Supporting Information

Highly elastic relaxor ferroelectrics for wearable energy storage

Experimental sections

Materials. The copolymer P(VDF-CTFE) 80/20 mol% was obtained from Arkema Piezotech. Dibenzoyl peroxide (BPO) and triallyl isocyanurate (TAIC) were purchased from Macklin and Meryer, respectively. Sodium hydroxide and acetone were obtained from National Medicines Group Chemical Reagent Co., Ltd. Triethylamine, *N,N*-dimethylformamide (DMF), ethanol, cyclohexanone, isophorone, and sulfuric acid were obtained from Aladdin. Gallium (Ga, liquid, 99.99%) and Sylgard ®™ 184 Silicone Elastomer Kit were purchased from Beijing Founde Star Sci. & Technol. Co. Ltd and Dow Chemical, respectively.

Synthesis of P(VDF-CTFE-DB). The synthesis procedure followed the reported method. Poly(vinylidene fluoride-chlorotrifluoroethylene) (P(VDF-CTFE)) copolymer (with 20 mol% CTFE) was procured from Piezotech/Arkema, France. In a 500 mL Schlenk flask, 18.29 g of P(VDF-CTFE) and 146 ml of dimethylformamide (DMF) were added. The mixture was heated and stirred in a 60 °C oil bath until the polymer completely dissolved. Subsequently, 15 ml of triethylamine was added, and the solution was stirred for 24 hours at 65 °C. After the reaction, 146 ml of DMF was added to dilute the solution. The diluted solution was then dropwise added to water with continuous stirring, resulting in the formation of flocculent precipitates. The precipitates were collected, dried, and subjected to Soxhlet extraction with ethanol for 24 hours, followed by vacuum drying at 80 °C for 8 hours. The brownish product obtained had a yield of approximately 82.56%. ^{1}H NMR was used to determine the copolymer's composition **Fig. S1.**

Thick-Film Preparation. A solution containing 200 mg of P(VDF-CTFE-DB) and varying amounts of BIPB and TAIC was prepared in 1 mL acetone using a vortex oscillator, with a feeding ratio of BPO to TAIC at 5:4. The crosslinking density in the article is defined as the mass ratio of BIPB to P(VDF-CTFE-DB). The resulting solution was drop-cast onto an OTS (octa-decyl trichlorosilane)-modified glass substrate in a fume hood and allowed to naturally dry for 24 h. After most of the solvent had volatilized, the film underwent further drying under vacuum at room temperature for 8 h, followed by crosslinking at 120 °C on heating panels in the air for 1 h. The resulting thick film was employed for mechanical measurements and other characterizations, including DSC (differential scanning calorimetry), DMA (dynamic mechanical analysis), FTIR, XRD, and gelation con-tent measurement.

Thin-Film Preparation. A solution containing 100 mg of P(VDF-CTFE-DB), 12 mg of BPO, and 9.6 mg of TAIC in 1 mL acetone was prepared. The solution was dropped onto an Au/Si wafer (10 mm × 10 mm), and spin-coating was performed at 500 rpm for 10 s and 2000 rpm for 35 s to create a uniform film. The film was left to air-dry naturally for 12 h, and after most of the solvent had volatilized, the film underwent further drying in a vacuum oven at room temperature for 8 h before being crosslinked at 120 °C on heating panels in the air for 1 h. Au electrodes, with a diameter of 200 μm and a thickness of 100 nm, were deposited via magnetron sputtering to form an Au/crosslinked P(VDF-CTFE-DB)/Au/Si structure. A control sample of pristine P(VDF-CTFE-DB) thin films for use in rigid devices (Au/P(VDF-CTFE-DB)/Au/Si) was also prepared using the same method. The resultant thin films were used for $P-E$ hysteresis loop tests and PFM characterization.

Preparation of fully elastic device Measurements. The Si/SiO$_2$ wafer underwent initial cleaning with oxygen plasma (150 W, 3 min). A dextran solution (10 wt% in water) was then spin-coated onto the wafer at 600 rpm for 10 s and at 1500 rpm for 40 s. The wafer was subsequently baked on a hot plate at 80 °C for 10 min and at 180 °C for 30 min to eliminate trapped water. A solution containing 100 mg of pristine

P(VDF-TrFE-DB), 12 mg of BPO, and 9.6 mg of TAIC in 1 mL acetone was prepared. The solution was spin-coated on top of the glucan layer at 500 rpm for 10 s and at 2000 rpm for 35 s. The film was left to dry naturally for 12 h, after most of the solvent had volatilized, the film underwent further drying in a vacuum oven at room temperature for 8 h and was subsequently crosslinked at 120 °C on a heating panel in the air for 1 h. After cooling to room temperature, liquid metal (LM, gallium (Ga)) was stencil printed on the surface of the crosslinked P(VDF-TrFE-DB) film to form strip electrode patterns, which were then encapsulated by Sylgard®™ 184 Silicone Elastomer (silicone elastomer base and curing agent were mixed at a ratio of 10:1) (PDMS) by spin-coating at 1500 rpm for 35 s. After curing at 50 °C 4 hours, the resultant film (thickness: ~100 μm) was placed in deionized water for 20 mins to dissolve the glucan layer and then was peeled off from the Si/SiO$_2$ substrate. A layer of LM (Ga) was then brushed in a direction perpendicular to the previous LM (Ga) electrode to form a Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS sandwich structure for a fully elastic capacitive array.

Measurement methods

^{1}H NMR measurement and high-resolution mass spectroscopy. ^{1}H NMR spectra were acquired using a Bruker 600 MHz spectrometer (Advance NEO 600, Switzerland). The acquisition involved 128 scans for each spectrum. High-resolution mass spectrometry was conducted using liquid chromatography-quadrupole time-of-flight tandem mass spectrometry (LC-Q-TOF-MS,4600, AB Sciex, USA) with methanol as the solvent.

Strain-stress measurements. The mechanical properties of the samples were assessed through strain–stress analysis using an Instron-5943 instrument. The initial dimensions of the film were set to 10 mm in length and 3 mm in width. A stretching rate of 4 mm/min was consistently applied for all stress–strain curves. Additionally, cyclic stretching curves shown in **Fig. 2D** were obtained with over 3000 repetitions utilizing a Cell Scale instrument (Univert S2, Canada).

DSC analysis. Differential scanning calorimetric (DSC) analysis was conducted on a DSC calorimeter (214, Netzsch, Germany) in a nitrogen atmosphere at a scanning rate of 10 °C/min during the heating and cooling cycles.

FTIR. Micro-infrared absorption spectra of the films were recorded using a microscopic infrared spectrometer (Cary660, Agilent, USA). The number of scans was set to 32 for enhanced accuracy.

X-ray diffraction. High-resolution X-ray diffraction measurements (Theta-2theta) were conducted using an X-ray Powder diffractometer (D8 ADVANCE DAVINCI, Bruker, Germany). The X-ray wavelength utilized was 1.54 Å (Cu Kα radiation, 40 kV, and 100 mA), and the scanning rate was maintained at 4 °/min.

P–E hysteresis loop. Electric P–E hysteresis loops at room temperature were acquired using a Premiere II ferroelectric tester from Radiant Technologies, Inc., USA. AC electric fields with increments of 50 MV/m were applied across the polymer films with a triangular waveform in the frequency range of 100 Hz to 10 kHz. Film thicknesses at three points were measured using a surface profiler (Dektak XT, Bruker, USA) to obtain the average thickness.

PFM characterization. PFM morphologies were characterized using a Scanning Probe Microscope (Dimension ICON, Bruker, USA).

Dynamic mechanical analysis. To discern the individual contributions of energy elasticity and entropy elasticity, the stress-temperature relationship of crosslinked P(VDF-CTFE-DB) was obtained using a dynamic mechanical analyzer (DMAQ800, TA instruments, America) within a specific temperature range.

Supplementary notes

The phase determination of P(VDF-CTFE-DB) and crosslinked P(VDF-CTFE-DB) using FTIR is summarized as follows:

1. For pristine P(VDF-CTFE-DB), the main phases are: α-phase: 761, 977 cm⁻¹; β-phase: 1272 cm⁻¹; γ-phase: 811, 831 cm⁻¹. Since no characteristic peak of the β-phase is observed at 840 cm⁻¹, the phase content is calculated assuming the sample contains only α- and γ-phases. The fraction of γ-phase (F(γ)) can be calculated using the following equations: $F(\gamma) = \dfrac{A_\gamma}{\left(\frac{k_\gamma}{k_\alpha}\right)A_\alpha + A_\gamma} \times 100\%$, where A_α and A_γ are the absorbance intensity at 761 and 832 cm⁻¹, respectively. K_α and K_γ are the corresponding absorbance coefficients, 0.365 and 0.150 μm⁻¹, respectively. The fraction of α-phase (F(α)): F(α)=1− F(γ). Using this method, we found that the main phases in pristine P(VDF-CTFE-DB) are α-phase and γ-phase, with respective contents of 14.70% and 85.30%.

