ChemComm

Nanoporous silica from amphiphilic block copolymer (ABC) aggregates: control over correlation and architecture of cylindrical pores

Christine G. Göltner,* Beate Berton, Eckart Krämer and Markus Antonietti

Max-Planck-Institute of Colloids and Interfaces, Kantstr. 55, 14513 Teltow/Seehof, Germany.
E-mail: goeltner@mpikg-teltow.mpg.de

Received (in Bath, UK) 20th August 1998, Accepted 9th September 1998

Novel nonionic ABCs are shown to be versatile templates for the sol–gel synthesis of nanoporous silicas, the structure can be fine-tuned by varying the template concentration.

Amphiphilic block copolymers (ABCs), consisting of one hydrophilic and one hydrophobic block, are gaining increasing importance as structure-directing agents in the synthesis of nanoporous ceramic oxides.[1,2] When mixed with water, these polymers undergo aggregation into lyotropic liquid crystalline phases, which are stable over a wide range of composition and temperature. These self-organizing systems, although not mechanically robust in their own right, are well suited as nanotemplates to imprint structure and porosity onto an otherwise dense and amorphous material, such as sol–gel-derived silica.[3–6] ABC templates help to extend the boundaries for pore size, wall thickness and mechanical strength beyond those of previously known nanoporous ceramic oxides.[7,8]

Cylindrical pores represent the closest approximation of one-dimensional cavities, which are of growing importance for a number of topochemical or spectroscopic applications and the generation of anisotropic nanostructured materials. The latter has been elegantly demonstrated by preparing monodisperse carbon nanotubules within nanopores of alumina.[9] Ordered nanoporous arrays were also utilized as tubular membrane separation devices.[10] There is a demand to increase the density of cylindrical pores to a filling factor (*i.e.* volume fraction of the voids) of 0.7 in hexagonally ordered silica to make similar ‘nanocapillary’ reactors very efficient.

Existing templating routes towards hexagonal porous silica, however versatile they may be, produce defect sites, which are reflected in the physical properties or even reproduced in the secondary cast of the porous material. For example, ABC templates of the poly(butadiene-b-ethylene oxide) (PB–PEO) type were shown recently to be suitable templates for the generation of a rich variety of pore structures in silica.[11] Although these polymers show good solubility in water, their structural polymorphism in these mixtures is such that often wide biphasic ranges occur. This phenomenon increases the number of defect sites over the statistically determined measure.

Therefore, there is a demand for self-organizing templates with a more pronounced tendency to form well ordered phases, which possess a smaller number of defect sites. In this contribution, we present new low-cost, nonionic polymer templates which form superbly stable, homogeneous lyotropic liquid crystalline phases. Such nanocasting media facilitate the control over correlation and architecture by simply varying synthetic parameters during the templating procedure, as opposed to selecting from a library of ABCs.

The results demonstrate the great potential inherent in ABC nanocasting as the method of choice for pore design in ceramic oxides. Poly[(ethylene-co-butylene)-b-(ethylene oxide)] (KLE-3729 and KLE-3736, see Table 1) were obtained from Th. Goldschmidt AG, Essen, Germany, and freeze-dried prior to use.

TMOS was obtained from Aldrich and used as received. HCl (1 M solution from Aldrich) was diluted using distilled water. Sol–gel synthesis of silica in the presence of ABC templates has been described in detail elsewhere.[1] Typically, the ABC (30, 50 or 70 mass% with respect to water) was dissolved in 2 g TMOS before adding 1 g of hydrochloric acid (pH 2). After the hydrolysis had abated, the flask was evacuated for 5–10 min in order to remove methanol, formed during the hydrolysis of TMOS. The birefringent, viscous mixture was then left to polycondense in an open container at 60 °C. The resulting inorganic–organic hybrid materials were calcined at 500 °C (12 h under nitrogen, 16 h under oxygen).

