Independent Fine-Tuning of the Intrawall Porosity and Primary Mesoporosity of SBA-15

Tomas Kjellman,*[,†] Nina Reichhardt,[†] Motolani Sakeye,[‡] Jan-Henrik Smått,[‡] Mika Lindén,[§] and Viveka Alfredsson[†]

[†]Physical Chemistry, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

[‡]Center for Functional Materials, Laboratory of Physical Chemistry, Department of Natural Sciences, Åbo Akademi University, Porthansgatan 3-5, FIN-20500 Turku, Finland

[§]Inorganic Chemistry II, University of Ulm, Albert-Einstein-Allee 11, 89081 Ulm, Germany

Ⓢ Supporting Information

ABSTRACT: We present a study in which the intrawall porosity and primary mesoporosity of SBA-15 are independently controlled by modifying the strength of the molecular interaction that governs the formation of the material. The interactions are targeted at specific times during the process of formation, which results in selective tuning of the porosity, while other characteristics of the SBA-15 material are retained. We show that the intrawall porosity can be considerably reduced by addition of NaI, but not NaCl, and that the shape of the primary mesopores can be influenced by a decrease in temperature, while the two-dimensional hexagonal structure and the particle morphology and size remain unchanged. The timing of the "tuning event" is imperative. We show that a decrease in intrawall porosity by addition of NaI is generic to Pluronic-based mesoporous silica syntheses. This work demonstrates that the material characteristic of mesoporous silica is not necessarily restricted by the initial synthesis conditions as the material properties can be tuned by "actions" taken upon the ongoing synthesis. The triblock copolymer Pluronic P104 was used as a structure director and tetramethyl orthosilicate as a silica source. The materials have been characterized primarily with nitrogen sorption and small-angle X-ray diffraction.

KEYWORDS: SBA-15, intrawall porosity, mesoporosity, N_2 sorption, mesoporous, Pluronic, molecular interaction, tuning
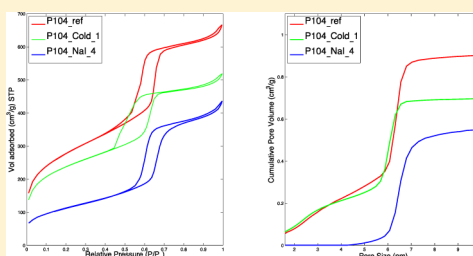
■ INTRODUCTION

Since the beginning of the 1990s, mesoporous materials have attracted considerable interest among chemists and material scientists. The properties of the materials make them attractive for a wide and diverse range of applications, for example, in separation processes,[1] as adsorbents,[2] and for drug release purposes.[3,4] For application purposes, it is important to be able to control several material properties, such as structure, chemical composition, particle size, morphology, and, of course, porosity. In this work, the aim is to tune the porosity of one of the most well-known structures of mesoporous material, namely SBA-15,[5] while also gaining some under-standing of the molecular interactions that control the process that governs the formation of the material. SBA-15 has a complicated bimodal pore system consisting of primary mesopores and complementary smaller (typically in the micromeso range) pores, hereafter termed intrawall pores,[6,7] that interconnect the primary mesopores. The structure is defined by plane group *p6mm*, and the unit cell parameter, which can be controlled by several synthesis parameters, is in the range of 100 Å.

In a previous paper, we reported on how we could reduce the intrawall porosity of SBA-15 by adding NaI to the ongoing synthesis.[8] We showed that the time of addition of the

electrolyte was important for the material properties. Additions made too early (0.5 h after the synthesis was initiated) produced a material with a less defined structure, and additions made too late (24 h after the synthesis was initiated) had a limited effect. We found that 4 h was an optimum time for the addition. For SBA-15 (according to the synthesis protocol used here), the percentage of intrawall pore volume (defined as <5.9 nm pores) with respect to the total pore volume is 36%. For materials synthesized via addition of NaI at 4 h, only 7% of the total porosity was due to intrawall pores. The effective removal of intrawall porosity was also demonstrated by the unsuccessful formation of a carbon replica, in which only a carbon "shell" was obtained (see the Supporting Information of ref 8). In this work, we present a follow-up study that has a trifold objective. We show that the approach of reducing intrawall porosity can be generally applied for synthesis systems using Pluronic molecules as structure directors. We extend porosity control to include the mesoporosity, where the intent is not to change the mesopore size but rather to target the corrugation, or roughness, of the mesopores. Changing the meosopore size

has previously been successfully achieved by using, for example, trimethylbenzene as the swelling agent.[5] Finally, we discuss the molecular interactions allowing for the pore tuning opportunities.

