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In situ Synchrotron SAXS/XRD Study on the Formation of Ordered Mesoscopic Hybrid Materials with Crystal-Like Walls

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The synthesis of a new class of organic−inorganic hybrid materials, called periodic mesoporous organosilicas (PMOs), was first reported in 1999.[1−3] These materials contain organic units covalently bonded and homogeneously distributed in an inorganic silica framework; they are obtained by hydrolysis and condensation of bridged organosilane precursors $(R'O)_3-Si-R-Si-(OR')_3$ in the presence of tetraalkylammonium halides as structure-directing agents. Larger pore sizes were obtained by using nonionic triblock copolymers as structure-directing agents,[4−6] and PMOs with special morphologies, such as thin films[7] or monodisperse spherical particles,[8] have also been reported. In most cases the pore walls of these materials are X-ray amorphous; however, Inagaki et al. were the first to synthesize periodic mesoporous organosilicas with crystal-like pore wall structures possessing molecular-scale periodicity with periodic distances of 0.76 nm in case of 1,4-phenylene-[9] and 1,3-phenylene-silica,[10] and 1.16 nm for biphenylene-silica.[11] So far there is no information about the formation process of this kind of periodic organosilica mesophases. Here we report the first in situ synchrotron SAXS/XRD studies of the formation process of a mesoscopically ordered biphenylene-bridged organosilica material with crystal-like pore walls. We demonstrate that the formation of periodicity both on the mesoscopic scale and within the pore walls occurs simultaneously as the result of a fully cooperative process.

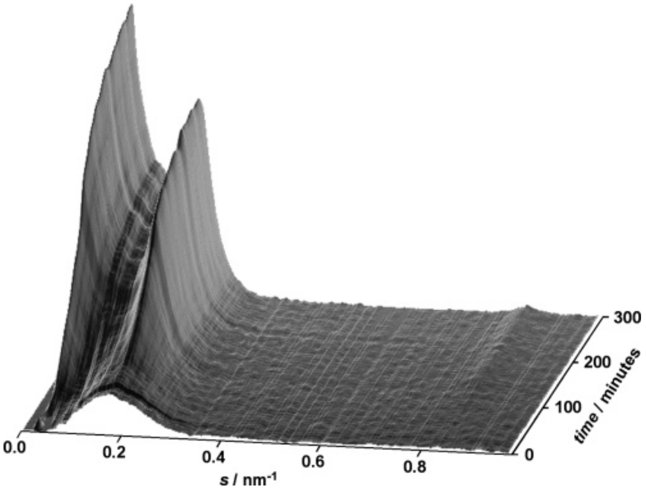

Figure 1. Temporal evolution of the SAXS/XRD pattern for the synthesis of a mesoscopically ordered biphenylene-bridged organosilica with crystal-like pore walls.

The measurements were conducted at the Austrian SAXS beamline at ELETTRA synchrotron, Trieste, Italy, utilizing the linear position-sensitive Gabriel detector. The SAXS camera was set to a length of 1.5 m and to a photon energy of 8 keV. The measurements were performed using a flow-through reactor, which has been described in detail elsewhere.[15] The vessel was connected to a reflux condenser and could thus be operated at atmospheric pressure at elevated temperatures (see Supporting Information). Octadecyltrimethylammonium chloride (OTACl) was dissolved in a NaOH solution (pH = 13.5) under stirring. After addition of the precursor, 4,4′-bis(triethoxysilyl)biphenyl, the reaction mixture was stirred for 24 h at room temperature. Then data acquisition was started (1 min per frame) and the solution was heated to 95 °C within about 3 min. The molar composition of the reaction mixtures was precursor/OTACl/NaOH/H_2O = 1:1.3:8.1:927. The experimental curves were corrected for variations of the primary intensity, and background was subtracted. The form factors of spheres and ellipsoids were modeled according to ref 13.

The SAXS/XRD pattern measured during the formation of the hybrid mesophase is shown in Figure 1. At short reaction times only diffuse scattering from micelles is observed. However, after a reaction time of about 60 min a low-angle reflection appears which

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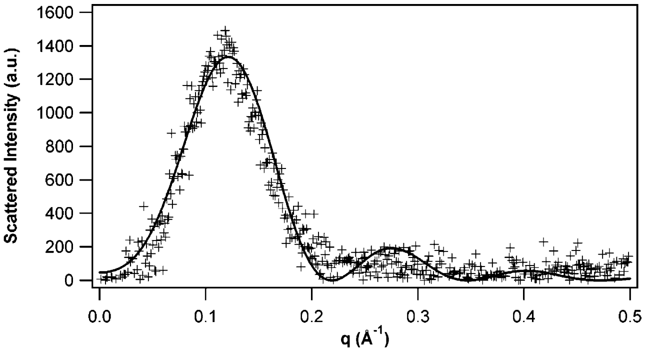

Figure 2. Experimental curve (+) after 40 min into the reaction with the form factor of sphere (solid line).