2. For crosslinked P(VDF-CTFE-DB), the main phases are: α-phase: 761, 977 cm⁻¹; β-phase: 1272, 840 cm⁻¹; γ-phase: 811, 831 cm⁻¹. Since the characteristic peak of the γ-phase at 1234 cm⁻¹ is absent, the γ-phase content is considered negligible, and the calculation is performed assuming the sample contains only α- and β-phases. The fraction of β-phase (F(β)) can be calculated using the following equations: $F(\beta) = \dfrac{A_\beta}{\left(\frac{k_\beta}{k_\alpha}\right) \cdot A_\alpha + A_\beta} \times 100\%$, where A_α and A_β are the absorbance at 761 and 840 cm⁻¹, respectively. K_α and K_β are the corresponding absorbance coefficients, 6.1 ×10⁴ and 7.7 × 10⁴ cm² mol⁻¹, respectively. The fraction of α-phase (F(α)): F(α)=1− F(β). Using this method, we determined that the main phases in crosslinked P(VDF-CTFE-DB) are α-phase and β-phase, with respective contents of 47.48% and 52.52%.
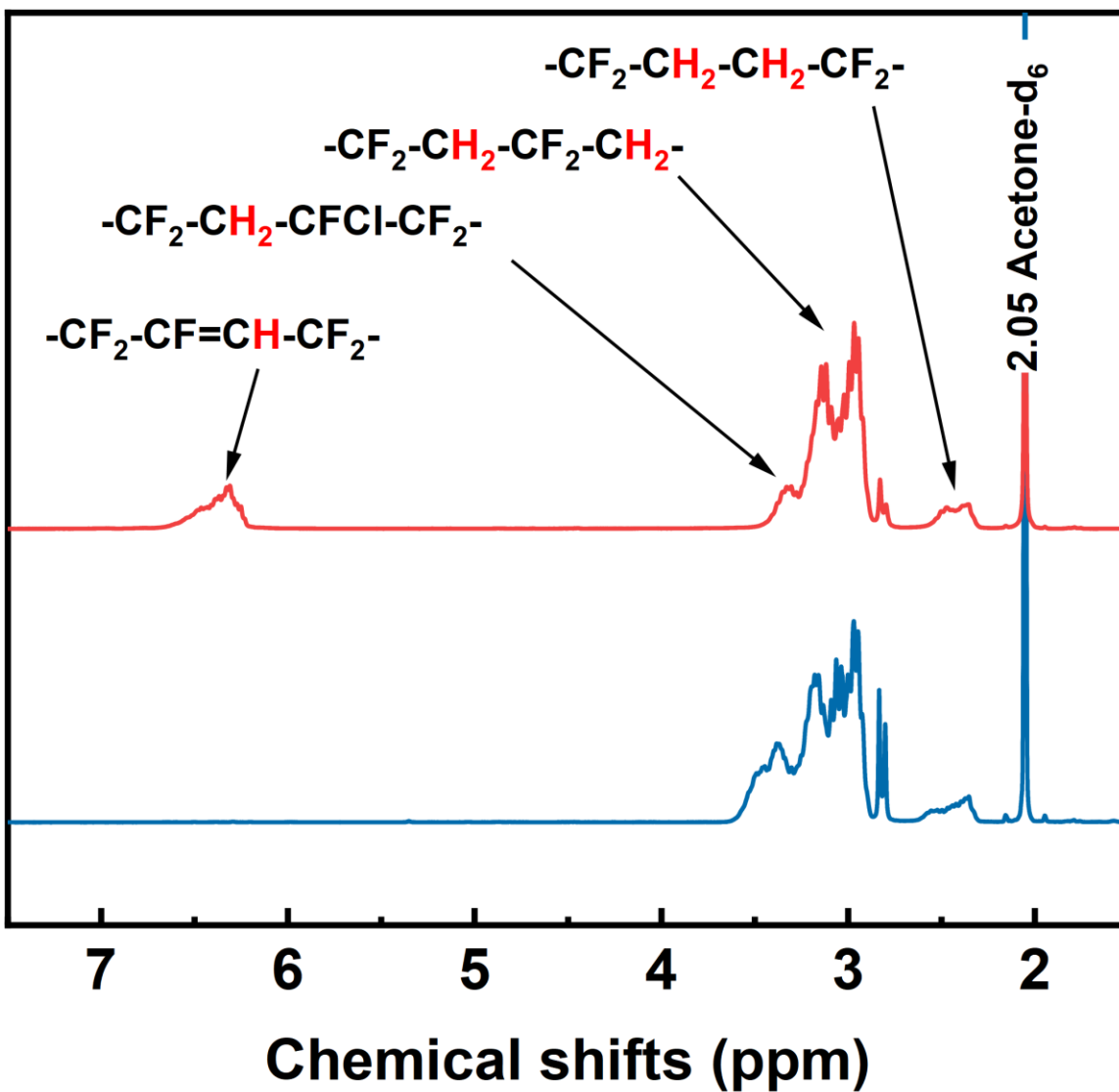
Figure S1. ^{1}H NMR spectra of P(VDF-CTFE) and pristine P(VDF-CTFE-DB) in actone-d_6.
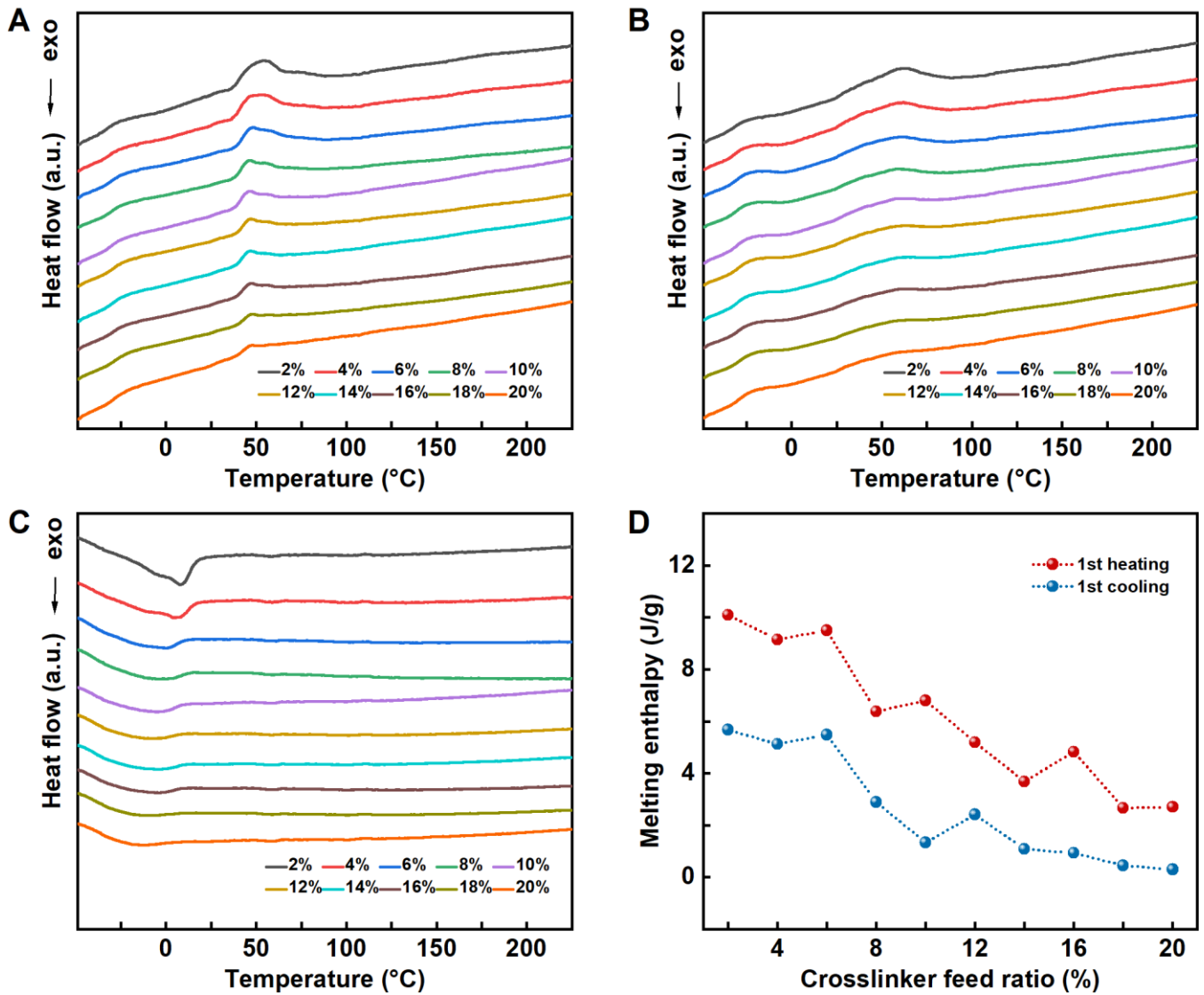
Figure S2. DSC curves corresponding to (a) first heating, (b) first cooling, (c) second heating, and (d) melting enthalpy of crosslinked P(VDF-CTFE-DB) films with different BPO ratios.
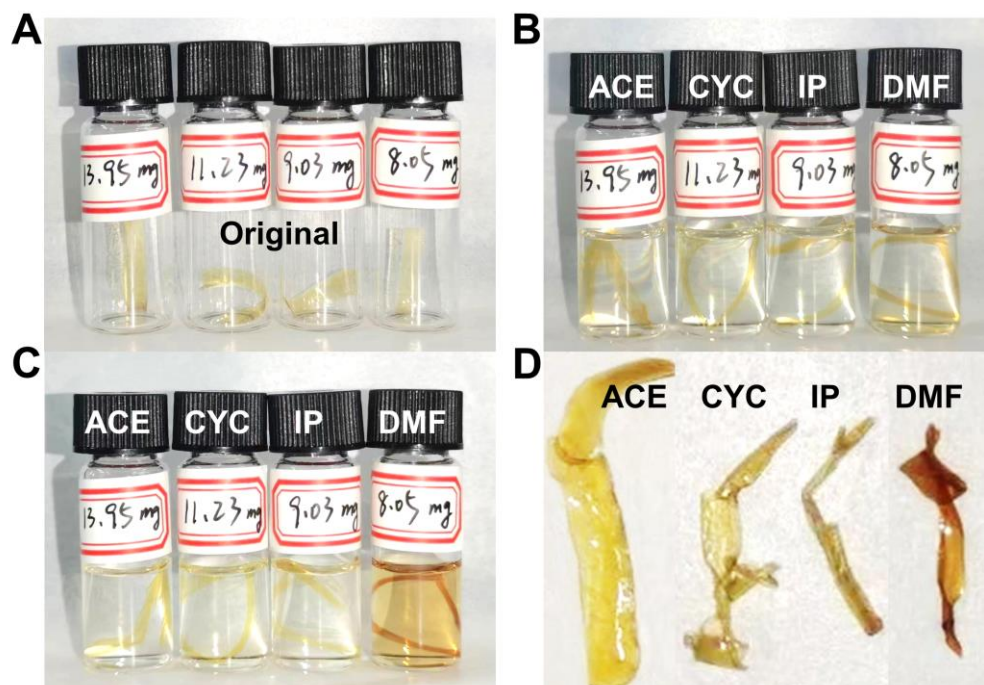
Figure S3 Photos of crosslinked P(VDF-CTFE-DB) films immersed in different solvents for different times: (A) before soaking; (B) after soaking in solvents for 30 min; (C) after soaking in solvents for 15 days; (D) after drying.

