ESRF	**Experiment title:** Light-induced Changes of Viscoelastic Properties in Photo-Rheological Fluids investigated by XPCS	**Experiment number**: SC3880
Beamline: ID10B	**Date of experiment**: from: 11/06/2014 to: 17/06/2014	**Date of report**: 02/10/2014
Shifts: 18	**Local contact(s)**: F. Zontone	*Received at ESRF:*

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Report:

Summary:
We studied the change of viscoelastic properties in photo-rheological fluids by X-ray Photon Correlation Spectroscopy (XPCS). Photo-rheological fluids alter their rheological properties upon light irradiation through a change in molecular structure. For instance it is possible to increase or decrease the shear viscosity. We studied a mixture of cetyl trimethylammonium bromide (CTAB) and trans-ortho-methoxycinnamic acid (OMCA) which forms wormlike micelles [1] and shows a strong response to UV irradiation (< 400 nm) [2]. Changing the isomerization from trans-OMCA to cis-OMCA by UV illumination weakens the interaction with CTAB since the cis-isomer of OMCA is less favourable for binding to the micellar interface. Additionally, cis-OMCA is less hydrophobic which further lowers the connectivity. First analysis results reveal fast dynamics in the range of tens of milliseconds for the high viscouos cases.

Set-up:
The photo-induced change of viscoelastic properties was probed by XPCS in SAXS geometry. Samples of different OMCA-CTAB ratios were prepared and filled in quartz capillaries. Here, the concentration of the ingredients and the thickness of the capillaries were chosen in order to ensure a homogeneous excitation of the whole sample volume. In order to increase the scattering signal, silica particles with a diameter of about 490 nm (Duke standard) were added.
As optical excitation source, a Hg-based UV lamp from Lot QuantumDesign with a power of about 100 W was used. The spectral range of the lamp covers the two absorption bands of the sample at 270 nm and 312 nm, which both can contribute to the photo-isomerization. The diameter of the light cone was as big as the length of the capillaries to transform the entire sample.
The experiment was performed using the standard SAXS chamber of the beamline ID10 without any special requirement on the temperature stability. The coherent and monochromatic X-rays with an energy of 8 keV were focussed down to 20 µm on the samples. The SAXS signal was collected by a Medipix detector.
In order to get access to the dynamical constants expected down to the millisecond regime, the fast shutter of the beamline was used with an opening time of 0.003 sec. We performed for each irradiation time three measurements on different sample positions with 10.000 images per measurement.

Results:

The investigated SAXS images show a strong contribution of the added silica particals (see Figure 1). An investigation of the radial-integrated pattern based on the Schultz distribution resulted in an averaged particle radius of 250 nm, which fits to the expected size of the spheres.

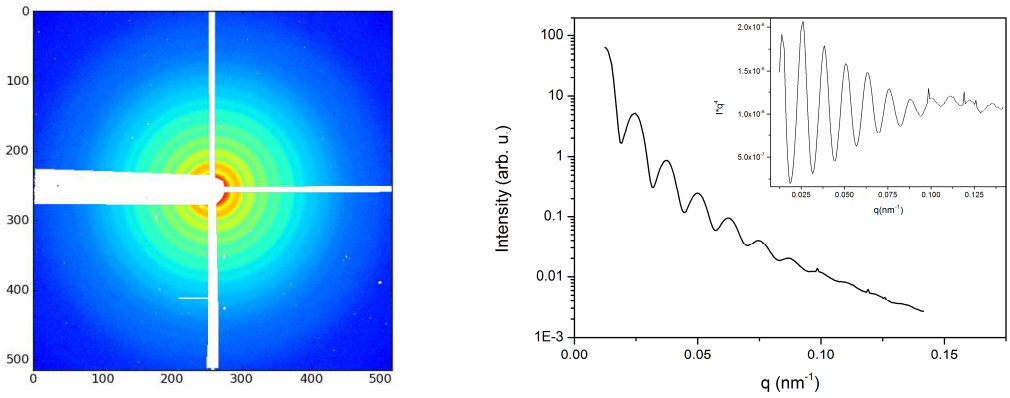

Figure 1: Left: SAXS image of the CTAB-OMCA mixture with silica particles. Right: Radial integration of the SAXS image. The position of the maxima of the curve point to the expected particle sizes of about 500 nm using the formular of the Schultz distribution.

