Non-ionic block copolymers leading to a highly ordered organosilica material

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Abstract. Phenylene-bridged periodic mesoporous organosilica (PMO) materials with hexaethylene glycol mono hexadecylether (C\textsubscript{16}(EO)\textsubscript{6}) as structure directing agent (SDA) in acidic solution were synthesised and the reaction was studied in different conditions, including \textit{in situ} small angle X-ray scattering at room temperature and at 60 °C. The \textit{in situ} SAXS investigations at 60 °C show the formation of a 2D hexagonal mesostructure after 3 hours reaction time. In contrast to these results the same reaction performed in the laboratory produced a powder that, after drying at room temperature, shows a large number of diffraction peaks, allowing identifying a lamellar structure, possibly in coexistence of a micellar cubic structure (space group \(Pm\textsubscript{3}n\)). Aposteriori removal of the surfactant from the powder synthesised in the laboratory led to the collapse of the lamellar structure.

1. Introduction
Periodic mesoporous organosilica (PMO) materials are a class of materials showing high ordering of pores in the mesoscopic, high specific surface areas up to 1000 m\textsuperscript{2}/g and narrow pore size distributions combined with a uniform distribution of organic functionalities in the pore wall matrix [1-3]. Hence, the PMO materials can be used in a wide field of applications like catalysis, separation and adsorption [4-7]. The synthesis, based on hydrolysis and condensation of an organically modified silica precursor of the formula \((OR)\textsubscript{3}Si-R\textsuperscript{-}Si(OR)\textsubscript{3}\) (R: methyl, ethyl, \(R\textsuperscript{-}\): any organic unit) in presence of an amphiphile structure directing agent (cationic, anionic or non-ionic surfactants or block copolymers) offers the opportunity to tune the resulting material to the designated properties, by choosing the appropriate organic unit \(R\textsuperscript{-}\).

By varying the synthesis parameters like temperature, concentration, reaction time and pH of the solution, different mesostructures can be obtained although the formation process is not yet fully understood. Most common structures of these materials are the lamellar (space group: \(p2\)), the two dimensional (2D) hexagonal (space group: \(p6mm\)) and several bicontinuous cubic (e.g. \(Im\textsubscript{3}m\), \(Fm\textsubscript{3}m\), \(Pn\textsubscript{3}m\), \(Ia\textsubscript{3}d\)) and micellar cubic structures (e.g. \(Pm\textsubscript{3}n\), \(P4\textsubscript{3}32\)). A comparatively very low number of publications about the synthesis of PMOs report the observation of a three dimensional (3D) hexagonal structure (\(P6/mmc\)) [1] and a cubic (\(Fd\textsubscript{3}m\)) [8, 9].

In 2002, an improvement of the structures of PMO materials was introduced by Inagaki et al. [10] with syntheses using cationic surfactants in basic solution. Additionally to the well-ordered 2D hexagonal pore system, an ordering of the organic units in the pore walls became possible. This was shown by powder X-ray diffraction (P-XRD) and transmission electron microscopy (TEM). These measurements showed a repeat distance of 0.768 nm between the aromatic units in the pore wall.
framework and were in good agreement with modelling results. Similar findings were then reported for materials containing highly conjugated units but showing a decrease in the mesopore ordering with increasing size of the organic unit of the organosilica precursor [11-13]. A PMO material showing a similar ordering achieved under acidic conditions was introduced recently [14].

2. Experimental section

2.1. Materials
1,4-bis(triethoxysilyl)benzene (BTEB) and hydrochloric acid (32 %) were purchased from Sigma-Aldrich and used without further purification, hexaethylene glycol mono hexadecylether (C_{16}(EO)_6) was purchased from Nikko Chemicals, Japan.

2.2. Synthesis
For the in situ measurements at a synchrotron a solution of C_{16}(EO)_6 in diluted hydrochloric acid (pH = 1) was prepared in a four neck vessel with a reflux condenser. The vessel was connected to a flow through capillary placed in the X-ray beam by flexible tubing and the solution was pumped through the setup with a speed of 5 mL/min. After measuring the pure surfactant solution, the organosilica precursor BTEB was added and data acquisition was started immediately afterwards. Measurements were carried out at 25 °C (room temperature) and 60 °C. For the synthesis in the laboratory the surfactant C_{16}(EO)_6 was dissolved in diluted hydrochloric acid and BTEB was added. The solution was stirred for 24 h at room temperature and then transferred into a Teflon lined steel autoclave and kept for another 24 h at 100 °C. After cooling the resulting solid was filtered off, washed with water and dried in air. Removal of the surfactant was accomplished by solvent extraction using a mixture of ethanol and hydrochloric acid (32 %) (100:3; v:v) in a Soxhlet apparatus for 12 h at 120 °C with subsequent drying in air.