The synthesis of SBA-15 relies on the interaction between siliceous species and the structure-directing Pluronic polymer. Pluronic polymers consist of three blocks, one central polypropyleneoxide (PO) block that is connected at both ends with a polyethyleneoxide (EO) block $[(EO)_x(PO)_y(EO)_x]$. The PO block is more hydrophobic than the EO blocks, and the polymer is thus amphiphilic. The properties of the Pluronic polymer can easily be influenced by temperature and electrolytes.[9−11] Pluronic molecules have reversed solubility behavior, with phase separation occurring at elevated temperatures (at the so-called cloud point). The molecular explanation has been proposed[12] to originate from the conformation of the ethylene oxide chains, with the oxyethylene group being in either the gauche conformation at low temperatures or the anti conformation (high-energy form) at high temperatures. The gauche conformation gives rise to a dipole moment and the observed hydrophilic behavior, whereas the anti conformation does not. Because of the reversed solubility behavior of PEO−PPO−PEO type block copolymers, the polymer will be dissolved as unimers, rather than forming micelles, when the temperature is low.[9] This lower limit of micelle formation is known as the critical micelle temperature (CMT). This feature is crucial when considering the effect of temperature on porous silica materials when synthesized with a Pluronic polymer structure-directing agent because below the CMT there are no micelles that can form the mesopores within the material.[13] The presence of electrolytes is believed to cause changes mainly in the EO part, and typically, anions have the strongest effect.[11,14] As the properties of the structure-directing polymer easily can be changed by electrolytes and temperature, these parameters are, not surprisingly, efficient means of controlling the synthesis of mesoporous silica. Typically, both a general ion effect and a specific ion effect can be identified in the formation of mesostructured SBA-15[15] performed in the presence of a series of electrolytes. The general ion effect is manifested as a diminished solubility of the EO blocks as the solvent becomes more polar with the addition. The specific ion effect counterbalances this. Some large polarizable ions, such as I^-, are known to interact positively with the EO blocks, and as a consequence, the EO blocks become more soluble.[14] Additions of, for instance, NaI and NaCl to an aqueous solution of Pluronic polymers hence give a different outcome, reflected in the different positions of the anions in the Hofmeister series.

The material properties of mesoporous silica are typically determined primarily by the initial synthesis parameters (e.g., reactants, concentrations, and synthesis temperatures). Generally, a synthesis is left to run for a specified time (typically 24 h) without interruption. Material properties are modified by choosing different synthesis parameters, for instance, the polymer:silica ratio,[16] or by additions made to the initial reaction solution, e.g., oil[17] or electrolytes.[18,19] Such additions are made prior to the addition of the silica source and the consequential onset of the synthesis. Other frequently employed means of control are the synthesis temperatures and stirring speeds.[20] The ensuing hydrothermal treatment[7,21] can also be used for modifying the material properties to a certain degree. In this work, we target specific formation steps during the ongoing synthesis, an approach that requires knowledge of the formation sequence.

The formation of SBA-15 has been the focus of many studies.[22−32] A number of these support a mechanism that can roughly be divided into a number of steps:[28−32] (i) formation of flocs consisting of globular micelles in a silica/water matrix (i.e., a nucleation and growth process), (ii) association of the flocs to larger units, (iii) development of the mesoorganized structure, and (iv) "maturing" of the silica framework (i.e., solidification of the soft matter flocs into hard matter particles). Figure 1 shows a time line of the synthesis indicating the
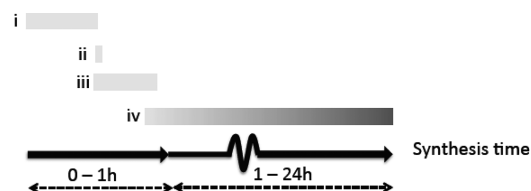

Figure 1. Schematic indicating the occurrence of major formation events in the SBA-15 synthesis and their approximate duration. The grayscale indicates the transition from a soft material to a more solid one. The steps are as follows: (i) floc formation, (ii) oriented aggregation, (iii) formation of structure, and (iv) solidification of the silica framework. Please note that the time scale is not linear.

occurrence and duration of the formation steps. Please note that the time axis is not linear. The ensuing hydrothermal treatment (not shown in the figure) further increases the extent of silica polymerization. It should be stressed that the hexagonal structure and the particle morphology are completed within the first three steps (~40 min after initiation by addition of TMOS).[30]

The driving force for the entire formation process is largely due to the interaction between the siliceous species and the EO blocks.[28,33] This positive interaction has been described to be a consequence of a hydrophobic attraction.[28] If this interaction were to be manipulated at the onset of the synthesis, all of the four steps mentioned above (i.e., i−iv) would be influenced, having an impact on all the thereby generated material properties. For example, with addition of an electrolyte at the onset of synthesis, the entire formation process (steps i−iv) will be altered.[15] In this study, and in a couple of previous studies,[34,35] we aim to selectively influence specific material characteristics by targeting specific formation steps by an action that targets the molecular interactions governing that particular step. We call these changes in the synthesis "tuning events" as the change tunes the properties of the material and does not transform it to, for instance, another structure. In a previous study, particle size was modified by tuning step ii.[34] In another study, mentioned above, the establishment of the intrawall pores was influenced by addition of salt during step iv (i.e., the maturing process).[8] The timing in the former study was critical (cf. Figure 1), and in the latter, it was important, but not crucial.

Our approach is different from that used previously by others,[6,7,21,36] where the temperature was changed during hydrothermal treatment, leading to alterations in the intrawall porosity. However, this always led to other alterations as well, such as an increase in the primary mesopore diameter and an increased total pore volume. The benefit of our approach is that the different porosities can be controlled independently of each other. We will show that with our approach, utilizing time-dependent tuning events, we can independently control the different porosities. For instance, as will be demonstrated, a

decrease in intrawall porosity is accompanied by a corresponding decrease in total pore volume, while the primary mesoporosity is unaffected. In addition, particle morphology and size remain constant regardless of the tuning event.

In summary, the knowledge obtained in this study provides an opportunity to selectively modify particular features (intrawall porosity and primary mesoporosity) of mesoporous silica materials while retaining others (like morphology and particle size). The materials generated can thus serve as good model materials for application studies where the porosity effect can be uniquely investigated.

