies of the synthesis of SBA-15 in the presence of TMB indicated that very-large-pore materials had a foamlike (mesocellular foam, MCF) structure instead of the 2D hexagonal structure, and the largest pore diameter achievable for the latter was 12 nm.[23]

Subsequent advances in the synthesis of ordered mesoporous materials with cylindrical pores were based on either the identification of appropriate swelling agents for Pluronic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) triblock copolymer surfactants, or the use of novel surfactants that form very large micelles. In particular, alcohols (butanol, pentanol, hexanol),[24,25] aliphatic hydrocarbons (pentane, hexane, heptane, octane, etc.),[25−28] or aromatic hydrocarbons (1,3,5-triisopropylbenzene)[16] were found suitable to increase the diameter of cylindrical pores in 2D hexagonal structures from $\sim$9 nm (typical of SBA-15)[17,18] to $\sim$12−15 nm. The (100) interplanar spacing, d_{100}, (which after multiplying by 1.155 provides the unit-cell parameter, a, which is equal to the distance between the pore centers), in some of these structures reached 16.8 nm. It should be noted that in the case of the use of the shorter-chain aliphatic hydrocarbons (hexane, pentane), the synthesis was performed at 12−15 °C,[26,27] which coincides with the initial temperature suitable for the synthesis of LP-FDU-12 silica with large spherical mesopores arranged in a face-centered cubic (*Fm*3*m*) structure.[29,30] On the other hand, the use of new surfactants, such as poly(ethylene oxide)-poly(methyl acrylate) diblock copolymers (PEO-PMA)[31,32] and poly(methyl acrylate)-poly(ethylene oxide)-poly(methyl acrylate) triblock copolymers (PMA-PEO-PMA)[33] afforded SBA-15 silicas with BJH pore diameters[34,35] of up to 21 nm and with d_{100} up to $\sim$16.5 nm (which corresponds to the distance between the pore centers up to $\sim$19 nm). It should be noted that for 2D hexagonal structure of separate cylindrical pores, the pore diameter must be smaller than the distance between the pore centers. The reported inconsistency may be attributed to the merging of adjacent mesopores, which was first demonstrated by Fan et al.,[36] or to the inaccuracy in the BJH pore diameter for very large pores.[28,37] In the case of the considered work on PEO-PMA-type copolymers, the latter explanation appears more likely, and thus the pore diameter limit of 20 nm reported therein[31,33] appears to be appreciably overstated. It is also relevant to mention silicas with large mesopores[38] templated by poly(ethylene-co-butylene)-poly(ethylene oxide) block copolymers. In this case, the formation of cylindrical pores of diameter up to 16 nm arranged in 2D hexagonal arrays was reported on the basis of TEM, but no X-ray diffraction (XRD) or small-angle X-ray scattering (SAXS) data were provided to cast light on the degree of structural ordering and symmetry.

As mentioned above, hexane and other aliphatic hydrocarbons were found suitable for the synthesis of SBA-15 silicas with pore diameters up to $\sim$15 nm.[26−28] Our study[28] of the synthesis involving hexane as a swelling agent suggested that the actual uptake of hexane by the surfactant micelles was very small. This is consistent with findings of Nagarajan et al.[39,40] that the uptake of linear alkanes by micelles of Pluronic copolymers was rather small and it increased as the alkane chain length decreased. The latter behavior explains why the pore size and (100) interplanar spacing increased for SBA-15 as the chain length of the alkane micelle expander decreased in a series from decane to pentane.[26,27] It was hypothesized that a moderate uptake of the swelling agent by the micelles led to the observed micelle size expansion without the loss of uniformity and without the alteration of the micelle shape.[28] On the basis of this reasoning, it is likely that the failure of many prior attempts at using micelle swelling agents to achieve uniform and appreciable pore size expansion in OMMs[23,41] was related to the excessively strong, and thus poorly controlled, swelling action of micelle expanders used.

SBA-15 has attracted much attention as an adsorbent;[42] medium for immobilization of biomolecules;[9,16,43,44] template for synthesis of ordered mesoporous carbons, oxides, sulfides, and other compositions with rodlike or tubelike structure;[45−47] support for high-surface-area polymer brushes;[48−51] catalyst

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support;[52−54] component of lasing device;[55] component of sensors;[56] and so forth. Well-defined materials with cylindrical pores are also important from the point of view of fundamental research on the effects of confinement on properties of matter.[37,57,58] The availability of SBA-15 in a much wider pore diameter range would significantly enhance the opportunities in the use of this remarkable material in its many prospective applications.

Herein, an approach for the identification of micelle expanders that are promising for surfactant-templated synthesis of ordered mesoporous materials is proposed. On its basis, TIPB, 1,3,5-triethylbenzene (TEB) and cyclohexane were identified as potentially useful in Pluronic-templated synthesis of SBA-15. It was shown that the use of moderate amounts of TIPB as a swelling agent for Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$) at initial synthesis temperatures of 12−20 °C allows one to obtain SBA-15 silicas with ultralarge unit-cell sizes (d_{100} up to 26 nm) and with cylindrical mesopores of diameter tunable in the range from 10 to as large as 26 nm (the nominal BJH pore diameter up to 34 nm). The pore size was continuously adjusted to even larger values (the BJH pore diameter up to ~70 nm), but with the loss of the 2D hexagonal ordering. Cyclohexane and TEB were also found to be promising swelling agents.

Materials and Methods

Materials. SBA-15 silicas were synthesized using triblock copolymer Pluronic P123 (BASF) as a template and TIPB as a micelle expander. In most cases, the molar composition of the synthesis mixture was TEOS:P123:TIPB:NH_4F:HCl:H_2O = 1:0.0168: 0.199x:0.0295:4.42:186, where TEOS stands for tetraethyl orthosilicate and x ranged from 0.5 to 3 (typically 1 or 2) and denoted the mass of TIPB (in grams) per 2.4 g of P123. A typical synthesis procedure was as follows: 2.4 g of P123 and 0.027 g of NH_4F were dissolved in 84.0 mL of 1.30 M aqueous HCl solution at room temperature. Subsequently, the solution was transferred to a water bath (nominal temperature accuracy of 0.01 °C) set at a temperature between 11.00 and 20.00 °C; after at least 1 h, a mixture of 5.5 mL TEOS and 1.2 mL (1.0 g) TIPB was added. The solution was stirred for 24 h at the selected initial temperature in an open container using a mechanical stirrer. Then, the product was either isolated (see below) or heated at 100 or 130 °C in a closed container for periods of time from 3 h to 5 days (usually 1 or 2 days). As-synthesized material was isolated by filtering, washing with water and drying at ~60 °C in a vacuum oven. Finally, the sample was calcined under air at 550 °C for 5 h (heating ramp 2 °C min^{-1}). The synthesis was also performed in a similar way with cyclohexane and 1,3,5-triethylbenzene as micelle expanders.