Table S1. The gel content of crosslinked P(VDF-CTFE-DB) immersed in different solvents

Solvent	Original mass /mg	Final mass /mg	Ratio of gel
ACE	13.59	12.23	89.99%
CYC	11.23	9.94	88.51%
IP	9.03	8.47	93.80%
DMF	8.05	6.78	84.22%

ACE: acetone; CYC: cyclohexanone; IP: isophorone; DMF: *N,N*-dimethylformamide
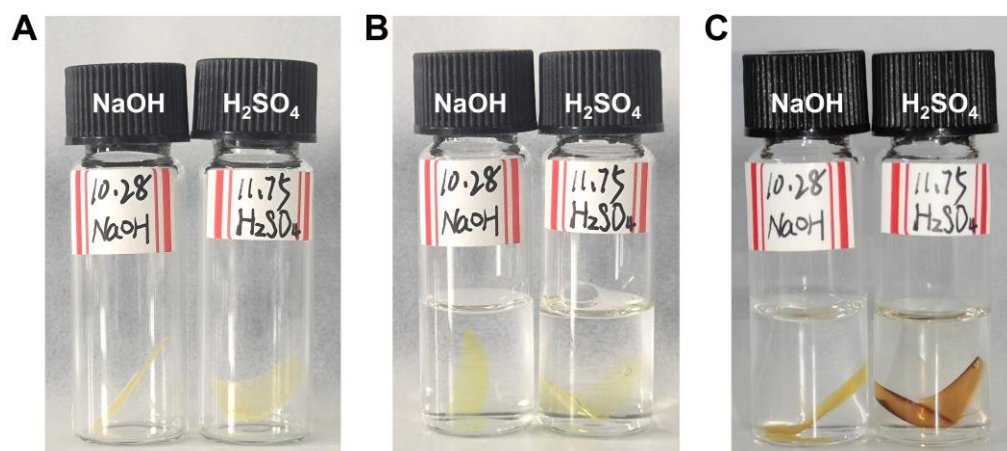
Figure S4 Photos of crosslinked P(VDF-CTFE-DB) films immersed in H_2SO_4 (98%) and saturated NaOH aqueous solution for different times: (A)before soaking; (B)after soaking in solvents for 30 min; (C)after soaking in solvents for 15 days.
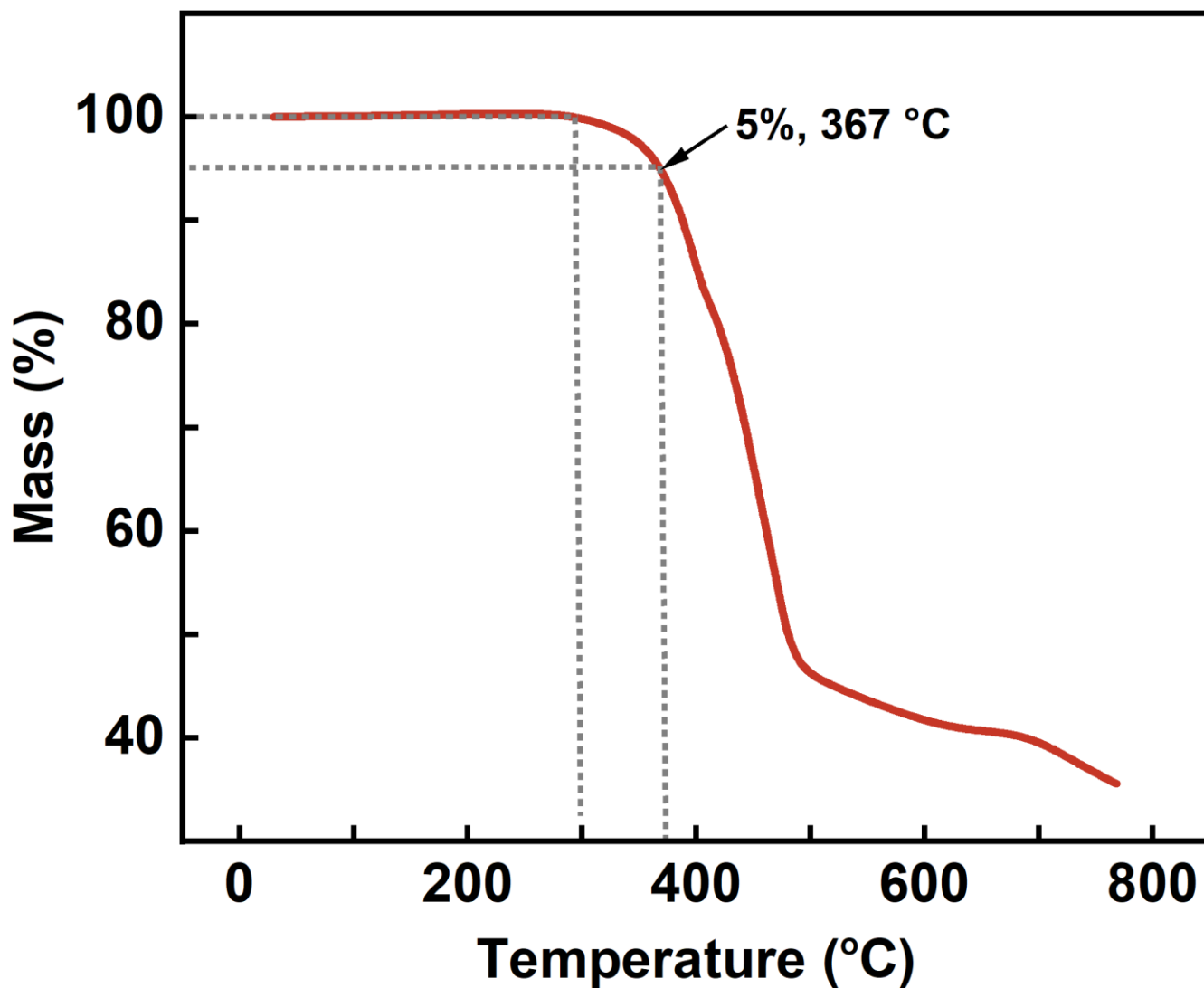
Figure S5. Thermogravimetric diagram of the crosslinked P(VDF-CTFE-DB) film with a crosslinking density of 10%.