This study also provides essential information regarding the nature of the molecular interactions and thereby improves our fundamental understanding of the formation, which eventually can provide enough tools to allow rational design of mesoporous materials.

In the paper, we first discuss the readiness of adaptation of the silica framework as a function of time. We then focus on the porosity control by discussing first the intrawall porosity (revisiting some of the results from our previous study) and then the tuning of mesoporosity. Finally, we reflect upon the mechanism responsible for the observed material characteristics.

■ MATERIALS AND METHODS

Materials. The chemicals Pluronic P104 ($EO_{27}PO_{61}EO_{27}$), P123 ($EO_{20}PO_{70}EO_{20}$), and F127 ($EO_{106}PO_{70}EO_{106}$) (BASF), NaCl, 37% (weight) HCl (Merck), tetramethyl orthosilicate (TMOS), and NaI (Sigma-Aldrich) were used as received.

The protocol is considered to have four practical steps: (1) synthesis, (2) hydrothermal treatment, (3) filtration and drying, and (4) calcination. All modifications were done during the synthesis (step 1), while the other steps were kept constant. Time zero is defined as the time of addition of TMOS.

The general synthesis protocol for SBA-15 is based on that reported by Zhao et al.,[5] modified by Linton et al.[31] Pluronic P104 (0.48 g) was dissolved in 1.6 M HCl (18.75 g) in a closed Teflon-lined polypropylene bottle and then heated to 55 °C using a water bath. The reaction was initiated by the addition of TMOS (0.715 mL), after which the solution was stirred vigorously for 1 min. The reaction solution was kept at the same temperature while being moderately stirred for 24 h. This was followed by hydrothermal treatment under static conditions at 80 °C for 24 h, filtration, washing with water, and subsequently drying in air. Finally, the acquired solid was calcined for 6 h at 500 °C. The material synthesized accordingly is termed P104_ref and serves as the reference material for syntheses performed with Pluronic P104.

For the synthesis of SBA-15 using P123, the same procedure and composition (but replacing P104 with P123) were used, with the exception of the synthesis temperature (35 °C). This material is denoted as P123_ref and is the reference material for syntheses in which Pluronic P123 was used.

For the synthesis using Pluronic F127, the following protocol was used. Pluronic F127 (0.48 g) was dissolved in 1.6 M HCl (18.00 g) at room temperature while being moderately stirred in a Teflon-lined polypropylene bottle. TMOS (0.745 mL) was added, and the stirring speed was increased for 1 min, after which the sample was left on the bench and stirring was maintained for 24 h. The remaining steps were equivalent to the steps listed above. This reference material is termed F127_ref.

The properties of the synthesized materials are modified by tuning events, i.e., changes to the synthesis conditions introduced at different times during the synthesis. They refer to either the addition of NaI or NaCl (to a concentration of 1.0 M) or a change in the temperature to 5 °C.

Salt, NaCl or NaI, was added (by simply opening the Teflon-lined polypropylene bottle and adding the dry solid) to the mixture in which

the synthesis was occurring at particular times, after which the synthesis proceeded according to the normal synthesis protocol. Please note that salt was added at 24 h, which was followed immediately by hydrothermal treatment. Salts were added to obtain a 1.00 M solution in the reagent mixture. Samples with salt are denoted P104_NaCl/NaI_z, where z is the time of addition in hours. For instance, P104_NaI_0.5 denotes a synthesis with P104 as the structure director to which NaI (yielding a 1.00 M solution) was added 30 min after the synthesis was initiated. For Pluronic P123 and F127, only additions of NaI at 4 h were performed (P123_NaI_4 and F127_NaI_4).

The synthesis temperature also was lowered by simply placing the Teflon-lined polypropylene bottle in a cold room held at 5 °C while the contents continued to be stirred. In this case, the total synthesis time was prolonged to 96 h instead of the 24 h to allow for a better polymerization. A reference sample kept at 55 °C for 96 h was also synthesized, termed P104_ref_96. The remainder of the protocol was unaltered. Samples placed in the cold room are denoted with the suffix cold_x, where x denotes the time, in hours, after TMOS addition, when the solution was placed in the cold room (e.g., P104_cold_4 denotes a sample placed in the cold room after 4 h at 55 °C and left in the cold room for an additional 92 h).

Methods. The surface area, mesopore dimensions, and pore volumes were determined by nitrogen physisorption measurements at 77 K (ASAP 2010, Micromeritics Co., Norcross, GA). The specific surface area was deduced using the BET method at P/P_0 ratios between 0.05 and 0.2. The total mesopore volume was taken at 0.98 P/P_o. The pore size for primary mesopores was determined using an NLDFT kernel developed for silica (Autosorb version 1.53, Quantachrome Instruments, Boynton Beach, FL) assuming cylindrical pores (equilibrium model). The shown cumulative pore volume plots were determined using an NLDFT kernel developed for silica (Autosorb version 1.53, Quantachrome Instruments) assuming cylindrical pores (adsorption model). The total pore volume (V_t) was obtained from the DFT kernel as the last cumulative value in the adsorption branch, and the volume of the intrawall pores (V_i) was obtained in a similar way but from the cumulative volume at a pore width of 5.9 nm.

The powder diffraction measurements were taken on SAXS beamlines I711 and I911-3 at MAXLAB (Lund, Sweden).[37−40] The raw data were normalized to the first-order (10) reflection. Scanning electron microscopy (SEM) micrographs were recorded with a JEOL JSM-6700 microscope operating at 5 or 10 kV. The samples were sputter-coated with gold before being examined.