Measurements. Small-angle X-ray scattering (SAXS) patterns were either acquired at Station D1 of Cornell High Energy Synchrotron Source (CHESS) at Cornell University or recorded using a Bruker Nanostar U SAXS/wide-angle X-ray scattering (WAXS) system with a rotating anode X-ray source and Vantec-2000 area detector. The Nanostar U system had a sample-to-detector distance of 72 cm and was in high-flux configuration. The powder samples were placed in a hole in a sample holder and secured from both sides using a Kapton or Scotch tape. Nitrogen adsorption isotherms were measured at −196 °C on a Micromeritics ASAP 2020 volumetric adsorption analyzer. Before the adsorption analysis, calcined samples were outgassed under a vacuum at 200 °C in the port of the adsorption analyzer. Transmission electron microscopy (TEM) images were recorded on a Philips CM 100 microscope operated at 80 kV or a FEI Tecnai G2 Twin microscope operated at 120 kV. Before the imaging, the samples were dispersed in ethanol through sonication and subsequently deposited on a carbon-coated copper grid.

Calculations. The specific surface area, S_{BET}, was evaluated from nitrogen adsorption data in the relative pressure range from 0.04 to 0.2 using the Brunauer−Emmett−Teller (BET) method.[59] The total pore volume, V_t, was determined from the amount adsorbed at a relative pressure of 0.99.[59] The micropore volume, V_{mi}, was evaluated using the α_s plot method[59,60] in the standard reduced adsorption (α_s) range from 0.9 to 1.2. The external surface area, S_{ext}, and the sum of the primary (ordered) mesopore volume, V_p, and the micropore volume, V_{mi}, were calculated using the α_s plot method in α_s range selected within 2.0−2.55 interval. The reference adsorption isotherm for macroporous silica was used in the α_s plot analysis.[60] For samples with pore diameter above ~18 nm, it was not possible to assess $V_p + V_{mi}$ using the α_s plot method, because it would require the calculations from adsorption data at pressures very close to the saturation vapor pressure ($p/p_0 > 0.95$), for which fully reliable reference adsorption data are not available. Moreover, any contribution from secondary (interparticle) porosity would have detrimental effect on the accuracy of the results. Therefore, $V_p + V_{mi}$ (which is used to evaluate V_p, which in turn is needed in pore size calculations using eq 1) was estimated as $0.783V_t$, the constant 0.783 being determined on the basis of data for samples for which the $(V_p + V_{mi})/V_t$ ratio could be determined with acceptable confidence. Pore size distributions (PSDs) were determined from adsorption branches of isotherms[35] using the Barrett−Joyner−Halenda (BJH) method[34] with the Kelvin equation for hemispherical meniscus and the statistical film thickness curve for macroporous silica.[60] The BJH pore diameter, w_{BJH}, is defined as a position of the maximum on the pore size distribution. For 2D hexagonally ordered samples, the diameter of ordered mesopores, w_d, was calculated using a geometrical equation for materials with 2D hexagonal structure of cylindrical pores that are separated by microporous walls[61]

$$w_d = 1.213 d_{100} \sqrt{\frac{V_p}{\frac{1}{\rho} + V_p + V_{mi}}} \qquad (1)$$

where d_{100} is the (100) interplanar spacing obtained from SAXS, and ρ is the density of silica framework (assumed to be 2.2 g cm^{-3}).

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It should be noted that although V_p for some of the samples was indirectly estimated as described above, even 10% error in V_p would result in less than 2% error in the pore diameter estimation (assuming that $V_p = \sim 1.0$ cm^3 g^{-1} and $V_{mi} = 0.02$ cm^3 g^{-1}, which is a good approximation for the samples under study), due to the nature of eq 1.[62]

Results and Discussion

Selection of Micelle Expanders for Significant Pore Size Enlargement with Retention of Structural Ordering. It is proposed herein that in order to obtain ultra-large-pore ordered mesoporous silicas using surfactant-templated synthesis with a micelle expander, one should select a micelle swelling agent with a moderate swelling ability to achieve an appreciable pore diameter enlargement while avoiding the change in the nanostructure type and/or the formation of a heterogeneous material. It is suggested to identify viable swelling agents based on the extent of solubilization of different organic molecules in micellar solutions. In particular, it was hypothesized that a further pore size enlargement for SBA-15 can be achieved through the identification of swelling agents that are solubilized in Pluronics to somewhat higher extent than the swelling agents successfully used earlier (such as linear hydrocarbons), and yet would solubilize to a smaller extent than TMB, which readily affords the MCF phase instead of SBA-15. As discussed above, SBA-15 with pore diameter up to ~15 nm was obtained when the alkyl chain length of the linear hydrocarbon swelling agent was decreased to 5−6 carbon atoms (in case of hexane and pentane).[26−28] On the basis of the finding of Nagarajan et al.,[39,40] that the uptake of linear alkanes by micelles of Pluronic copolymers was rather small and it increased as the alkane chain length decreased, one would expect that the use of shorter-chain alkanes (butane, etc.) could afford SBA-15 with larger pore sizes. However, these alkanes are gases at room temperature and thus are not convenient to use in hydrothermal synthesis. On the other hand, cyclohexane solubilizes in Pluronics to a larger extent than its linear counterparts[39,40] and it is postulated herein that it can serve as a continuation of the aliphatic hydrocarbon series. Additional opportunities arise for aromatic hydrocarbons, whose extent of solubilization was reported to decrease as the number and length of alkyl substituents on the benzene ring increase in a series: benzene > toluene > xylene.[39,40] One can envision a continuation of this series with TMB, 1,3,5-triethylbenzene, and 1,3,5-triisopropylbenzene. The compounds at the beginning of the above series solubilize in PEO-PPO-PEO copolymers to much greater extent than linear hydrocarbons do,[39,40] but one can expect that trialkylbenzenes, especially TIPB, will have the extent of solubilization gradually approaching that of the linear alkanes series. TIPB has already been employed in the synthesis of large-pore MCM-41,[63] alkylammonium-templated periodic mesoporous organosilicas (which were weakly ordered),[64] and Pluronic P104-templated large-pore SBA-15 with a d_{100} of ~14 nm,[16] although in the cases of MCM-41 and SBA-15, the adsorption properties of the resulting materials were not reported. TIPB was also employed as a swelling agent in syntheses involving Pluronic P123 block copolymer, which resulted in the formation of silicas with vesicular morphology,[65] or foamlike morphology (MCF).[66] Hereafter, it is shown how TIPB can be used to achieve SBA-15 with diameter of cylindrical pores reaching 26 nm and with nominal BJH pore diameters up to 34 nm, which is beyond the range of BJH pore sizes (up to 30 nm) reported initially for SBA-15 synthesized in the presence of TMB,[17,18] which may have been MCFs, as inferred from the subsequent study.[23]

