Mesoporous Silica from Lyotropic Liquid Crystal Polymer Templates

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Mesoporous nanostructures are regularly structured solids with pore sizes between 20 and 500 Å and a narrow pore size distribution. They are a welcome supplement to classical zeolites, the application of which was previously restricted because of their limited highest pore diameter of 13 Å.[1,2] Mesoporous ceramic oxides have large specific surface areas and are potential candidates for chemical and physical processes, such as chromatography and catalysis.[3–5] Since the discovery of M41S in 1992,[6] many research groups have focused their interests on mesoporous materials.[7] M41S is formed by a surfactant-assisted reaction pathway as a result of the attractive electrostatic interaction between a ceramic precursor and an ionic amphiphile (sometimes counterion-mediated), upon which a surfactant-rich gel phase precipitates from solution.[8-11] The structure of M41S-type materials depends sensitively on the preparation conditions, as a delicate balance between charge density and volume has to be maintained. Since M41S is obtained as a fine, porous precipitate from a heterogeneous reaction mixture, these nanostructured ceramic oxides have extraordinarily large specific surface areas.[12]

An alternative approach to mesoporous molecular sieves is the exploitation of nonionic surfactants (primary amines) at low concentration,[13] which affords similar materials to M41S. Mesoporous ceramic oxides obtained in the presence of oligoethylene oxide surfactants[14] are less regular than M41S (as determined by X-ray diffraction, which usually reveals just one diffraction peak), but still exhibit high specific surface areas and narrow pore size distributions. Pinnavaia et al. attributed the templating effect to the presence of wormlike surfactant micelles.[14,15] Their results clearly show that there is a displacement mechanism caused by nonionic micellar aggregates.

An alternative route towards ordered mesoporous ceramic nanostructures is the utilization of lyotropic liquid crystal phases as structure-directing media.[16,17] Here, the sol–gel synthesis of the inorganic nanostructure takes place in the ordered environment of a bulk surfactant mesophase: the polycondensation of a water-soluble monomer (e.g., silicic acid) is confined within the aqueous domains of a microphase-separated medium, which acts as a template for the nanostructure. The bulk liquid crystal approach has many advantages over previous routes towards inorganic nanostructures. The resulting ceramic oxide is a direct cast of the liquid crystalline phase, which indicates a high degree of control over the structure. Further, mesoporous ceramic oxides prepared in liquid crystalline phases can be obtained as monoliths (large, crack-free objects, which usually are not macroscopically aligned), because the product is generated by solidifying a homogeneous bulk liquid crystal as opposed to being precipitated from a heterogeneous mixture in the case of M41S. (A certain particle size, if required, can always be achieved after synthesis by grinding and subsequent sifting, and a large particle size of heterogeneous catalysts also facilitates catalyst recovery.)

Using the lyotropic phases of classical nonionic surfactants (low molecular weight amphiphiles) as templates typically affords particles sizes from 300 mm to several millimeters. This big particle size of silica has the effect that the surface area is to a large extent determined by the internal nanostructure and not by the particle surface, an important aspect with respect to size-exclusion processes.[12]

In this paper we describe the preparation of mesoporous silica from lyotropic liquid crystalline polymer templates. Amphiphilic block copolymers (ABCs), like low molecular weight surfactants, can form micelles when mixed with water or other suitable solvents.[18] Accordingly, more complex aggregate structures, namely, lyotropic liquid crystalline phases, are formed at higher polymer concentrations.

ABC templates are expected to show a number of advantages. Firstly, the compatibility of a polymeric amphiphile can be chemically adjusted to the desired product by established procedures of polymer chemistry. Thus, a significant extension of the chemical toolbox for the preparation of mesoporous materials is provided. Secondly, the higher molecular weight slows down exchange and structural relaxation kinetics of the aggregation structures, which makes these lyotropic liquid crystals kinetically less sensitive to phase changes. At the same time, a larger size of the templating lyotropic aggregate is achieved, which directly determines the pore diameter as well as the wall thickness of the mesoporous materials. In addition, such templates should facilitate the preparation and handling of large monoliths, because the resulting hybrid materials are expected to show an improved elasticity and ductility.