Table S2. FTIR characteristic peaks of P(VDF-CTFE-DB) and crosslinked P(VDF-CTFE-DB)

Name	α/cm^{-1}	β/cm^{-1}	γ/cm^{-1}
P(VDF-CTFE-DB)	977,761	1272	811,831
C-P(VDF-CTFE-DB)	977,761	1272,840	811,831
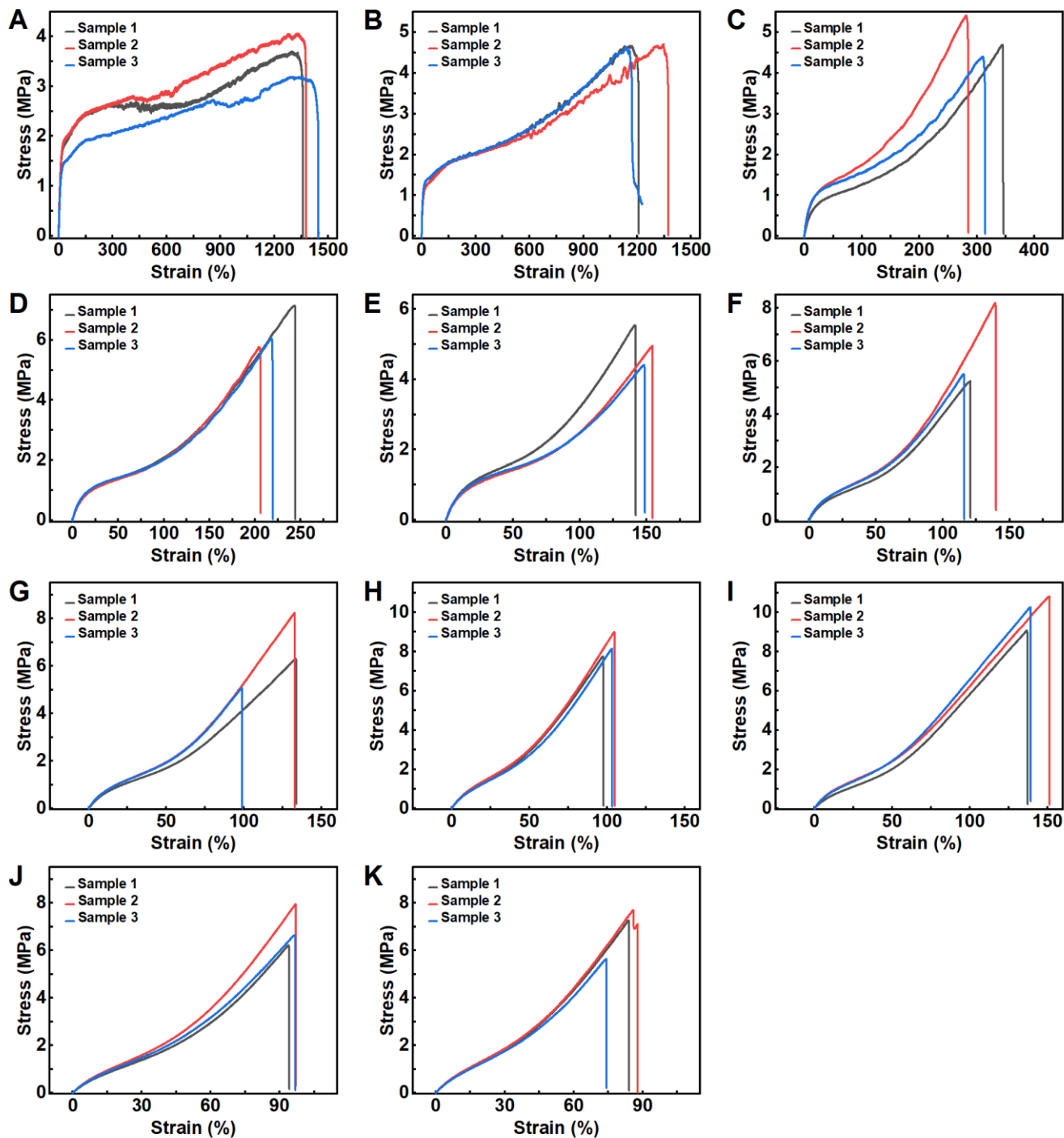
Figure S6. Stress–strain curves of pristine (A) and crosslinked P(VDF-TrFE-DB) thick films at various BPO ratios of 2% (B), 4% (C), 6%(D), 8%(E), 10% (F), 12% (G), 14% (H), 16% (I), 18% (J), and 20% (K).
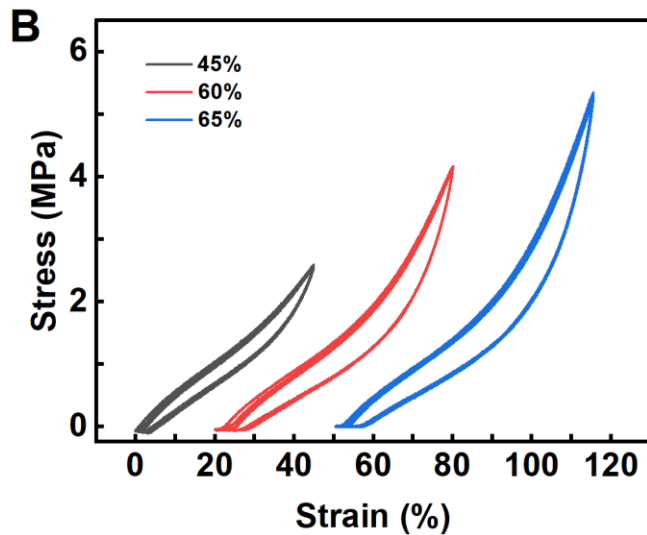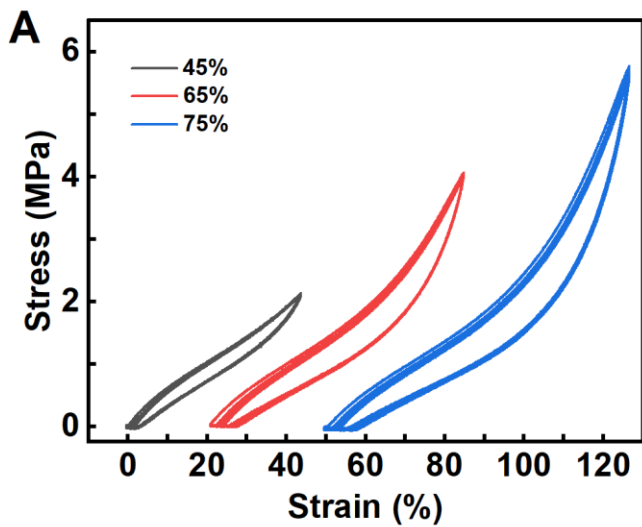
Figure S7. Cyclic stress-strain curves of the crosslinked P(VDF-CTFE-DB) films with a BIPB ratio of 12% (A) and 18% (B).
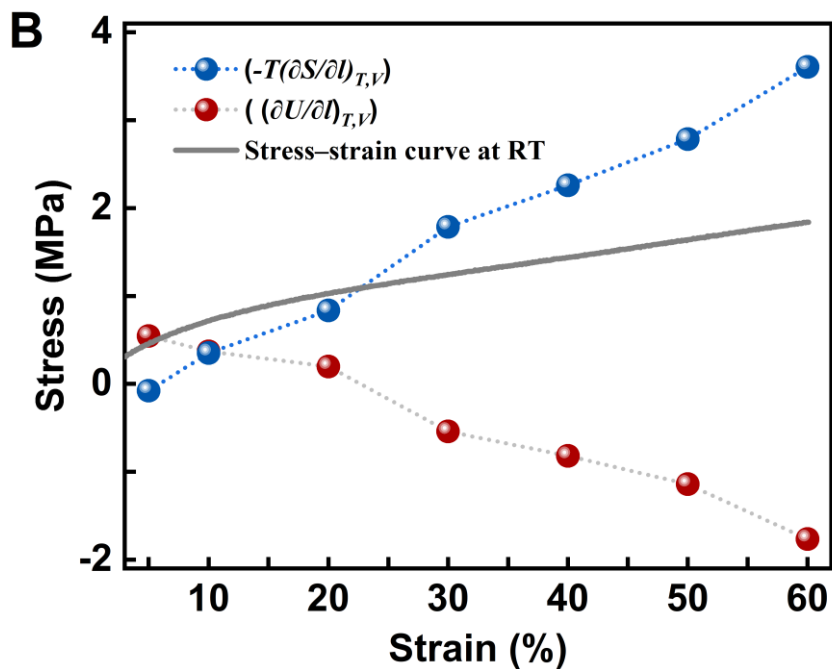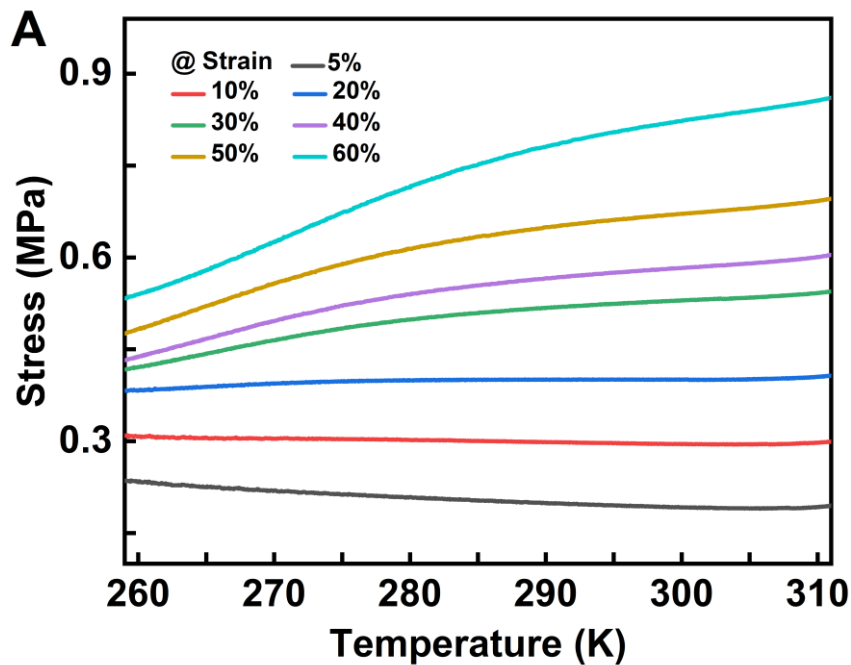