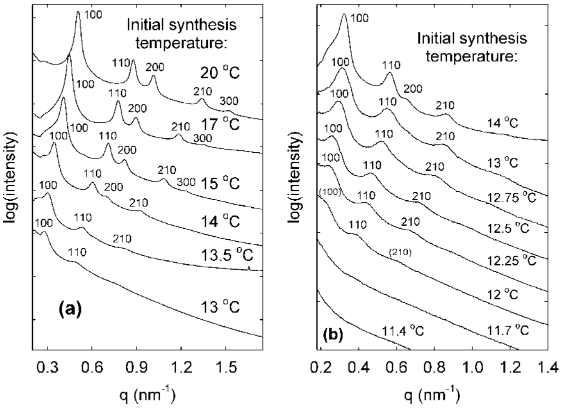

Figure 1. Small-angle X-ray scattering patterns for calcined silica samples synthesized at different initial temperatures with surfactant (P123): swelling agent (TIPB) mass ratio of (a) 2.4:1, with hydrothermal treatment at 100 °C for 2 days; (b) 2.4:2 (except for samples synthesized at 12.25 and 12 °C, for which ratios of 2.4:2.5 and 2.4:3 were employed), with hydrothermal treatment at 130 °C for 1 day. Data in (a) and the uppermost pattern in (b) were collected using SAXS with synchrotron X-ray source. Other data shown in (b) were collected using a laboratory SAXS setup.

Effect of Initial Synthesis Temperature. Shown in Figure 1 are SAXS patterns for calcined silicas synthesized with surfactant (Pluronic P123) to micelle expander (TIPB) mass ratio of 2.4:1 at initial temperatures from 13 to 20 °C. In the case of these samples, TIPB was mixed with the silica source (TEOS) and simultaneously added to the surfactant solution under mechanical stirring. The initial synthesis temperature was maintained for one day under stirring, and then the synthesis mixture was transferred to an oven and heated in a closed container for 2 days at 100 °C. Relative positions of SAXS peaks for the samples prepared at 13.5−20 °C corresponded to the 2D hexagonal structure characteristic of SBA-15. The patterns were somewhat less well resolved for the samples prepared at 14 and 13.5 °C. In the case of the sample synthesized at 13 °C, there was only one well-pronounced peak, and a shoulder at a position where (110) reflection of 2D hexagonal structure would be expected. The peaks on the SAXS patterns shifted to lower *q* values as the initial synthesis temperature was lowered, indicating the increase in the unit-cell size. The position of the main peak on the SAXS pattern corresponded to (100) interplanar spacings of 12.6 to 20.7 nm for 2D hexagonal

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Table 1. Structural Properties of Materials Synthesized under Different Conditions[a]

initial temperature, hydrothermal treatment temperature and time, P123/TIPB mass ratio	$d_{100\ \mathrm{UC}}$ (nm)	d_{100} (nm)	S_{BET} ($\mathrm{m^2\ g^{-1}}$)	V_t ($\mathrm{cm^3\ g^{-1}}$)	V_{mi} ($\mathrm{cm^3\ g^{-1}}$)	V_p ($\mathrm{cm^3\ g^{-1}}$)	w_{BJH} (nm)	w_d (nm)
20 °C, 100 °C, 2 days, 2.4:1	13.0	12.6	620	1.38	0.05	(1.03)[b]	13.9	12.5[c]
17 °C, 100 °C 2 days, 2.4:1	14.4	14.1	680	1.40	0.08	1.01	15.0	13.8
17 °C, 100 °C, 2 days, 2.4:1.5	15.8	15.4	570	1.49	0.02	1.10	16.3	15.6
17 °C, 100 °C, 2 days, 2.4:2	16.8	16.3	530	1.48	0.03	(1.13)[b]	17.4	16.5[c]
17 °C, 100 °C, 2 days, 2.4:3	17.8	17.2	580	1.85	0.07	b	18.4	d
15 °C, 100 °C, 2 days, 2.4:1	15.8	15.4	590	1.28	0.08	0.90	15.7	14.8
14 °C, 100 °C, 2 days, 2.4:1	19.4	18.6	570	1.13	0.05	0.81	20.4	17.7
13.5 °C, 100 °C, 2 days, 2.4:1	21.3	20.7	520	1.05	0.07	(0.75)[b]	24.6	19.3[c]
13 °C, 100 °C, 2 days, 2.4:1	23.3	22.6	520	1.04	0.02	[b]	30	[e]
12 °C, 100 °C, 2 days, 2.4:1	[f]	[f]	520	0.95	0.04	[b]	~50	[e]
14 °C, 130 °C, 1 day, 2.4:2	19.9	19.4	350	1.30	0.04	(0.98)[b]	22.6	19.2[c]
13 °C, 130 °C, 1 day, 2.4:2	20.8	20.1	350	1.34	0.02	(1.03)[b]	25.5	20.2[c]
12.75 °C, 130 °C, 1 day, 2.4:2	22.6	21.6	330	1.29	0.02	(0.98)[b]	27.8	21.4[c]
12.5 °C, 130 °C, 1 day, 2.4:2	24.5	24.2	330	1.33	0.03	(1.01)[b]	29.8	24.2[c]
12.25 °C, 130 °C, 1 day, 2.4:2.5	26.0[g]	25.8[g]	360	1.50	0.02	(1.15)[b]	33.9	26.3[c]
12 °C, 130 °C, 1 day, 2.4:3	[h]	[h]	300	1.40	0.01	b	42	[i]
11.7 °C, 130 °C, 1 day, 2.4:2	[f]	[f]	300	1.21	0.00	b	52	[e]
11.4 °C, 130 °C, 1 day, 2.4:2	[f]	[f]	290	1.09	0.00	b	71	[e]

