

Periodically Mesoporous Silica Monoliths from Diol-Modified Silanes

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Despite a drastic progress in the synthesis of porous inorganic materials with control of pore sizes over length scales from Angstroms to micrometers, the preparation of materials with a simultaneous tailoring of morphology and pore structures on different scales still remains a challenging task. Periodic mesoporous materials can be obtained by applying long-chain surfactants or amphiphilic block copolymers as structure-directing agents.^{1,2} However, the synthesis of materials with a high degree of mesoscopic order in combination with macroscopic morphologies such as large monoliths is still difficult to achieve and only a limited number of examples is known from the literature.^{3–7} Anderson et al. demonstrated a successful route to surfactant-templated silica aerogel monoliths using hexadecyltrimethylammonium bromide as a structure-directing agent followed by supercritical drying with liquid carbon dioxide. The resulting material showed hexagonally arranged mesopores within spherical particles but no hierarchical structural buildup of the network is described.⁷

The situation becomes even more problematic when materials with pore sizes on different length scales are desired, for example, materials that combine small (micro- and mesopores) and large pores. For these materials multiple benefits arise from each of the pore size regimes, for example, micro-/mesopores for size- or shape-selective applications and macropores for a reduction of diffusion limitations to the active sites. Thus, the advantages of producing hierarchical pore structures within one material are evident. Dual or multiple

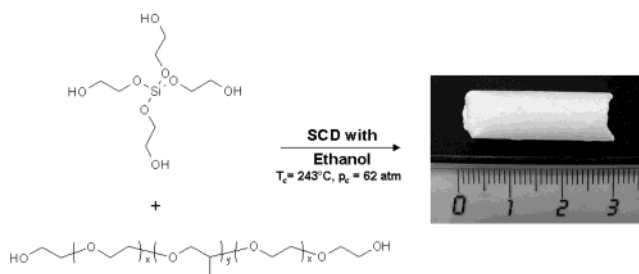


Figure 1. Schematic representation of the precursors and a representative photograph of the mesostructured gel (SCD = supercritical drying).

templating approaches have been used for the production of materials with a bimodal pore size distribution; however, no morphological control is reported.^{8–11} Another approach is based on phase separation strategies in combination with sol–gel processing for the preparation of monolithic materials for chromatography purposes; however, no or only weak regular arrangements of the mesopores are achieved within a rather bulky network structure in the micrometer range.¹²

Here, we report the synthesis of silica monoliths with a hierarchical organization of the pores in the macro- and mesopore size regime within an extremely filigrane inorganic backbone, combined with very low densities. Our synthetic route is based on a templating mechanism of a water-soluble, ethylene glycol-modified silane as an inorganic precursor with an amphiphilic triblock copolymer, followed by supercritical extraction with ethanol to remove the surfactant phase (Figure 1). The modified silane offers two major advantages compared to the conventionally used tetraethoxy- or tetramethoxy-silanes. First, the precursor is water-soluble and thus allows a direct mixing with the lyotropic liquid-crystal-like phase of the block copolymer in water; second, it does not require a catalyst to start the hydrolysis and condensation reactions. In addition, the ethylene glycol, which is released during the hydrolysis and condensation reactions, is not detrimental for most of the liquid-crystal surfactant mesophases as Hoffmann et al. showed in previous studies for an anionic surfactant/silica/ethylene glycol mixture.¹³ We extended this work to ethylene oxide-containing block copolymer surfactants since a stronger interaction with the inorganic precursor can be expected due to transalkoholysis reactions and thus a more pronounced influence on the mesostructure is anticipated. To our knowledge, this is the first report on hierarchically porous monolithic materials with meso- and macropores. The mesopores show a regular arrangement due to the structure-

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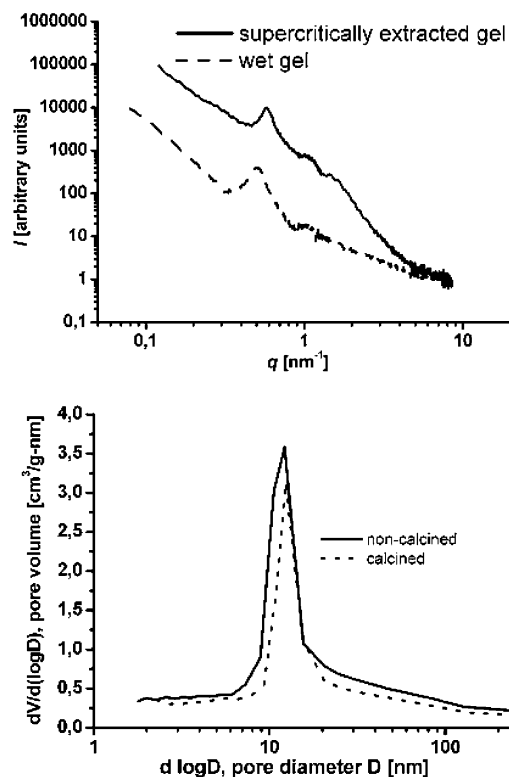


Figure 2. Small-angle X-ray scattering profiles of monolithic samples prior to supercritical extraction with ethanol ("wet" gel) and of the dry gel after extraction with ethanol (top). The BJH pore size distribution (bottom) calculated from the adsorption branch of the supercritically extracted and calcined gel.

directing effect of the amphiphilic block copolymer and the inorganic network is built up from a filigrane fibrous, interwoven structure, instead of the typically expected spherical silica particles.

