ESRF	**Experiment title:** Combining time-resolved SAXS and WAXD with flash DSC for polymer crystallization studies	**Experiment number**: SC-4263
Beamline: ID13	**Date of experiment**: from: 21 April 2016 to: 23 April 2016	**Date of report**:
Shifts: 6	**Local contact(s)**: Dr. Martin Rosenthal	*Received at ESRF:*

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Report:

The aim was to collect SAXS/WAXD based structural information during the isothermal crystallization and subsequent melting of a series of polyamides (PA) (and syndiotactic polystyrene) at sampling rates compatible with the scanning rates typical of fast scanning calorimeters. To do so, an existed Mettler-Toledo Flash DSC 1 was modified in such a way that the chip can be controlled outstide the FSC housing and presented in front of an X-ray beam. This was successfully tested in (four) different sessions at the DUBBLE (BM26B) beamline. However during these sessions, we were unable to collect SAXS signals. Therefore the work done at ID13 was a continuation of experiments performed at the DUBBLE beamline, with the great advantage that SAXS signals could be captured.

The assigned beam time was used as efficient as possible, starting with the allignment of the sample sensor with the X-ray beam. For this beam time a new, much thinner sample box needed to be constructed. Two types of experiments were performed on PA11 and PA12 samples using this sample box. Due to the limited time (6 shifts instead of the requested 9 shifts) we were not able to perform experiments on syndiotactic polystyrene as well.

The first experiments consisted of isothermal crystallization experiments in which one SAXS/WAXD pattern was collected at the end of the isothermal segment on T_c and one after cooling to room temperature. Time-resolved experiments were not possible, since this would lead to severe radiation damage. From these experiments, the SAXS (local) crystallinity, crystallite sizes with crystalline and amorphous layer thicknesses

and contrast values were calculated. These results are used to propose models for the solid phase formed during the isothermal crystallization. Depending on the T_c the models differ in fraction of mesomorphic and crystalline phase present.

During the second type of experiments, the heating runs after isothermal crystallization were followed in a temperature-resolved mode. A heating rate of 500 °Cs^{-1} was chosen and combined with an acquisition time of 4ms, resulted in a temperature interval of 2 °C of which an example is shown in the figure below (PA11). The arrow gives the heating direction with the blue pattern at 25 °C and the red at 220 °C. In the WAXD region, the α-to-δ phase transition (Brill temperature) and the solid-to-liquid transition is observed. From the SAXS signals, the crystallinity, crystallite sizes with crystalline and amorphous layer thicknesses and contrast values were calculated. This experiment gives insight in the recrystallization/reorganization and melting behavior of the solid phase formed during the prior isothermal crystallization segment.

The results are processed and published in the PhD thesis of D. Baeten. A paper is written and ready to be submitted.