The correlation functions show two main decays (see Figure 2) and were fitted by a double Kohlrausch-Williams-Watts exponential form:

$$g^{(2)}(\tau)=b_1\cdot\exp(-2(\tau\cdot\Gamma_1)^{\gamma_1})+ b_2\cdot\exp(-2(\tau\cdot\Gamma_2)^{\gamma_2})+a$$

where b_1 and b_2 are optical contrasts, Γ_1 and Γ_2 the relaxation rates, γ_1 and γ_2 the individual KKW exponents, and a is the baseline.

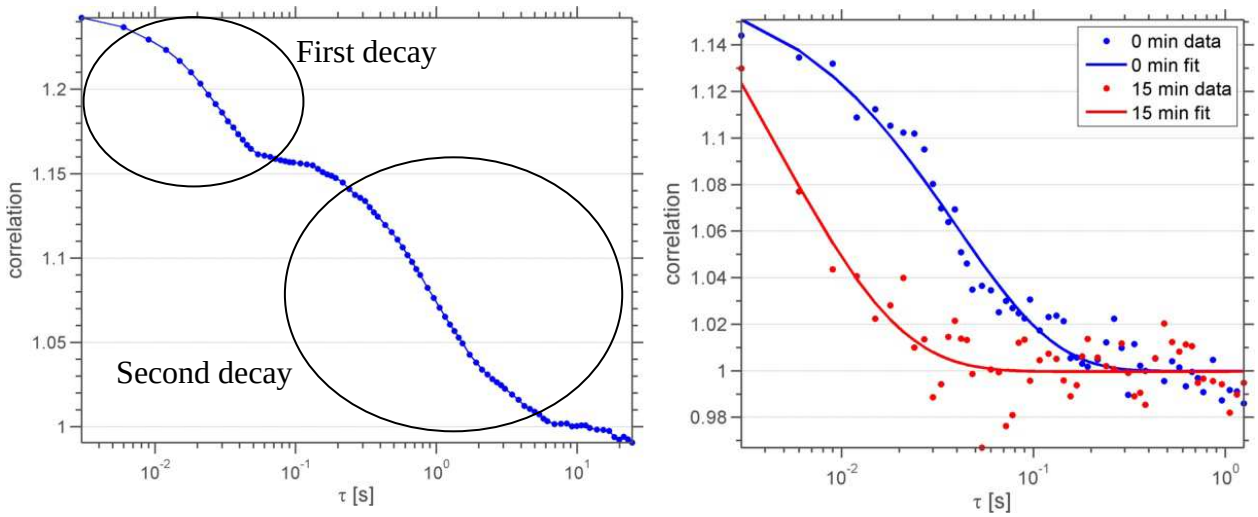

Figure 2: Left: Correlation function of OMCA-CTAB mixture after 25 min irradiation at q=0.025nm^{-1}. The two different time constants are clearly visible. Right: Comparison of the fast decay for 0 min (black curve) and 15 min (red curve) UV-irradiation duration. An influence of the UV excitation on the fast dynamics of the OMCA-CTAB mixture is evident.

Upon UV-irradiation, the dynamics of the system changes clearly and a systematic investigation of the influence on the different CTAB-OMCA concentrations is ongoing.

References:

[1] M. E. Cates and S. J. Candau, J. Phys.: Condens. Matter **2**, 6869 (1990)

[2]A. M. Ketner *et al*., J. Am. Chem. Soc. **129**, 1553 (2006)