

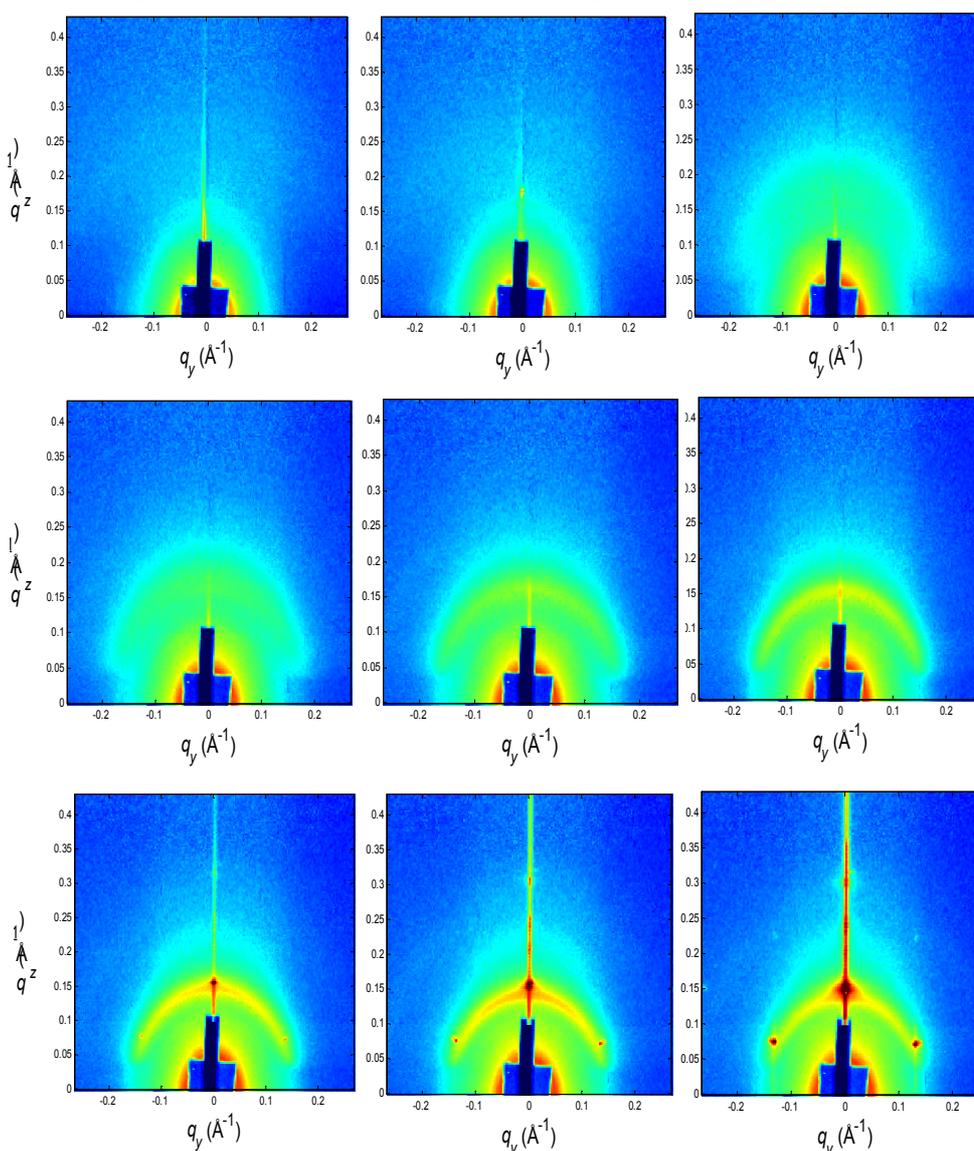
GISAXS Measurements of the Slow Evaporation of Meso MCM41 Phases: From the Liquid Solution to the Dry Film

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Beamline(s): X22B

We have conducted a time-resolved *in situ* GISAXS experiment of the slow evaporation of a liquid film of surfactant molecules dissolved in a mixture of TEOS and ethanol at various pH. The final composition was the liquid film was deposited on a silicon substrate which was itself on the plateau of a weighing balance. In this manner, it was possible to measure the mass of evaporated ethanol and to obtain an estimation of the surfactant concentration in the liquid film. The measurements were performed on the liquid spectrometer of the X22B beam line of the NSLS (National synchrotron Light Source, BNL, USA). The sample was kept horizontal during the course of the measurements and the incident beam was deflected by a Ge monochromator so that it could impinge at a controlled incident angle on the surface of the liquid film. At each incident angle, the height of the sample and of the detector was adjusted accordingly. The incident wavelength was fixed to 1.5826Å. The scattering was monitored either with a point detector mounted on the detector arm of the spectrometer or with a MAR CCD two D detector sitting above the point detector.

The aim of this study was to follow in a reasonable time the evolution of the scattering pattern of a liquid film during the process of self-assembly. The measurements were carried out continuously during the evaporation. As shown in figure 1, the GISAXS patterns beautifully evolve during the course of the measurements. The first image



(top left corner) exhibits the characteristic pattern of a liquid film with a long diffuse streak normal to the surface of the sample. This streak is the diffuse scattering coming from the capillary waves existing at the surface of the liquid. Then the Bragg spot clearly visible in the specular direction shows that the film has undergone a smectic ordering. This is quickly followed by an undulating phase in which the layers of the smectic phase oscillate out of phase. This stage corresponds to the creation of cylindrical micelles which finally order into a hexagonal phase.

For the first time, we show with this experiment how the mechanism of self-assembly proceeds from the liquid phase to the silica templated mesophase. From the first analysis of these results one can state that the self-assembly occurs in five different stages which correspond to the liquid phase, smectic phase, undulating assembly, 2D hexagonal phase and the distorted 2D hexagonal phase.

Figure 1: Illustration of the change in the GISAXS scattering patterns of the liquid film during the slow evaporation of the ethanol solvent.