Figure S8. Contributions of energy elasticity and entropy elasticity in crosslinked P(VDF-CTFE-DB). (a) Force-temperature relationships (*f–T* curves) of crosslinked P(VDF-CTFE-DB) film under various strain. (b) Internal energy and entropy contributions of tensile stress as functions of strain for crosslinked P(VDF-CTFE-DB) film, compared to the stress–strain curves at room temperature.
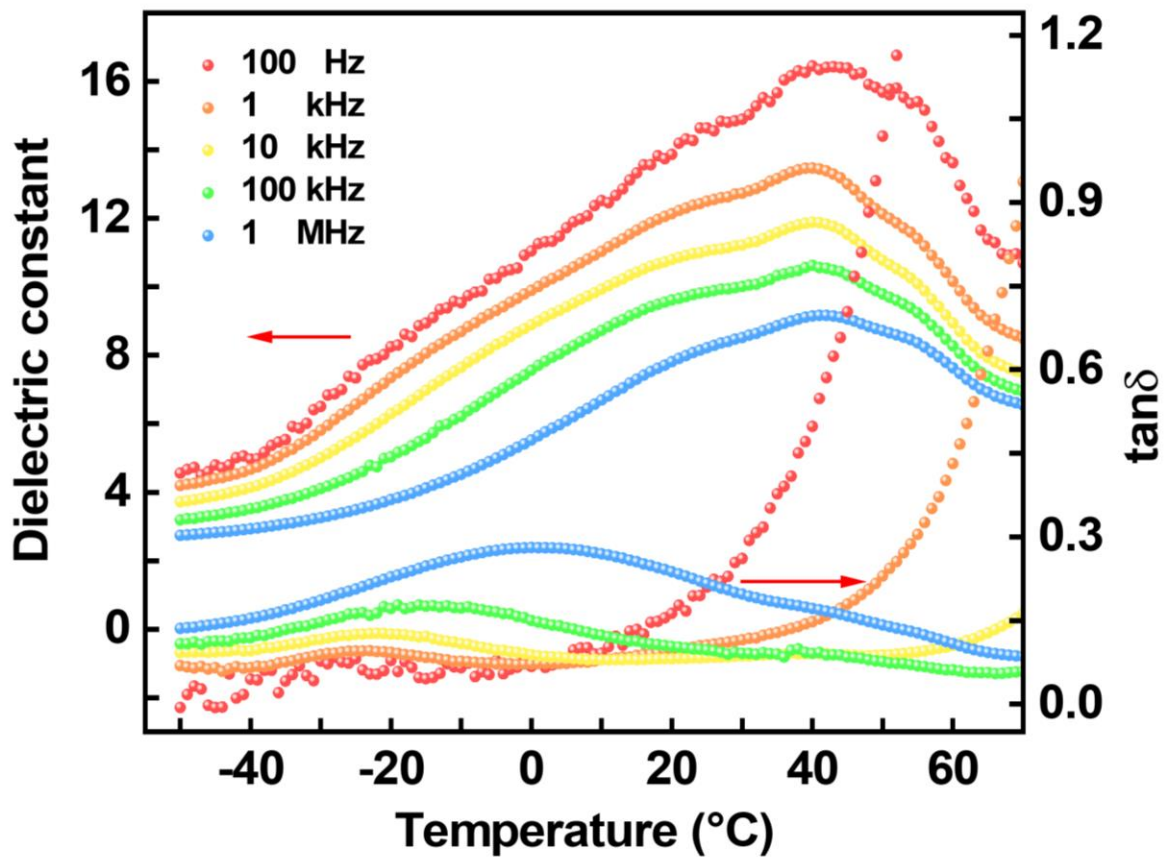
Figure S9. Temperature-dependent ε of pristine P(VDF-TrFE-DB) films at different frequencies.
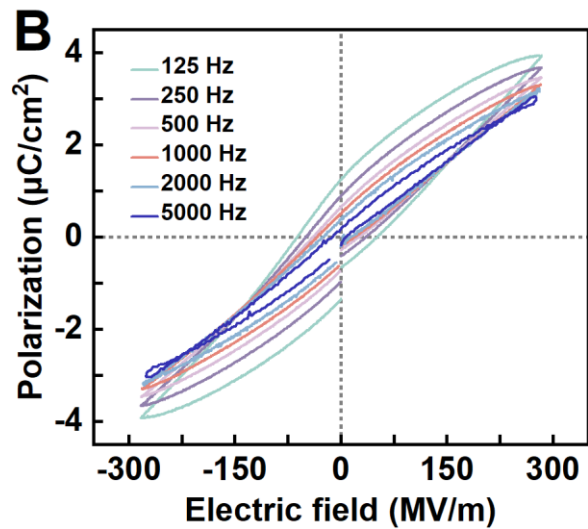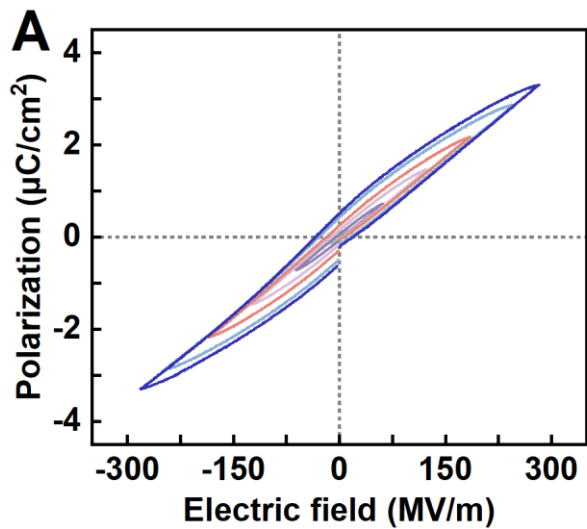
Figure S10. P–E loops of pristine P(VDF-CTFE-DB) under increased electric fields at 1000 Hz (A) and with increased frequencies (B).
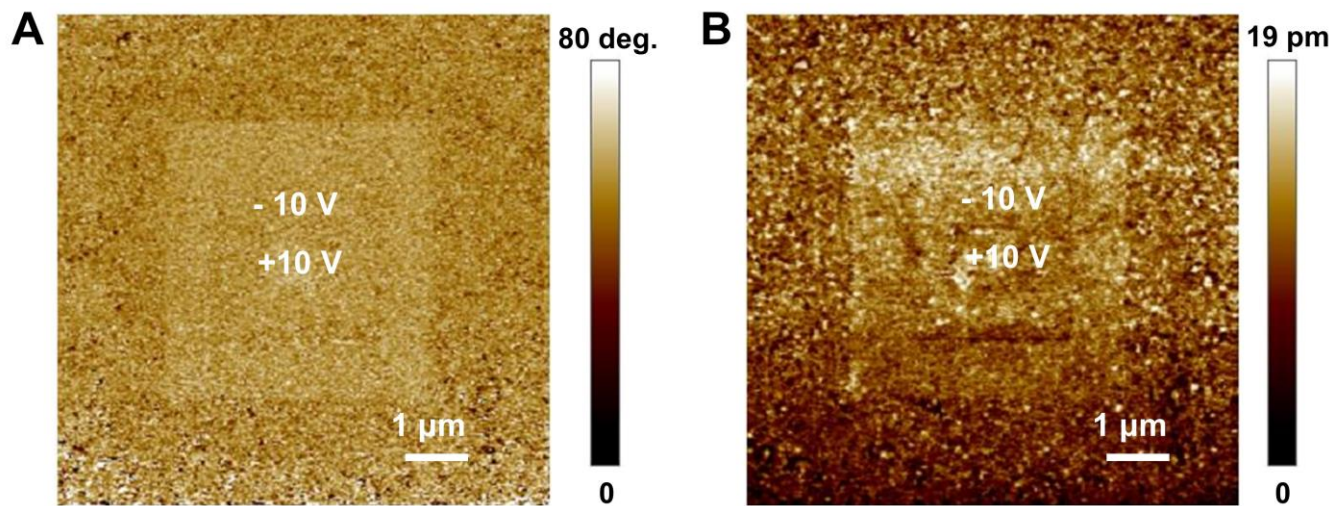
Figure S11. PFM of pristine P(VDF-CTFE-DB). (A) Phase and (B) amplitude mapping.
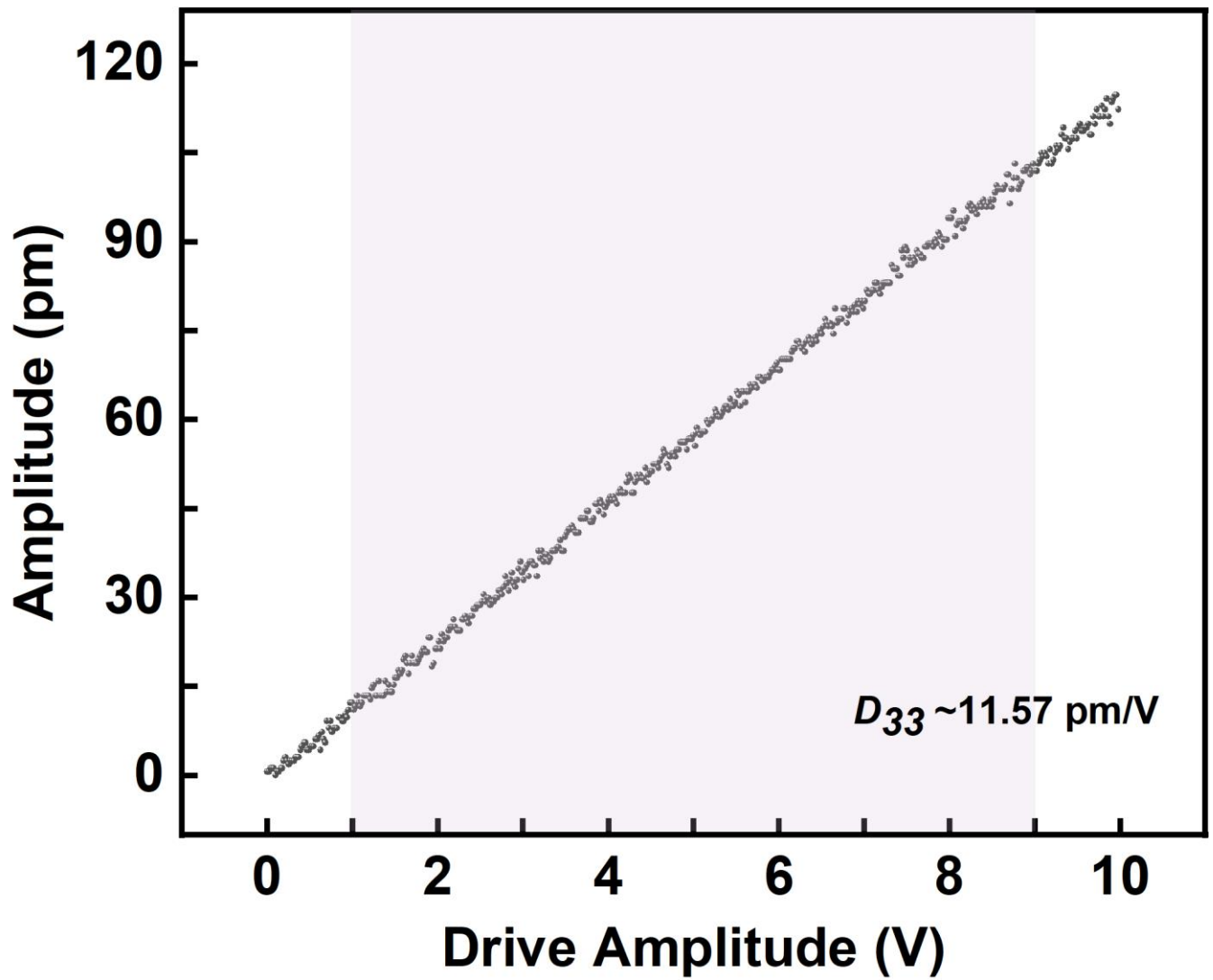