[a] Notation: $d_{100\ \mathrm{UC}}$, (100) interplanar spacing for uncalcined sample; d_{100}, (100) interplanar spacing for calcined sample; S_{BET}, BET specific surface area; V_t, total pore volume; V_{mi}, micropore volume; V_p, primary mesopore volume; w_{BJH}, BJH pore diameter; w_d, pore diameter calculated using eq 1. [b] Could not be calculated with acceptable accuracy using α_s plot method. Values in parentheses are estimates on the basis of V_t and V_{mi} values for the particular sample (see Calculations section). [c] Value based on the estimated value of V_p. [d] Could not be estimated with acceptable accuracy due to a significant uncertainty in the value of V_p. [e] Could not be calculated using eq 1 because the lack of clear evidence of 2D hexagonal symmetry. [f] No observable peaks on SAXS pattern. [g] Estimated on the basis of position of (100) and (110) peaks. [h] (100) peak not fully resolved. [i] Could not be estimated because (100) peak was not fully resolved.

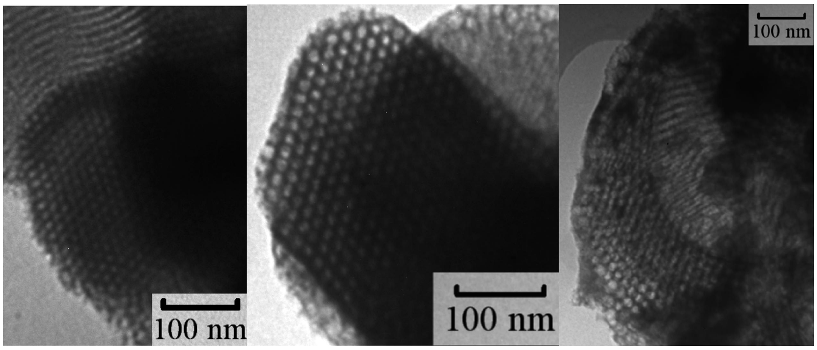

Figure 2. TEM Images of Calcined Silica Samples Synthesized at: (left) 17 °C, (middle) 15 °C, and (right) 13.5 °C with surfactant (P123):swelling agent (TIPB) mass ratio of 2.4:1.

structures (see Table 1), the latter being exceptionally large. The less well-defined sample obtained at 13 °C had d_{100} of 22.6 nm. As discussed above, commercially available Pluronic block copolymers[16,24−28] and purposefully synthesized PMA-PEO-PMA block copolymers[33] are suitable for the synthesis of SBA-15 with (100) interplanar spacings up to ~17 nm (for calcined samples). The synthesis procedure described above extends the achievable d_{100} range for 2D hexagonal structure to 21 nm. For a sample prepared at initial temperature of 12 °C, the SAXS pattern (not shown) was featureless. The 2D hexagonal structure of samples prepared at 13.5−20 °C was confirmed by TEM (see Figure 2 for images for selected samples). In the case of the sample prepared at 13 °C, TEM indicated that the pores were channel-like and their arrangement was similar to that for 2D hexagonal (honeycomb) structure, but with some imperfections. Finally, TEM images for the sample prepared at 12 °C showed channel-like, spherical, and irregularly shaped pores with a wide distribution of sizes. It should be noted that MCF impurity was observed in some samples of well-ordered 2D hexagonal materials (see, for instance, the upper right corner of Figure 2(middle)). The occurrence of MCF domains was not correlated with the initial synthesis temperature. Perhaps the MCF impurity formed sporadically as a result of less-effective local mixing in the reaction mixture.

Nitrogen adsorption isotherms for the samples synthesized at initial temperatures from 12 to 20 °C (Figure 3a) featured capillary condensation steps whose relative pressure at midpoint systematically shifted from 0.85 to 0.96. In particular, the sample synthesized at 13.5 °C exhibited capillary condensation at relative pressure of 0.917. The highest relative pressure of capillary condensation of nitrogen at −196 °C observed for well-defined SBA-15 silica with cylindrical mesopores was ~0.87 for materials templated by Pluronic block copolymers,[26,28] and ~0.90 for silicas templated by PEO-PMA or PMA-PEO-PMA block copolymers,[31−33] which is much lower than that observed for our aforementioned sample. This provides strong evidence that our material exhibited higher pore diameter than other silicas with 2-D hexagonal pore structure documented to date. It should be noted that SBA-15 silicas with large-mesopore connections between ordered mesopores[28,36] are not taken

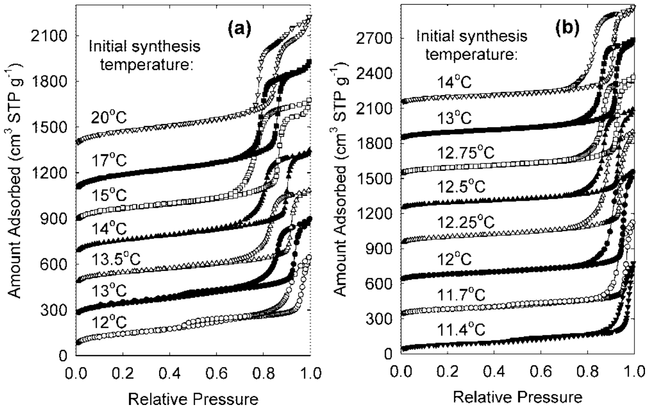

Figure 3. Nitrogen adsorption isotherms for calcined silica samples synthesized at different initial temperatures with surfactant (P123):swelling agent (TIPB) mass ratios of: (a) 2.4:1, with hydrothermal treatment at 100 °C for 2 days; (b) 2.4:2 (except for samples synthesized at 12.25 and 12 °C, for which ratios of 2.4:2.5 and 2.4:3 were employed), with hydrothermal treatment at 130 °C for 1 day. For clarity, in (a), the isotherms for samples prepared at 13, 13.5, 14, 15, 17, and 20 °C were offset vertically by 200, 400, 600, 800, 1000, and 1300 cm^3 STP g^{-1}) and in (b), the isotherms for samples prepared at 11.7, 12, 12.25, 12.5, 12.75, 13, and 14 °C were offset vertically by 300, 600, 900, 1200, 1500, 1800, and 2100 cm^3 STP g^{-1}.

