Electronic Supplementary Information

Manipulation of the Oriented Amorphous Fraction of Poly(vinylidene fluoride-co-trifluoroethylene) Films by Thermal Annealing for High Piezoelectricity

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1. EXPERIMENTAL SECTION

1.1 Materials

Commercial P(VDF-TrFE) 80/20 mol% (FC20) random copolymer is supplied by Piezotech, Arkema, France. The weight-average molecular is 450000 g/mol. The polymer powder is used directly without any purification.

1.2 Sample preparation

Electrospinning process. First, the FC20 nanofiber films were obtained by electrospinning (TL-Pro-BM, Shenzhen Tongli Micro Nano Technology Co., Ltd, China). Specifically, FC20 powder was dissolved in a mixed solvent of *N, N*-dimethylformamide (DMF) and acetone (volume ratio of 3:2). Then, the solution was stirred at the speed of 500 rpm for 12 h to obtain a homogeneous electrospinning solution. Electrospinning was carried out at a constant feed rate of 1.0 mL/h under a constant DC voltage of 16 kV at 25 ºC and 40-50% relative humidity. The tip to collector distance was maintained at 12 cm and the drum speed was 1500 rpm. The resulting nanofiber films were dried at 55 ºC for 24 h for further research.

Annealing process. The dried electrospinning films were annealed in a muffle furnace (KSL-1200X, Hefei Kejing Material Technology Co., Ltd, China) at different temperatures (120, 125, 130, 135, and 140 ºC) under atmospheric pressure for 8 hours. These samples are labeled as EFC20-Ax (where x = 120, 125, 130, 135, and 140 ºC), and the sample without annealing was labeled as EFC20-0.

1.3 Characterizations

The crystallization behavior of nanofiber films was investigated by differential

scanning calorimetry (DSC, DSC 25, TA Instruments, USA). Approximately 2 mg of sample was heated from -50 ^{o}C to 200 ^{o}C at a rate of 10 ^{o}C/min in a dry nitrogen atmosphere (flow rate = 40 mL/min). Field emission scanning electron microscopy (FE-SEM, SU-70, Hitachi, Japan) was used to observe the morphology of the sample. The operating voltage is 5 kV. The conformation of different samples was characterized by a Fourier transform infrared spectrometer (FTIR, Nicolet 6700, Thermo Fisher Scientific, USA) in an attenuated all-trans (ATR) mode with a resolution of 4 cm^{-1} in the range of 3200 to 300 cm^{-1}. 2D WAXS and 2D SAXS measurements were performed using a fully automated small-angle wide-angle ultra-small-angle scattering station (SAXSpoint5.0, Anton Paar GmbH, Austria). The beam wavelength is 0.154184 nm. The sample-to-detector distance for WAXS and SAXS is 64.2 mm and 476.4 mm, respectively. The 2D WAXS patterns were integrated to obtain 1D curves of the intensity (I) as function of scattering vector (q). The frequency-dependent dielectric constant of the film was measured using a broadband dielectric spectrometer (BDS, Novocontrol Concept 40, Novocontrol Technologies, Montabaur, Germany) at room temperature. A 1.0 Vrms (i.e., root-mean-square voltage) is applied during the BDS test, and the test frequency ranges from 1 Hz to 10^7 Hz. Prior to the test, gold (Au) electrodes with diameters of 6 mm were sprayed on two surfaces of the sample using a VTC-16-SM plasma magnetron sputtering coater (Hefei Kejing Material Technology Co., Ltd., China). The Displacement – Electric (D-E) loop measurements were performed using a ferroelectric tester (Precision Materials Analyzer, RADIANT TECHNOLOGIES, INC. USA) in combination with a high-voltage amplifier (EEL 1102.05.2,

