New insights into the initial steps of the formation of SBA-15 materials: an *in situ* small angle neutron scattering investigation†

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Time-resolved *in situ* SANS investigations have provided direct experimental evidence for the three initial steps in the formation of the SBA-15 mesoporous material: an induction period is followed by a shape transformation of the micelles from spherical to cylindrical ones followed by the precipitation of a two-dimensional hexagonal phase.

Mesostructured materials with adjustable porous networks have shown considerable potential in heterogeneous catalysis, separation processes and novel applications in optics and electronics. One of the most promising mesoporous materials is the silica based SBA-15, prepared using non-ionic tri-block copolymers, such as Pluronic P123, as the structure-directing agent.[1] During the synthesis, silica precursors, tetralkyl orthosilicates, are added to acidic solutions of the non-ionic copolymers at 30–100 °C. When the solid structure is formed, the template species can be removed by calcination or solvent extraction. The resulting structure is characterised by a 2D hexagonal array of mesopores with the pore diameter typically between 2 and 30 nm and the wall thickness up to 6 nm, which can be controlled to a certain degree by varying the reaction conditions. The preparation procedures and general features of the self-assembly mechanisms for the formation of these mesostructured materials are now well documented.[2] However, direct experimental information about the key initial stages of the synthesis is lacking, because of the difficulty in performing *in situ* studies.

Recently, several *in situ* studies have been devoted to this question. A number of spectroscopic techniques, including EPR,[3] NMR[4] and IR, have been used as well as transmission electron microscopy (TEM)[4,5] and time-resolved small angle X-ray scattering (SAXS).[6,7] However, the results obtained are not always directly comparable, as the experimental conditions vary from one study to another. In addition, TEM, NMR and EPR characterisation generally involve quenching of the synthesis solutions, which may introduce undesirable modifications of the investigated structures. In this paper, we present the first *in situ* time-resolved small angle neutron scattering (SANS) study of the initial stages of the SBA-15 synthesis.‡ SANS is now established as a powerful means for structural characterisation of some of the most challenging systems. SANS experiments are particularly well suited for *in situ* studies under realistic conditions, and they do not require quenching procedures of the reaction mixtures. Furthermore, unlike TEM imaging and SAXS, for which the contrast between the micelles and the solvent is very weak, so that the signal can be detected only when the silica species are sufficiently linked to the micelles, neutron scattering provides a very high contrast between the organic micelles and the deuterated solvent. Therefore, the very first stages of the cooperative self-assembly can be investigated when the silicate species just begin to interact with the organic micelles.

Figs. 1 and SI-1 show neutron scattering patterns and relevant photographs of the reaction mixture, both of which were taken simultaneously in real time with a temporal resolution of 1 minute.

Prior to the addition of TEOS, the acidic Pluronic solution appeared transparent. After the addition of TEOS, the solution immediately became turbid and became increasingly opaque until a thick white precipitate formed after about 23 minutes of reaction time. The changing turbidity of the mixture and the formation of the precipitate are indicative of a number of physical and chemical processes taking place in the reaction vessel. These include TEOS hydrolysis, condensation reactions involving silicate species, density fluctuations, emulsion and suspension formation, and growth of long cylindrical micelles.

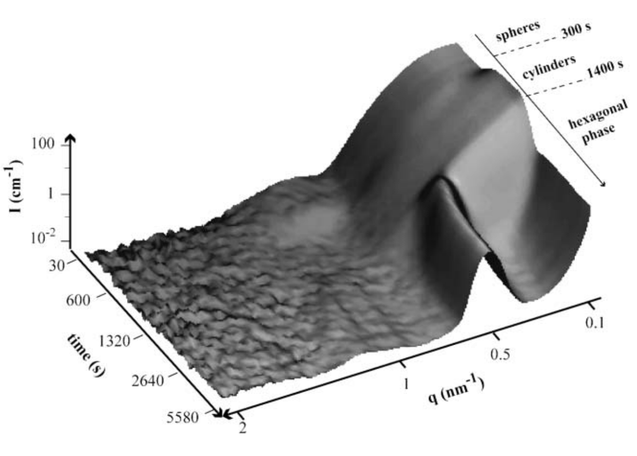

Fig. 1 The real time SANS measurements recorded at a sample–detector distance of 5 meters.

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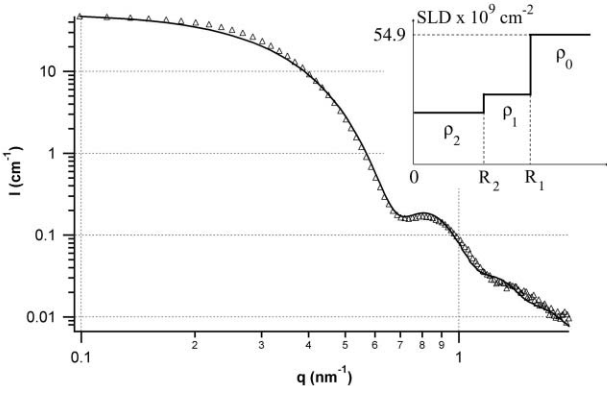

Fig. 2 The acidic P123 solution at 40 °C before TEOS addition is well described by non-interacting spherical micelles with R_2 = 4 nm, R_1 = 7.1 nm and β = 0.26. The polydispersity σ equals 0.05.