■ RESULTS

The materials were investigated with small-angle X-ray diffraction (SAXD), N₂ sorption, and SEM. The results are found in Figures 2–6 (SAXD and N_2 sorption) and in the Supporting Information (Figures S1–S4). Please note that two different SAXD setups were used, and therefore, the baseline can be quite different for some of the samples. Materials synthesized with Pluronic P104 as the structure director were indexed to the expected two-dimensional (2D) hexagonal plane group *p6mm* [(10), (11), (20), and other higher-order reflections were identified (see Figures 2−5)], and the SEM micrographs revealed that the characteristic size and morphology of the particles were conserved irrespective of whether the synthesis had been subjected to any tuning event (i.e., addition of NaI or NaCl or transfer to the cold room). These initial results show that the primary objective of the investigation was satisfied; i.e., the principal features of SBA-15 were not influenced by the tuning events. Also, for the syntheses made with Pluronic P123 and F127, the expected structures were obtained (see Figure 4 and Figure S5 of the Supporting Information).

For the P104 samples, we define intrawall pores as those pores that have a diameter of <5.9 nm. This value was chosen
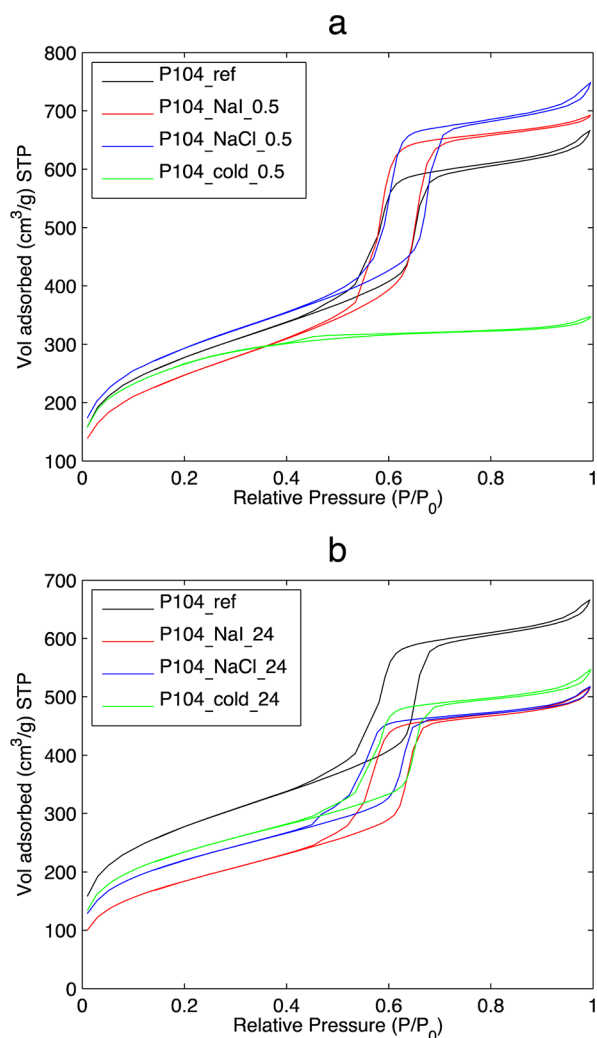
Figure 2. (a) N_2 isotherms of the SBA-15 materials having gone through a tuning event 0.5 h into the synthesis. (b) N_2 isotherms of the SBA-15 materials having gone trough a tuning event 24 h into the synthesis. The reference material (P104_ref) is included for comparison in both diagrams.

as it corresponds to the onset for the hysteresis loop, i.e., the onset of capillary condensation in the main mesopores.

The data in Table 1 show that the cell parameter is only slightly affected by the tuning. It varies between 9.2 and 10.1 nm. The nitrogen sorption data on the other hand show larger variations. The BET values lie in the range between ∼400 and 1100 m²/g. Only P104_NaI_x samples show significant changes, first decreasing to 400 m²/g for P104_NaI_4 and then increasing to 670 m²/g for P104_NaI_24. This is consistent with the changes in porosity discussed below. The main mesopore diameter is quite constant (∼6.6 nm) but diverges significantly for two samples, P104_cold_0.5 and P104_cold_1. As it turns out, some tuning events may be too harsh for the material at such an early stage of the synthesis, and this will be discussed below.

Timing of Tuning Events in General. Figure 2 shows the nitrogen sorption isotherms for all the different tuning events, i.e., addition of NaI or NaCl or transfer to the cold room, at 0.5 h (Figure 2a) and 24 h (Figure 2b), including in both cases the isotherm of P104_ref. The corresponding diffraction data are included in Figures 3−6. It is clear from the isotherms that

alterations made at 0.5 h could be detrimental to the formation of the material, as demonstrated by the isotherm obtained from sample P104_cold_0.5. It is known that 30 min into the synthesis the material has evolved the 2D hexagonal structure and the particles have been established;[30,32] however, the silica framework is apparently very soft, and a temperature decrease is detrimental to this delicate structure. We note that, despite the lack of order, the morphology of the particle is retained (see the micrographs in Figures S1−S3 of the Supporting Information). The additions of salt on the other hand do not destroy the structure. This is not surprising as the formation of SBA-15 proceeds successfully in the presence of high salt concentrations.[15,19,41] When the material has proceeded through undisturbed synthesis for 24 h, the tuning events result in markedly smaller effects (Figure 2b). The two series demonstrate the importance of timing. The prerequisite for the tuning technique is that the material has established both structure and particle morphology but that the silica polymer is able to adapt to the response of the structure director on the tuning event. In other words, the Pluronic molecules respond to the tuning events, and in turn, the silica polymer or oligomers adapt to the Pluronic response.