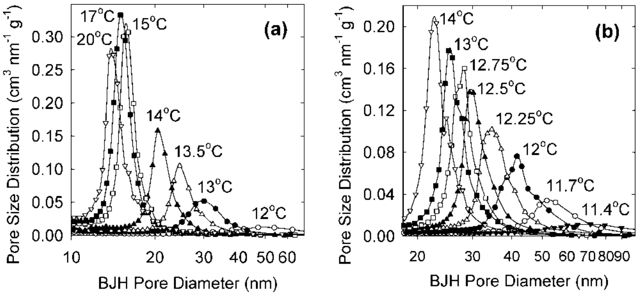

Figure 4. Pore size distributions for calcined silica samples synthesized at different initial temperatures with surfactant (P123): swelling agent (TIPB) mass ratio of: (a) 2.4:1; (b) 2.4:2 (except for samples synthesized at 12.25 and 12 °C, for which ratios of 2.4:2.5 and 2.4:3 were employed), with hydrothermal treatment at 130 °C for 1 day.

into account, because in such cases, the adjacent mesopores are merged to a significant extent and thus the pore shape deviates significantly from cylindrical. It appears that such materials can readily be generated using the present synthesis method when extended hydrothermal treatments (2 days or more) at high temperature (130 °C) are applied (see the Supporting Information, Figure S1). For regular SBA-15 materials, the capillary condensation pressure is correlated with the pore diameter determined using eq 1 or simulations of XRD/SAXS patterns,[37] following the behavior observed earlier for MCM-41 silicas.[35] In the cases of SBA-15 suspected of the merging of adjacent mesopores, the capillary condensation pressure was much higher than that for similar samples hydrothermally treated for shorter time at 130 °C or at lower temperatures.

It should be noted that the samples prepared with P123: TIPB ratio of 2.4:1 at an initial temperature of 13 °C or lower clearly exhibited an additional hysteresis loop in a relative pressure range ca. 0.45−0.7 (see Figure 3a), which is indicative of the presence of mesopores of size 5−8 nm, which is much smaller than the size of the main mesopores. SBA-15 prepared at 13.5 °C also exhibited such a feature on its isotherm, although its relative magnitude was much smaller. TEM images did not provide any clear indication as to the nature of this additional porosity. As this porosity is fully or largely eliminated by increasing the copolymer: swelling agent ratio (such samples are discussed below), it is suggested that these additional pores might be present in disordered domains that were micelle-expander-depleted.

Pore size distributions (PSDs) for the discussed samples, calculated from the nitrogen adsorption isotherms using the BJH method, are shown in Figure 4a. To better show the full range of relevant pore diameters, the logarithmic scale was used. The pore diameter increased as an initial synthesis temperature decreased. PSDs for samples prepared at 13.5−20 °C were narrow, but as the temperature decreased further, a significant broadening of PSD was observed. The BJH pore diameter for samples that exhibited 2D hexagonal ordering, as inferred from SAXS and TEM, reached 25 nm. This BJH pore size is significantly larger than that of ~16 nm reported for SBA-15 templated by Pluronic block copolymers[26,28] (except for those in which the adjacent mesopores were shown to be, or are likely to be, merged with one another) and that of 21 nm reported for SBA-15 templated by PEO-PMA or PMA-PEO-PMA.[31−33] While the BJH PSDs calculated from adsorption branches of isotherms allow one to compare a relative magnitude of size of pores of a particular geometry, they overestimate the diameter of large cylindrical mesopores (above 10 nm).[37,67] Such an overestimation is caused by an inaccuracy in the relation between the pore diameter and the capillary condensation pressure (in the considered case, this relation is the Kelvin equation), which is a crucial component in PSD calculations. Therefore, eq 1 was used herein to obtain reliable estimates of actual pore diameters for samples for which the 2D hexagonal ordering was confirmed. As can be seen in Table 1, the actual pore diameters for the 2-D hexagonally ordered samples were 12 to ~19 nm.

Effect of Amount of the Swelling Agent. In typical syntheses with micelle expanders, the pore diameter can be adjusted in a wide range by changing the amount of the micelle expander.[15,17,41] In the case of the low-temperature synthesis with TIPB, the behavior was more complicated. At 20 °C, the material exhibited a significant secondary mesoporosity even when the P123:TIPB mass ratio was 2.4:1 and the increase in this ratio to 2.4 to 2 enhanced the secondary mesoporosity even further. Thus, the increase in the amount of the swelling agent was not beneficial. At somewhat lower temperatures (14−17 °C), the pore diameter can be tailored to some extent by changing the amount of TIPB. For instance, when the initial synthesis temperature was 17 °C, highly ordered SBA-15 silicas with (100) interplanar spacings up to 16.3 nm were obtained when the mass of TIPB was increased to 1.5 and 2 g per 2.4 g of P123 (see Table 1). Five pronounced reflections and two additional less well-resolved reflections were observed on SAXS patterns for these samples (see the Supporting Information, Figure S2). TEM (see the Supporting Information, Figure S2) provided a confirmation of the structural uniformity. Although the increase in the amount of TIPB to

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(67) Kim, S. S.; Karkamkar, A.; Pinnavaia, T. J.; Kruk, M.; Jaroniec, M. *J. Phys. Chem. B* **2001**, *105*, 7663.

