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Electronic Supporting Information (ESI)

Solid-state-processing of δ -PVDF

Jaime Martín^a, Dong Zhao^b (赵冬), Thomas Lenz^{b,c}, Ilias Katsouras^d, Dago M. de Leeuw^{b,e} and Natalie Stingelin^{a,f*}

^a Department of Materials and Centre of Plastic Electronics, Imperial College London, London SW7 2AZ, UK
^bMax-Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
^cGraduate School Materials Science in Mainz, Staudinger Weg 9, 55128 Mainz, Germany
^dHolst Centre, High Tech Campus 31,5656AE Eindhoven, The Netherlands
^eFaculty of Aerospace Engineering, Delft University of Technology, Kluyverweg 1, 2629 HS Delft, The Netherlands
^f School of Materials Science and Engineering and School of Chemical & Biomolecular Engineering, Georgia Institute of Technology, 311 Ferst Drive, Atlanta, Georgia 30332, USA

[*] E-mail: natalie.stingelin@mse.gatech.edu

Materials and Methods

Materials

Poly(vinylidene fluoride), PVDF, with a weight-averaged molecular weight, \overline{M}_w , of 543,000 g mol⁻¹, was purchased from Sigma-Aldrich Co. and used as received.

Processing

For solid-state-processing PVDF structures, as-received powder (10-20 mg) was placed in a manual hot press (Rondol Autopress), followed by compression molding at temperatures ranging from 100 to 150 °C (see Figure S1); i.e. at temperatures many commodity plastics such as polyethylenes are processed. During the compression molding process, the pressure was

progressively increased up to ~10 to 30 kN/cm² thereby avoiding rapid application of pressure and keeping the final pressure for a period that depended on the applied temperature. Typical conditions used were 150 °C, ~20 kN/cm² and 5 min. We note that these pressures are relatively moderate in order to enable materials flow, as described in Ref. 24 of the main manuscript. The PVDF samples were then cooled to room temperature under pressure to obtain ~30 μ m thick films.



Fig. S1. Photographs of (a) the as-received powder (α -PVDF) prior to solid-state-processing and (b) the solid-state pressed PVDF film which is clear and highly transparent. For small-angle X-ray measurements, PVDF films were produced via drop-casting from N,N-dimethylformamide (DMF).

Free-standing films of PVDF were in addition prepared by spin-coating for comparison. To that end, 50 nm films of PEDOT:PSS (Clevios P VP 4083, Heraeus) were spin-coated onto cleaned glass substrates (10 s at 500 rpm, followed by 60 s at 1500 rpm). Then, a PVDF solution (340 mg/ml in DMF) was spin-coated onto the PEDOT:PSS films at 250 rpm for five minutes, followed by the annealing of the samples at 200 °C for two hours. Samples were then slowly cooled down to room temperature and immersed in a water bath in order to detach the PVDF films from the substrate. The resulting free-standing films are by definition in the α -phase, as they were obtained by slow cooling from the melt (after spin-coating). They serve as reference for the electrical characterization.

Characterization

The electric displacement as a function of electric field was measured using a Radiant precision multiferroic test system (Radiant Technologies, Inc.). The strain as a function of electric field was measured simultaneously with the displacement, using a MTI 2100 photonic sensor interfaced with the Radiant tester. Leakage was avoided by using a Sawyer-Tower setup, where the electric displacement were derived from the charge on a reference capacitor. The hysteresis loops were obtained from shunt measurements using a resistor in series with the ferroelectric capacitor.

Since fatigue effects can influence the hysteresis D-E loop we compared solid-state processed and spin cast films. On both 20 nm Au electrodes were evaporated; the thickness as well as the surface roughness of both types of films was comparable, allowing us to produce similar PVDF layer/electrode interfaces between the two types of samples. Furthermore, all measurements were done on freshly made samples to avoid any fatigue issue; i.e.all the samples investigated in our work can be regarded as ferroelectric-only capacitors.

Owing to the soft nature of our PVDF films, which easily flex/deform, only unrealistic d33 values could be deduced when using a standard d33 meter. We have therefore extracted the piezoelectric coefficient for our structures by using the model fitting. We have verified the validity of this method by using rigid PZT pellet samples, whose d33 value was found in agreement to the one measured by a standard d33 meter.

Wide-angle X-ray scattering (WAXS) $\theta/2\theta$ scans were recorded at room temperature on a PANalytical X'Pert Pro MPD using Cu K α radiation. The analyzed scattering vector, q ($q = 4\pi/\lambda \sin\theta$) was thereby parallel to the out-of-plane direction of the films. The amount of the different PVDF phases present in solid-state pressed structures was quantified by fitting the WAXS pattern using the *PeakFit4.12* software, taking as an assumption that the final crystallinity of the samples should be around 40 - 50 %. The peaks were fitted to Voight functions, while the amorphous halo was fitted as the sum of 2 peaks. One of the main reasons for the latter is the strong diffuse scattering in the region that is present between $15^\circ - 20^\circ$, which renders description of the diffuse scattering of the amorphous PVDF fraction intricate. WAXS patterns for hypothetically defect-free α - and δ -PVDF were calculated using the Mercury 3.8 software (Figure S2).