The evolution of the scattered neutron intensity, shown in Fig. 1 as a three-dimensional representation of the data obtained over the first 90 minutes of the synthesis, reveals information about the structure of the reaction mixture on a much smaller length scale, 3 to 200 nm ($q = 2\pi/d$), compared to that for visual observation.

The data are spatially averaged for the sampling volume of about 0.1 cm^3 which is within the neutron beam. It should be noted that SANS is sensitive to changes in the size, shape and distance between micelles as well as in their scattering length densities and ordering in the course of the reaction.

Our results indicate that the synthesis proceeds in three steps:

First, during an induction period of about 5 minutes, the scattering curves remain identical. They reach a plateau at low q-values and the oscillation (around q = 0.8 nm^{-1}) is characteristic of relatively monodisperse objects.

Between 5 and 23 minutes, the increase of the intensity at low q is due to the growth of the micelles in solution, the polydispersity in size increases since the oscillation disappears. It should be noted that after *ca.* 18 minutes the 2D scattering pattern shows a slight elongation in the direction perpendicular to the flow. This effect has already been observed in the *in situ* SAXS and demonstrates the presence of anisotropic objects which are aligned in the observation cell by the flow rate.[7]

After 23 minutes, the sudden occurrence of the Bragg peak reveals the condensation of the inorganic species around the micelles within a 2D hexagonal structure.

For SANS data modelling, the micelles are described using core-shell objects of different shapes: spheres, ellipsoids or cylinders. Details of the model are included in the supplementary information.

Before the addition of TEOS, the SANS data are well described by a solution of spherical micelles using a core-shell model without any interaction term. An example of data fitting is presented in Fig. 2. The dimensions found for the micelles compared well with other data on P123 available in the literature.[8] This result shows that the shape of the micelles is still spherical even under strong acidic conditions.

Within the first 5 minutes, the scattering curves are similar to the one measured before addition of TEOS, except at very low q values, where a slight increase in the intensity is detected. During this period, the Pluronic micelles are still the same, and no silica species are linked to them. The increase in the intensity at very low q-regime (q < 0.06 nm^{-1}) can be explained by the formation of a biphasic emulsion of hydrophobic TEOS droplets with a size around 100 nm, before TEOS is completely hydrolysed, which may be responsible for the turbidity of the reaction mixture during the same period.

Between 5 and 23 minutes, the SANS data show a continuous evolution, mainly characterised by the increase in the intensity at low q and a q^{-1} slope in a log–log graph (see Fig. SI-2) that is the signature of 1D objects. This can be described by a transformation of the shape of the micelles from spherical to cylindrical.

For data recorded between 9 and 15 minutes of the reaction time, the scattering is well modelled by cylindrical micelles of aspect ratio increasing from 1.4 to 3.7 (Table 1 and Fig. 3). These are only average dimensions of the hybrid micelles and considerable polydispersity of the objects is probable. Moreover, coexistence of different shapes can be expected as observed by TEM.[5]

When the precipitation is observed after 23 minutes, the (10) diffraction peak of the 2D hexagonal packing is detected in the SANS patterns (Fig. SI-2). The position of this diffraction peak corresponds to a distance between the cylinders of 14.2 nm. According to our previous detailed SAXS[7] investigations, this distance is continuously decreasing with the reaction time. Our current SANS study confirms that the precipitation can be attributed to the packing of cylindrical hybrid micelles inside macroscopic particles of SBA-15. *Ex situ* SAXS analysis of the precipitate and of the calcined mesoporous material has verified the structural characteristics of the obtained SBA-15 solid (see supporting information for more details).

These results confirm the transformation from spherical to elongated micelles before precipitation, which is in complete agreement with a recent TEM study.[5] A three-stage mechanism of

Table 1 Results of SANS data modelling. The parameters are the following: R_1 is the shell external radius (sphere) or section (cylinder), R_2 is the core radius (sphere) or section (cylinder), L is the length of the objects (cylinder) and ε the aspect ratio. β is the density contrast coefficient, σ is the polydispersity coefficient and D are the sample–detector distances used for the data

Time (min)	R_2 (nm)	R_1 (nm)	$R_1 - R_2$ (nm)	L/2 (nm)	Shape	ε = L/2R_1	$\beta = (\rho_1 - \rho_2)/(\rho_0 - \rho_1)$	σ	D (m)
without TEOS	4.0	7.1	2.9		spherical	1	0.26	0.05	5
0 (TEOS addition)	4.1	7.1	3.0		spherical	1	0.25	0.05	5
1.5	4.6	7.2	2.6		spherical	1	0.33	0.075	5
9	3.2	7.3	4.0	10	cylindrical	1.4	0.4	0.075	5 and 17
11	3.1	7.1	4.0	14	cylindrical	2.0	0.4	0.06	5 and 17
13	3	7	4.0	18	cylindrical	2.6	0.4	0.06	5 and 17
15	2.9	6.8	3.9	25	cylindrical	3.7	0.4	0.06	5 and 17