In our experiments we employed amphiphilic block copolymers consisting of an apolar polystyrene block (S) and a polar polyethylene oxide block (E) of equal molecular weight (the SE tensides) as polymer templates.[19] The average molecular weight was 1000 $\mathrm{g\,mol^{-1}}$ per block for SE 10/10 and 3000 $\mathrm{g\,mol^{-1}}$ per block for SE 30/30. The polyethylenoxide block's distribution was narrow, whereas the polystyrene block exhibited the Schulz–Flory distribution as a result of a radical polymerization mechanism.

The lyotropic phases of the polymeric SE surfactants investigated are extraordinarily stable. SE 10/10 is characterized by birefringent fluid phases between 45 and 80% (w/w) above 45°C, although the diffuse textures do not allow any

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phase assignment into the classical scheme of liquid crystal phase structures. SE 30/30, as expected, is less soluble in water than its smaller analogue, and it has a higher melting point and Krafft temperature. However, like SE 10/10, it forms a broad mesophase between 45 and 65% (w/w). The liquid crystalline phases of both block copolymers are thermally very stable, as no clearing point was observed up to 100°C. Mesoporous silica was prepared in the same way as reported previously.[16,20] In the following the polymer-templated silica will be referred to as SE 10/10-silica and SE 30/30-silica, depending on the template in which it was generated.

As expected, the use of lyotropic polymer templates for the synthesis of nanostructured ceramic oxides has the advantage that macroscopic, transparent monoliths are obtainable, which, once the template is removed, could be suitable for separation processes. The crack-free monoliths can be obtained in considerable size (Figure 1) from the lyoptropic phase of SE 10/10 and are stable in a closed vessel. Exposure to dry air causes cracks to appear in the monolith; future studies will reveal which method of drying can avoid this problem.

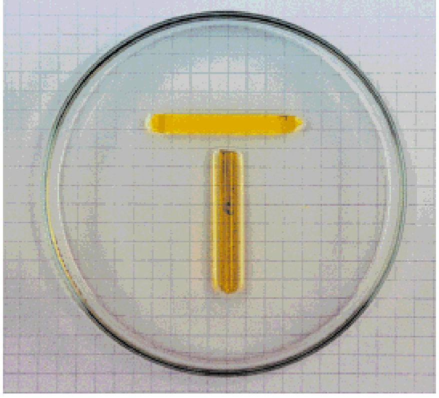

Figure 1. Silica monoliths (dyed with methyl orange for better visibility) templated with SE 10/10. The background lines are 5 mm apart.

After calcination the mesoporous silicas obtained from liquid crystalline polymer templates exhibit specific surface areas of about 500 $m^2 g^{-1}$, as found by nitrogen BET measurements.[22] From the type II adsorption–desorption isotherm (Figure 2), a narrow pore size distribution around 3 nm can be calculated (see the Horvath–Kawazoe plot in Figure 2). Thermogravimetric analysis (TGA) revealed an average content of organic matter of 53% (w/w), which can be completely removed by either calcination or solvent extraction. Transmission electron microscopy (TEM) pictures of the ultramicrotomed, calcined materials shows the regular, porous structure of the polymer-templated silicas (Figure 3).

Quantitative evaluation of the TEM data reveals a larger pore diameter for SE 10/10-silica than that calculated from the desorption branch of the adsorption iotherm, but it confirms the narrow pore size distribution. This deviation can be explained by the "ink bottle" shape of the pores, which gives rise to the type II isotherm with its pronounced hysteresis.[21] The evaluation of the sorption data according to Barret, Joyner, and Halenda (BJH) gave an average pore radius of 4 nm as calculated from the adsorption branch of the isotherm, and 3 nm calculated from the desorption branch. The interpretation of the sorption data with respect to pore diameter should therefore be regarded with caution.

