ESRF	**Experiment title:** **Rheo-SAXS on thermotropic and lyotropic liquid crystals using a vertically deflected X-ray beam**	**Experiment number**: 26-02 714
Beamline: BM26B	**Date of experiment**: from: 20/01/2015 to: 02/02/2015	**Date of report**: 30/03/2015
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Report: *In situ* structure determination of the structural response in complex fluids to shear flow by small angle X-ray scattering has proven to be a successful methodology. Recently we extended the possibilities of this technique by building in Desy, Hamburg, a set-up where a vertically deflected X-ray beam is passed through a plate / plate or couette geometry of a rheometer . One of the main advantages of this set-up, namely the possibility to probe the flow-gradient plane, has thus far not been exploited. More recently, we have successfully installed a next generation mobile version of the vertical detection line at BM26B.

The complete installation of the system lasted effectively two days: one to build the set-up, which was done during the machine day, and one to align the beam and direct it to a small beam stop just in front of the camera close to the ceiling of the hut. The whole procedure really took much longer due to the restart of the synchrotron and big problems with the synchrotron.
As a result of the initial beam instability and alignment delays, the proposed measurement schedule was changed, such that we mainly focused on the Gibbsite system in glycerol in order to complete out data set on the response of nematic Gibbsite dispersions in Large Amplitude Oscillatory Shear flow. On our last beam-time, we focused on strain-controlled measurements, whereas this time most of the experiments were stress-controlled. Moreover, we were able to obtain data on the effect of confinement at selected amplitude-frequency combinations, by using a plate / plate geometry at 0.5 and 1 mm gap distances. Unfortunately, when using the couette geometry we were not able to scan the gap, as proposed, since the size of the beam was only slightly smaller than the gap and we decided to focus on the stress response.
We observed novel symmetry breaking in the response of the angle θ of the director with respect to the gradient direction for selected stress amplitude-frequency combinations in the form of a decaying slope in the offset of the response of angle θ, as well as in the offset of the response of the system, see fig. 2, blue diamonds and squares respectively. In addition, the black squares in fig. 2 show a power law dependence of the response amplitude with respect to increasing frequency.
Furthermore, to avoid spending beam-time to realign the setup for WAXS, we conducted few explorative experiments with industrial T4T (“hard”) / pTHF (“soft”) multiblock copolymers in which the crystallization of the hard units leads to a dramatic increase of the mechanical properties through the formation of three-dimensional network. The latter may be described at different length scales from the T4T segments (≈1 nm) to large agglomerates (≈1 μm) through the formation of 2D crystallite (≈10 nm) separated by a characteristic distance dependent of the chain composition. Among other results, SAXS experiments during a temperature ramp allowed to evidence the formation of those intermediate objects (building blocks of the network) highlighting the presence of an important structure factor in the signal (peak + correlation hole). This result

greatly helps for the interpretation of previous USAXS-SAXS measurements performed on ID02 with the same materials.

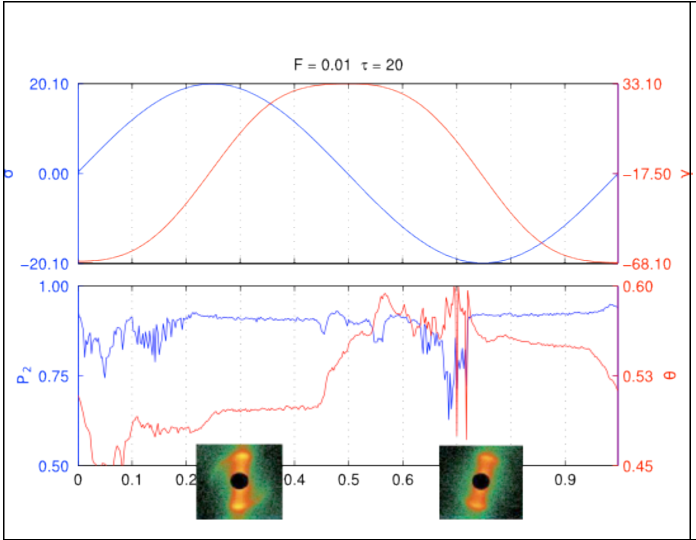

Figure 1: The response of Gibbsite platelets in the nematic phase during Large Oscillatory Shear Flow. And the response of the angle of the director (θ) and the orientational ordering given by the average second Legendre polynomial $\langle P_2 \rangle$ at applied stress of 20 Pa and frequency of 0.01 Hz.