Tuning of Intrawall Porosity via Addition of Electrolytes. In our previous study,[8] we showed that addition of NaI to the mixture in which the synthesis was ongoing decreased the intrawall porosity of SBA-15 while preserving the primary mesoporosity. From tuning events with NaI (to a final concentration of 1.0 M) undertaken at 0.5, 4, and 24 h, it was established that the optimal time for the addition was 4 h into the synthesis. This was revealed by the nitrogen sorption isotherms and the corresponding cumulative pore volume plots. Carbon replicas made from the materials corroborated the results. Here we show the isotherms (Figure 3a) and corresponding cumulative pore volume plots (Figure 3b) obtained from an equivalent series, extended with two additional samples (additions of NaI at 1 and 2 h). The lowest intrawall porosity was also obtained for the 4 h sample (P104_NaI_4), in which only 7% of the total porosity is assigned to <5.9 nm pores. The SAXD patterns for the samples are shown in Figure 3c. A typical feature for the SAXD pattern for a SBA-15 synthesis using P104 as the structure promoter is that the third-order reflection (20) is more intense than the second-order reflection (11) (see P104_ref in Figure 2c). This is the opposite of what is generally observed for syntheses conducted with P123 as the structure promoter. The intensity relation between these reflections is dependent upon the intrawall porosity.[42,43] If we disregard the first reflection that will always have the highest intensity, Impéror-Clerc et al.[42] showed that for SBA-15 syntheses performed with P103 or P123 the (20) reflection has the larger value for as-synthesized samples whereas the (11) reflection dominates after the hydrothermal treatment. This change in intensity was caused by the reduction in "microporosity" (i.e., intrawall porosity) that occurs during the hydrothermal treatment. The presence of "holes" in the wall was also shown, from computer simulations, to cause a stronger (20) reflection, the intensity of which decreased when the holes were filled.[43] The relative intensities are also sensitive to changes in the ratio of the pore wall thickness to the pore diameter, but as demonstrated in Table 1, this value remains almost constant. In our case, the (20) reflection is dominating over the (11) reflection in P104_ref [enlargement of the SAXD data focusing on the (11) and (20) reflections are shown in the Supporting Information],

Table 1. Properties of the Different SBA-15 Silica Samples Synthesized with P104, Obtained by N$_2$ Sorption and SAXD^a

name	BET (m^2/g)	V_t (cm^3/g)	V_i (cm^3/g)	V_i/V_t (%)	D_{Des} (nm)	a_0 (nm)	R
P104_ref	1000	0.97	0.35	36	6.6	10.01	0.52
P104_ref_96	912	0.93	0.29	31	6.3	10.01	0.59
P104_NaI_0.5	898	1.02	0.25	24	6.6	9.47	0.43
P104_NaI_1	593	0.75	0.16	21	6.3	9.55	0.52
P104_NaI_2	501	0.67	0.11	16	6.3	9.67	0.53
P104_NaI_4	408	0.63	0.05	7	6.8	9.41	0.38
P104_NaI_24	670	0.75	0.20	27	6.3	9.47	0.50
P104_NaCl_0.5	1055	1.09	0.32	29	6.8	b	b
P104_NaCl_1	919	0.91	0.29	32	6.6	9.98	0.51
P104_NaCl_2	978	0.95	0.31	33	6.6	10.02	0.52
P104_NaCl_4	999	0.94	0.33	35	6.6	10.02	0.52
P104_NaCl_24	793	0.75	0.32	42	6.1	9.62	0.58
P104_cold_0.5	952	0.50	0.47	93	2.8	9.20	2.29
P104_cold_1	852	0.75	0.36	48	5.1	9.92	0.94
P104_cold_2	863	0.82	0.30	36	6.3	9.92	0.58
P104_cold_3	924	0.92	0.30	32	6.6	10.01	0.52
P104_cold_4	931	0.91	0.29	32	6.6	10.10	0.53
P104_cold_24	843	0.79	0.28	36	6.6	9.29	0.41

^{a}V_t is the total pore volume, V_i the intrawall pore volume (pore diameter of $\leq$5.9 nm), D_{Des} the primary mesopore diameter, and a_0 the unit cell parameter. R is the ratio of the pore wall thickness to the primary mesopore diameter, i.e., $(a_0 - D_{Des})/D_{Des}$. ^{b}Not measured.
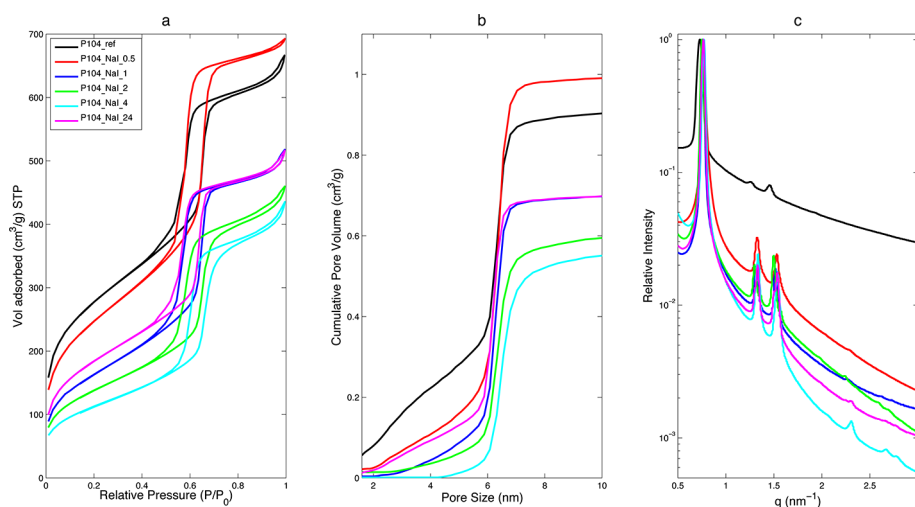