ELECTRICAL ENERGY LIMITED, USA). The dynamic piezoelectric response of samples was tested by a home-made testing device as shown in Fig. S1. The samples were first sealed into a CR2032 cell to avoid any contact of moving friction. The force was provided by a LinMot linear motors (C1100-GP-XC-0S-000). The output voltage signal is recorded by a Keithley 6500 electrometer (DMM6500, Tektronix). Piezoelectric response force microscopy (PFM, Dimension ICON, Bruker) was used to detect the inverse piezoelectric coefficient (d_{33}) of the sample. Specifically, the sample is first prepared on a conductive substrate, which is grounded to the platform of PFM. Then, the measurement is operated in a contact mode by applying an additional alternating voltage to the conductive tip. The sample deformation caused by the voltage is monitored by the conductive tip and the resulting cantilever oscillation is measured by the locking amplifier. The d_{33} can be calculated by:

$$d_{33} = \frac{A - A_0}{V - V_0}$$

where A and V are the amplitude and voltage at the maximum amplitude change, and A_0 and V_0 are the amplitude and voltage at the intersection.

2. SUPPLEMENTARY FIGURES

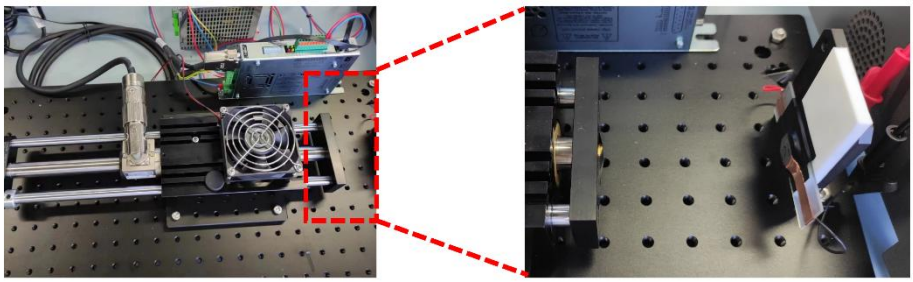

Fig. S1. The home-made dynamic piezoelectric testing apparatus

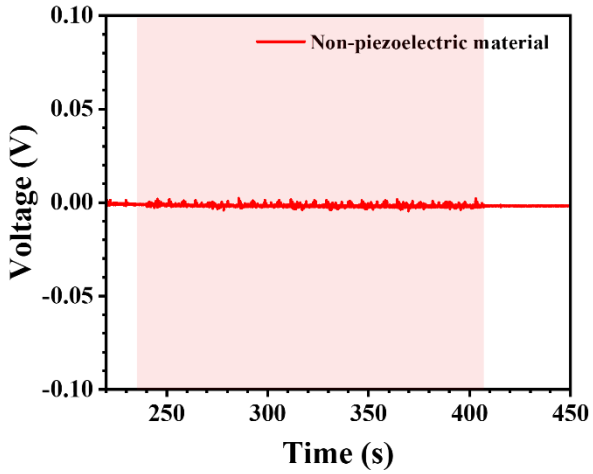

Fig. S2. The piezoelectric voltage of the non-piezoelectric film under a periodically applied force.

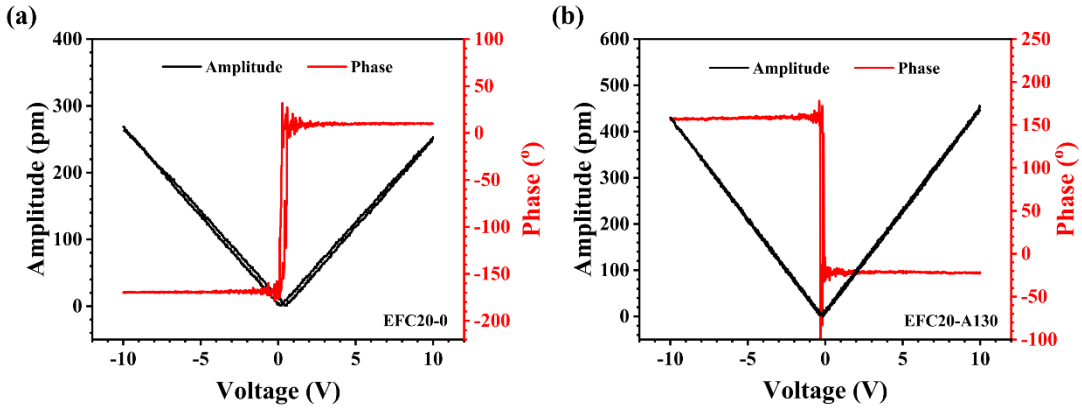

Fig. S3. Phase and amplitude loops of (a) EFC20-0 and (b) EFC20-A130.

