

# Electrical and Microstructural Changes of $\beta$ -PVDF under Uniaxial Stress Studied by Scanning Force Microscopy

J. Serrado Nunes<sup>1, a</sup>, V. Sencadas<sup>1, b</sup>, A. Wu<sup>2, c</sup>, P.M. Vilarinho<sup>2, d</sup>,  
S. Lanceros-Méndez<sup>1, e</sup>

<sup>1</sup>Departamento de Física, Universidade do Minho, 4710-057 Braga, Portugal

<sup>2</sup>Dept. Eng. Cerâmica e do Vidro, CICECO, Universidade de Aveiro, Portugal

<sup>a</sup>jivago@fisica.uminho.pt, <sup>b</sup>vsencadas@fisica.uminho.pt, <sup>c</sup>aiying@cv.ua.pt,  
<sup>d</sup>paulas@cv.ua.pt, <sup>e</sup>lanceros@fisica.uminho.pt

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**Abstract.** Chain reorientation may be induced in polyvinylidene fluoride (PVDF) in its  $\beta$ -phase by applying a deformation perpendicular to the pre-oriented polymeric chains. This reorientation begins right after the yielding point and seems to be completed when the stress-strain curve stabilizes. As the deformation process plays an important role in the processing and optimisation properties of the material for practical applications, different deformation stress was applied to the PVDF lamellas and their topographic change and piezoelectric response were studied by means of scanning force microscopy in a piezo-response mode.

The experimental results confirm the previously observed chain reorientation that occurs right after the yielding point and that is completed when the yielding region is passed. This reorientation is accompanied by a stretching of the granular structures observed in the topographical images and variations in the domain response. The observed results help to explain the variations in the macroscopic response of the material.

## Introduction

Poly(vinylidene fluoride), PVDF, in its  $\beta$  phase is known for its piezo-, pyro-, and ferroelectric properties, which are found applicability in the field of sensors and actuators. In many of these applications the material may be subjected to severe conditions, such as temperature changes or mechanical stresses. A strong mechanical stress dependency of the piezoelectric coefficient has been detected [1,2].

One relevant issue is the dependence of the electrical and mechanical properties on the structure of PVDF. The distribution of lamella thickness, the degree of perfection of the two-phase structure, and the orientation of the chain elements in the amorphous region of PVDF are structural parameters, which influence the electrical, mechanical and electromechanical response of the material. It should be also taken into account that PVDF alters its crystal modification under thermal or stress treatment [3,4]. Of the five known modifications of PVDF, the  $\alpha$ - and  $\beta$ -modifications are the most common. The unpoled  $\alpha$ -crystalline material is usually isotropic, whereas PVDF in the  $\beta$ -modification is highly oriented [4] and responsible for the outstanding piezoelectric properties of PVDF.

Further, the interphase between the crystalline and amorphous phases is of eminent importance for the polarization in PVDF [2]. In this interphase, a stress dependent orientation correlation of the molecular electric moments can exist, which in turn is induced by the complete orientation correlation of the moments in the crystalline phase, particularly in  $\beta$ -crystalline material. It randomizes only in the amorphous bulk. Estimations of the chain conformation in this interphase show that its thickness amounts to about 1 nm. At usual supermolecular structure, particularly, at crystallinity around 50%, this interphase carries about one third of the overall polarization.

Considering the extensibility of the amorphous phase with stress and with change of temperature, it is obvious that the structure and the dynamic of the amorphous phase will play an important role in the ferroelectricity, piezoelectricity and pyroelectricity of this material [2].

In this investigation, we have extended previous investigations on the dependence of the different properties of  $\beta$ -PVDF upon a transversal deformation [5,6,7]. The differences in the topological and domain morphologies have been investigated by scanning force microscopy in a piezo-response mode and correlated with previous results.

## Experimental

The starting material was a poled 28  $\mu\text{m}$  thick commercial  $\beta$ -PVDF film from Measurements Specialties, Inc. (Fairfield, NJ, USA). Some samples were prepared by controlled deformation at different degrees (from 18% to break (max. 140%)) in the perpendicular direction to the initial chain orientation. For this preparation, a Minimat testing machine from Polymer Laboratories in the tensile mode at test velocities of  $dl/dt = 2 \text{ mm/min}$  on ca. 4 cm x 1 cm rectangular samples was used.