Figure S12. Response amplitude versus drive amplitude of the crosslinked P(VDF-CTFE-DB) thin film. Insert shows the piezoelectric coefficient (d_{33}).
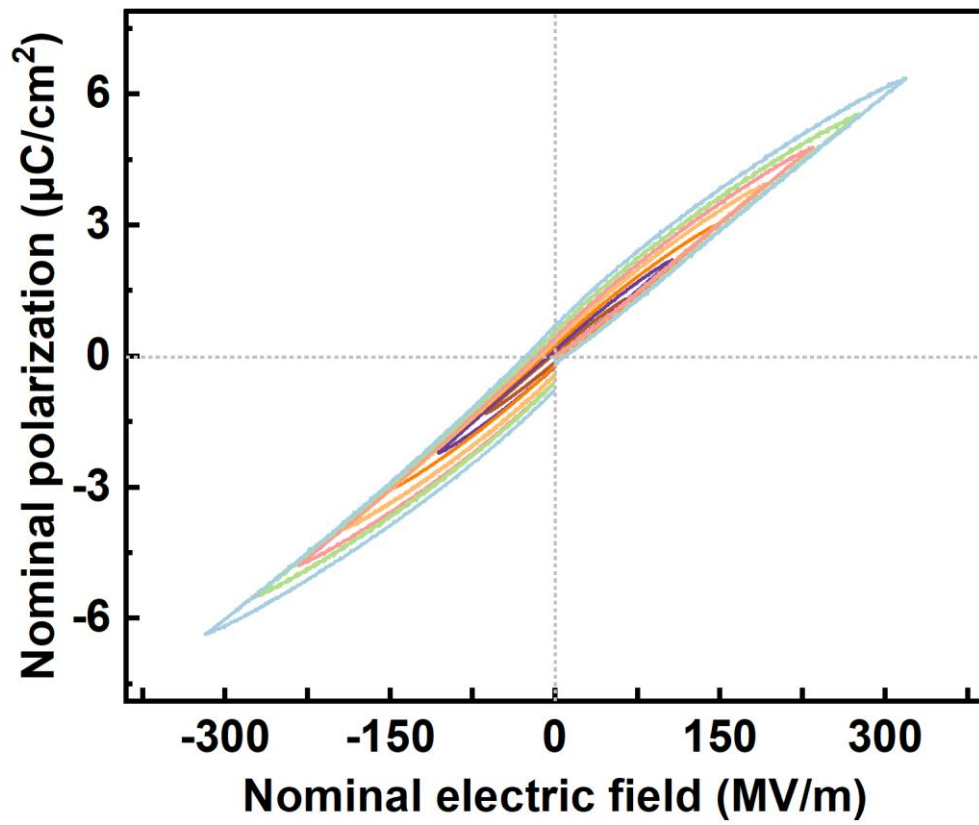
Figure S13. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS without stress at 1000 Hz.
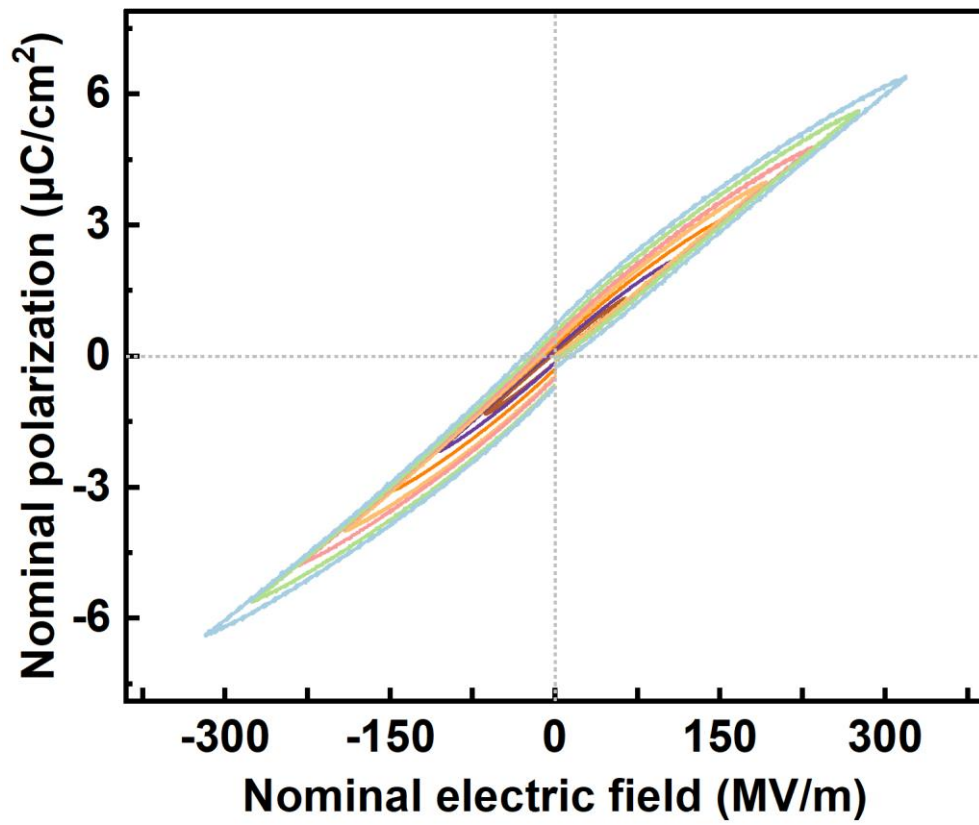
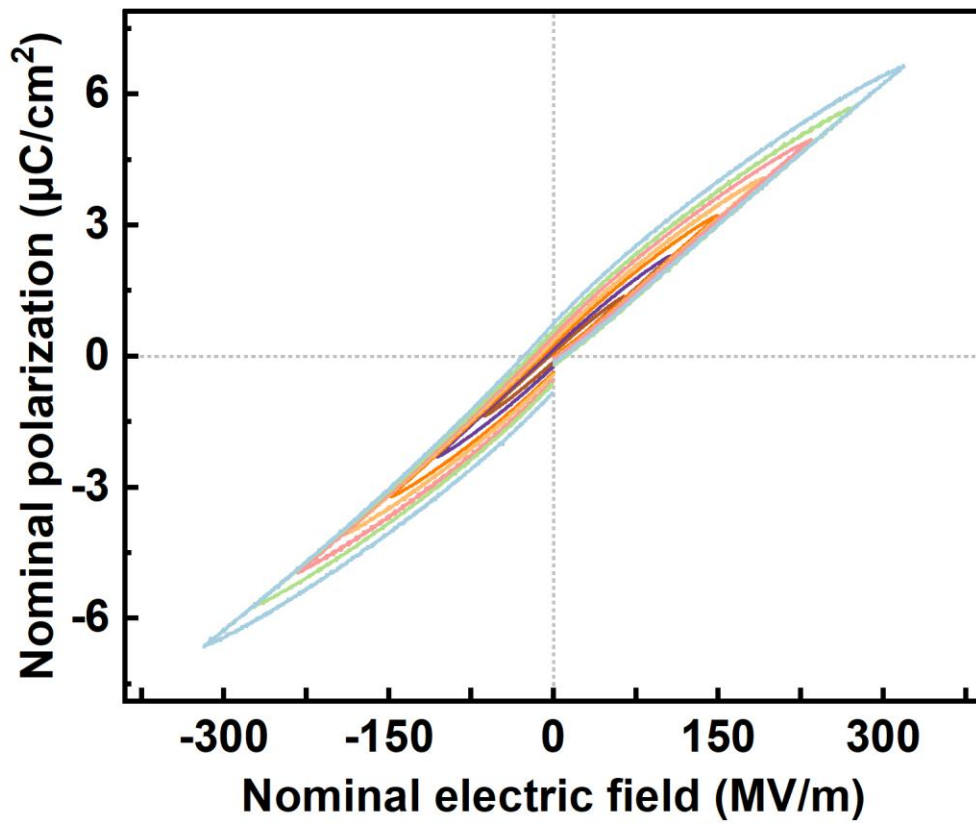**Figure S14.** *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 10% tensile strain at 1000 Hz.
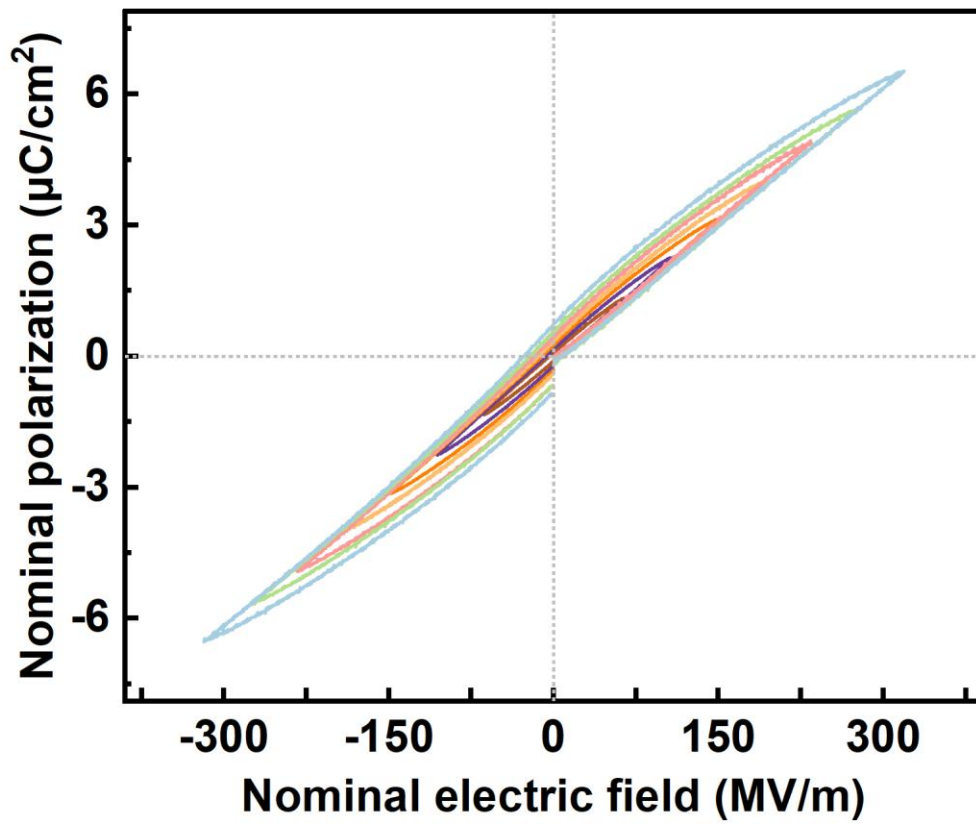
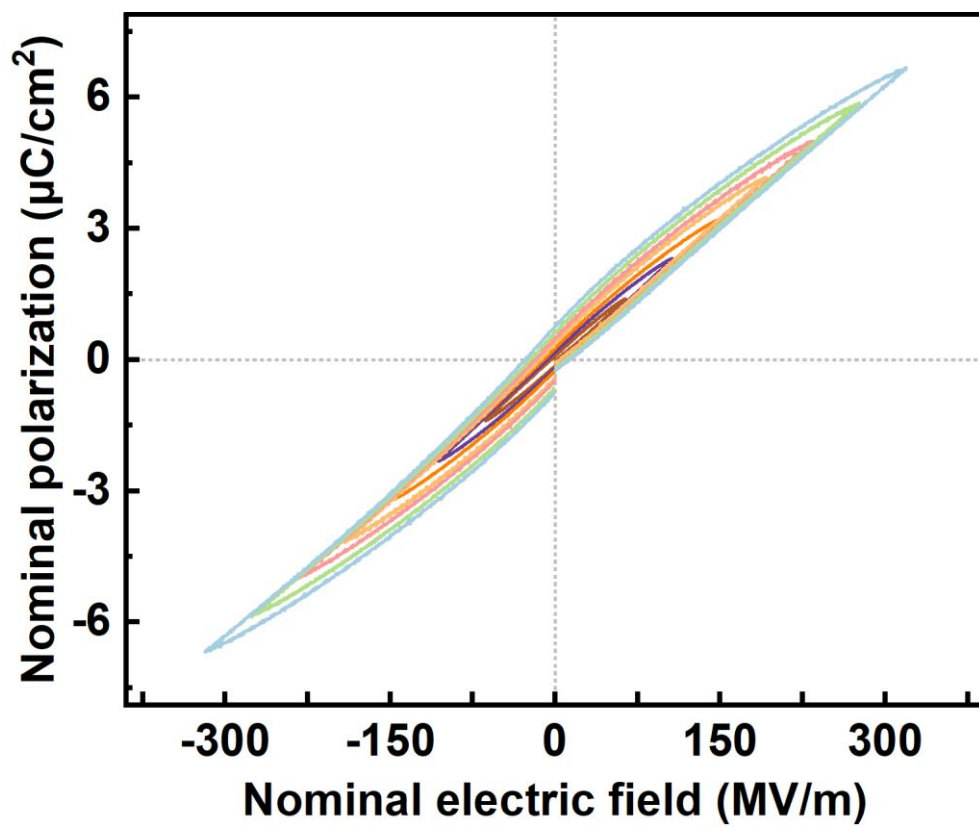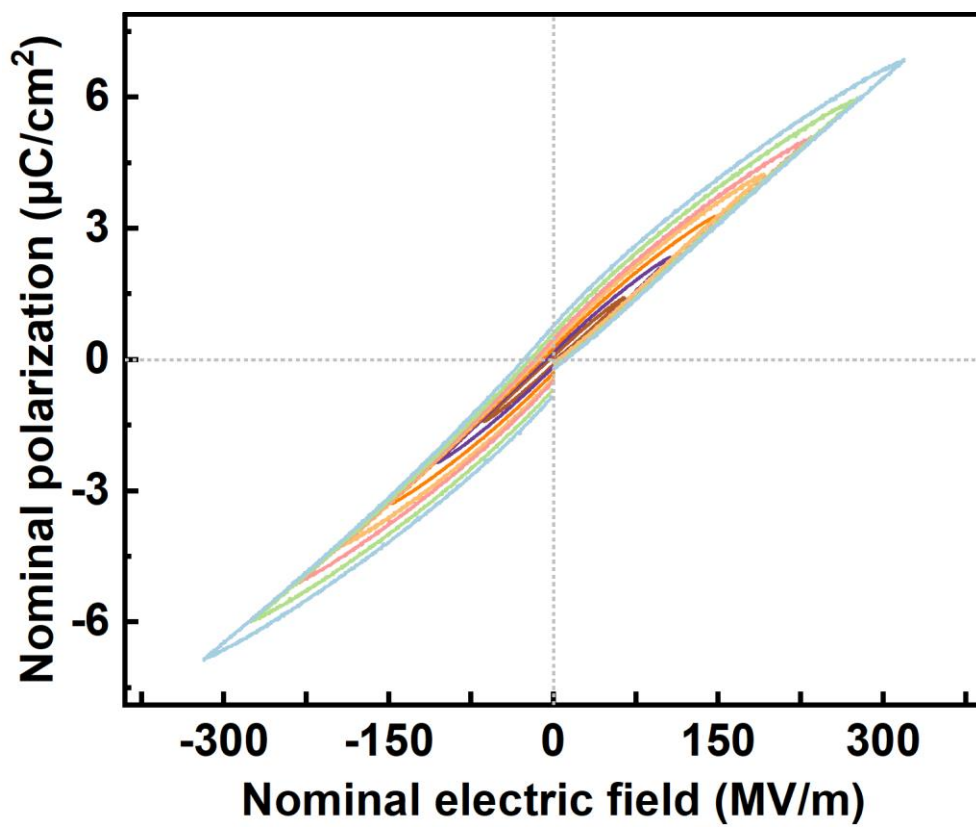**Figure S15.** *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 20% tensile strain at 1000 Hz.
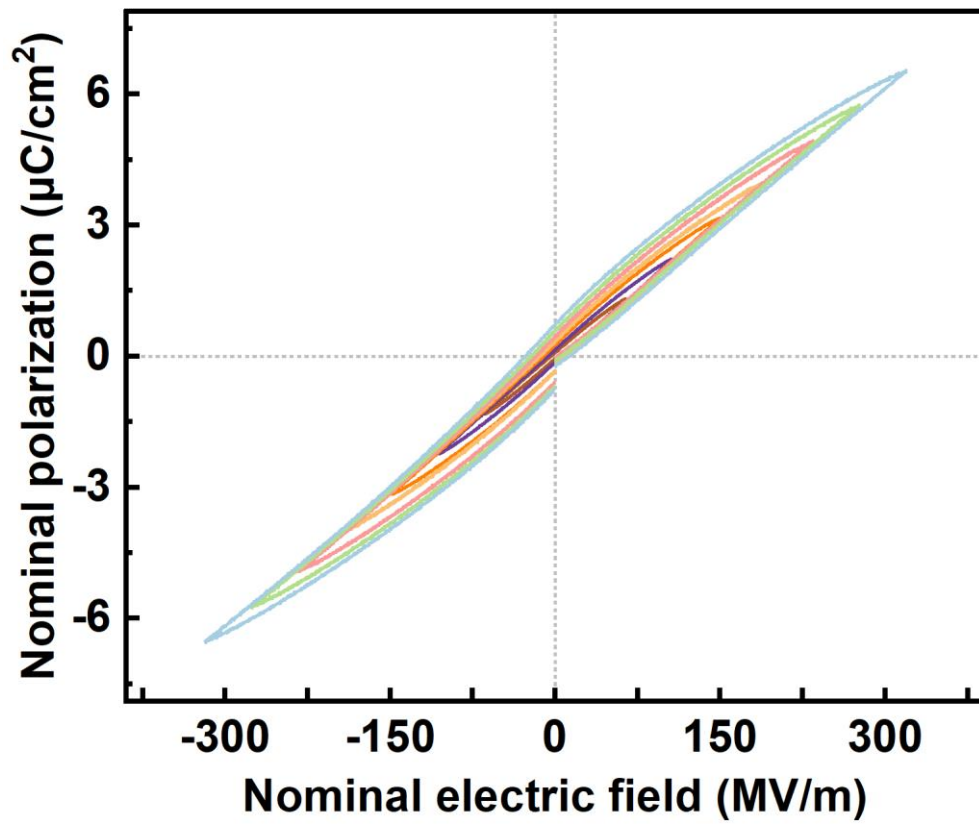
Figure S16. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 30% tensile strain at 1000 Hz.

