



	Experiment title: Gelation of poly (ethylene oxide) induced by transition metal ions	Experiment number: 26-02-766
Beam line: BM26B	Date of experiment: from: 30/01/2016 to: 02/02/2016	Date of report: 01/04/2016
Shifts: 9	Local contact(s): Daniel Hermida Merino	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): J. Hendricks ^{1*} , K. Verbeke ^{1*} , P. Lettinga ^{2*} , C. Clasen ^{1*} ¹ Department of chemical engineering, KU Leuven, Belgium ² Department of physics and astronomy, KU Leuven, Belgium		

Report: Rheo-optical techniques are well described in literature to study flow induced structure, using in-situ light scattering, neutron scattering and X-ray scattering. Regarding X-ray scattering, rheo SAXS is performed [1,2], neglecting the possibilities WAXS can offer. The main advantage of rheo-WAXS compared to rheo-SAXS lies in the robustness of these measurements. However, the use of rheo-WAXS to investigate structural changes under flow is still unexplored. The performed WAXS measurements had two aims. The first one was the optimization of the utilized setup [3] comprising a new for the highly mobile setup modified rheometer and a new oven (TU Eindhoven). All modifications of the current setup can be considered to have a positive effect on the measurement performance. 2 maintenance days were used to set up the instrument followed by 1 day of beam time to align the beam. This beam time was successful because of the significant insights we obtained on the flow behaviour of poly(ethylene oxide) – transition metal salt melts and emulsion crystallized hydrogenated castor oil (HCO) and the insights we gained on the experimental setup itself.

We could probe a significant amount of samples. Unfortunately, the proposed investigations of supramolecular polymers in solution utilizing a tailored Couette cell were not successful due to low torque of the rheometer and low scattered intensity of the samples. In addition we measured polymer melts of 10 kg/mol poly(ethylene oxide) mixed with nickel chloride (Figure 1). At room temperature two sharp peaks at large q-values were detected corresponding to the crystalline structure of PEO at room temperature. When heating the sample, the peaks disappeared and changed over to an amorphous halo. At 90°C the scattering pattern changed significantly: two additional peaks appeared at low scattering angles and one broad peak around $q=25$ 1/um indicating a structure build-up. Furthermore the PEO halo seems to decrease. Applying low shear rates results in an increase of the PEO halo and a shift of the dominant peak around $q=10$ 1/um towards larger q values which might be a result of shear induced crystallization or pronounced network formation due to increased mobility of the polymers. After stopping the flow, the original structure reforms. Applying larger shear rates (3 1/s and 10 1/s) does not result in a changed scattering pattern as with lower shear rates (0.5 1/s and 1 1/s) which might be due to occurring wall slip or breakage of bonds due to larger shear stress. Nevertheless, performed oscillatory shear measurements after each shear rate indicate a dropping complex modulus with increasing shear rate (Figure 1, inset).