2.3. Instrumentation
In situ small angle X-ray scattering (SAXS) measurements were performed at the Soft Condensed Matter Beamline A2 at DORIS III synchrotron at DESY. Data acquisition was started after the addition of BTEB to the reaction solution with 60 s exposure time followed by a 60 s break between the measurements. The measurement was interrupted when the capillary was blocked by the occurring solid in the solution. Powder-X-ray diffraction measurements were carried out at Beamline G3, small angle X-ray scattering measurements of the powders at Beamline B1 (both DORIS III at DESY).

3. Results

3.1. In situ experiments
The evolution of the in situ SAXS patterns of a reaction containing C_{16}(EO)_6 as structure directing agent (SDA) and BTEB as organosilica precursor measured at 60 °C is shown in Figure 1a. After about 55 min reaction time a transition structure showing only one reflection starts evolving and remains present for about 30 minutes. Upon decreasing of this single reflection a new diffraction peak evolves and another phase transition takes place, leading to a 2D hexagonal structure after 100 min (Figure 1b). Due to the appearance of only one reflection of the metastable transition state, an indexing to a certain structure is not possible. We assume this structure to be lamellar due to the concept of charge density matching introduced by Monnier et al. [15], which says that the surface curvature of the liquid crystal changes with the changing number of charges on the silica surface due to hydrolysis and condensation reactions. A low number of charges on the silica surface (e.g. at the
beginning of the hydrolysis) forces the liquid crystal into a highly curved surface (e.g. micellar cubic) while a high number of charges on the silica surface leads to a low curved surface (e.g. lamellar). For the described results this let us assume that a lamellar structure is formed at the time many silica species are hydrolysed and with on-going condensation the number of charges decreases and the curvature of the liquid crystal increases until the formation of the final 2D hexagonal structure. The observation of a selected frame after 100 min reaction time illustrates the quality of the scattering pattern. It can be seen, due to the peaks broadness, that the structures were “loosely” formed, however still enabling a structure assignment.

Figure 1 a and b. a) Evolution of the in situ SAXS patterns of a sample containing C_{16}(EO)_6 as SDA and BTEB as organosilica precursor at 60 °C and pH 1; b) SAXS pattern collected after 105 min showing the (100), (110) and (200) reflections of the 2D hexagonal structure.

In order to test the temperature relevance for the formation of the lamellar intermediate structure and its stability, we repeated the reaction at room temperature. Selected frames of the in situ measurement are shown in Figure 2a. Due to the slower kinetics, the on-going chemical reaction could be monitored for more than 180 min without blockage of the capillary. However, as can be seen from Figure 2a no clear structure could be identified. Phase transitions are on-going until the last recorded pattern showing one broad peak and one more intense sharp peak. This last pattern remains unchanged over a long time period. A single pattern recorded after 24 hours reaction time did not show significant changes compared to the last frame of the sequence taken at 180 min (Figure 2b). This clearly illustrates a significant influence of the reaction temperature on the resulting structure.

Figure 2a and b. a) Selected frames of the sample measured in situ at 25 °C and pH 1; b) SAXS pattern of the solution collected after 24 h at 25 °C.
3.2. Powder samples

The investigation of powder samples as synthesised (as), or upon extraction of the surfactant (ex) show different results and leads to the assumption that the structure found at the end of the in situ measurements not necessarily represents the final and stable structure.

Prior to the surfactant extraction, the dry powder shows some rather broad and weak features, Figure 3a, that can tentatively be attributed to a micellar cubic phase with the space group $Pm\bar{3}n$. However, the pattern is too poor for an unquestionable structure determination. The powder diffraction at wide angles reveals a well-defined set of sharp peaks, despite low intensity (Figure 3b) that index a lamellar structure. It is noticeable that we can identify up to 14 orders of diffraction from this structure. As far as we are aware, such large number of diffraction orders has not been reported before. Moreover, the coexistence of two different structures with so different lattice parameters; a large cubic phase seen at small angles and a lamellar at wide angles is remarkable. Similar samples synthesised with C$_{12}$(EO)$_6$ or C$_{18}$(EO)$_6$ did not show diffraction patterns with so many peaks suggesting that such degree of ordering to be surfactant specific. The removal of the surfactant from such samples leads to a collapse of the lamellar structure which was expected (Figure 3b), considering the absence of the surfactant layers between the silica layers. However, the small angle diffraction pattern remains almost the same, showing the poor ordering in the small angle region.