Figure S17. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 40% tensile strain at 1000 Hz.
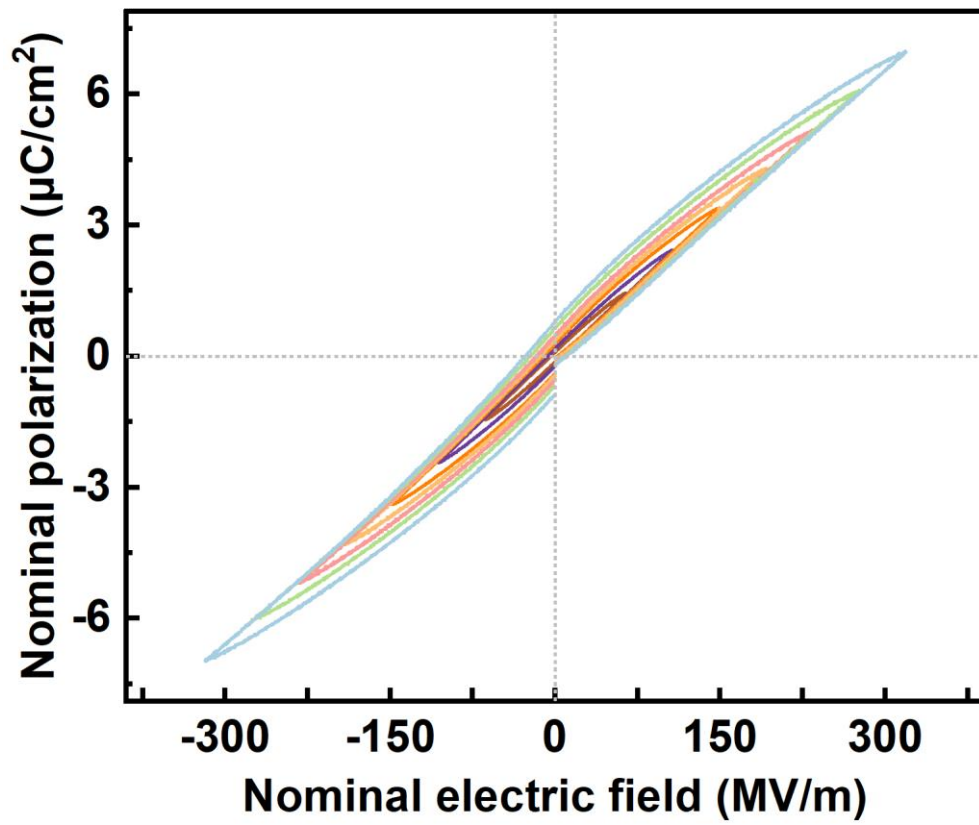
Figure S18. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 50% tensile strain at 1000 Hz.