Figure 3. (a) N$_2$ isotherms for SBA-15 synthesized with addition of NaI at different times. (b) Corresponding cumulative pore volume plots. (c) Corresponding SAXD pattern. The equivalent data for the reference material (P104_ref) are included for comparison.

indicating the comparatively strong prevalence of intrawall pores in the SBA-15 material when using this structure director. (It should be noted that P104 has longer EO chains, with 27 EO units, than P123, with 20 units.) However, upon adding NaI, we observe that the intensity of the (20) reflection is no longer stronger than that of the (11) reflection, indicating that the extent of holes has diminished and confirming the sorption results.

To show the generic applicability of this approach, we added NaI (to a final concentration of 1.0 M) to mixtures in which two other Pluronic molecules were serving as structure directors: SBA-15 with P123 as the structure director and SBA-16 with F127 as the structure director. The additions of NaI were made 4 h into the syntheses. Figure 4 shows the data obtained for the P123 system. In this case, intrawall pores were defined as those below a pore width of 6.1 nm. The percentage of intrawall pores decreased from 27 to 23% upon addition of NaI. Even though the decrease is less notable, the tendency is clear. Knowing that the kinetics of the P123−TMOS system (at

37 °C) is notably slower[44] than the kinetics of the P104−TMOS system (at 55 °C),[32] we were not surprised to find that 4 h is likely not the optimal time for the addition of NaI, and the result can likely be improved by optimizing the time of the addition. The data for SBA-16 synthesized using F127 are shown in the Figure S5 of the Supporting Information, and also in this case, a decrease in the intrawall porosity is obtained. In SBA-16, it will not be possible to remove all small pores because the windows between the main pores in the cubic structure will always be present, with or without any tuning of the porosity.

When NaCl is added (data shown in Figure 5) instead of NaI, there is no obvious change in the intrawall porosity. This is most clearly seen in the cumulative pore volume plot in Figure 5b. The percentage of <5.9 nm pores remains around 35% (29−42%), similar to that of P104_ref, which has an intrawall porosity of 36% (see Table 1). The SAXD pattern confirms this, and the expected intensity sequence with the third-order reflection being more intense than the second-order reflection
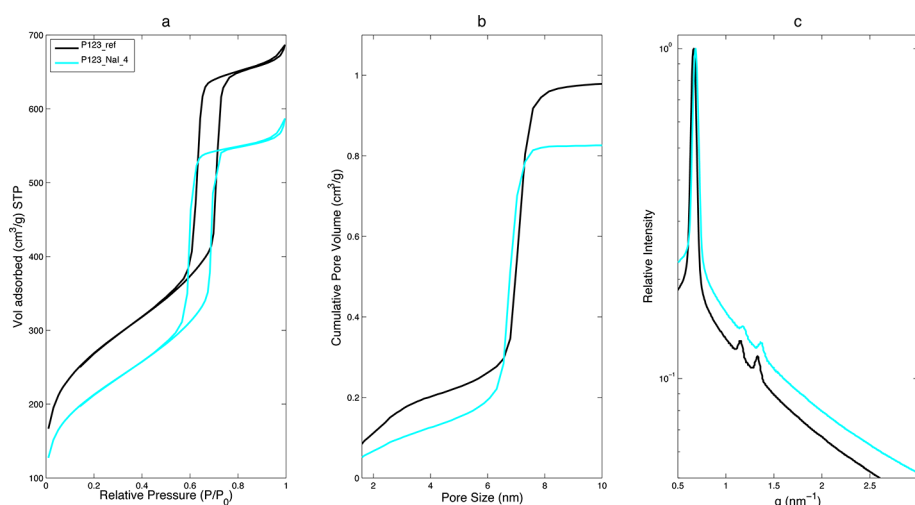
Figure 4. (a) N_2 isotherm for SBA-15 synthesized using P123, with addition of NaI at 4 h (P123_NaI_4). (b) Corresponding cumulative pore volume plot. (c) Corresponding SAXD pattern. The equivalent data for the reference material (P123_ref) are included for comparison.
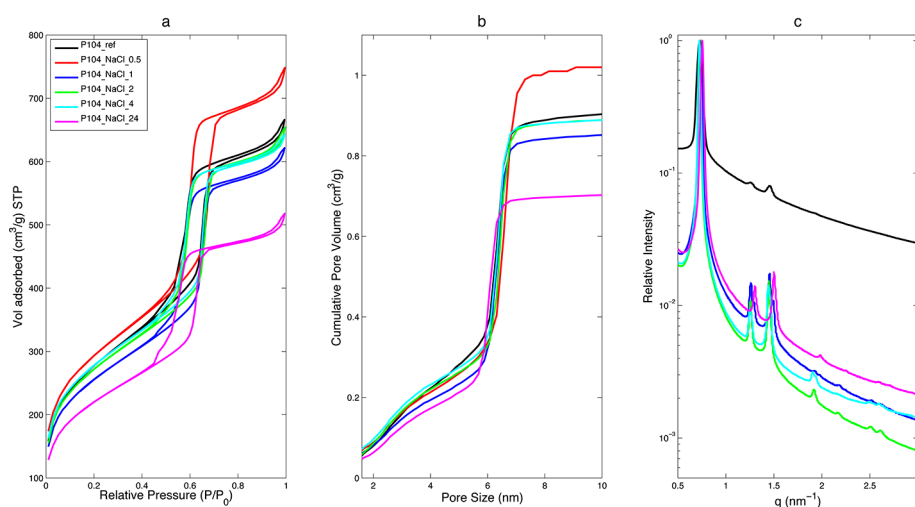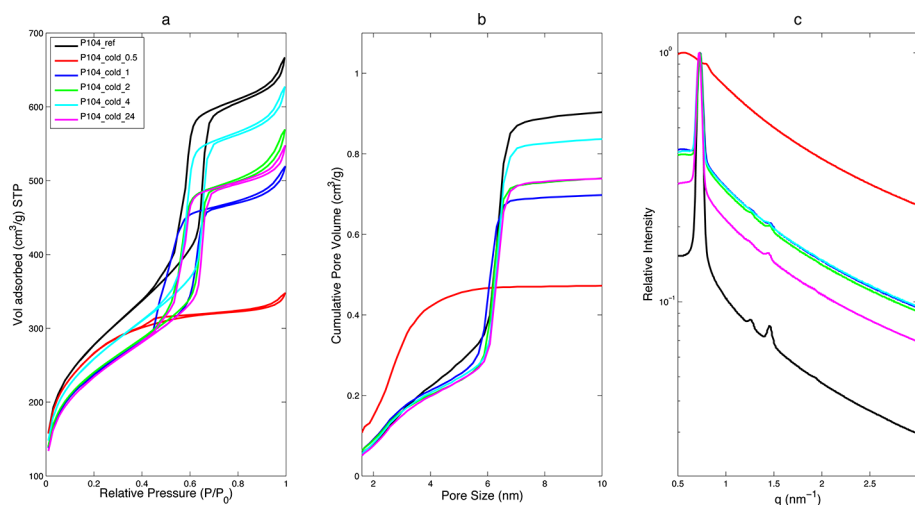

