



Experiment title:
In-situ alignment of “bio-inspired” liquid-crystalline organic-inorganic nanocomposites in a magnetic field

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SC-1944

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Report:

Mesostructured silica gels with controlled structure are of great importance for many technologies such as filtration, catalysis etc. and also optical applications [1]. Despite the tremendous progress in spatially patterning the deposition of inorganic solids in the presence of organic templates in the lab, the structure formation kinetics is highly dependent on the system and in many cases poorly understood. In our laboratory we fabricated monoliths of mesostructured hybrid materials using the sol-gel process with liquid crystal (LC) templating [2,3]. Commercially available alkoxy silanes, however, are typically not compatible with liquid crystal-like phases due to the presence of alcohol. We have developed an innovative approach using novel silica precursors (different polyol modified silanes) to synthesize macroscopic silica monoliths with a periodic mesoscopic nanostructure. To induce phase separation, various surfactants are used.

In the present study we investigated the formation kinetics of hierarchically structured silica monoliths with micro- and macroporosity based on phenylene bridged EGMS (ethylene glycol modified silane) as precursor and Pluronic P123 as structure directing agent. These systems do not lend themselves to magnetic alignment that was previously planned, but are very interesting for correlation of self-assembly processes and formation of the network and phase separation during sol-gel-synthesis. Therefore time resolved *in-situ* SAXS studies were performed at ESRF, beamline ID02 in order to

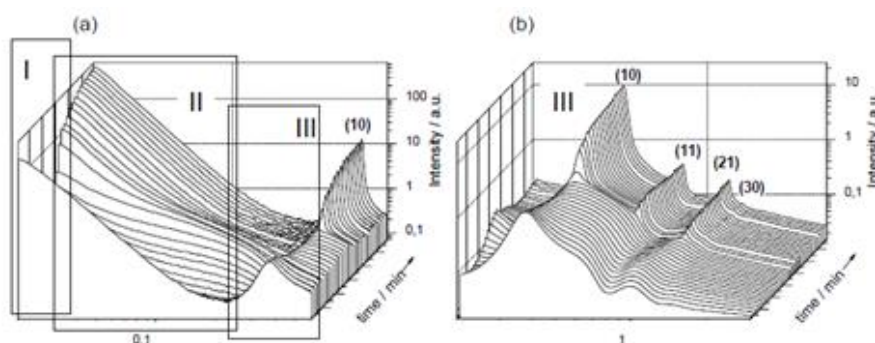


Figure 3.4.11. Time-resolved synchrotron SAXS patterns from a P123-mediated sol-gel-synthesis of the phenylene bridged silica-precursor leading to a macroporous network consisting of highly ordered, hexagonally arranged cylindrical mesopores. (a) SAXS-measurements carried out with a sample-detector distance of 10 m and (b) of 1.5 m.

follow the structure formation at two length scales: evolution of the periodic mesostructure in a q range of $0.18 < q < 4 \text{ nm}^{-1}$, and the evolution of sub-micron structure (“macromorphology”) in the range of $0.018 < q < 0.6 \text{ nm}^{-1}$, measured at two different sample to detector distances (1.5 and 10 m). The overlap in q was used as support to identify same points in time during a measurement time of approx. 2 h.

During the gelation of this system, three stages of development could be distinguished from the time-resolved SAXS curves shown in Figure 3.4.11 (a): For the first 15-35 minutes, a mixing and formation of new aggregates, respectively, is observable in the low q -regime (q -region I), as well as in the amplitude loss of the remaining liquid crystalline structure (q -region III: $> 0.2 \text{ nm}^{-1}$). From 40 to 65 min in time (prior and parallel to the mesostructure formation) the evolution of an “intermediate phase” is observed in the q -range smaller than 0.2 nm^{-1} (q -region II). In stage 3 the mesostructure develops (see Figure 3.4.11 (b)). The systems start with the structure-directing agent already in or close to the liquid crystalline phase (mixed phase of cubic and hexagonally close-packed spheres). Although ethylene glycol is compatible with the LC phases, the phase diagram is influenced and the long range order of the supramolecular assembly is partly destroyed. Following this dissolution process, a characteristic shoulder evolves in the measured SAXS curves, which can be interpreted as an intermediate phase, consisting of particles that are spherical to cylindrical with a maximum radius of 11 - 12 nm, growing in number and diameter prior to the establishment of long range order of the evolving mesopores.

The influence of the fraction of fluid phase (dilute HCl) in the sol on gelation kinetic and mesostructure formation was investigated by studying samples with different ratios of silane/ 10^{-2} M HCl weight ratios: (A) 48/70, (B) 48/90 and (C) 48/110. As the fluid phase content increases, the time, at which the evolution of the hexagonally ordered cylinders starts, decreases. For all three systems the observed time of phase separation coincides approximately with mesostructure formation, whereas gelation was observed afterwards. The time interval between phase separation/mesostructure formation and gel time increases at higher fluid phase fraction.

The macroporous network (as seen in the TEM images on dried gels at the top of Fig 2) develops due to a phase separation into silica-surfactant rich and solvent-rich regions and stops when sol-gel transition is complete. The growth kinetic and mesostructure evolution determines the final macromorphology of the network. Size of the macromorphological features was estimated by the coherence length L for the liquid crystalline domains. At the onset of mesostructure formation, the domains exhibiting periodical arrangement are already very large at or shortly after phase transition. The coherence length increases during the course of synthesis. Surprisingly, we find much lower values for L in aged gels. The loss of domain size in the aged gels is probably caused by micro-cracks. For systems B and C that exhibit a platelet like macromorphology, the relatively uniform platelet thickness is also detected in the USAXS signal (580 and 590 nm final size, corresponding very well to TEM measurements of dried gels). The time resolved scattering curves thus allowed following of the kinetic of structure evolution hierarchically structured mesoporous silica gels *in situ* on two length scales simultaneously [4].

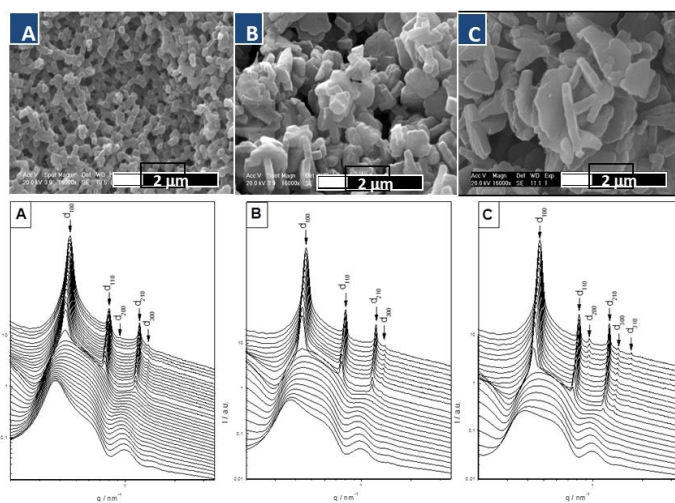


Figure 2: gelation from sols with different amount of fluid phase. Changes in macromorphology observable in SAXS and USAXS.

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