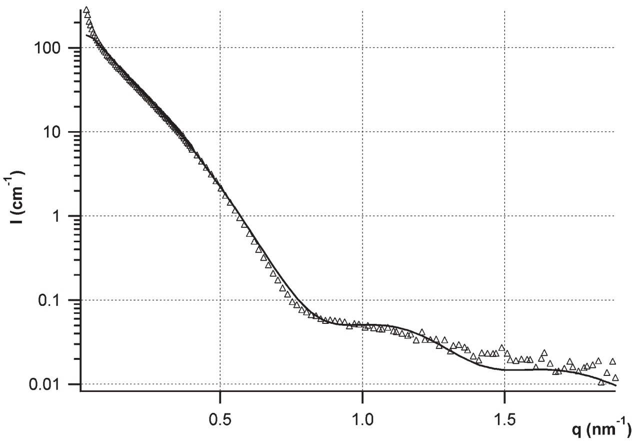

Fig. 3 After 15 minutes, the experimental curve is well described by a solution of non-interacting cylindrical micelles with R_2 = 2.9 nm, R_1 = 6.9 nm, L = 22 nm and β = 0.4. The polydispersity σ equals 0.075.

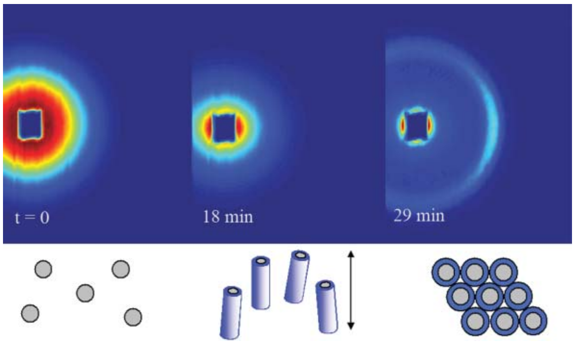

Fig. 4 The three steps of the synthesis: Pluronic spherical micelles are observed within the first 5 minutes. Then, a solution of hybrid elongated micelles is detected. The black arrow is along the flow direction. After 23 minutes, these micelles pack together within the precipitate.

the cooperative self-assembly of the SBA-15 synthesis is illustrated in Fig. 4. Spherical micelles of Pluronic 123 are observed within the first 5 minutes. Following the 5-minute induction period, hybrid organic–inorganic elongated micelles are detected. The transformation of the hybrid micelles takes place until the precipitation occurs, and their size increases with time. The slight anisotropy of the 2D picture reveals their tendency to align along the direction of the flow (black arrow). After ~ 20 minutes, the micelles begin packing together and the precipitation is observed after 23 minutes of the reaction time accompanied by the appearance of the (10) diffraction peak, which proves that the precipitation phenomenon is associated with the self-assembly of hybrid cylindrical micelles into a two-dimensional hexagonal structure of SBA-15.

At this stage of the data analysis, we cannot rule out the coexistence of spherical and elongated micelles. A more refined model including both types of micelles should give a detailed picture of the evolution of hybrid micelles. In addition, light scattering experiments could help in revealing the nature and role of different phases present in the synthesis mixture. Combined with SANS, this could provide a new insight into the interaction between the silica species and the organic micelles. Further *in situ* SANS studies will explore the role of experimental conditions such as the temperature and the nature of the inorganic source to ascertain if alternative pathways are possible for the self-assembly of hybrid micelles in the synthesis of mesoporous materials.

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Notes and references

‡ The experimental procedures were as follows. The molar composition used for the SBA-15 synthesis was: 1 TEOS : 1.68 10^{-2} P123 : 6 HCl : 172 D_2O : 21 H_2O. P123 block copolymer (poly(ethylene glycol)-poly(propylene glycol)-polyethylene glycol, average molecular mass 5800, Aldrich) was dissolved in a mixture of deuterated water and concentrated HCl under stirring. Tetraethyl orthosilicate (TEOS) was the last component added to the synthesis mixture. The use of D_2O instead of H_2O did not affect the kinetics. Vigorous stirring conditions were applied during about 30 s when TEOS was added to the solution. The synthesis was carried out at 40 °C in a 250-ml glass flask equipped with a magnetic stirrer. The reaction mixture was circulated continuously through a 2-mm quartz flow-cell using a peristaltic pump. This experimental set up was similar to the one previously used for *in situ* SAXS experiments.[7]

The *in situ* SANS data were recorded on the small angle instrument D22 at the ILL (Grenoble). The wavelength of the neutrons was set to λ = 0.6 nm ($\Delta\lambda/\lambda$ = 10%), the peak flux of the instrument. In order to get a sufficient q-range, the same kinetic experiment was repeated for two different sample–detector distances: 5 m (q-range 0.1–2 nm^{-1}) and 17 m (q-range 0.03–0.6 nm^{-1}). The detector offset of 400 mm was used to extend the dynamic q-range (q_{max}/q_{min}) to 20.

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