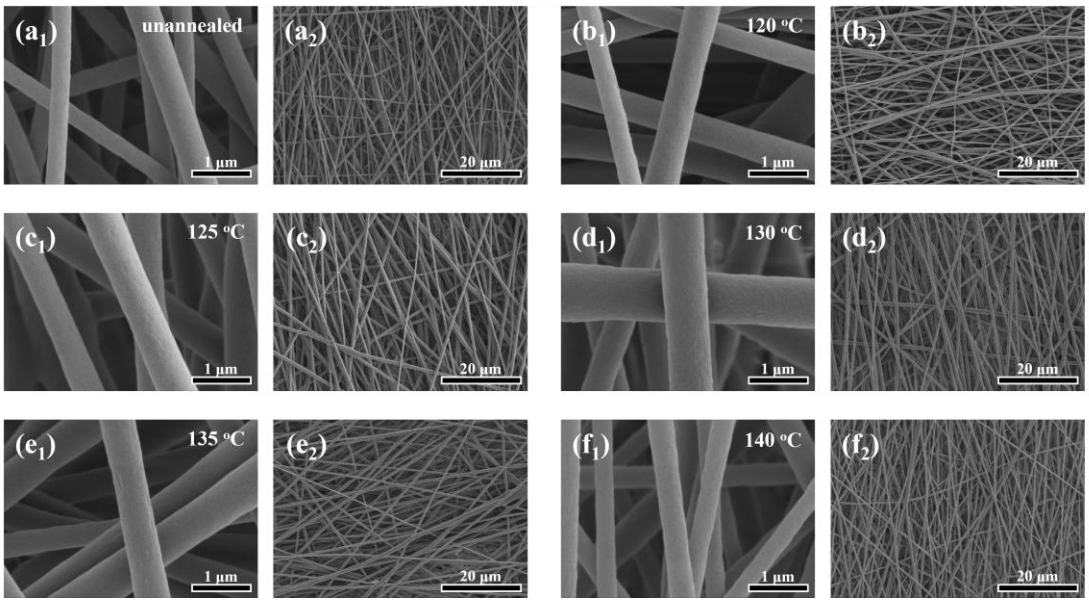

Fig. S4. Morphologies of (a) EFC20-0 and (b) EFC20-A130, (c) EFC20-A135, and (d) EFC20-A140 at different manifications.

