ESRF	**Experiment title:** **Investigation of crystal transformations in poly(vinylidene fluoride)with microfocus WAXS/SAXS**	**Experiment number**: MA-274
Beamline: ID13	**Date of experiment**: from: 04.04. to:07.04.2007	**Date of report**: 28.08.2007
Shifts:9	**Local contact(s)**: *Dr Richard DAVIES (e-mail: richard.davies@esrf.fr)*	*Received at ESRF:* *N. E. Zafeiropulos* *Denis Anokhin* *Martin Rosenthal* *Dimitri Ivanov*

Names and affiliations of applicants (* indicates experimentalists):

M. Rosenthal[1], D. V. Anokhin[1*], D.A. Ivanov[1*], N. E. Zafeiropoulos [2*]

[1]Institut de Chimie des Surfaces et Interfaces, CNRS UPR9069, 15, rue Jean Starcky, BP 2488, 68057 Mulhouse CEDEX, France.
[2]Leibniz-Institut für Polymerforschung Dresden e.V, Hohe Strasse 6 D-01069 Dresden Germany

Report:

Poly(vinylidene fluoride), PVDF, has been extensively investigated for the last forty years because of its unique high performance properties exploited in various technological applications[1,2]. Thus, PVDF has excellent mechanical behavior, high chemical resistance, good thermal stability as well as high pyro- and piezo-electric coefficients. Many of these properties crucially depend on the polymer processing conditions as they determine the resulting crystal phase composition. Apart from the polar β-phase phase, PVDF crystallizes in at least two nonpolar phases: α-phase (with the lattice parameters **a**=4.96Å, **b**=9.64Å and **c** (fiber repeat)=4.62Å, chain conformation TG^+TG^-)[3,4] and γ-phase (**a**=4.97Å, **b**=9.66Å, **c** (fiber repeat)=9.18Å, chain conformation $T_3G^+T_3G^-$)[5,6]. In thin films crystallized from the melt two types of spherulites can be identified by optical microscopy[7]: large spherulites of the α-form [7,8] and smaller spherulites of the γ-form[6]. In cross-polarized light the α-spherulites show high birefringence and regular concentric banding, whereas for the γ-spherulites the birefringence is lower and banding does not appear due to their morphological irregularity[9] Upon annealing of thin films at a high temperature (160-170°C) a solid-state transformation of the α-spherulites to a higher-melting crystalline form occurs[7]. Based on infra-red and optical microscopy data, this phase was assigned to the γ-form[9,10,11]. However, these methods do not provide direct structural information on the formed crystal phase. To elucidate this, we have undertaken a morphological study of two-dimensional spherulites using microfocus X-ray scattering.

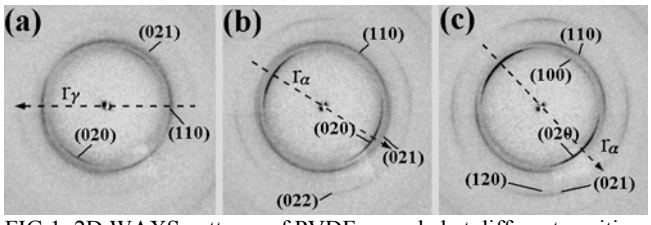

FIG 1. 2D WAXS patterns of PVDF recorded at different positions along the scan. They correspond to two different crystalline modifications. a) γ-modification (within the γ-spherulite); b) γ_α-modification (within the α- spherulite); c) α-modification (banded spherulite).

PVDF (Mw = 1.66x105 g/mol, Mw/Mn=1.7) films were prepared by solution-casting from DMF on glass. The obtained films were dried in vacuum, molten at 210°C and subsequently crystallized for 88 hrs at 165°C. For micro-focus X-ray scattering experiments the films were recovered from glass by floating them off in water. The 2D micro-focus X-ray scattering experiments were carried out at the ID13 beam line at the European Synchrotron Radiation Facility. A monochromatic circular-section X-ray beam with a diameter of 0.5μm (FWHM) and a wavelength of 1.0 Å was used. The experiments were performed in transmission geometry with the sample surface normal to the X-ray beam. The region of interest was selected with an upstream on-axis optical microscope using the morphological difference between the α- and γ- spherulites. The sample was scanned by means of an x-y gantry. The diffraction patterns were collected using a step of 1.0 μm.

The micro-focus WAXS diffraction patterns measured along the scan show three different crystalline structures (FIG 1). The patterns in FIG 1(b) and 1(c) were recorded within the banded spherulite whereas pattern 1(a) was taken within the γ-spherulite. It should be noted that the well-pronounced (020) and (110) reflexes are identical for both, α- and γ-modifications, and therefore they are present on all the patterns. The

$(021)_\alpha$ reflex is superposed with the $(022)_\gamma$. The identification of the phases thus can be done using the unique reflexes of each of the phases such as the $(021)_\gamma$ reflex of the γ-phase and $(100)_\alpha$ and $(120)_\alpha$ reflexes of the α-phase.

The X-ray pattern of the first region (FIG. 1(a)) is characterized by the $(021)_\gamma$ reflex at 3.3Å and the absence of $(021)_\alpha$ reflex at 4.27Å, which indicates that it is a pure γ-phase. The orientation of the $(110)_\gamma$ reflex changes randomly along the scan direction, which can be accounted for by the orientational disorder of lamellar crystals. The latter observation is in agreement with the curled lamellar morphology found for the γ-spherulite from optical microscopy and AFM.

