

To monitor the structure changes, XRD structure modeling was performed using the continuous density function (CDF) approach¹¹ and the derivative difference minimization full-profile refinement.¹² The density distribution in *fcc* and *bcc* materials was simulated by a three-dimensional array of spherical cavities arranged in accordance with the face-centered cubic and the body-centered cubic packing respectively. For the 2-D hexagonal phase the density distribution function described in ref. 11 was applied assuming the cylindrical pore model. The cavity (or pore) diameters and the lattice parameters were varied to obtain the best agreement between the experimental and calculated XRD profiles. As shown in Fig. 1, the structure models provided full matching between the experimental and calculated XRD peak positions and intensities for all the samples. The structure parameters are summarized in Table 1. The addition of butanol induced prominent increase of the cavity diameter, while the lattice parameter expansion was minor. The lattice parameter of *bcc* structure cannot be directly compared to that of *fcc*. Instead, we can compare the unit cell volumes normalized to the number of cavities per unit cell. For samples S0, S1, S2, and S3 these specific volume values are 2488, 2502, 2666, and 2513 nm³ respectively. The specific volumes per cavity for sample S0 and S3 differ only by 1%, which suggests negligible lattice expansion. On the other hand, the nearest distance between the cavity surfaces, which is given by $a\sqrt{2}/2 - D$ for *fcc* and $a\sqrt{3}/2 - D$ for *bcc* and can be used as a measure of the silica wall thickness, decreased from 6.2 nm for sample S0 to 3.8 nm for sample S3. From the above considerations we may conclude that butanol causes minor swelling of the mesostructure lattice but major decrease of the silica wall thickness, presumably due to the dehydration of the PEO blocks.^{6b} The XRD pore diameter for sample S4 appeared to be smaller than those of S3 and S2. However, the nitrogen physisorption analysis for this sample suggested an intermediate pore shape between cage-type and cylindrical (ESI†). In this respect, the pore diameter 9.7 nm for S4 should be considered as an effective value since the XRD modeling for this sample was done applying a simplified cylindrical pore model.

The present study demonstrates unambiguously that the introduction of butanol to a triblock copolymer-based mesoporous silica synthesis provides an extremely efficient means of tuning the material structure. Such straightforward tailoring of the phase behaviour is made possible under the low HCl concentrations conditions utilized. Butanol is known to act as a co-surfactant participating together with the block copolymer in forming the polar/apolar interfaces. Specifically, it is believed that butanol is mainly located at the hydrophilic–hydrophobic interface (EO/PO) stabilizing the micellar aggregates and determining the surface curvature.⁶ We could speculate that the evolution of the mesophase from the cage-type *fcc* and *bcc* to the near-cylindrical pore 2-D

hexagonal structure may, therefore, originate from changes in the interfacial curvature and the hydrophobic to hydrophilic volume fractions. Similar transition between *Im3m* and *p6mm* phases resulting from the reduced hydration of the polar headgroups and lowering curvature has been observed, for example, in a polyalkylene oxide-based surfactant–water system where, besides, an epitaxial relationship between both phases was evidenced.¹³ In our case, it is possible that the curvature of the micellar aggregates could be reduced due to the combined swelling of the micelles and decrease in hydration of the polyethylene oxide groups caused by increasing amounts of butanol.^{6c} In addition, the location of butanol at the hydrophilic–hydrophobic interface may be responsible for the shift of the silica region in the micelles, which resulted in reducing the silica wall thickness and, consequently, in the pore opening.

In conclusion, we demonstrated a facile and systematic control over the formation of mesoporous silica with tailored pore architecture. The structural evolution is exclusively due to the addition of different amounts of butanol as the unique phase-controlling agent. Phase transitions from face-centered cubic *Fm3m*, to body-centered cubic *Im3m* (SBA-16) to, finally, 2-D hexagonal *p6mm* (SBA-15-like) mesostructures accompanied by pore widening and opening were observed upon increasing the amount of the co-surfactant. With regard to this, we stressed that combining experimental and simulated powder XRD patterns and TEM could ensure the precise structure characterization. Furthermore, it is reasonable to consider synthesis of mesostructured materials using other organic additives that can affect the hydrophilic–hydrophobic interface of the triblock copolymers. Therefore, we expect this particular synthesis route and the principle described herein to be readily and widely adopted.

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Notes and references

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Table 1 Structure characteristics of samples synthesized with different amounts of butanol^a

Sample	Lattice type	<i>a</i> (nm)	<i>D</i> (nm)
S0	<i>Fm3m</i>	21.51	9.0
S1	<i>Fm3m</i>	21.55	9.6
S2	<i>Fm3m</i>	22.01	10.2
S3	<i>Im3m</i>	17.13	11.0
S4	<i>p6mm</i>	14.52	9.7

^a *a*, the lattice parameter; *D*, the cavity (or pore for *p6mm*) diameter determined from XRD modeling.