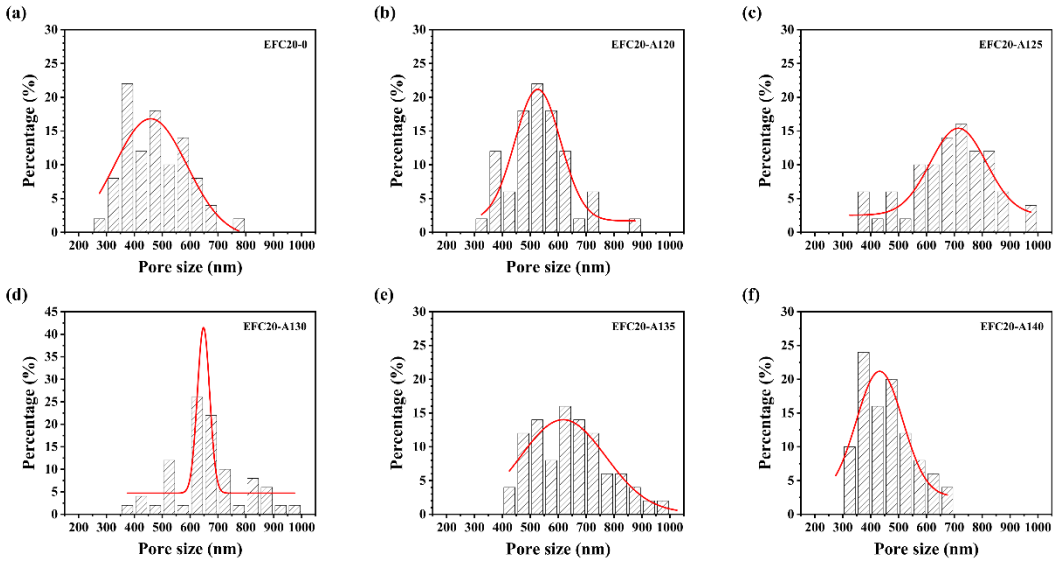

Fig. S5. Fiber diameter distribution statistics of (a) unannealed P(VDF-TrFE) nanofiber membranes and annealed at (b) 120°C, (c) 125°C, (d) 130°C, (e) 135°C and (f) 140°C electrospun membranes.

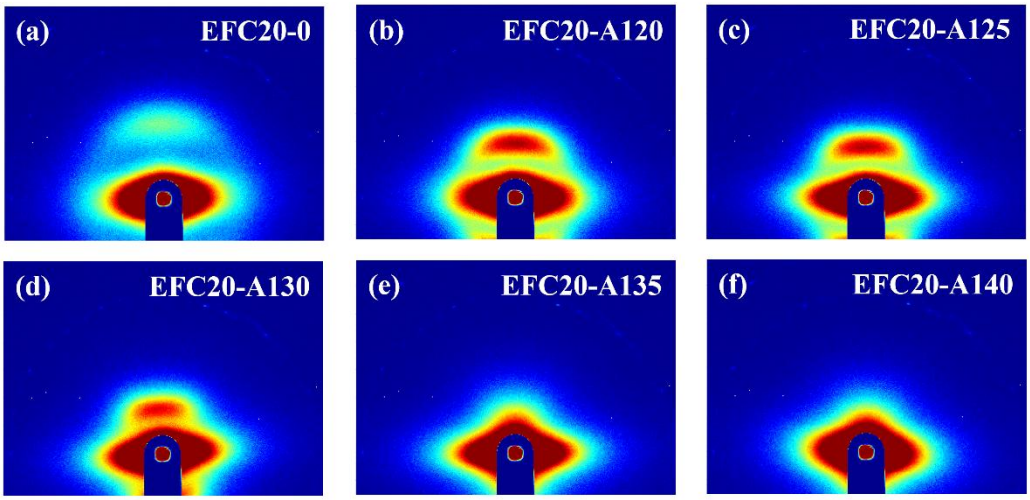

Fig. S6. 2D-SAXS plots of P(VDF-TrFE) nanofiber membranes before and after annealing heat treatment.

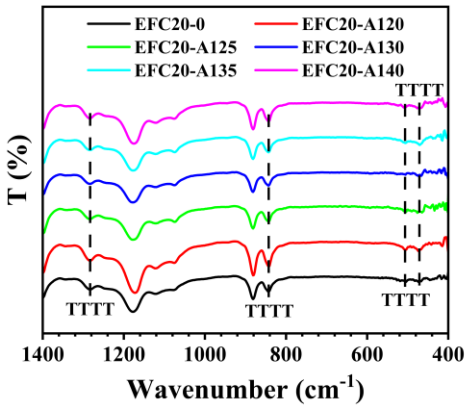

Fig. S7. FTIR of EFC20-0 and EFC20-Ax samples.