Scanning force microscopy (SFM, Nanoscope IIIA, Multimode, Digital Instruments) in a piezo-response mode was performed under the following conditions: silicon cantilever (Nano world Innovative Tec.) with spring constant 14 N/m, resistivity: 0.01-0.02  $\Omega\text{cm}$ , resonance frequency: 110-150kHz. When measure domain contrast, the applied ac field used is 6V at 50kHz. Scan rate is 0.5Hz. In order to check the reliability of the measurements, soft tips (NSG01/Pt, NT-MDT Co.) with force constant  $\sim 5\text{N/m}$  were also used.

## Experimental results

In the following figures the results obtained by scanning force microscopy in a piezo-response mode for a poled  $\beta$ -PVDF sample with several permanent transversal deformations are presented (Figures 1 to 3). For all figures, the image on the left represents a three dimensional image, the figure in the middle a two dimensional image and the one on the right the domain contrast image. Two kinds of SFM tips were applied to analyze the morphology and piezo-response signal of the samples. Consistent results are obtained indicating the obtained images are typical and no tip dependence.

Comparing the microstructure observed by SEM [7] and SFM, the low magnification images of SFM show consistent microstructural features with the ones obtained by SEM. On the other hand, high magnification SFM image revealed more detailed features than SEM. In the following we will concentrate to discuss those images.

Original PVDF sample (deformation 0%) (Figure 1) show unstrained grain structure with surface roughness around 27 nm. The microstructure has a matrix and granular grains inlaid on this matrix. The matrix has a strip like undulation.

After applying small deformation (9%) perpendicular to the preferred chain orientation (Figure 2), SFM microstructure show the some additional undulation strip with the direction across the original strip on the matrix and grains stressed and elongated along the stretch direction. The surface roughness in big area image is similar as the first one.

By further elongation (119%) along the transversal direction far beyond the yielding (Figure 3), SFM microstructure show that the original strip in matrix gets enhanced and grains deformed as a bended granule towards the strip direction. Grains are stressed and this stress of grains may contribute to the macroscopic properties of the sample. The surface roughness in big area image is also similar as the first one (Figure 1).

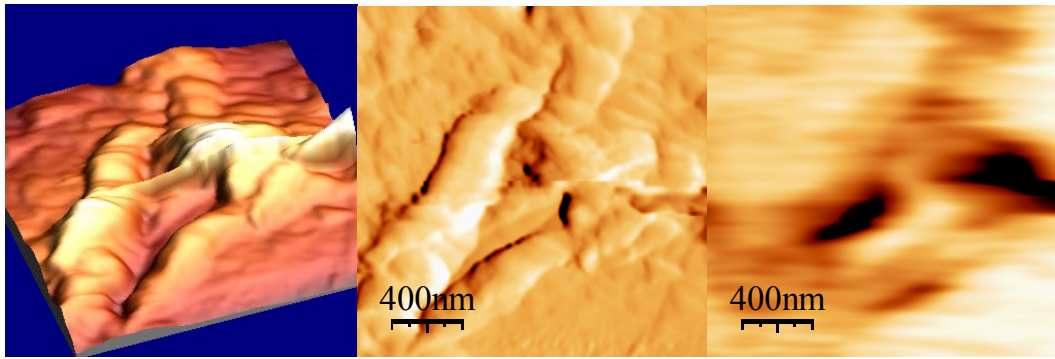


Fig. 1. From left to right; three dimensional, two dimensional and domain contrast image for a  $\beta$ -PVDF undeformed poled sample obtained by SFM.