3 g per 2.4 g of P123 resulted in further increase in d_{100}, the degree of structural ordering was significantly diminished, as also seen from a significant broadening of PSD (see the Supporting Information, Figure S2). Moreover, the shape of the nitrogen adsorption isotherm for the considered sample differed from the shape of adsorption isotherms for the other samples, as the amount adsorbed continued to significantly increase after the completion of the capillary condensation in ordered mesopores (see the Supporting Information, Figure S2). This behavior suggests a major population of secondary (disordered) mesopores with broad size distribution overlapping with the size distribution of the ordered mesopores. At 14 °C, it was possible to reduce the amount of TIPB to 0.5 g per 2.4 g of P123 while still achieving a BJH pore diameter of ~16.5 nm (see the Supporting Information, Figure S3), thus achieving for a micelle-expander/copolymer mass ratio as low as ca. 1:5 the pore diameter comparable to the highest reported earlier for Pluronic-templated synthesis of SBA-15. On the other hand, the increase in the amount of TIPB at 14 °C or lower allowed us to achieve a major improvement of quality of materials and to achieve much higher unit-cell sizes and pore diameters with retention of 2D hexagonal ordering.

Further Extension of Pore Size Range for SBA-15 via Adjustment of the Amount of Swelling Agent. At 14 °C, the change in P123: TIPB mass ratio to 2.4:2 resulted in a slight pore diameter enlargement, but more importantly, it led to a major improvement of the quality of the material. For the resulting SBA-15, the SAXS pattern was very well resolved featuring a strong (210) peak, which was a clear improvement over the sample prepared with P123:TIPB mass ratio to 2.4:1 (compare Figure 1a and the Supporting Information, Figure S4), whereas d_{100} was somewhat larger for the former. The mesopore volume was also increased. It should be noted that a broadening of the hysteresis loop on nitrogen adsorption isotherms was observed for the samples prepared at 14 °C or lower with 2 g or more of TIPB per 2.4 g of P123 (see for instance the Supporting Information, Figure S4), indicating the development of minor constrictions in the mesopores. When the hydrothermal treatment at 100 °C was prolonged to 5 days, or its temperature was increased to 130 °C, the hysteresis loops became narrower (see the Supporting Information, Figure S4), indicating the elimination of these constrictions.

Shown in Figures 1b, 3b, 4b, and 5 are SAXS patterns, nitrogen adsorption isotherms, PSDs and TEM images for SBA-15 silicas synthesized with increased relative amount of TIPB (P123:TIPB = 2.4:2, 2.4:2.5 and 2.4:3) at initial temperatures decreasing from 14 to 11.4 °C and subsequently hydrothermally treated at 130 °C for 1 day. SAXS patterns indicated that 2D hexagonal structure formed at temperatures from 14 to 12.25 °C and d_{100} interplanar spacing for calcined materials increased from 19.4 to 25.8 nm as the temperature decreased, but the patterns became less well resolved as the temperature decreased, indicating a gradual decrease in degree of structural ordering. All the considered materials exhibited (100), (110) and (210) peaks on SAXS patterns (see Figure 1b; Figure S5 in the Supporting Information shows additional data for SBA-15 synthesized at 12.25 °C with different hydrothermal treatment times/temperatures). It should be noted that although the silica synthesized at 12.25 °C with the P123:TIPB ratio of 2.4:2 also exhibited three reflections on SAXS pattern, the increase in the ratio to 2.4:2.5 made the pattern better-resolved. TEM images (Figure 5) provided further corroboration of 2-D hexagonal structures of the materials, as patterns of parallel stripes (which are known to be side projections of the honeycomb)[68] and honeycomb patterns were observed. For some samples, TEM also showed a minor fraction of domains with larger mesopores arranged in less orderly way (see, for instance, the Supporting Information, Figure S6). SAXS pattern of the sample synthesized at initial temperature of 12 °C was less well resolved, but on the basis of the SAXS patterns of the samples discussed above, it appears that the shoulder at $q \approx 0.23$ was a residual (100) peak, and the feature observed at $q \approx 0.39$ was (110) reflection, which would correspond to $d_{100} \approx 28$ nm. TEM confirmed the presence of honeycomb domains in the aforementioned material (see Figure 5), but these domains were accompanied by a significant fraction of less-well-defined domains with appreciably larger pores, some of which were apparently cylindrical in shape (see the Supporting Information, Figure S7). The silicas formed at 11.7 and 11.4 °C, whose SAXS patterns were featureless (see Figure 1b), also comprised similar domains (see the Supporting Information, Figures S8 and S9).

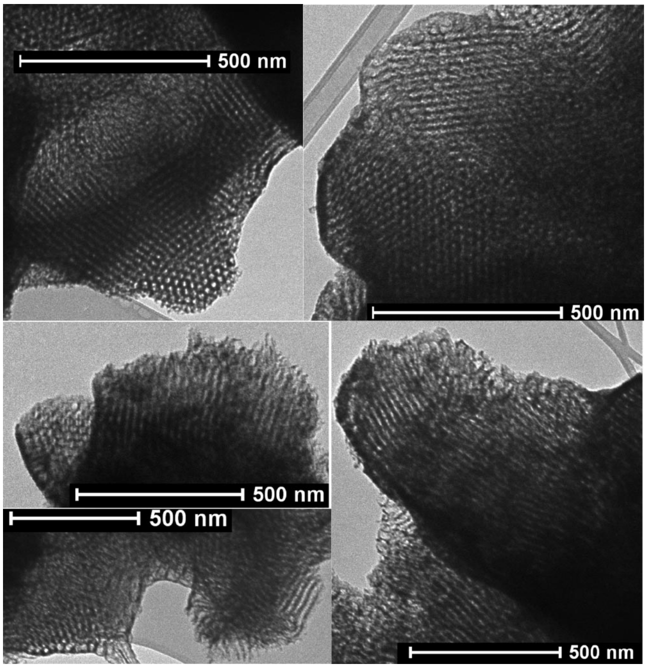

Figure 5. TEM images of calcined silica samples synthesized at: 14 °C (top, left), 12.75 °C (top, right), and 12.5 °C (middle, left) with surfactant (P123):swelling agent (TIPB) mass ratio of 2.4:2; 12.25 °C (bottom, right) with P123:TIPB mass ratio of 2.4:2.5; and 12 °C (bottom, left) with P123: TIPB mass ratio of 2.4:3.

