ESRF	**Experiment title:** The bimodal temperature dependent crystallization rate of selected polyesters	**Experiment number**: 26-02-762
Beamline: BM26B	**Date of experiment**: from: 30 October 2015 to: 3 November 2015	**Date of report**:
Shifts: 9	**Local contact(s)**: Dr. Daniel Hermida Merino	*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 semi-crystalline polymers at sampling rates compatible with the scanning rates typical of fast scanning calorimeters to elucidate the origin of their temperature dependent bimodal crystallization kinetics. A previous beam time, which was scheduled after the proposal deadline, learned us that collecting SAXS signals during a FSC protocol was not possible with the setup available at the DUBBLE beamline. Therefore some adaptations to the original project were made.

Instead of focussing solely on the isothermal crystallization of a selection of polyesters, we extended the research goals to examining the isothermal crystallization of polyamides (PA11 and PA12) aswell. The reason for this is the failed previous beamtime (july 2015, n° 26-02-733), in which the goal was to study the bimodal crystallization rate dependence on temperature for polyamides based on both SAXS and WAXD signals. However problems with the SAXS setup, described in the previous experimental report, prevented us to perform *in-situ* FSC/WAXD experiments at that time. Therefore it was necessary to move this study to our next beam time. In this beam time the goal is to investigate the peculiar crystallization rate behavior of a selection of semi-crystalline polymers, thus the research questions concerning PA crystallization fitted perfectly in the proposed project. PA11 and PA12 were subjected to isothermal crystallization protocols using a fast scanning chip calorimeter and *in-situ* WAXD collection was asured using an in-house developed sample holder, which is accessible for X-rays [1-2]. At this moment, the data processing of PA11 is completed and the results are published in the PhD thesis of D. Baeten. In addition a paper is written and ready to be submitted.

Interpretation of the PA12 data is more difficult due to complex polymorphism in the sample and thus the data processing is still ongoing.

In the second part of the beam time we examined the crystallization behavior of a polyester. Poly(butylene terephthalate) (PBT) is chosen out of the three proposed polyesters (PBT, polylactic acid (PLA) and poly(ε-caprolactone (PCL)). PLA has the drawback of slow crystallization kinetics, which would took too long for the remaining beam time, leaving no time for studying multiple T_c's. For PCL the crystallization kinetics are situated at very low temperatures and from the previous beam time (july 2015, n° 26-02-733) we learned that reaching these temperatures was not possible with the available cooling unit. Therefore both non-isothermal as isothermal experiments were performed on PBT. During the non-isothermal experiments the crystallization and melting at different rates (between 20 and 200 $°Cs^{-1}$) was followed by temperature-resolved WAXD patterns (acquisition times of 47 or 17 ms). Depending on the scanning rate used one or two FSC peaks are observed, probably referring to crystal and/or mesomorphic phase formation. The isothermal crystallization experiments are similar to the once performed on PA11 and PA12 and show two crystallization rate peaks. The WAXD data from the non-isothermal and isothermal experiments are still waiting to be processed, which are scheduled after the PA12 processing is completed. At the end the PBT, PA11 and PA12 results will be compared with each other hopefulling elucidating their peculiar crystallization behavior.

[1] D. Baeten et al., *Macromol. Rapid Commun.* **2015**, *36(12)*, 1184
[2] D. Baeten et al., In C. Schick & V. B. F. Mathot (Eds.) *Fast scanning calorimetry* (first edition, pp.327-359), Switzerland, Springer International Publishing