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Supplementary Information

Exclusive self-aligned β-phase PVDF films with high piezoelectric coefficient via phase inversion

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1. Materials

Poly(vinylidene fluoride) pellets (Solef 1008) with a density of 1.78 g/cm^3 and a molecular weight (M_w) of 244,000 g/mol were obtained from Solvay Solexis, France.[1] N, N-dimethyl formamide (DMF, extra pure) and Glycerol was obtained from Acros Organics Ltd. and were used as-obtained.

2. Membrane preparation

A 30 wt.% solution of Poly(vinylidene fluoride) (PVDF) was prepared in N,N-dimethylformamide (DMF) solvent by heating at 70ºC, with continuous and vigorous magnetic stirring for about 3 hr. The PVDF films were then deposited via spin-coating on highly polished glass substrates. A small volume (~1.5 ml) of PVDF/DMF mixture was placed on the glass substrate and then processed at a spin speed of 750 rpm for duration of 75 sec (SPIN150 Single Substrate Spin Processor). The spin-coated films were then immediately immersed in the precipitation bath of deionized water kept at a desired temperature (-20 °C to 100 °C) for 30 min for complete elimination of DMF by quenching. For -20 °C bath, a mixture of deionized water and glycerol was used. The as-prepared films were then washed thoroughly with water to remove any traces of solvent and then dried overnight in air at room-temperature

(~25 °C) before undertaking any further characterisation. The complete removal of solvent was further confirmed through Fourier transform infrared spectroscopy (FTIR) analysis.

3. Membrane Characterisation

A Hitachi S3400N scanning electron microscope (SEM) was used to characterise the microstructure of the PVDF films. The vibrational characteristics of the films were examined by FTIR spectroscopy (Thermo Scientific IS10 Nicolet). Vendor provided OMINIC software was used to analyse the results, including the calculation of β-phase content. The spectra were recorded at a nominal resolution of ±2 cm^{-1} for a total of 64 scans. Differential scanning calorimetry (DSC) was used to investigate the crystalline phase of the polymer films on a TA Instruments DSC Q2000. The samples, approximate weight 5 mg, were heated at 5 ºC/min from -50 ºC to 200 ºC under 50 ml/min N_2 flow. X-ray diffraction scans were collected on a D2 Phaser (Bruker) system employing a Co-Kα (λ= 1.78897 Å) source, operating at 30 kV and 10 mA. The sample was scanned at a speed of 0.02 º/sec from 10º to 40º (2θ).

The piezoelectric response of the PVDF thin films was investigated using piezoresponse force microscopy (PFM) (Bruker Nano Inc, Santa Barbara, CA, USA). For PFM imaging, a Pt-Ir coated conductive probe (SCM-PIT) with spring constant of 2.8 N/m and resonant frequency of 75 kHz was used. The amplitude of the detected piezoelectric signal is related to the piezoelectric coefficient (d_{33}) of the material, whereas the phase of the signal reflects the direction of the polarisation of the domains. An average of ten different locations on one sample was used to compute the average value of piezo-response amplitude. Before imaging the PVDF film samples, the PPLN (Periodically Poled Lithium Niobate) test sample was used for standard PFM imaging verification. The vertical piezoresponse was calibrated using deflection sensitivity of the AFM cantilever tip obtained from the force-displacement curve. The d_{33} measurement procedure is described below:

d_{33} (nm/V) = Amplitude (in V) * deflection sensitivity (nm/V) / (vertical deflection gain (16) * Applied AC Bias)

where deflection sensitivity: 109.44 nm/V, Vertical deflection gain: 16X and applied AC bias: 3V

Substituting above values, d_{33} = 2.28*A (V)

Table 1: Measured d_{33} values for various PVDF samples obtained from PFM amplitude

Sample (T_Q)	**PFM amplitude (mV)**	**d_{33} (pm/V)**
-20°C	21.76	49.61
0°C	20.326	46.34
60°C	13.52	30.89
100°C	11.18	25.49

4. X-ray Diffraction analysis of the PVDF films

The crystalline phases were characterised using the XRD analysis. Fig. S1 shows the XRD spectra of the PVDF films at various quenching temperatures, and a sequential change of the three peaks located at approximately 21.1°, 23°and 24° can be observed. The peaks at 21.1° and 23° correspond to the (020) and (110) planes of the α-phase with the corresponding d-spacing of 4.84 Å and 4.45 Å, whereas the peak at 24° corresponds to the β-phase and is a combination of (200) and (110) planes with the corresponding *d*-spacing of 4.38Å.[2,3] It can be observed clearly that with the reduction in the quenching temperature, the peaks at 21.1° and 23° gradually disappear, while that around 24° becomes stronger and dominant. The broadening of the β-phase peak can be attributed to multiple factors such as small crystallite size and defects in crystalline lattice due to occurrence of unit cells with deviating dimension.