For the preparation of the ethylene glycol-modified silane, tetraethoxysilane (TEOS) was mixed with a 4-fold molar excess of ethylene glycol and heated to 150 °C under argon. Continuous distillative removal of ethanol resulted in the formation of an oily liquid.¹⁴ The silica monoliths were prepared by a neutral sol-gel route using a nonionic poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (P123, EO₂₀PO₇₀EO₂₀) mixed with the ethylene glycol-modified silane and water in a molar ratio of 0.03:1:23. Gelation took place after 10 min and the gels were aged for 7 days at 30 °C. In a final step drying of the gel bodies was performed with supercritical ethanol ($T_c = 243$ °C, $p_c = 62$ atm).

White, crack-free monolithic silica monoliths were reproducibly obtained after the supercritical extraction process. Although the theoretical density of the monoliths was adjusted (by the amount of water) to 0.088 g cm⁻³, the measured bulk densities of the final extracted material were in the range of 0.310 g cm⁻³ with a corresponding shrinkage of 40% (compared to the volume of the wet gel body). After calcination at 450 °C in air, the monoliths retain their macroscopic shapes, size, and appearance.

Chemical analysis of the sample prior to calcination showed a very low carbon content. By ¹³C CP MAS NMR

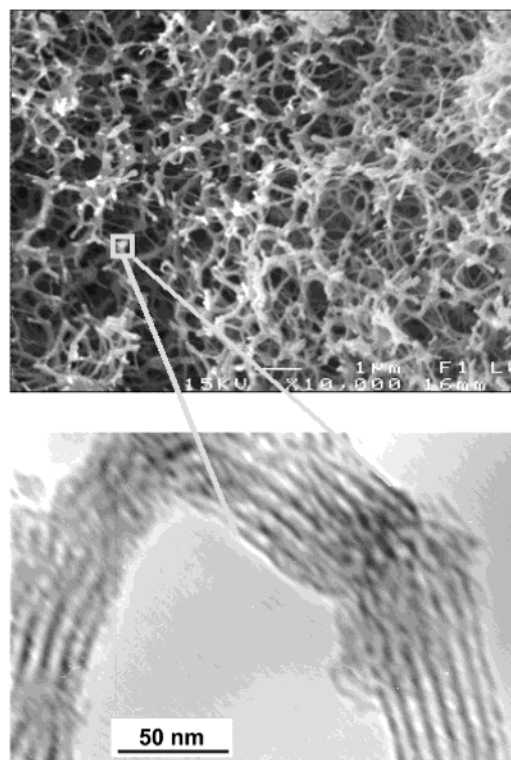


Figure 3. Representative SEM (top) and TEM image (bottom) of a macro-/mesoporous silica monolith templated with P123.

peaks at $\delta = 15.6$ and 58.2 ppm were found, which can be assigned to residual ethoxy groups. This was also confirmed by thermogravimetric analysis, which indicates an almost complete removal of the block copolymer template from the monoliths during supercritical extraction. However, due to the reaction conditions during drying, reactive Si-OH groups undergo transesterification reactions to form ethoxy moieties, resulting in a hydrophobic material. Calcination of the monoliths does not induce cracking of the gel body but results in the removal of the ethoxy groups, rendering the material hydrophilic (increase weight loss up to 150 °C).

Small-angle X-ray scattering measurements for the "wet gel", and supercritically extracted sample, proved the existence of long-range ordered domains with two broad reflections and a corresponding d spacing of the (100) peak of 12.3 nm for the wet gel and 10.8 nm for the supercritically extracted sample (Figure 2, top). The small shrinkage during supercritical extraction is due to further condensation of the silica network and removal of water. Consistent with the presence of uniform mesopores, the nitrogen adsorption-desorption isotherm shows the expected type IV adsorption behavior with a BET surface area of 510 m² g⁻¹. The BJH pore size distribution (Figure 2, bottom) also indicates a uniform distribution of the pores with a fairly broad maximum at around 11 nm for the adsorption branch and 8 nm for the desorption branch. The long-range ordering of the pores is retained even after calcination of the material as the BJH pore size maximum does not shift.

For all investigated materials, scanning electron microscopy images show a weblike macrostructure throughout the whole material with pores in the range of 200–800 nm (Figure 3). The single strands of the web have an open periodic mesoporous structure which was

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confirmed by transmission electron microscopy images of both supercritically extracted and calcined samples. Highly ordered parallel lines can be observed in the TEM image, relating to a hexagonal arrangement of mesopores (side view). In other images (not shown), the uniform hexagonal mesostructure could be seen from the top.

The typical spherical structural arrangement of a silica aerogel monolith, which has also been observed for aerogels from tetrakis(2-hydroxyethyl)silane/water mixtures without template, has completely vanished.¹⁵ Thus, it can be expected that the block copolymer not only directs the structure of the mesopores but also has a strong influence on the hydrolysis and condensation behavior of the ethylene glycol-modified precursor. This is probably associated with the ease of further transesterification reactions with the ethylene oxide groups in the hydrophilic domains of the block copolymer.

In conclusion, this synthetic method is well-suited for the synthesis of hierarchically porous, mesostructured silica monoliths in which the silica network forming the macroporous structure (200–800 nm) is built up from periodic interconnected mesoporous (8–11 nm) silica-based strands. The whole process gains profit from the combination of (a) the high compatibility of tetrakis(2-hydroxyethyl)silane with lyotropic liquid-crystal-like phases of block copolymers in purely aqueous solution and (b) standard processing techniques in the synthesis of highly porous materials such as supercritical extraction.

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