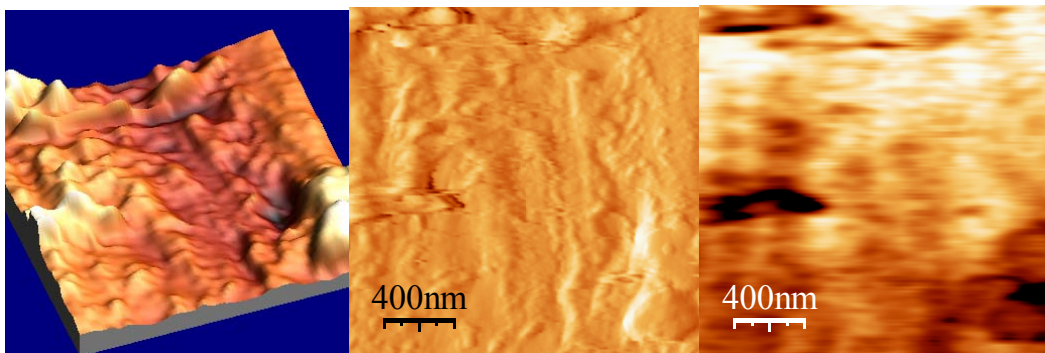


Fig. 2. From left to right; three dimensional, two dimensional and domain contrast image for a  $\beta$ -PVDF poled sample obtained by SFM. Transversal deformation (bottom-up, in the image) 9%..

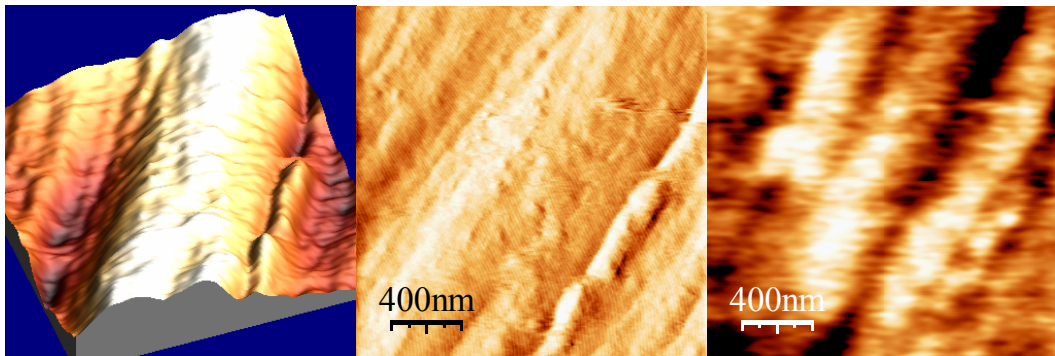


Fig. 3. From left to right; three dimensional, two dimensional and domain contrast image for a  $\beta$ -PVDF poled sample obtained by SFM. Transversal deformation (bottom-up, in the image) 119%.

These results corroborate the previously obtained [5,6,7] that indicated a chain reorientation towards the stretch direction when the sample is subjected to transversal stretching. The chain reorientation is accompanied by changes in the domain configuration, as can be observed in the piezo-response images. The contrast in the piezo-response images reflects the semi-crystalline nature of the polymer, as it is expected a larger electric activity in the crystalline regions, responsible for the main part of the piezoelectric response of these materials. A destabilization of the ferroelectric phase upon deformation seems to be confirmed by the images. This effect was already reported in P(VDF-TrFE) [8,9]. On the other hand there is some effect of the morphology on the contrast and may be some effect of electrostatic effect, as the following analyses reveal

(Figure 4). In order to clarify this issue, a comparative analysis of poled and non-poled samples is being performed.