The third region (FIG. 1(c)) is characterized by the presence of $(100)_\alpha$ and $(120)_\alpha$ reflexes located at 5.0Å and 3.5Å, respectively. The pattern does no contain any γ- peaks. The maximum of the azimuthal intensity distribution of the $(020)_\alpha$ peak points along the radial direction of the banded spherulite r_α indicated with a dashed arrow (FIG. 1(b,c)). Therefore the growth direction of the α-spherulite is parallel to the **b**-axis of the α unit cell.

The second, or intermediate, region (FIG. 1(b)) exhibits only the peaks typical of the γ-crystalline phase (cf. FIG 1a). Therefore we can identify the high-melting phase (i.e. the intermediate region) as the γ-modification formed from the α-phase, which will be denoted in the following as γ_α. The morphological difference between γ and γ_α phases consists in the fact that the γ_α phase exhibits orientation for the (020) peak, which is similar to what is observed for the α-phase. The radially-integrated diffraction intensity was plotted as a function of position along the scan line (ordinate) and the norm of the reciprocal space vector **s** (FIG 2 (a)). The intensity of (110) reflection within the γ_α-.and α-regions exhibits oscillations (cf. FIG 2 (b)) with a spatial frequency of about 5μm/cycle, as found from the power spectral density function (FIG 2(c)). This intensity variation within the banded spherulite can be attributed to a regular twist of the lamellar crystals, which are coming in and out of the reflection conditions during the scan.

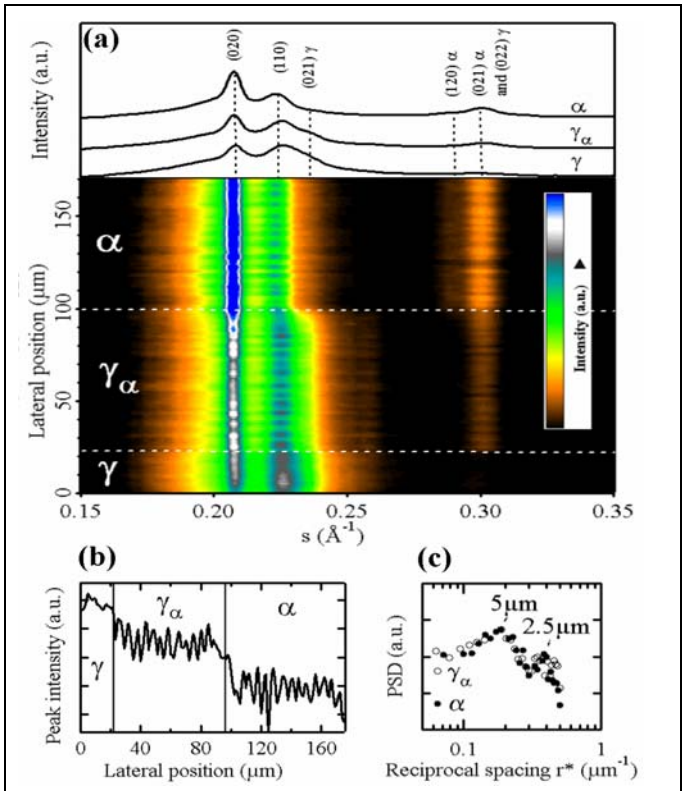

FIG 2. (a) radially-integrated diffraction intensity along the scan displaying three different crystalline morphologies: γ, γ_α and α; (b) intensity of the (110) reflex as a function of distance along the scan; (c) 1D power spectral density of the γ_α and α regions of (b) revealing a distinct peak at 5.0 μm corresponding to the band width along the scan.

The observed solid-state $\alpha \rightarrow \gamma$ transformation occurs upon long-time annealing at small supercoolings. The α-spherulites gradually transform into the γ-phase starting from the interface between the γ- and α-spherulites. The transformation front propagates radially, i.e. parallel to **b**-axis of the α-modification. This growth mechanism accounts for the jagged boundary between the phases such as observed in optical microrgraphs. As soon as the transformation front reaches the center of an α-spherulite, the subsequent growth of the γ_α phase spreads from the spherulite center radially in all directions. The increase of the melting temperature of the γ_α-phase compared to the original γ-phase can be explained by a higher crystal thickness and perfectness of the transformed γ_α-lamellae.

References:

[1] D. A. Seiler, Modern Fluoropolymers, (2nd ed., Wiley, Chichester, 1998)
[2] A. J. Lovinger, Developments in Crystalline Polymers, (Applied Science Publications, London, 1981)
[3] W. W. Doll, J. B. Lando, Macromol. Sci.-Phys., B4, 309, (1970)
[4] M. A. Bachmann, J. B. Lando, Macromolecules, 14, 40, (1981)
[5] S. Weinhold, M. H. Litt, J. B. Lando, J. Polym. Sci.,Polym. Lett. Ed., 17, 585, (1979)
[6] A. J. Lovinger, H. D. Keith, Macromolecules, 12, 919, (1979)
[7] G. Gianotti, A. Capazzi, V. Zamboni, Chim. Ind., 55, 501, (1973)
[8] W. M. Prest Jr, D. J. Luca, J. Appl. Phys., 46, 4136, (1975)
[9] A. J. Lovinger, J. Polym. Sci.-Polym. Phys. Ed. 18, 793, (1980)
[10] W. M. Prest Jr, D. J. Luca, J. Appl. Phys., 49, 5042, (1978)
[11] M. A. Bachmann, W. L. Gordon, J. L. Koenig, J. B. Lando, J. Appl. Phys., 50, 6106, (1979)