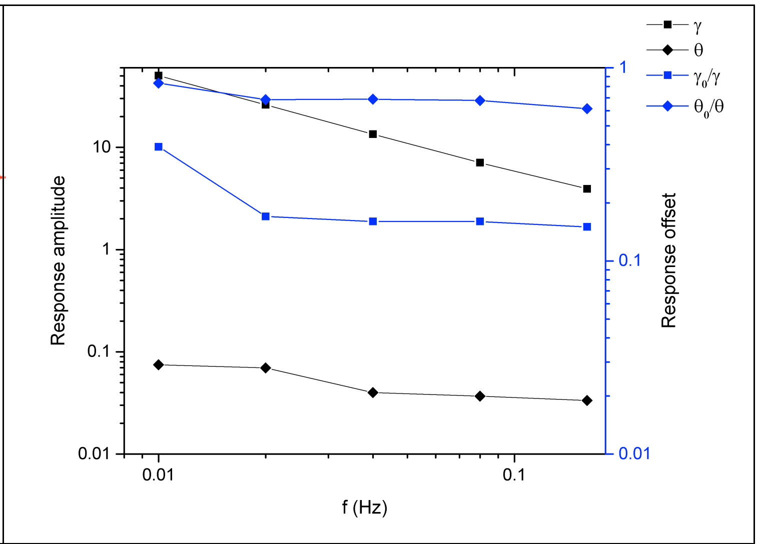

Figure 2: The amplitude of the response and the offset in the response of the angle of the director (θ) at applied stress of 20 Pa and a range of frequencies.

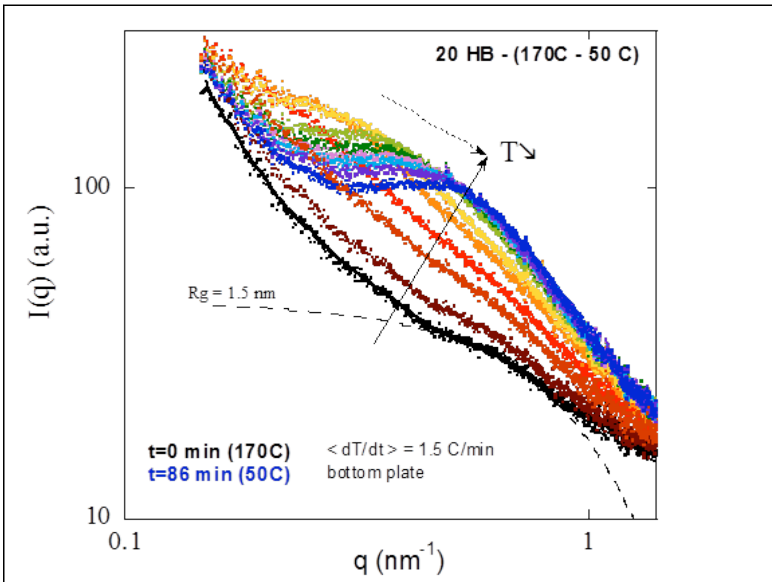

Figure 3: Crystallization of the T4T units in industrial multi-block copolymers. The size of the elementary segment can be extracted from the SAXS pattern at high temperature (Guinier) while a clear structure factor appears at low temperature pointing the distance between crystallites responsible for the enhancement of mechanical properties. The low-q upturn is the signature of much bigger agglomerates made of these intermediate sized objects.

References

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