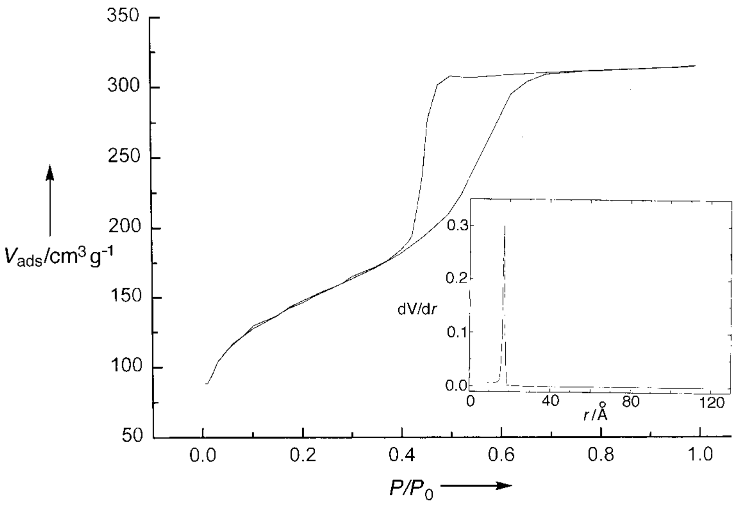

Figure 2. Nitrogen BET adsorption isotherm of SE 10/10-silica. Inset: Horwath–Kawazoe plot, depicting the pore size distribution. P is the equilibrium pressure of the adsorbate, P_0 the saturation pressure of the adsorbate at the temperature of the adsorbent; dV/dr is the derivative of the nitrogen volume adsorbed with respect to the pore diameter r of the adsorbent.

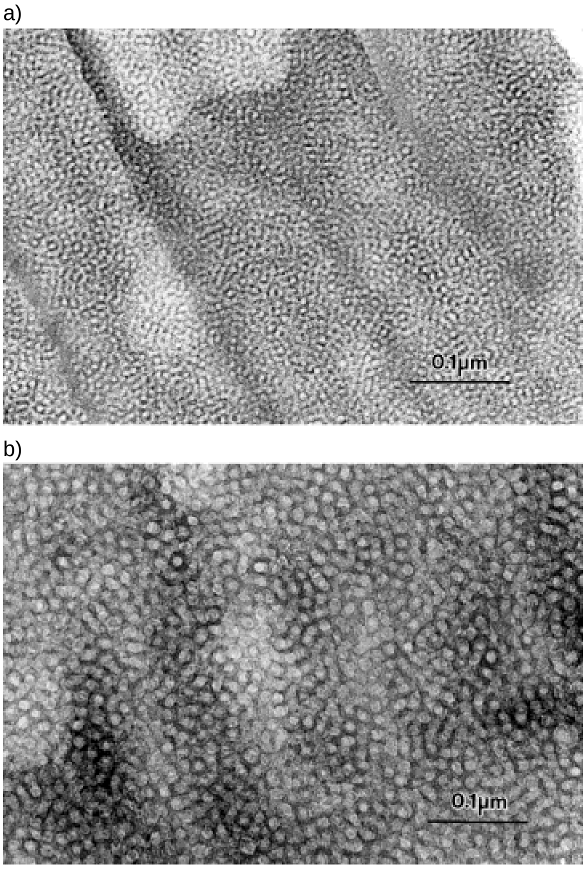

Figure 3. TEM micrographs of calcined silicas: a) SE 10/10 silica, b) SE 30/30 silica. Both samples were embedded in epoxy resin and ultramicrotomed.

The TEM pictures clearly demonstrate that both polymeric templates produce equally structured, highly porous materials. With knowledge about the stoichiometry and the absence of macroscopic volume shrinkage during gelation (as proven by the monolith production), we can calculate a porosity of about 80 vol% which is very high for a material with three-dimensional form stability.