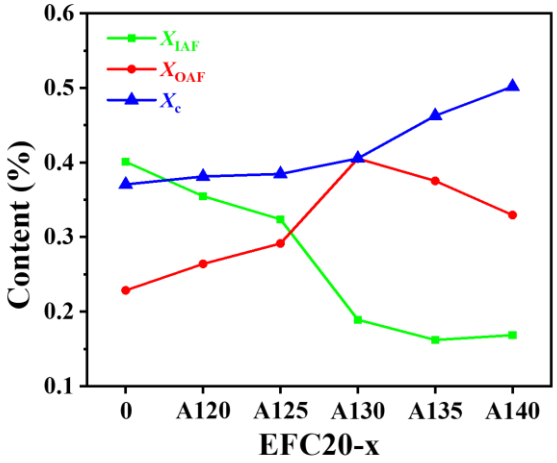

Fig. S8. Comparison of X_C, X_{IAF}, and X_{OAF} of EFC20 films before and after annealing.

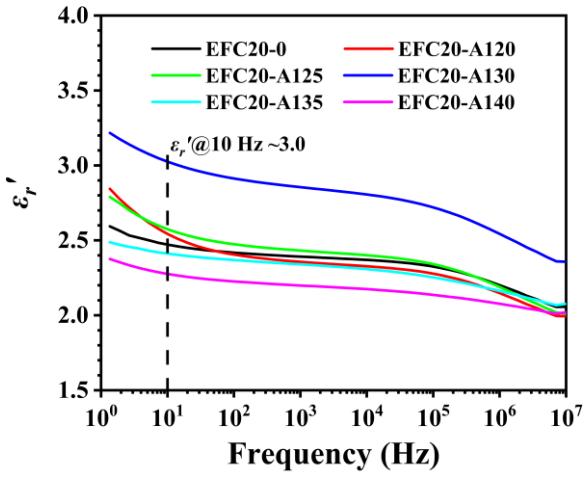

Fig. S9. BDS measurement of EFC20 films before and after annealing.

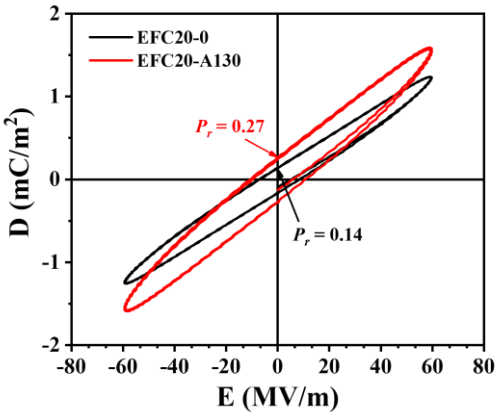

Fig. S10. *D-E* loop of P(VDF-TrFE) films before and after annealing at 130 °C under the electric field of 60 MV/m.

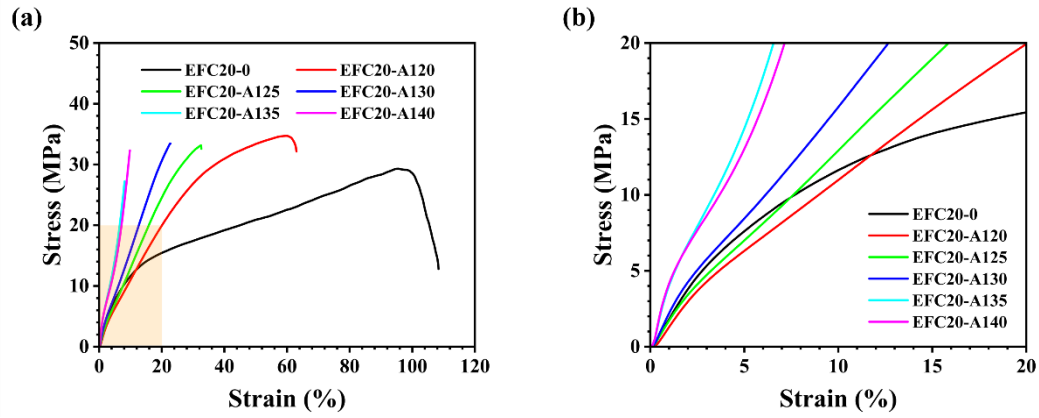

Fig. S11. (a) Mechanical properties of P(VDF-TrFE) nanofiber membranes before and after annealing heat treatment, (b) is an enlarged image of (a) orange dotted line.