rapidly increases in intensity. This reflection coexists with the diffuse micellar scattering up to a reaction time of about 150 min. This low-angle reflection corresponds to the formation of a surfactant−organosilane mesophase with an initial repeat distance of 5.25 nm. However, opposite to what has been previously observed for nonbridged precursors,[12] the repeat distance *increases* with time to reach 5.36 nm after 300 min, indicating that there might be some rearrangement in the silane portion. The formation of the mesophase is also slower than that with nonbridged precursors, which is to be expected, since the hydrolysis and condensation under basic conditions proceed slower with organically modified siloxane precursors. No high-order reflections appear at any stage of the process, which is typical for this type of bridged silane. However, the synthesis is known to result in a quasi-2D hexagonal material. Parallel to the intense low-angle reflection, another reflection with a repeat distance of 1.17 nm appears in the diffractogram, the intensity of which also increases with time. This reflection has no crystallographic relation to the intense low-angle reflection, and originates from the formation of periodic order within the walls of the hybrid mesophase; its relative position and intensity (as compared to the low-angle reflection) are in line with the powder patterns of the final solid product.[11] Since both reflections appear at the same time we can conclude that the formation of the mesophase serves to induce the local ordering in the walls and that both processes occur simultaneously; i.e., the crystallinity in the walls is a result of a fully cooperative process.

The micellar scattering was fitted according to procedures the same as those we recently used to analyze the SAXS pattern measured during the formation of block-*co*-polymer templated silica.[14] The scattering pattern can only be fitted assuming a spherical shape of the scattering objects up to a reaction time of 60 min. An example of the fitted curves is shown in Figure 2 for a reaction time of 40 min, and the parameters used in the fit are summarized in the Supporting Information. All scattering curves measured at reaction times shorter than 55 min can be fitted using the same set of parameters. Thus, we can conclude that the micelles remain spherical until the nucleation and growth of the hexagonal mesophase occurs. The presence of spherical micelles, despite the long hydrocarbon tail of the surfactant, can be understood, since the synthesis is carried out at elevated temperatures. However, at 60 min into the reaction, the fitting parameters show a slight increase, indicating that the micelles are growing. At this stage the low-angle Bragg reflection appears. The exponential decay of this region is −1.47 at 55 min and becomes −1.1 at longer reaction times, which is close to the value of −1 expected for infinite cylinders. This indicates that there is a growth of the micelles long after the formation of the ordered phase. As seen in Figure 1, the scattering intensity at very low angles increases dramatically with time after the formation of the mesophase. The results are thus in line with previous reports stating that the formation of the hexagonal mesophase in dilute systems undergoes a liquid−liquid phase separation process, where spherical inorganic-surfactant micelles separate into one phase rich in surfactant and inorganic precursor and one rich in solvent.[14−17] The nucleation and growth of cylindrical micelles then occurs in this concentrated phase.

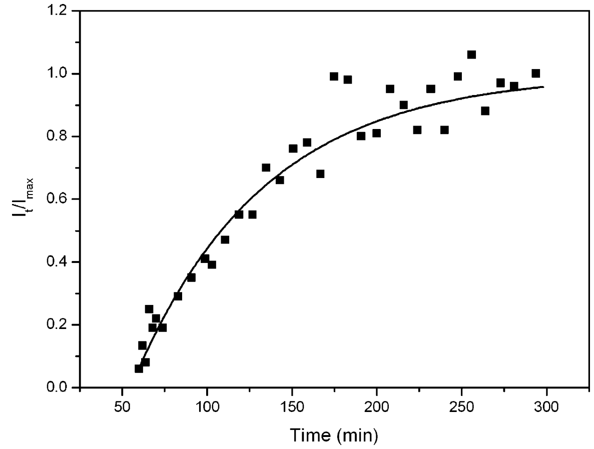

Figure 3. Temporal evolution of the relative intensity of the low-angle Bragg reflection (points) with a fit of the Avrami equation (n = 1; line).

The reaction order can also be deduced from analysis of the time-dependency of the integrated area of the low-angle Bragg reflection according to the Avrami equation

$$\ln(1 - I_{t-t_0}/I_{max}) = -k\,(t - t_0)^n \qquad (1)$$

where I_{t-t_0} and I_{max} are the integrated intensities of the low-angle Bragg reflection at time = $t - t_0$ and t = infinite, respectively, where t_0 is the time at which the Bragg reflection appears in the diffractogram (55 min); the ratio I_t/I_{max} is used to describe the fraction transformed, k is the rate constant, and n is the reaction order. In the Avrami formalism, the value of the exponent gives the dimensionality of the transformation and thus also includes information on the nucleation process, and has been used previously for kinetic analysis of phase transitions[18] between, and nucleation and growth[15] of, inorganic-surfactant mesophases. A plot of I_t/I_{max} versus t is shown in Figure 3 together with a fit of eq 1 to the data with n = 1. Neither n = 2 nor n = 3 result in a satisfactory description of the data. Since n = 1 corresponds to the one-dimensional growth of the objects, these results are again in good agreement with the results obtained based on analysis of the diffuse

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scattering at the low-angle region. Due to the low signal-to-noise ratio of the Bragg reflection originating from the order in the walls, no similar analysis was carried out for this reflection. However, one should not expect a similar dependence anyway, since the diffracting planes are orthogonal to each other and the sizes of the scattering domains are different. In summary, we can conclude that our data clearly suggest that (a) the hybrid micelles are spherical before nucleation and growth of the mesophase occurs, (b) the ordering in the walls is a direct consequence of the ordering effect of the micelles building up the mesophase, and (c) the nucleation and growth of the mesophase follows first-order kinetics and proceeds notably slower than that for comparable syntheses with nonbridged siloxane precursors.

Supporting Information Available: Schematic drawing of the experimental setup and table of parameters obtained from the fitting of form factor of spheres to the experimental curves (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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