Figure 5. (a) N_2 isotherms for SBA-15 synthesized via addition of NaCl at different times. (b) Corresponding cumulative pore volume plots. (c) Corresponding SAXD pattern. The equivalent data for the reference material (P104_ref) are included for comparison.

Figure 6. (a) N_2 isotherms for SBA-15 for which the synthesis temperature was lowered from 55 to 5 °C at specific times during the synthesis. (b) Corresponding cumulative pore volume plots. (c) Corresponding SAXD pattern. The equivalent data for the reference material (P104_ref) are included for comparison.

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is observed (see also Figures S6 and S7 of the Supporting Information).

Tuning of Mesoporosity via a Temperature Decrease. Figure 6 shows the isotherms (Figure 6a), the corresponding cumulative pore volume plots (Figure 6b), and the SAXD pattern (Figure 6c) of the P104_cold_x samples. A change in the synthesis temperature is expected to result in both a decrease in silica polymerization kinetics and a change (increase) in the hydrophilicity of Pluronic molecules. To ensure a sufficiently high degree of silica condensation, the total synthesis time was extended to 96 h for the samples placed in the cold room (5 °C).

When the temperature was decreased 0.5 h into the synthesis (P104_cold_0.5), the mesostructure characteristics were lost. The SAXD pattern revealed only a faint (10) reflection, and no mesoporosity was detected. If, however, the temperature was altered at a later stage, a rather surprising effect was observed. While the isotherms for P104_cold_2 to P104_cold_24 had the typical isotherms obtained from the hexagonal structure (hysteresis loop H1), P104_cold_1 had an isotherm resembling that of a cubic structure with spherical pores connected by smaller pores (hysteresis loop H2). The SAXD data in Figure 6c however show that the structure of the material is defined by plane group *p6mm*, i.e., 2D hexagonal. This indicates that the cylindrical micelles responsible for "templating" the 2D hexagonal structure revert to a more spherical shape upon cooling, which is mirrored by the silica. Even so, the micelles are stacked as rods, as indicated by the retained *p6mm* symmetry. This suggests that the silica wall for P104_cold_1 is more corrugated than that for materials having the isotherm with the usual hysteresis loop H1.

■ DISCUSSION

We recall that the tunings are most efficient at a rather early stage of the synthesis, a stage at which the material can be considered as a soft matter system controlled by weak intermolecular interactions and thus responsive to changes made to the interactions. This is prior to silica having developed a highly interconnected network that arrests the structural evolution. Obviously, the interactions between siliceous species and Pluronic molecules are the central interactions and the driving force for the formation of the material. The tuning events are primarily aimed at influencing these weak interactions. As the hydrophilicity of the polyethylene oxide blocks of the Pluronic molecules is readily controlled by additions of electrolytes or by a temperature change, we target the central molecular interactions between silica and the structure director by influencing the Pluronic molecules, more specifically the hydrophilic EO blocks.