Nitrogen adsorption isotherms of the obtained SBA-15 silicas with ultralarge unit-cell sizes are shown in Figure 3b. It can be seen that the capillary condensation step shifted from the relative pressure of ~0.91 to 0.94 as the initial synthesis temperature was lowered from 14 to 12.25 °C. As

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(68) Chenite, A.; Le Page, Y.; Sayari, A. *Chem. Mater.* **1995**, *7*, 1015.

noted above, the highest relative pressure of capillary condensation (for nitrogen adsorption at −196 °C) observed for previously reported and well-documented silicas with 2D hexagonal structures was ∼0.90, which is well-below the range observed for our samples considered here. This clearly indicates that the latter samples had larger pore diameters than their literature counterparts. Even if the TMB-expanded material reported in the first disclosure of SBA-15[17,18] had been 2-D hexagonally ordered, which is unlikely based on the subsequent report on the mesocellular foam nature of large-pore TMB-expanded silicas,[23] its capillary condensation pressure was ∼0.92, which is in the lower range of values observed for our 2D hexagonal samples whose isotherms are shown in Figure 3b. Further insight regarding the magnitude of pore diameters of the present silicas relative to the diameter of cylindrical pores of 2D hexagonal silicas reported earlier can be gained by comparing nominal pore diameters assessed from adsorption branches of isotherms using the BJH method.[34] The BJH pore diameter of our samples ranged from 21 to as high as 34 nm (see PSDs in Figure 4b). The BJH pore diameters of well-documented SBA-15-type silicas reported to date were up to ∼21 nm.[31−33] The BJH pore diameters initially reported for SBA-15[17,18] ranged to 30 nm, although it was later reported that the 2D hexagonal structure persists only up to 12 nm.[23] In any case, the BJH pore diameter for our SBA-15 silicas was beyond that reported earlier for SBA-15. It is interesting to note that even at temperatures of 12 °C or lower, in which case the 2D hexagonal structure was partially or fully lost, the pore diameter still systematically increased as the initial synthesis temperature decreased and the BJH pore diameter reached 70 nm. One can conclude that the initial temperature adjustment in the present synthesis affords materials with pore diameters in the entire upper part of the mesopore range. Although the adjustability of the pore size over most of the mesopore range using swelling agents has been demonstrated earlier,[66] our synthesis gives an unprecedented range of diameters for cylindrical pores. It should be noted that the improvement in quality of the sample prepared at 12 °C was reached through a further increase in the P123:TIPB mass ratio to 2.4:3. Clearly, larger relative amounts of TIPB are beneficial in the synthesis of silicas with very large mesopores at initial temperatures of ∼12 °C.

The BJH pore size calculations from adsorption branches of isotherms provided the information about the shape of pore size distribution and allowed for a reliable comparison of pore diameters for different samples. However, a more accurate pore diameter evaluation is desirable, and can be achieved using eq 1, which allows one to assess the diameter of cylindrical pores on the basis of (100) interplanar spacing, primary mesopore volume and micropore volume. As can be seen in Table 1, the resulting pore diameters ranged from 19 to 26 nm, the latter being exceptionally large. It can be inferred from Table 1 that the nominal BJH pore diameter of ∼21 nm corresponds to the actual pore diameter of 18 nm (see Table 1). Therefore, one can conclude that our work extended the upper limit of the pore size range achievable for silicas with ordered cylindrical pores from 18 to 26 nm.

Effect of the Hydrothermal Treatment Time and Temperature. A pore diameter adjustment was also achievable through the change in the duration of the hydrothermal treatment (see the Supporting Information, Figures S4, S5, and S10), which is a known feature of SBA-15 synthesis.[17,28,69] For instance, in the case of the initial synthesis temperature of 17 °C, the BJH pore diameter could be adjusted from 10 to 15 nm by extending the hydrothermal treatment time from 0 h to 2 days. It should be noted that adsorption/desorption hysteresis loops on adsorption isotherms for the samples prepared without a hydrothermal treatment, or with short treatments, exhibited broadening and/or tailing to lower pressures, which was similar to the behavior of SBA-15 synthesized using hexane as a swelling agent.[28] Such an adsorption behavior indicates that the ordered mesopores exhibited constrictions, which were gradually diminished during the hydrothermal treatment.[28]

The increase in the hydrothermal treatment temperature allows one to achieve larger pore sizes[17] in a shorter period of time.[28] For instance, the heating at 130 °C for 1 day afforded a larger pore size than the heating at 100 °C for 2 days (see the Supporting Information, Figure S11). As noted above, long hydrothermal treatment times at high temperatures (e.g., 2 days at 130 °C) appear to lead to the merging of adjacent cylindrical mesopores.

Influence of the Order of Addition of Silica Source and TIPB. The pore size increase was also achieved in case where TIPB was added 3 h before the addition of TEOS instead of adding both at the same time, as in our standard procedure. For initial synthesis temperature of 17 °C, d_{100} interplanar spacing of the obtained SBA-15 was 15.6 nm (see SAXS data in the Supporting Information, Figure S12), which is 1.5 nm larger than d_{100} obtained in our standard procedure. The pore diameter was also increased (compare data in Table 1 and the Supporting Information, Figure S12). In case of the synthesis at an initial temperature of 14 °C, the pore size was also increased when TIPB was added prior to TEOS, but SAXS pattern featured only one broad peak (see the Supporting Information, Figure S12), indicating a low degree of structural ordering, unlike in the case of the standard procedure.

Accelerated Synthesis of Large-Pore SBA-15. The overall time of the synthesis of large-pore SBA-15,[16,24−28,31,33] is from one to several days. In the case of the present synthesis procedure, this time can be shortened to ∼12 h (including the preparation of the copolymer solution) while still achieving a well-ordered 2D hexagonal structure with BJH pore diameter of 13 nm (see the Supporting Information, Figure S13).

Cyclohexane and Triethylbenzene As Swelling Agents. As noted in the introduction, our expectation was that swelling agents of moderate tendency of solubilization in Pluronics are suitable as micelle expanders in the synthesis of large-pore SBA-15. In addition to TIPB, which was found to be an excellent swelling agent, 1,3,5-triethylbenzene (TEB) was evaluated in a synthesis outlined in the Experimental Section, but with TEB substituted for TIPB with the same mass ratio.

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(69) Fulvio, P. F.; Pikus, S.; Jaroniec, M. *J. Mater. Chem.* **2005**, *15*, 5049.