The structure of these silicas has nothing in common with any simple lyotropic phase structure. The TEM pictures can be compared with those reported by Pinnavaia et al., who used ethylene oxide monoethers and Pluronics as templates.[14] This research group applied the surfactants in concentrations much lower than the ones necessary to provide a lyotropic liquid crystalline phase. The structure of those materials was described as distorted hexagonal; however, no cylindrical structure of the silicas, which would be expected for a classical hexagonal lyotropic mesophase (H_I-phase), could be detected. Furthermore, similar structures have been observed for block copolymers and assigned to a hexagonal phase.[22] It is interesting to note that a very similar silica mesostructure was found in marine diatoms[23] and named "continuous silica". Such structures seem to be an optimal compromise between porosity and mechanical stability in nature for the purpose of lightweight design.

Small-angle synchrotron X-ray scattering[24] provides a deeper insight into this novel structure of mesoporous silicates. The small-angle X-ray diffractograms of SE 10/10-silica and SE 30/30-silica (Figure 4) show the same qualitative and quantitative features, indicating that both materials belong to the same type of phase structure. As expected, the X-ray reflections are shifted according to the different molecular weight and size of the template employed. The diffractograms typically show three reflections, of which the higher order ones are not resolved as simple peaks. The degree of order exceeds the one of the corresponding systems described by Pinnavaia et al., who reported only one broad first-order scattering peak. Since the diffractograms of SE 10/10 and SE 30/30 contain several scattering reflections, an L_3-phase as a template can be excluded.[25]

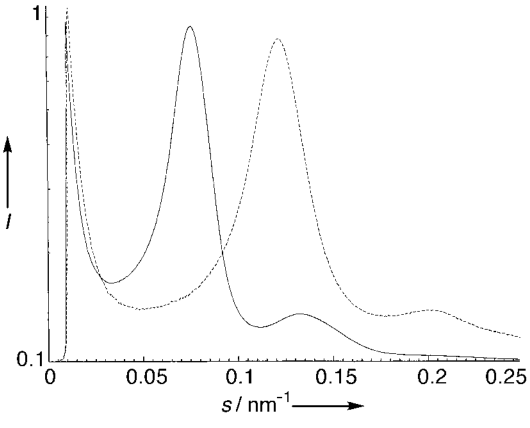

Figure 4. Synchrotron X-ray diffractograms of SE 10/10-silica (broken line) and SE 30/30-silica (solid line). I = rel. intensity.

From the first-order scattering peak, we calculate a Bragg distance of 8.2 nm (SE 10/10 silica, 8.7 nm before calcination) and 13.3 nm (SE 30/30 silica, 14.1 nm before calcination). This is in good agreement with the pore-to-pore distances observed in the transmission electron micrographs. The the next higher-order peak can be described by the superposition of two Lorentz peaks, and fitting these reveals that they can be indexed according to a two-dimensional hexagonal packing. The high intensity and broadening of the peaks can be attributed to high order on a local scale, but also to a low correlation length ξ. From the width of the scattering peaks, the ξ value, a measure of the size of coherent hexagonal domains, is calculated to be of the order of about four times the pore-to-pore distance. The size of these hexagonal domains is limited by frequent branching points at a typical 120° angle ("tripods", as observed in the TEM pictures), which interconnect the silica rods and give rise to a three-dimensional continuity of the silica phase. This phase structure might be located between a cylindrical hexagonal, the bicontinuous cubic (gyroid), and a hexagonally perforated lamellar phase (the latter two consisting of tripods connected with a defined rotation angle), as it exhibits a statistical arrangement of structural elements of all three "pure" symmetry groups.

This phase structure turned out to be independent of temperature, amphiphile concentration, and silica content over wide ranges, as shown in a set of experiments in which the composition of the reaction mixture is varied. The structure of the materials does not change upon solvent extraction and calcination, as shown by small-angle X-ray diffraction studies at all stages. The volume shrinkage of 6–7% on calcination is much less than that observed when using low molecular weight surfactant phases as templates (up to 21%).

It was shown that the lyotropic liquid crystalline phases of amphiphilic block copolymers are very promising templates for the generation of mesoporous materials. It is not only possible to extend the long Bragg distance of classical mesoporous materials to 8–13 nm; macroscopic monolithic objects can also be obtained. The resulting phase morphology of a hexagonal continuous silica turned out to be stable over a wide range of accessible experimental parameters. Further experiments with more homodisperse model templates will show whether this is due to the polydispersity of the polymeric template or whether it is a general feature of such strongly segregating block copolymers.