From the series of additions of NaCl and NaI, we conclude that the observed effects have an ion specific nature and are not of a simple electrostatic nature. It is, as previously mentioned, well-known that ions have a strong effect on the solubility and phase behavior of polyethyleneoxide-based amphiphiles, such as Pluronic triblock copolymers, in aqueous solution. It has also been shown that silica syntheses in the Pluronic-based systems are dependent on the presence of salt and also that this dependence is ion specific.[14] We thus infer that the observed effects are primarily a consequence of the EO block solubility characteristics. Typically, a solution containing NaCl is a worse solvent for EO than a solvent containing NaI, as I⁻, a large polarizable anion, attaches to the EO chains, thereby making them more soluble.[14] Apparently, during formation, in the

competition between being in the aqueous phase or attaching to the siliceous species, the EO block favors the siliceous species, and this leads to the formation of the initial particles and the subsequent entrapment of the EO inside the silica walls (which upon calcination forms the intrawall pores). Additions of salt can change this balance. In the case of additions of NaI, the volume of intrawall pores decreases. We interpret this decrease as being related to the increased hydrophilicity of the EO, caused by attachment of I⁻ to the EO chains. We suggest that this leads to EO preferring the aqueous solution to the silica, and hence, the EO chains are "pulled out" of the silica framework. If additions are made too late, the silica framework is less apt to respond. If, on the other hand, additions are made too early, the whole formation process may be affected. At a certain point in time, the conditions should be optimal for the tuning process. For SBA-15, synthesized according to the protocol presented here, this timing was found to be 4 h after TMOS addition.

The temperature decrease will as previously mentioned slow the silica kinetics as well as increase the hydrophilicity of the EO blocks of the Pluronic molecules. Apparently, this is a rather harsh tuning as it destroys the structure when performed at 0.5 h. This is not too surprising if we look to the literature. For the synthesis protocol used here, the silica network is just about strong enough to maintain the particle morphology during a freeze-drying process after synthesis for 30 min.[30] Also, for P104 in an aqueous solution at a concentration of 2.5 wt %, the CMT is around 20 °C,[9] but with the Cl⁻ ions present in our system, the CMT is likely lower. Combining these two observations, it is possible that decreasing the temperature to 5 °C after synthesis for only 30 min at 55 °C leads to the dissolution of the cylindrical micelles into unimers, because there is no observed mesoporosity remaining.[13] A temperature decrease 1 h after the synthesis was initiated resulted in a significant effect on the mesoporosity. The isotherm (Figure 6a), with a H2 hysteresis loop (an enlargement of the isotherm is shown in the Supporting Information), suggests that the silica wall is more corrugated or even that the cylindrical pores have become globular or spherical. Although the structure is maintained as shown by the SAXD (Figure 6c), the increased hydrophilic behavior of the EO blocks of the Pluronic molecules promotes a more curved spontaneous curvature. This would drive the cylindrical micelles toward spherical, or at least globular, micelles. As the 2D hexagonal structure is maintained, we envisage this transformation to be unidirectional as depicted in Figure 7. There will be a tendency toward transformation of the micelles from rods to spheres, but the rigidity of the silica walls will more or less inhibit the transformation. Evidently, at 1 h, the wall is flexible enough and can to some extent adapt to a more globular micellar shape. This is reflected in the H2 hysteresis loop.

It is interesting to note that while addition of NaI or a decrease in the synthesis temperature after 4 h is viable the combined tuning event results in destruction of the structure of the material.

■ CONCLUSIONS

The properties of a mesoporous material are not limited by the synthesis conditions at the onset of formation. Certain formation events can be fine-tuned during the process, allowing detailed control of the resulting material characteristics. With previous knowledge of the timing of the formation events and with a basic understanding of the central molecular interactions,
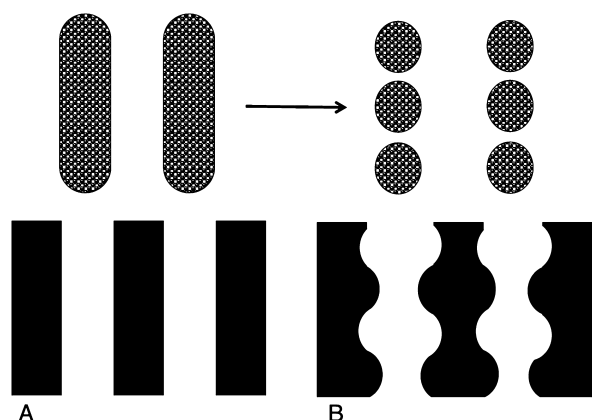
Figure 7. Schematic illustration of the evolution of the micelles and the ensuing corrugation of the pores when the synthesis temperature is decreased from 55 (A) to 5 °C (B) at a time when the material is still adaptive (cf. P104_cold_1).

specific formation events can be targeted. In this work, we show that the porosity of the material (both intrawall porosity and primary mesoporosity) can be tailored without affecting other principal material characteristics.

Changing the solubility behavior of the ethylene oxide block of the Pluronic molecule modifies the balance between its interaction with H_2O and silica. This is done by addition of salt or by a change in temperature at certain times in the formation sequence. It is clear that addition of NaCl and NaI gave different results demonstrating that there is a specific ion effect. Addition of NaI decreased the intrawall porosity, and with a decrease in the temperature of the synthesis solution, the level of corrugation of the primary mesoporosity was increased. The effect of the tuning events is dependent on timing and the corresponding state of the evolving composite materials. We also show that this simple approach of controlling material characteristics can be generally applied for mesoporous silica syntheses using Pluronic block copolymers as structure directors.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
SEM micrographs, additional nitrogen sorption, and SAXD data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Notes
The authors declare no competing financial interest.

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