Fig. S2. Calculated WAXS pattern for defect-free α -PVDF and δ -PVDF calculated using the Mercury 3.8 software. For this calculation, the diffraction peaks were assumed to be of an arbitrary width.

Two-dimensional wide-angle X-ray scattering (2D-WAXS) measurements were performed at the D-line of the Cornell High Energy Synchrotron Source (CHESS). The WAXS intensity was recorded along the q_z and q_{xy} , *i.e.* the scattering vectors normal and parallel the plane of the film, respectively. A wide band-pass (1.47%) X-ray irradiation of a wavelength of 1.155Å was used, selecting an incidence angle between 0.5° and 1°. A Pilatus 200k detector with a pixel size of 172 µm was placed at a distance of 28.9 cm from the samples. A 1.5 mm wide tantalum rod was used to block the intense scattering in the small-angle area. The exposure time was 1s. The 2D-WAXS analysis was limited to angles ψ (defined by the rotation of the sample around an axis contained in the plane of the film) between 0° and 65° due to the shadowing of a certain detector area by the sample. The (100) and the (020) reflections were computed together as their peaks overlapped.

Small-angle X-ray scattering (SAXS) experiments were conducted on a Rigaku 3-pinhole PSAXS-L equipment operating at 45 kV and 0.88 mA, employing Cu K α radiations with a wavelength $\lambda = 1.54$ Å. The flight path and the sample chamber in this equipment were kept under vacuum. The scattered X-rays were detected on a two-dimensional multiwire X-ray detector (Gabriel design, 2D-200X). This gas-filled proportional type detector offers a 200 mm diameter active area with ca. 200 µm resolution. The azimuthally averaged scattered intensities were obtained as a function of *q*. Reciprocal space calibration was performed using silver behenate as standard. PVDF films were placed perpendicular to the incident X-ray beam and

analyzed in transmission geometry. For the sake of comparison, α -PVDF films were also analyzed. These were processed from N,N-dimethylformamide (DMF) solution.

Differential scanning calorimetry (DSC) was performed on a Mettler–Toledo DSC1 Star system using heating- and cooling rates of 10 °C/min. 3-5 mg of freshly prepared solid-state-processed films were used for the analysis. We used the 1st heating thermogram to obtain information on the thermal behavior of solid-state-processed PVDF, while from the 2nd heating thermogram insights were gained on melt-processed material that leads to α -PVDF. Measurements were also conducted on as-received PVDF powder.

Supplementary data

Comparison between the intensity along the z direction (normal to the film) and the intensity averaged over all y-angles

A preferred crystal orientation seems to be obtained by solid-state pressing PVDF powder. This can be deduced also from the direct comparison between the WAXS intensities along the *z*-direction (normal to the film) and the intensity averaged over all ψ -angles. For example, the (021) reflection is almost absent along the *z*-direction but it is present in the diffractogram that accounts for the intensity averaged over all the ψ -angles. In fact, just (*hkl*) diffractions with zero *l*-indices are observed in the diffractogram along the *z*-direction. These reflections are associated with planes that are parallel to the chain directions in the crystals. Therefore, it can be concluded that, in general, chains are oriented parallel to the plane of the film in solid-state-processed PVDF films.



Fig. S3. Comparison between the recorded intensity along the *z*- direction (normal to the film; grey line with circles) and the intensity averaged over all ψ -angles (solid orange line).

Lamellar crystal thickness and long period of solid-state-processed films

The crystallinity X of, respectively, solid-state- and melt-processed PVDF material was estimated from DSC data. Fig. S4a displays the first heating thermogram for solid-state pressed PVDF (dark blue line), while the second heating run was used to obtain information of melt-crystallized material that leads to the α -phase (light blue line). Both thermograms were measured using a heating rate of 10 °C/min. For comparison, the first heating run of the as-received PVDF powder used for the solid-state processing is also shown (light blue dashed line).

In Fig. 4b we display small-angle X-ray scattering data for solid-state pressed (dark blue line) and solution-cast PVDF films (light blue line). We find a well-defined Bragg peak in the low q region of both X-ray scattering profiles, both for the solid-state-processed material and for the solution-cast films, which will be predominantly in the α -form. The peak in the solid-state pressed sample pattern is centered at $q \sim 0.049$ Å⁻¹, which corresponds to a characteristic length of the periodic stack, *i.e.* the so called long period, $L \approx 12.8$ nm. For the solution-processed PVDF, the peak maximum is located at $q \sim 0.052$ Å⁻¹, which corresponds to a long period, $L \approx 12.1$ nm.



Fig. S4. (a) DSC thermograms of solid-state processed PVDF (dark blue solid line), PVDF crystallized from the melt (light blue solid line, α -phase) and as received PVDF powder (light blue dashed line, α -phase). (b) Lorentz-corrected SAXS data for solid-state processed PVDF (dark blue line) and solution-crystallized material (deposited from N-N-dimethylformamide) that leads to the α -phase (light blue).