In addition, the full potential of polymeric templates, which is gained by the careful chemical adjustment (using chemical functionality) of the interface between template and casting should allow the extension of this technique to other materials, such as mesoporous polymers or semiconductors. Finally, the regular porous structure of such structures is expected to be useful for enclosing nanometer-sized objects, such as enzymes and chemically active colloids.

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[20] The amphiphilic block copolymer (2 g) is dissolved in tetramethylorthosilicate (TMOS, 4 g), which is then hydrolyzed by adding dilute hydrochloric acid (pH 2, 2 g). Initially, an isotropic mixture is obtained. Methanol is removed by evaporation in vacuo (25 Torr, 30°C), upon which the reaction mixture turns viscous and birefringent. The subsequent sol–gel process is carried out at room temperature (50°C for SE30/30) in an open flask. After 12 h the liquid crystalline mixtures are solid and, after extraction of a major portion of the template with acetone for 24 h, are calcined at 550°C (12 h under nitrogen, 12 h under oxygen).

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[25] The X-ray data were fitted with Lorentzian functions. The normalized peak positions for the first three peaks are 1.00, 1.73, and 2.00, which indicates a hexagonal symmetry of the packing.

Why Does the Active Form of Galactose Oxidase Possess a Diamagnetic Ground State?**

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Dedicated to Professor Gottfried Huttner
on the occasion of his 60th birthday

The fungal enzyme galactose oxidase (GO) contains in its active site a square-pyramidally coordinated Cu^{II} ion (d^9) with an O-bound tyrosyl radical (Tyr 272) in the equatorial plane (see Figure 1). This catalytically active copper(II)–tyrosyl radical form is EPR-silent and has been proposed to possess a diamagnetic ground state ($S = 0$).[1a] The unpaired electron in the $d_{x^2-y^2}$ magnetic orbital of the Cu^{II} ion is then intramolecularly *antiferromagnetically* coupled to the electron of in the half-occupied π orbital of the tyrosyl radical. This is somewhat surprising, because in all known Cu^{II}–semiquinonate complexes this intramolecular exchange coupling is *ferromagnetic*, yielding an $S = 1$ ground state.[2] What is the mechanism of the exchange coupling in GO?

A catalytically inactive form of GO (pH = 4.5) containing a reduced Cu^{II}-tyrosinate moiety has been characterized by X-ray crystallography (Figure 1).[3] It has been shown that the conformation of the coordinated Tyr 272 ligand is fixed by π stacking with the tryptophane residue Trp 290. It is assumed that one-electron oxidation of Tyr 272 yielding the coordinated tyrosyl ligand does not change the conformation of the phenyl ring or the Cu-O-C bond angle significantly.

Recently Tolman et al.[4] and we[5] have reported some low molecular weight, structurally characterized Cu^{II}–phenolate complexes that can be chemically or electrochemically oxidized to generate relatively stable Cu^{II}-phenoxyl species.[6] These complexes are EPR-silent; they possess a diamagnetic ($S = 0$) ground state.[7] In these compounds the coordinated phenolate ligands are connected to the coordinated macrocycle 1,4,7-triazacyclononane (Figure 2); a six-membered chelate ring $\overline{\mathrm{Cu^{II}NCCCO}}$ is formed. It is then natural to assume that the conformation of the chelate ring does not change upon one-electron oxidation of the phenolate to a coordinated phenoxyl.

A qualitative analysis of the relative orientations of the magnetic orbitals of the Cu^{II} ion ($d_{x^2-y^2}$) and of the phenoxyl radical (the half-occupied π orbital) reveals that they are strictly orthogonal at an Cu^{II}-O-C bond angle α of 180°, irrespective of the dihedral angle β between the x,y plane at the Cu^{II} ion and the phenyl ring of the radical ligand (Figure 3). According to the Goodenough–Kanamori rules

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