ESRF	**Experiment title:** Studies of the thermal behavior of "semi-thin" films of PVDF on a local scale	**Experiment number**: SC-3099
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Report:

Poly(vinylidene fluoride), PVDF, has been extensively investigated over the last forty years because of its excellent mechanical behavior, high chemical resistance, good thermal stability as well as high pyro- and piezo-electric coefficients [1,2]. Many of these properties critically depend on the polymer processing conditions, as they determine the resulting crystal phase composition. Depending on the crystallization conditions, PVDF exhibits an interesting polymorphic behavior [3-5]. Thus, during crystallization from the melt at 150-170°C PVDF forms two crystalline modifications: α (with the lattice parameters **a**=4.96Å, **b**=9.64Å and **c**=4.62Å, chain conformation TG^+TG^-) [3,4] and γ (**a**=4.97Å, **b**=9.66Å, **c**=9.18Å, chain conformation $T_3G^+T_3G^-$) [5,6]. The structural details of these phases have been described in the literature. In thin melt-crystallized films two types of spherulites can be identified by polarized optical microscopy (POM): large spherulites of the α-form and smaller spherulites of the γ-form [7]. In POM micrographs, the α-spherulites show high birefringence and regular concentric banding (Fig1., A, point I), whereas the birefringence is lower and banding does not appear for the γ-spherulites due to their morphological irregularity (Fig.1, A, point II). However, the γ-modification is considered to be more thermodynamically stable and shows higher melting temperature – 182°C compared to 174°C for the α-phase. As one can see from POM image at 180°C (cf. Fig.1), only spherulites of the γ-phase are remaining at this temperature. Micro-focus X-ray diffraction at variable temperature allows to address the structural changes occurring in regions with different morphology during thermal treatment.

In the present work, we study the thermal behavior of "semi-thin" films of PVDF (20μm) crystallized from the melt at 162.5°C. The measurements were performed on free-standing films using a CCD camera. The sample-to-detector distance was adjusted to record both SAXS and WAXS signals. For the measurements at elevated temperatures a Linkam heating stage was employed. The energy of X-ray photons used in the experiment was 10keV.

At room temperature, the X-ray pattern measured on the α-spherulite (Fig.1, B, Point I) reveal 020 (4.83Å) and 110 (4.42Å) reflections, which are identical for both crystalline modifications. In addition, two reflexes are detected which are specific to the α-phase: 100_α at 4.98Å and 120_α at 3.48Å. The pattern does not contain any γ-peaks. The maximum of the azimuthal intensity distribution of the 020_α peak points along the radial direction of the banded spherulite. Therefore the growth direction of the α-spherulite is parallel to the **b**-axis of the α-unit cell. The SAXS signal was found to be perpendicular to the radial direction. The

diffractogram measured on a γ-spherulite (Fig.1, E, point II) besides 020 and 110 peaks exhibits the 021_γ peak at 3.31Å typical of the γ-phase. Similar to the α-spherulite, the 020 reflex is parallel to the radial direction.

Despite the non-banded morphology of the γ-spherulite the SAXS signal is clearly pronounced which indicates that at least part of the lamellae are oriented edge-on in respect to the film surface.At 180°C the film morphology is changed drastically. X-ray pattern measured at point I shows the absence of any crystalline reflexes and SAXS signal (Fig. 1, C). In contrast, at point II (γ-spherulite) the crystalline peaks of the γ-modification are still present (Fig. 1, F). Moreover, the orientation and angular distribution of these reflections stay unchanged as compared to room temperature (Fig. 1, B). Thus, one can follow the local melting process of α-spherulites, which is in good agreement with POM data (Fig. 1, D). At the same moment the structure of the γ-spherulite does not display any significant structural changes at 180°C.

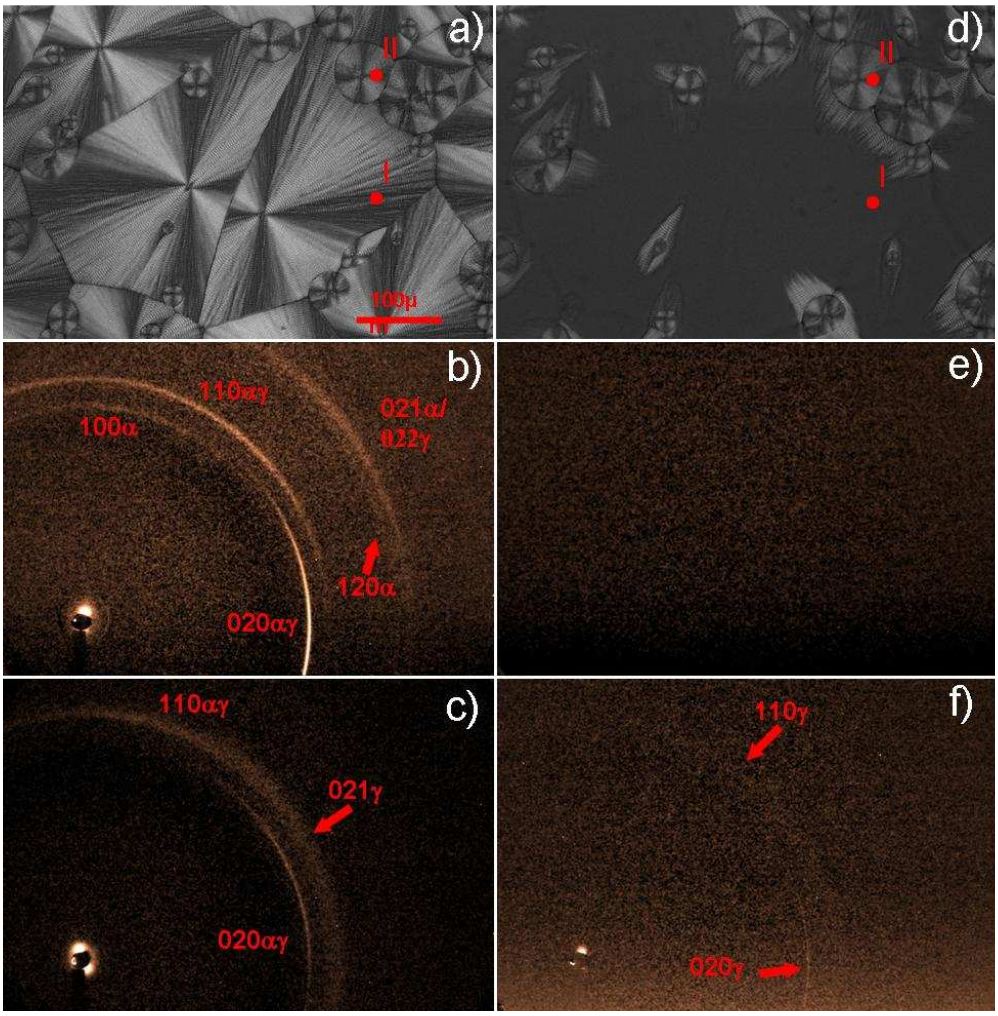

Figure 1. Structural characteristics of the PVDF film at room temperature (left column) and 180°C (right column). Optical microscopy images (A,D), the red circles indicate the measurements points. X-ray patterns measured at point I (B,E) and point II (C,F).

In conclusion, the variable-temperature micro-focus X-ray diffraction is a powerful tool to study the local-scale structural changes occurring during heating or cooling. More specifically, it allows addressing the type of the crystalline modification, orientation, perfectness, as lamellar orientation and long period of the polymer material in a large temperature range.

References

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