ESRF	**Experiment title:** Real time WAXS investigation of structuring in polyvinylidene fluoride at high supercooling using fast scanning chip calorimetry	**Experiment number**: 26-02-786
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Shifts: 9	**Local contact(s)**: Dr. Daniel Hermida Merino	*Received at ESRF:*

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Report:

Polyvinylidene fluoride (PVDF) is known to exist in several crystal modifications (α, β, γ, δ) of which the β- and δ-phases are the most interesting ones due to their ferroelectric, pyroelectric and piezoelectric properties. One way to obtain the β phase is by crystallization from the melt using very high cooling rates (above 2000 $°Cs^{-1}$) or by isothermal crystallization at high supercooling with the maximum crystallization rate around 20 °C. Another way to ease the formation of β-phase is by introducing artificial conformational defects, such as TrFE (trifluoroethylene) and CFE (chlorofluoroethylene), resulting in P(VDF-TrFE) and P(VDF-TrFE-CFE) copolymers.

PVDF and its copolymers are subjected to (non-)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]. This sample holder was connected to a liquid nitrogen dewar in order to reach a low surrounding temperature (0 °C) and allow fast linear cooling rates. The non-isothermal experiments consisted of cooling the samples at different rates (between 30-1300 $°Cs^{-1}$) and one WAXD pattern was collected at 0 °C. The cooling rates were too fast to follow the crystallization with WAXD in a temperature-resolved way. The samples were also isothermally crystallized at temperatures between 60 and 140 °C and the solid phase formation was followed with time-resolved WAXD.

Preliminary results are reported in a master thesis (by Eline Baes and supervised by D. Baeten and prof. B. Goderis), but require some additional experiments and data processing before publication in a scientific journal is possible. Some of the findings are reported below:

- β-phase not (or barely) observed in isothermally crystallized PVDF. Lower T_c's are needed which could not be reached with our setup
- β-phase observed in isothermally crystallized 70/30 P(VDF-TrFE)
- β-phase observed in isothermally crystallized 80/20 P(VDF-TrFE at temperatures in the high range of the crystallization rate vs temperature plot. (α-phase observed at lower T_c's)
- β-phase not observed after cooling (rates up to 1300 $°Cs^{-1}$) PVDF to room temperature
- β-phase observed after cooling 70/30 P(VDF-TrFE) to room temperature at all rates
- A mixture of β- and α-phase observed after cooling 80/20 P(VDF-TrFE) to room temperature

[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