The birefringence of the lyotropic phases was studied between crossed polarizers of an Orthoplan-Pol microscope (Leitz) equipped with a hotstage. Nitrogen sorption measurements were recorded on a Micromeritics Gemini surface analyzer. The sample morphologies were studied with a Zeiss DSM 940 scanning electron microscope operating at an acceleration voltage of 20 kV. Standard TEM investigations were carried out on ground samples. TEM pictures were recorded with a Zeiss EM 912 Omega TEM operating at an acceleration voltage of 120 kV. Optical textures of the ABCs in water revealed that both polymers presented here form lyotropic liquid crystalline phases between 15 and 85% (m/m). Both ABCs show lyotropic phases of normal topology only, as expected from the length ratios of the blocks. This was confirmed by the water-miscibility of the polymer–water phases at all compositions within the phase diagrams.

Sol–gel synthesis of silica in the lyotropic phases of KLEs resulted in homogeneous hybrid materials, which showed no indication of phase separation, as estabished by SEM analysis. The silica monoliths were calcined to completely remove the template.

At low polymer concentrations, casts of spatially non-correlated, cylindrical micelles with low degree of intermicellar order are observed [Fig. 1(a)]. At higher concentrations (50%), these cylinders are closely packed into hexagonal arrays [Fig. 1(b)]. Further increasing the template concentration causes the formation of a lamellar/vesicular structure [Fig. 1(c)], which collapses upon calcination. The deterioration of the lamellar/vesicular structure is expected, as calcination removes the ‘scaffolding’ ABC template, which keeps individual lamellae apart.

The nitrogen adsorption–desorption isotherms show pronounced hysteresis, making the determination of the pore size distribution by non-imaging methods unreliable. However, the transition from the cylindrical morphologies into a lamellar structure is manifested in the different shape of the nitrogen adsorption-desorption isotherm, with the lamellar sample

Table 1 Physical data of the amphiphilic block copolymers used as templates

ABC	M_n	M_w/M_n	N_A[a]	N_B[a]	Block ratio
KLE-3729	6.6	1.069	68	66	1 : 1
KLE-3736	7.3	1.103	68	82	1 : 1.2

[a] Number of repeat units.