The space between the crystal planes can be calculated from the XRD spectrum. The α-phase has a *d*-spacing of about 4.84 Å and 4.45 Å, while that of the β-phase is about 4.38 Å, in agreement with the reported values.[3,4] Table 2 is the summary of the properties of the crystal structure as a function of quenching temperature.

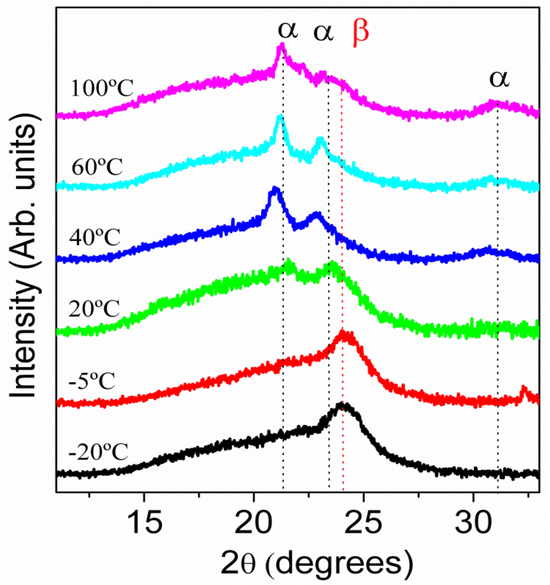

Fig. S1 XRD spectra of PVDF membranes quenched at different temperatures. The shift in the diffraction peak from β-phase to α-phase can be clearly observed.

Table 2. Summary of PVDF films synthesized at different quenching temperatures.

Quench temp. (^{o}C)	2θ (degrees)	d (Å)	Crystal phase
-20	23.67	4.366	β
-5	23.03	4.38	β
20	21.43 23.73	4.816 4.349	α β
40	20.99 22.93	4.90 4.349	α α
60	21.21 23.13	4.864 4.466	α α
100	21.30 23.19	4.843 4.639	α α

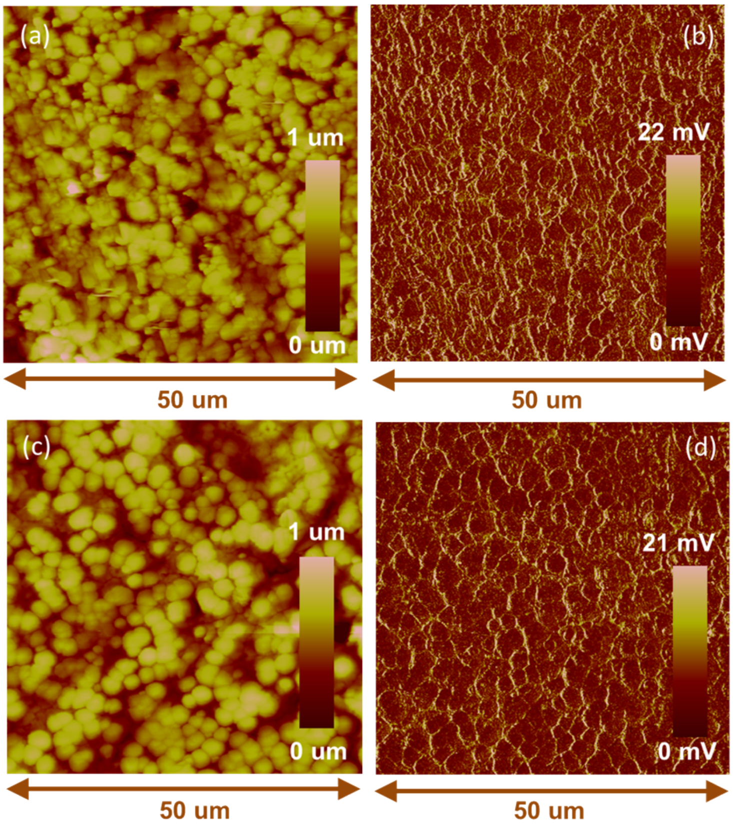

Figure S2(a-d): Topography and piezoresponse of the sample quenched at -20^{o}C (after storage in ambient laboratory conditions over twelve months, followed by subsequent annealing at 50 ^{o}C).

References

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