Standard Project

Experimental Report

Proposal title: Nucleation/growth of hybrid silica-surfactant particles with controlled morphology followed by in-situ SAXS		**Proposal number:** SC-3470
Beamline: ID02	**Date(s) of experiment:** from: 01/02/13 to: 05/02/13	**Date of report:** 21/06/2013
Shifts:	**Local contact(s): Pawel Kwasniewski**	*Date of submission:*

Objective & expected results:

The aim of this proposal was to follow upon time the nucleation/growth of hybrid particles for new morphology controlled by the synthesis conditions, like platelet, needle and torus shapes for 2D-hexagonal materials. Focusing on the USAXS region, two types of contributions are expected. The first one will be the signal of the hybrid silica/surfactant micelles. In the case of 2D-hexagonal materials, we expect to get time resolved information about the length and/or flexibility (wormlike micelles model) of hybrid elongated micelles. The second one will come from the shape of the particles and flocs during the nucleation/growth period. It is expected that the dynamics of formation play a significant role in the determination of particle size and possibly of the morphology. The comparison upon time of the hybrid micelles properties and of the particles size and morphology should give important information about the formation mechanism of the particles.

Results and the conclusions of the study:

SAXS experiments have been recorded on January 31 to February 05, 2013 on the ID02 beam-line to follow in real time the kinetics of self-assembly of silicas and organosilicas with ordered porosity. These powders obtained in solution via precipitation, are composed of surfactant micelles periodically organized and surrounded by siliceous species. After removal of the surfactant, one obtain a silica framework functionalized or not by organic groups, and whose porous architecture is controlled by the micellar aggregates. Hybrid particles are formed by the mixing of a non ionic Pluronic ® (P104, P123) and a silica precursor (TMOS : $Si(OMet)_4$, TEOS : $Si(OEt)_4$) in acidic medium.
The ID02 beamline allows to study the kinetics of formation on two different setup :
- SAXS configuration, use of the CCD camera, for the following q-range : $3.5*10^{-3} \leq q \leq 0.27$ Å^{-1}
- USAXS configuration, use of the Bonse-Hart setup, for the following q-range : $1.3*10^{-4} \leq q \leq 10^{-2}$ Å^{-1}
Every kinetic was made twice, in order to have the signal at both configurations.

During this session, a total of 20 kinetics were recorded:
- 12 kinetics were performed at 56°C : Compare the systems P123/TEOS and P104/TMOS and the effect on stirring on the particles formed. (4 kinetics + 2 for reproductibility, at both configurations)
- 8 kinetics upon temperature : with the system P123/TEOS, at 37°C, 40°C (repeated for reproductibility) and 50°C.

Thanks to this study, we were able to follow succesfully the particles formation upon time, see Figure 1, conducting to the formation of particles of various shapes, like platelets (Figure 2), rice-grains, short and long rods, or nano-torus (Figure 3). Due to the relative monodispersity of the formed particles, the form factor of this objects can be extracted from the low q regim.
Stirring of the solution allows further aggregation and thus “bigger” particles, which translates in a thinner (10) pics of the hybrid 2D hexagonal mesophase in the material, but it also disturbs the systems, preventing some shape like torus to form.

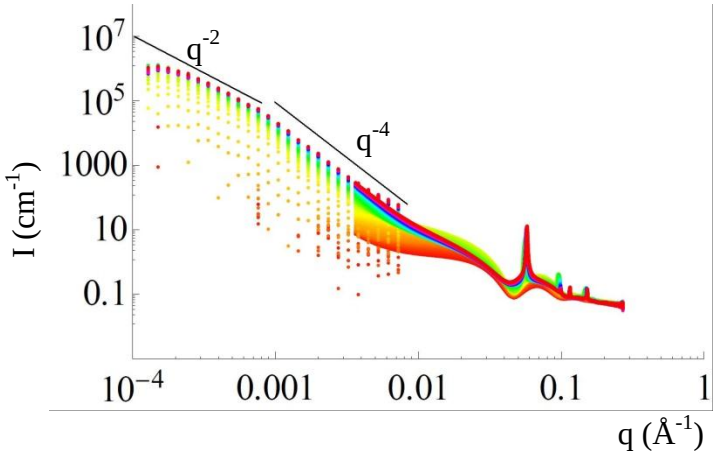

Figure 1 :
P104+TMOS at 56°C with stirring

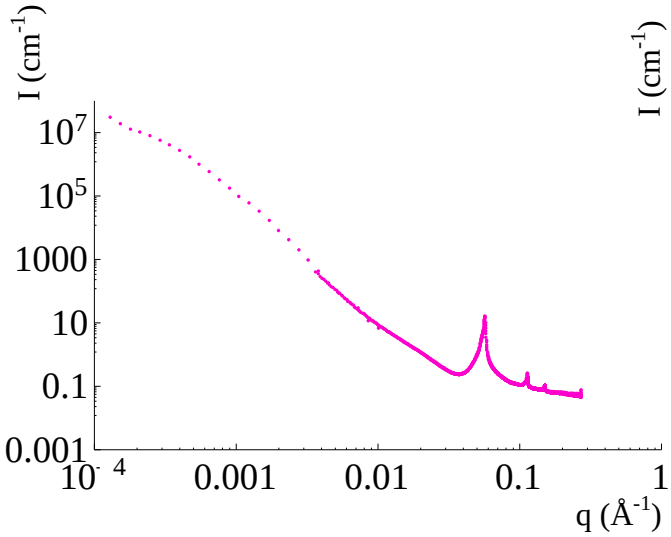

Figure 2 :
P104+TMOS at 56°C without stirring
End of kinetic

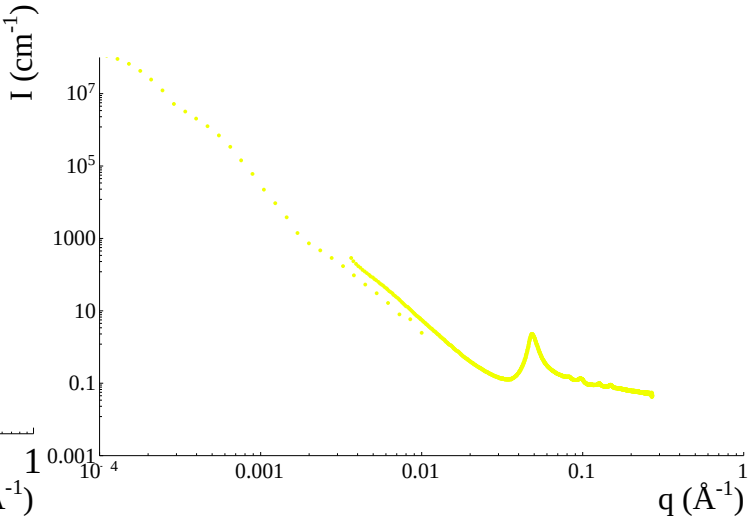

Figure 3 :
P123+TEOS at 56°C without stirring
after 20 min