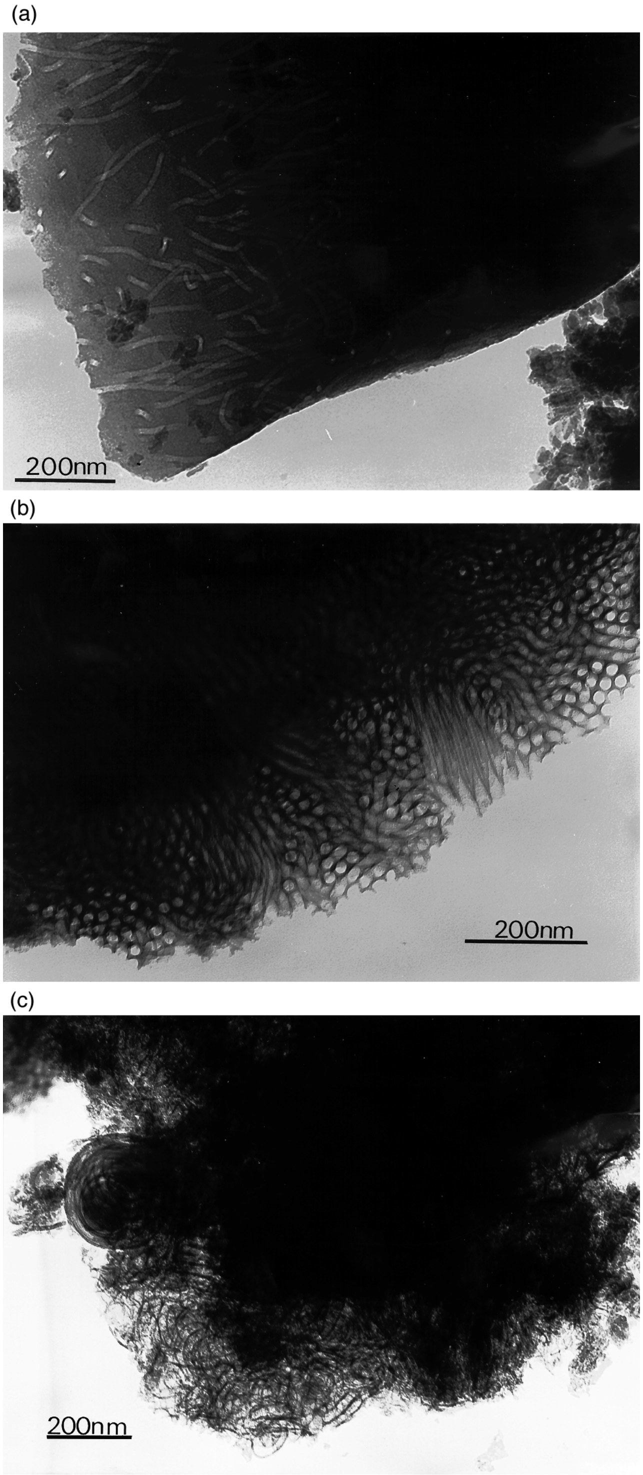

Fig. 1 TEM micrographs of KLE-3729-templated silicas: (a) 30% template (m/m with respect to water): isolated cylinders (diameter 14 nm) display no spatial order with respect to each other and are separated by up to 50 nm thick walls; (b) 50% template: hexagonally packed cylinders (diameter 16 nm, wall thickness 7 nm), (c) 70% template collapsed lamellae and multilamellar vesicles.

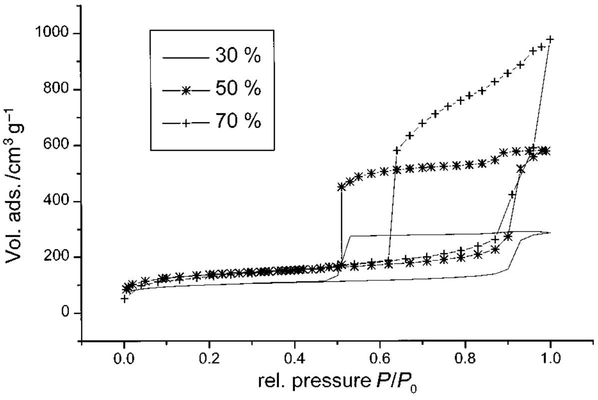

Fig. 2 Nitrogen adsorption–desorption isotherms of KLE-3729-templated silicas depending on the template content: 30% and 50%: typical isotherms showing pore condensation with pronounced hysteresis; 70%: the lamellar/vesicular structure, which is partially collapsed, expectedly does not show distinct pore condensation in the mesopore regime.

lacking distinctive pore condensation. For the cylindrical systems, the specific surface area increases with increasing template content, demonstrating the contribution of each individual ABC molecule to the overall interface area (Fig. 2).

Amphiphilic block copolymers of the KLE type have proven to be exceptionally well suited for the synthesis of nanoporous silica with cylindrical pore shape. The pore density can be controlled *via* the template content between 30 and 50%. Traversing this concentration regime, isolated cylindrical pores with low spatial correlation evolve into correlated ones with high degree of packing order. Adjusting the pore density and thus the packing order of the cylindrical pores allows control over the pore curvature, as the packing into an hexagonal array automatically goes along with a considerable straightening. Future work will focus on the synthesis of curved and straight nanowires with high aspect ratios. For this purpose, KLE-templated silicas appear to be the most promising candidates presently available.

The authors would like to thank R. Pitschke for graphical work, Th. Goldschmidt AG for generously providing the KLE-type ABCs, the Max-Planck Society and the Deutsche Forschungsgesellschaft (Sfb 1623) for financial support.

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Communication 8/06701E