![Figure 3 a and b](image)

**Figure 3 a and b.** a) Small angle powder diffraction measurement of the sample synthesised in the laboratory; b) Small and wide angle diffraction measurements of the dry powder sample (as: as synthesised, ex: extracted).

In Table 1 we list the lamellar peaks identified, noting that some of them are common to both lamellar and cubic phases, suggesting an epitaxial relationship between the structures.

![Table](image)
Table 1. s-values of the experimental diffraction peaks, the respective repeat distances and associated Miller indices.

| s [nm⁻¹] | d [nm]  | hkl   |
|----------|---------|-------|
| 0.144    | 6.94    | 001   |
| 0.284    | 3.52    | 002   |
| -        | -       | 003   |
| 0.560    | 1.79    | 004   |
| 0.697    | 1.43    | 005   |
| 0.835    | 1.19    | 006   |
| 0.972    | 1.03    | 007   |
| 1.110    | 0.90    | 008   |
| 1.248    | 0.80    | 009   |
| 1.385    | 0.72    | 0010  |
| 1.523    | 0.66    | 0011  |
| 1.660    | 0.60    | 0012  |
| 1.798    | 0.56    | 0013  |
| 1.936    | 0.52    | 0014  |

The sequence of the diffraction peaks belonging to the lamellar structure listed in Table 1 is plotted with the s-value versus diffraction order (Figure 4). The fit of this data leads to a perfect linear correlation confirming the structure assignment.

Figure 4. Linear correlation between the s-values and lamellar diffraction order of the detected peaks.
4. Discussion
The results obtained from the dry powder samples first lead to the assumption that the diffraction peaks in the wide angle region originate from an additional ordering in the pore walls as already described by Inagaki et al. [10]. However, two aspects disagree with this assumption. First, the calculated distance of the first wide angle reflection should have been around 0.768 nm, which corresponds to the length of one condensed precursor unit. One would expect a diffraction peak with this repeat distance as well as higher orders of it. This is, as visible from Table 1, not the case. The second aspect is, as can be concluded from Figure 4, the correlation of the diffraction peaks in the small and the wide angle regions excluding the peaks specific for the micellar cubic structure mentioned above. These diffraction peaks all belong to the same lamellar system. That means that all appearing reflections are related to the existing mesostructure and not to an additional ordering of organic units in the pore walls.

The existence of two different structures in the final powder material, a possible micellar cubic and the lamellar, would suggest that we have an epitaxial growth [16] during the chemical reactions leading to the final structures observed.

A diffraction pattern of the reaction solution that was recorded after a stirring time of about 24 hours is shown in Figure 2b. This was the last pattern collected before heating the material in an autoclave to obtain the final powder. As one can see there is coexistence of two different, not very well ordered structures. Comparing this pattern with the patterns of the final powder after heating the reaction mixture to 100 °C for 24 hours, the ordering process is significantly changed by increasing the reaction temperature. Following the reaction at room temperature on time (Figure 2a) shows that after 3 hours no significant changes take place. Thus, the evolution of the structure is clearly temperature dependent. The high temperature during the in situ experiment (Figure 1a + b) and for the synthesis of the powder samples the heating step is necessary if high ordering of the structure is desired. The temperature difference between the in situ measurement and the heating temperature of the powder sample of 40 °C leads to different final structures, the 2D hexagonal for the in situ measurement (60 °C) and the cubic plus the lamellar for the powder sample (100 °C).

5. Conclusion
From our results we conclude that under the given synthesis conditions such as acidic medium with pH 1 and the non-ionic surfactant hexaethylene glycol mono hexadecylether different synthesis temperatures lead to different structures of the final material. The formation of the structure during the powder synthesis in the laboratory passes a really highly ordered liquid crystal leading to a lamellar structure. Such high ordering covering a wide angular range is totally untypical for mesoporous materials and, to the best of our knowledge, has never been observed before. It should also be noticed that the final structure observed in the in situ reaction is different from the ones observed in the respective dry powders, illustrating that the dehydration is also a driving force for the structure formation, in addition to the temperature, as mentioned before. Moreover, the extraction of the surfactant leads to a collapse of the lamellar ordering which is at the same time the evidence for the correct indexing of the structure. The less dominating micellar cubic structure remains at the end.

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