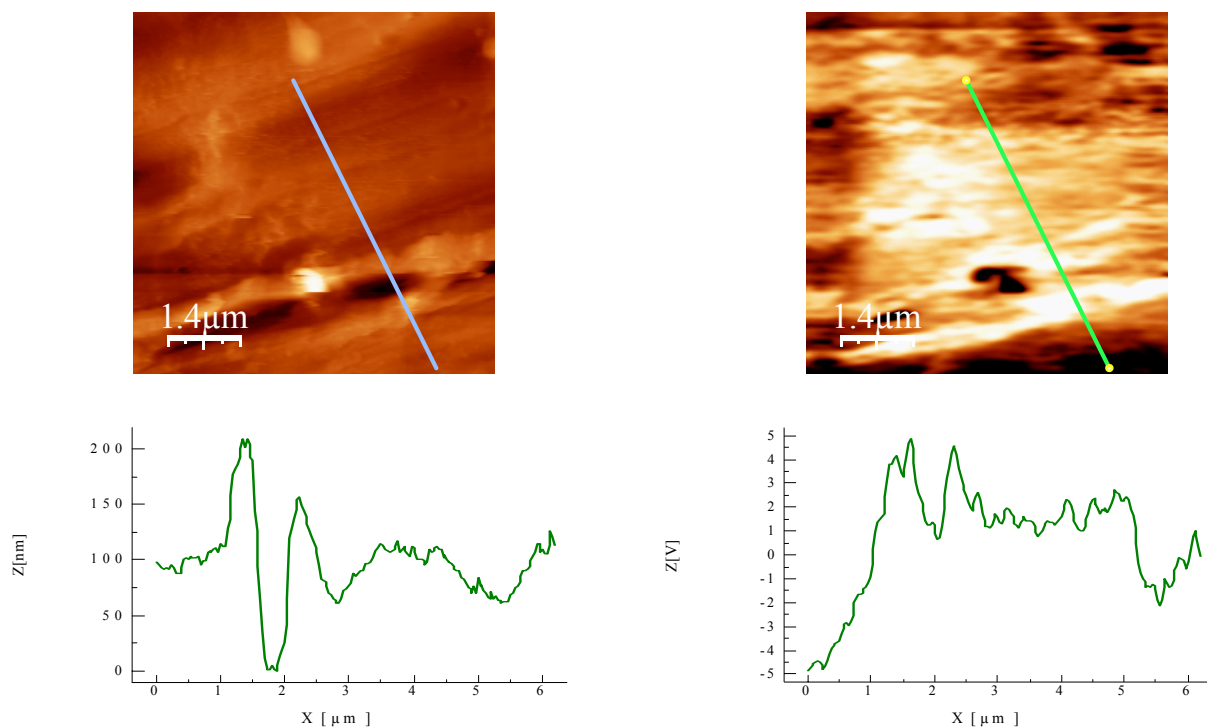


Fig. 4. Topographic image (top left) and domain contrast image (top, right) and corresponding line profiles (bottom).

Morphology and piezo-response signals were also obtained by scan on different area of the sample using the same scan condition and magnification values. Images with the same magnification but obtained in different region show similar results with respect to chain orientation and direction as well as with respect to the piezo-response. On the other hand, the surface roughness values are not equal in different area of the film. The average roughness value is  $42 \pm 6$  nm. Further, scans parallel or perpendicular to the chain direction showed no obvious difference was observed, only the image turns  $90^\circ$ .

## Discussion

In semi-crystalline polymers, yielding involves considerable disruption of the crystal structure. Slip occurs between the crystalline lamellae, which slide by each other; and within the individual lamellae. The latter process is the dominant one, and leads to molecular orientation, since the slip direction within the crystal is along the axis of the molecule. As plastic flow continues, the slip direction rotates systematically towards the tensile axis. Ultimately, the slip direction (i.e. the molecular axis) coincides with the tensile axis, and the polymer is then oriented and resists to further extension.

Previous FTIR experiments showed a polarisation switching when the material was subjected to tensile stress perpendicular to the draw direction [5,6]. This switching occurs progressively within this region [6] and is accompanied by a decrease in the degree of crystallinity with no changes in the crystalline lamellae thickness [6].

These previous results, together to the present ones obtained by SFM, point out to a model of plastic deformation occurring by fusion and incomplete recrystallisation of the crystal phase present in the

semi-crystalline polymer [10]. This can account for the static and dynamic behaviour of the dielectric parameters [7].

The variations observed in the domain images point out a contribution of the amorphous region both in the deformation process as well as in the piezoelectric response of the material. Though the chains in the amorphous bulk state could be hardly associated to the process leading to permanent deformation, as their relaxation times are very small at room temperatures, the presence of trapped entanglements among such segments could contribute as load transfer for permanent deformation. The interface region, i.e. the amorphous region related to the tie-chains that directly link adjacent crystalline lamellae and tie-chains linking the crystalline and the amorphous phases are expected to be highly taut and highly constrained and will dominate the mechanical behaviour in the plastic region. The activation of such tie-chain may contribute to change the orientation of the crystalline lamellae.

## Conclusion

A chain reorientation is confirmed in  $\beta$ -PVDF upon transversal deformation that affects the degree of crystallinity, the domain distribution and configuration and the macroscopic properties of the material. In the case of the studied oriented  $\beta$ -PVDF film, we expect that the tie-chains of the interphase will dominate the plastic behaviour of the material and deeply influence the macroscopic properties of deformed samples.

The decrease of crystallinity and the behaviour of the dielectric parameters upon transversal deformation, together with the domain images that support a destabilisation of the ferroelectric phase, support the model of melting and incomplete recrystallization as the mechanisms underlying the reorientation process.

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