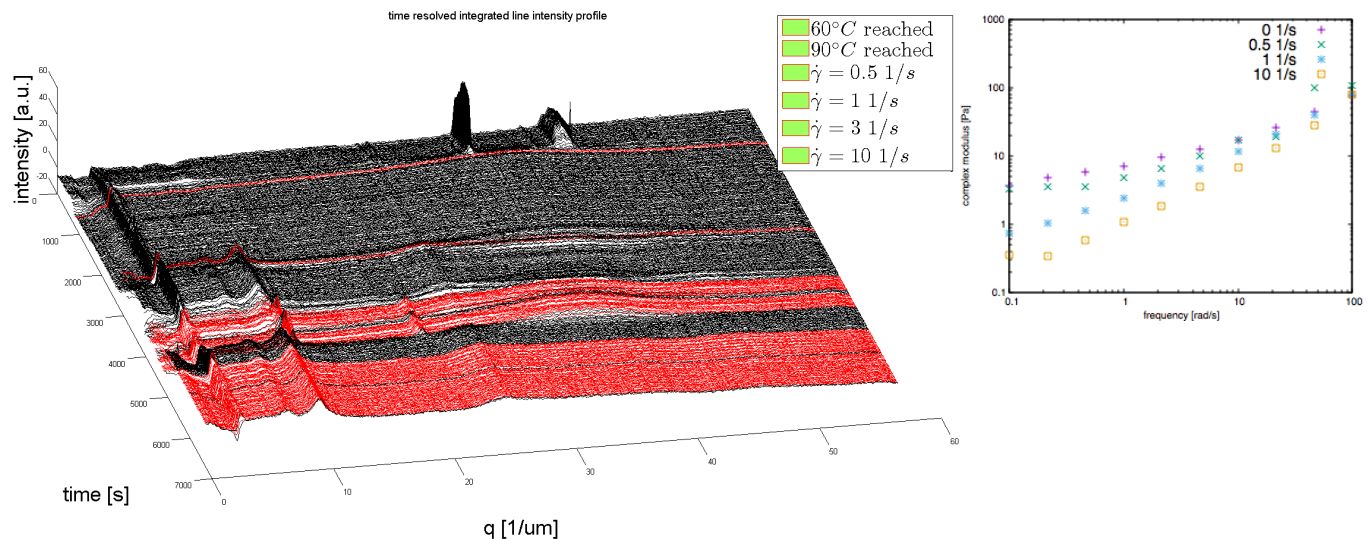


Figure 1: Time resolved integrated line intensity profile of a poly(ethylene)oxide melt mixed with nickel chloride. The temperature was increased from room temperature ($t=0$) to 60°C (first red line) to 90°C (second red line). At 90°C the sample was subjected to steady shear with shear rates of 0.5 1/s , 1 1/s , 3 1/s and 10 1/s . After each steady shear measurement small amplitude oscillatory shear measurements (inset) were performed.

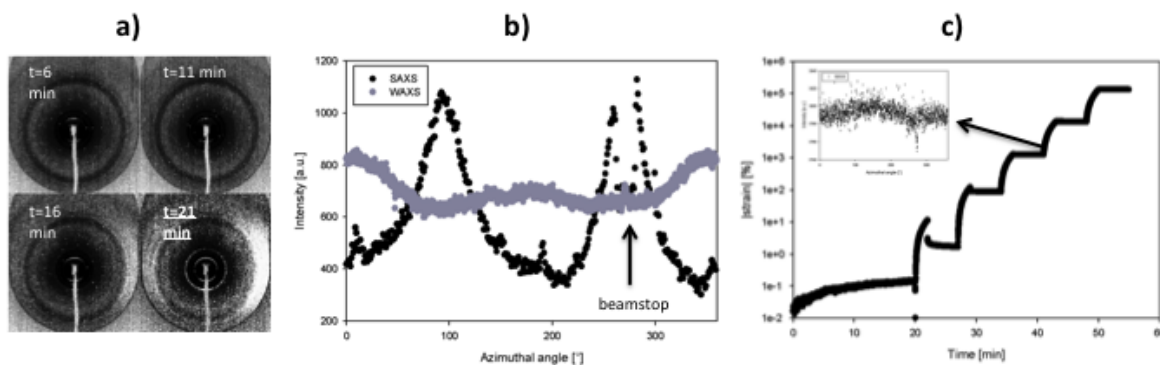


Figure 2 a) Anisotropy in the vorticity direction is observed in the scattering pattern for the emulsion crystallization of HCO at a constant cooling rate of $3.3^{\circ}\text{C}/\text{min}$. and 5 1/s shear rate b) scattering pattern versus azimuthal angle in bright WAXS and SAXS band, at $t=21\text{ min}$. c) Subsequent creep and stress relaxation measurements ($0\text{ Pa}; 0.001\text{ 1/s}; 0\text{ Pa}; 0.01\text{ 1/s}; 0\text{ Pa}; 0.1\text{ 1/s}; 0\text{ Pa}; 1\text{ 1/s}; 0\text{ Pa}; 10\text{ 1/s}; 0\text{ Pa}$) on a diluted HCO crystal suspension, inset showing an azimuthal WAXS pattern, with a slight anisotropy observed in the velocity gradient direction.

Investigation of an emulsion crystallization of hydrogenated castor oil (HCO) under flow [4] leads to more insights into the capabilities of the Rheo-WAXS/SAXS setup. During the cooling process crossed anisotropic patterns at small and large q -values are observed, as indicated in Figure 2 a) and b). The discovery of anisotropy at wide angles is a promising result, since simultaneous gathering of information about, both the crystal polymorphs and their orientation due to flow, can be obtained. Measurements of a dilute suspension of HCO crystals give a good summary of the rheometrical capabilities of the rheometer (Figure 2 c). However, in stress relaxation and creep experiments at sufficient torque the results already provide reliable data. As shown in the inset, only a slight anisotropy was observed. The origin of this behavior is unclear, but is assumed to be both due to the sample, and the relatively low intensity beam in the current setup. In addition to that, the velocity gradient direction was probed using a plate-plate geometry, where anisotropy is expected to be the most clear-cut in the vorticity direction [5].

- [1] Burghardt et al. Phys. Rev. E, 2012, 85
- [2] Dykes et al., Polymer 2010, 51
- [3] M.P. Lettinga, O. Korculanin, et al., report 26-02 714, (2015).
- [2] De Meirleir et al., Cryst. Growth Des. 2015, 15 , 635–641
- [3] Pfeleiderer et al, Rev. Sci. Instrum. 2014,85