



	Experiment title: Effect of Crystallization Conditions on the Crystal Structure and Thermal Behaviour of Poly(vinylidene fluoride)	Experiment number: 26-02-293
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Report:

Poly(vinylidene fluoride) (PVDF) exhibits remarkable chemical, electrical and mechanical properties and continues to attract significant interest as a potential material for piezoelectric applications [1]. PVDF is a semi-crystalline polymer with complex polymorphic behaviour [2]. Nonpolar α (chain conformation TG₁TG₂) and γ (chain conformation GTTT) modifications form on crystallization from the melt. Relative contents of the two modifications depend on the crystallization temperature. During drawing of the samples in the temperature in range 130-160°C the α - and γ -forms transform into the polar β -polymorph (trans-zigzag conformation) which is responsible for the piezo- and the pyroelectrical properties [3]. Despite the fact that, since 1970s, numerous publications addressed the thermal behaviour of PVDF, a detailed investigation of the effect of crystallization temperature on its final structure is still missing.

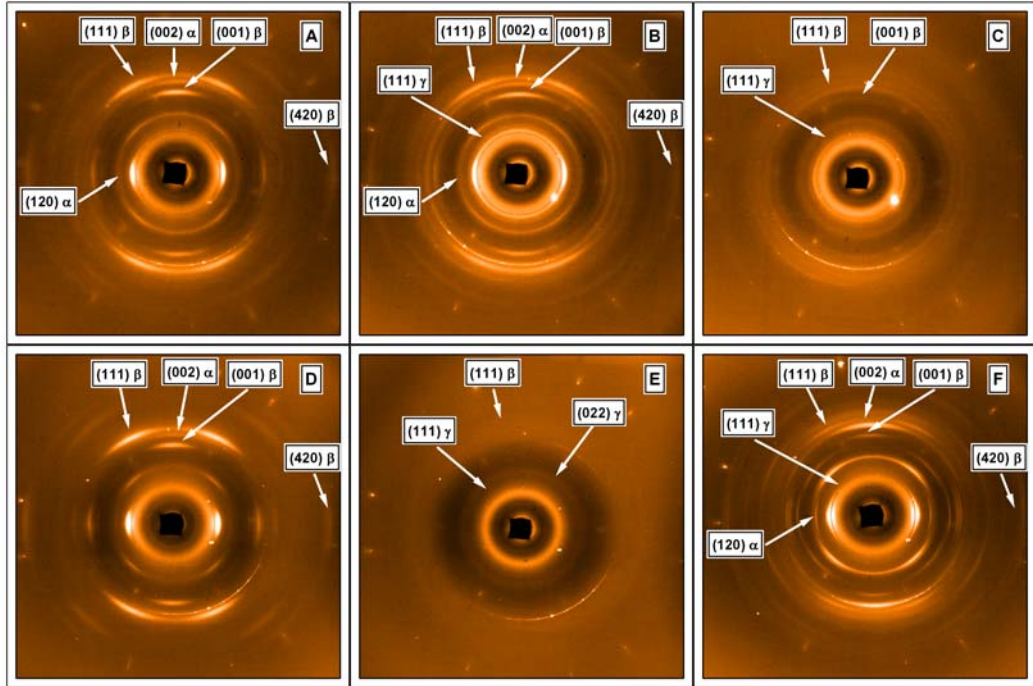


Fig.1 X-ray patterns of PVDF fibers which were crystallized (T_c), subsequently drawn (T_d) and measured (T_m) at the following respective temperatures (T_c - T_d - T_m): 160°C-148°C-160°C (A); 162.5°C-148°C-160°C (B); 162.5°C-148°C-180°C (C); 165°C-148°C-160°C (D); 165°C-148°C-180°C (E); 165°C-165°C-160°C (F).

In the frame of the present project, we studied the effect of crystallization conditions on morphology of PVDF fibers. The sample of SOLEF 6010 was donated by SOLVAY company. Uniform films were formed from powders by heating them up to 220°C and crystallizing isothermally at T_c of 160, 162.5 and 165°C. The films were subsequently drawn ($\epsilon \approx 300\%$) at T_d of 148 and 165°C respectively. The crystal structure of the fibers was determined from 2D X-ray diffraction patterns measured at T_m . Relative contents of different crystal modifications of the PVDF fibers were determined from the ratio of the structure factors corresponding to (120) peak of the α -phase, (111) peak of the β -phase and (111) peak of the γ -phase, respectively.

The WAXS patterns of the samples crystallized at 160°C and drawn at 148°C show at T_m of 160°C the crystalline peaks (020), (001), (111) corresponding to the β -phase and (100), (020), (110), (120), (130) and (021) reflexes of the α modification (Fig. 1A). At the same time, the intense peak (111) of the γ -form is not observed. As this peak was previously found for non-oriented films, we suggest that $\gamma \rightarrow \beta$ and $\alpha \rightarrow \beta$ solid-state transformations occur on drawing. The X-ray pattern of the sample drawn at 165°C reveals a different structure: the γ -form is

Table 1. Relative contents of different polymorphs in PVDF fibers

T_c - T_d - T_m	α -phase	β -phase	γ -phase
160°C-148°C-160°C	0.10	0.90	0
160°C-165°C-160°C	0.69	0.31	0
160°C-165°C-170°C	0.63	0.37	0
162.5°C-148°C-160°C	0.13	0.69	0.18
162.5°C-148°C-175°C	0.28	0.45	0.17
162.5°C-148°C-180°C	0	0.45	0.55
162.5°C-165°C-160°C	0.64	0.31	0.05
165°C-148°C-160°C	0.07	0.93	0
165°C-148°C-170°C	0.11	0.86	0.03
165°C-148°C-180°C	0	0.37*	0.63*
165°C-165°C-160°C	0.74	0.15	0.11

* peaks are very weak

also absent but the content of the α -phase is significantly higher than for the sample crystallized at 160°C (Tabl.1), which is probably due to a limited extent of the $\alpha \rightarrow \beta$ transformation at this temperature. The fiber crystallized at 162.5°C and drawn at 148°C in addition to reflexes mentioned above exhibits additional reflexes that can be indexed to (111) and (042) peaks of the γ -form (Fig. 1B). On heating to 180°C, individual reflexes of the α -form disappear due to melting of this phase (Fig. 1C). It should be mentioned that, on heating, the γ/β ratio increases and the crystals of β - and γ -modifications preserve their orientation. Such behavior can be explained by a $\alpha \rightarrow \gamma$ high-temperature transformation paralleled with a partial melting of the β -phase. The crystal structure of the samples crystallized at 165°C and stretched at 148°C appears similar to the sample crystallized at 160°C for which only reflexes of α and β -modifications are present (Fig. 1E). The relative amount of the γ -phase is increased due to melting of the α and β -forms. At T_m of 180°C the crystallinity is very small and the crystallites are disoriented. We therefore suppose that β -modification mechanically stabilizes the fiber up to the melting point above which the γ crystals loose their orientation. On the diffractogram of the sample drawn at 165°C the (021) and (111) reflexes of the γ -modification appear (Fig. 1E) probably because of a high content of the phase in the originally non-oriented film. Relatively lower content of β -phase (Tabl.1) reveals that the processes of the $\alpha \rightarrow \beta$ and $\gamma \rightarrow \beta$ transition do not proceed completely on drawing at high temperature (higher than 160°C).

In conclusion, PVDF fibers demonstrate complex polymorphic behavior, which is dependent on crystallization conditions and the drawing temperature. The solid-state transformations taking place upon thermal and mechanical treatments were explored using variable temperature 2D X-ray diffraction.

References

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