ESRF	**Experiment title:** **Phase separation and self-assembly of block copolymers in a solvent with tunable selectivity**	**Experiment number**: SC-4870
Beamline: ID02	**Date of experiment**: from: 08/09/2018 to: 11/09/2018	**Date of report**: February 28. 2019
Shifts: 9	**Local contact(s)**: Micael Sztucki	*Received at ESRF:*

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Report:

Proposal Summary

Biocompatible poly-ethylene(oxide)-*block*-poly-ε-caprolactone (PEO-PCL) block copolymers exhibit a temperature controlled phase separation in ethanol, while they self-assemble in water. Preliminary studies suggested that a remarkably complex self-assembly behavior emerges in water-ethanol mixtures, where different kinds of mesoscale and nanoscale assemblies can be obtained varying the solvent composition and temperature. Using high resolution Small Angle X-ray Scattering (SAXS) we aimed at understanding the structure of these aggregates and how their formation is affected by the solvent mixture composition and temperature.

Beamline Setup

The experiments were performed at the ID02 beamline**.** Most of the experiments were performed using a Linkham stage, which allows control over a wide temperature range. For some room temperature experiments a flow cell was used, which provide a better background subtraction. Three different detector distances were used, 3,10 and 31 meters.

Preliminary resylts

The allocated beam time was sufficient to analize a set of 4 copolymer and 2 homopolymer solutions in 6 different water/ ethanol mixtures.
Each sample was analyzed in a temperature range between 60 and -20 degrees with various cooling rates (between 0.5 and 50 °C/min). From the preliminary results it appears that the collected scattering data have sufficient quality and contrast to probe the thermally induced transitions in the different copolymer dispersions (See Fig. 1 for an example).
It appears that the cooling rate has an important effect on the temperature at which varous transitions take place. Performing SAXS and waxs analysis allowd to study the copolymers aggregation and crystallization at the same time. The data obtained in pure ethanol will provide a better understanding of the crystallization of block copolymers from dilute solutions. From a preliminary analysis it seems that the competition between phase-separation, self-assembly and crystallization can be controlled with the solvent mixture composition and temperature.

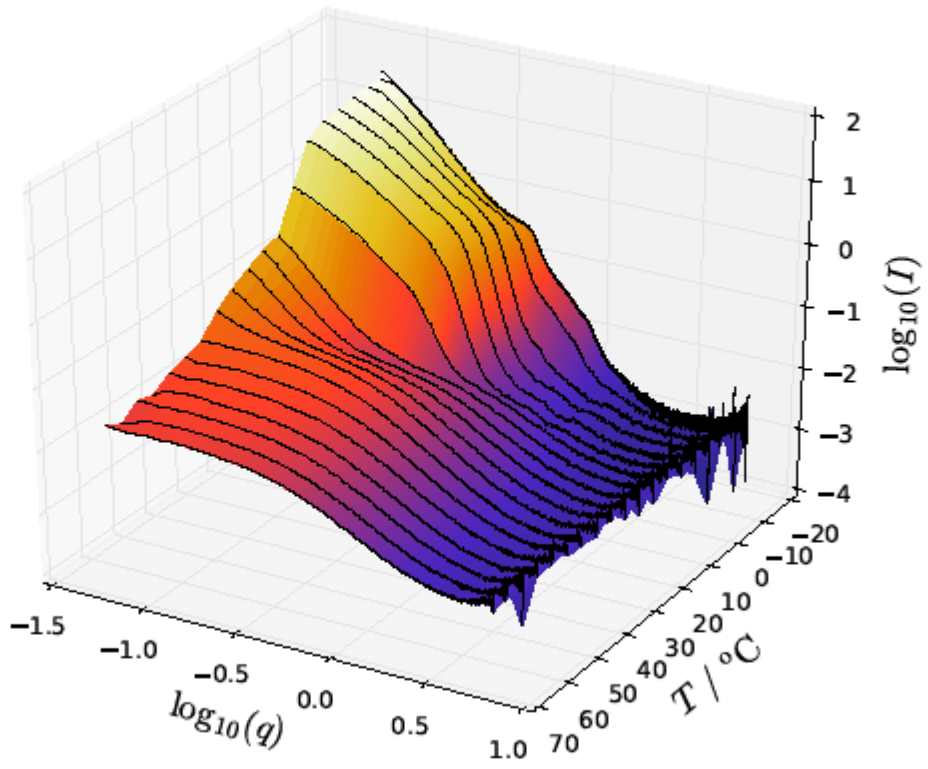

Fig 1. Background-subtracted scattering data for one of the copolymers in pure ethanol as a function of temperature.