A large-pore material with disordered structure (as inferred from featureless SAXS pattern) was obtained, showing that TEB is indeed a powerful swelling agent, but it leads to uncontrolled swelling under the considered conditions (for data, see the Supporting Information, Figure S14). It should be noted that silica synthesized under similar conditions using the common swelling agent TMB (2 g per 2.4 g of P123) did not feature any uniform mesopores, thus showing that TIPB, which is expected on the basis of its structure to solubilize in Pluronics to the least extent among TIPB, TEB, and TMB, is by far the most suitable for the synthesis of ultra-large-pore SBA-15. It was also conjectured that cyclohexane is likely to be a potent swelling agent in SBA-15 synthesis. The synthesis at an initial temperature of 15 °C using 1 g of cyclohexane per 2.4 g of P123 indeed afforded a large-pore SBA-15 (BJH pore diameter of ~13 nm; see the Supporting Information, Figure S14), whereas the use of 8.5 g of cyclohexane per 2.4 g of P123 (this is the mass ratio analogous to that used in the synthesis of Sun et al. involving hexane[26,28] that affords SBA-15 with pore diameter of ~15 nm) afforded a material with a broad PSD centered at ~20 nm and with a quite featureless SAXS pattern (data not shown). Clearly, cyclohexane is a powerful swelling agent that is useful in the synthesis of large-pore SBA-15.

Proposed Pore Size Expansion Mechanism. It was reported that in the synthesis of SBA-15, the use of TMB as a swelling agent allows one to expand the diameter of cylindrical pores only to a limited extent, while mesocellular foams with spherical mesopores form when higher relative amounts of TMB are used.[23] If the micelle expander solubilizes in the hydrophobic core of the micelle (which in the present case consists of poly(propylene oxide) blocks of the triblock copolymer), the volume ratio of the hydrophilic domains to the hydrophobic domains decrease, promoting lower-surface-curvature micellar structures (cylindrical, gyroid, lamellar) rather than high-surface-curvature micelles (spherical).[23] Therefore, the formation of MCFs templated by high-surface-curvature domains can be understood as a result of templating by oil-in-water microemulsions, in which oil (TMB) droplets are stabilized by the block copolymer surfactant.[23,70] In contrast, TIPB is shown herein to promote the formation of silicas with cylindrical mesopores with a wide range of sizes (10−26 nm), thus indicating the templating by TIPB-swollen micelles (rather than microemulsions), whose sizes can be adjusted in a wide range by changing the initial synthesis temperature and the amount of micelle expander.

The temperature-dependent gradual pore size enlargement in the SBA-15 synthesis in the presence of TIPB is an exceptional behavior. While the influence of the initial synthesis temperature was studied for aliphatic hydrocarbons used as micelle expanders, the change from SBA-15 to vesicular phase or MCF was observed.[71] Our study of SBA-15 synthesis with hexane swelling agent in the temperature range of 12−17 °C revealed essentially no variation in the pore diameter. Moreover, changes of initial synthesis temperature from 10 to 15 and 20 °C had little effect on the pore size for cyclohexane used as a swelling agent. In the case of the synthesis of LP-FDU-12 with spherical mesopores arranged in fcc structure templated by Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) block copolymer, the pore diameter increased as the temperature was lowered to 15 °C, but then stabilized until the temperature was lowered so much that the ordered material no longer formed.[29,30] On the basis of this survey, the temperature behavior observed in the synthesis involving TIPB does not seem to have any reported counterpart, although it bears some resemblance of the behavior observed in the synthesis of LP-FDU-12. Perhaps the interactions between TIPB and $EO_{20}PO_{70}EO_{20}$ change significantly as the temperature is lowered in the 11−20 °C range. It is notable that at lower temperatures, a larger relative amount of TIPB is needed to achieve a higher degree of structural ordering and to suppress the formation of disordered domains, whose presence is indicated by the occurrence of additional mesopores of size below 10 nm with concomitant lowering of the total pore volume. At the same time, the diameter of the uniform mesopores does not vary much as the amount of the swelling agent is increased, and the extent of the pore volume increase is smaller than the extent of increase in the sum of volumes of the block copolymer template and the micelle expander (unlike in some other cases, where there is a proportional increase[41]). These findings suggest that only a part of available TIPB is solubilized in the micelles, similarly to the case of the use of hexane as a swelling agent, wherein hexane is supplied in large excess.[28] The micelle diameter in the presence of TIPB is primarily temperature-dependent, being much less dependent on the relative amount of TIPB. This suggests that the temperature modifies the extent of stretching of the PPO block in the micelles in the presence of TIPB, whereas it affects the extent of solubilization of TIPB to a lesser extent. In this context, the fact that the increase in the relative amount of TIPB leads to improvement in quality of samples synthesized at lower temperatures might suggest that a significant excess of TIPB promotes the homogeneity of the material, suppressing the separation into more uniform, TIPB-rich domains and disordered, TIPB-depleted domains.

Conclusions

Considerations of the extent of solubilization of hydrophobic molecules in micelles of Pluronic block copolymers allowed us to identify TIPB, TEB, and cyclohexane as potentially suitable for the synthesis of large-pore SBA-15. Following this identification, the synthesis of ultralarge-pore SBA-15 (ULP-SBA-15) with pore diameter up to 26 nm (BJH pore diameter up to 34 nm) was accomplished using commercially available Pluronic P123 triblock copolymer as a template and 1,3,5-triisopropylbenzene (TIPB) as a micelle expander. In comparison to other micelle expanders, TIPB appears to exhibit a moderate extent of solubilization in PEO-PPO-PEO copolymer, which is likely to be a key factor in avoiding an uncontrolled swelling and loss of structural uniformity of the micelles. In the case of the synthesis involving TIPB, the pore diameter of SBA-15 was

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adjusted primarily by the selection of the initial synthesis temperature. However, the pore diameter fine-tuning was achieved through the change in the amount of the micelle expander (relative to the copolymer surfactant), or the change in the duration of the hydrothermal treatment or its temperature. Cyclohexane and 1,3,5-triethylbenzene were also verified as swelling agents for the synthesis of large-pore silicas and the former was demonstrated to be suitable for synthesis of large-pore SBA-15.

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Supporting Information Available: SAXS patterns, adsorption isotherms, pore size distributions, TEM images (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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