Figure S19. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 60% tensile strain at 1000 Hz.

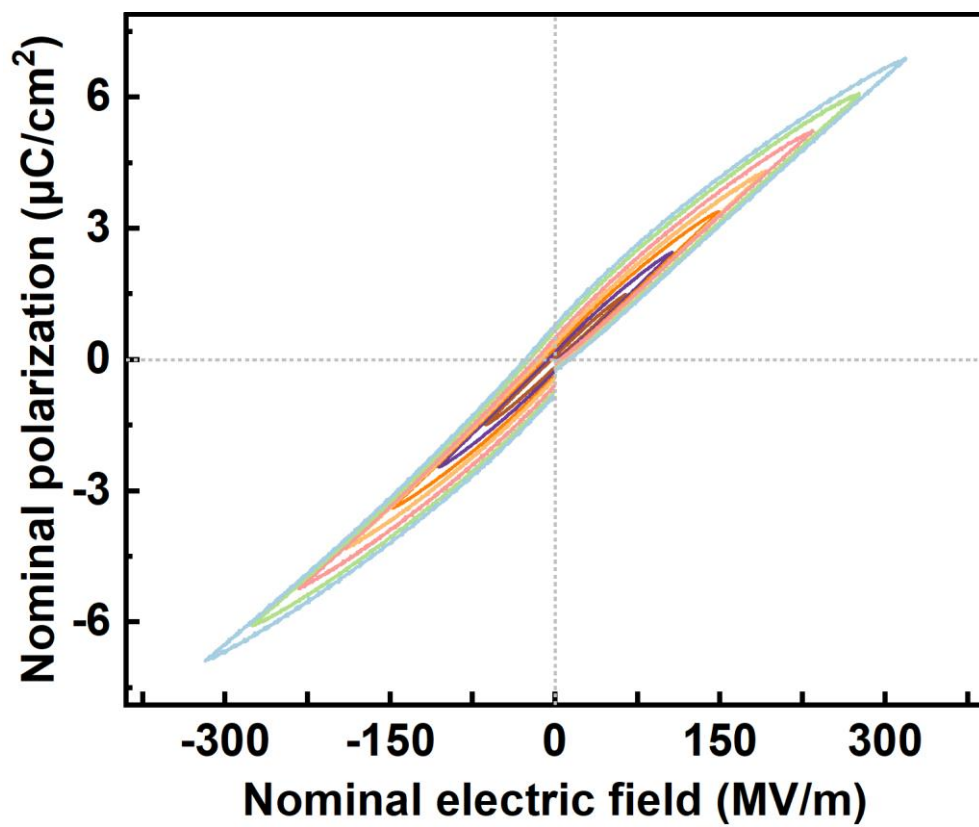**Figure S20.** *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 70% tensile strain at 1000 Hz.

Figure S21. *P–E* hysteresis loops of Ga/crosslinked P(VDF-CTFE-DB)/Ga/PDMS under 80% tensile strain at 1000 Hz.
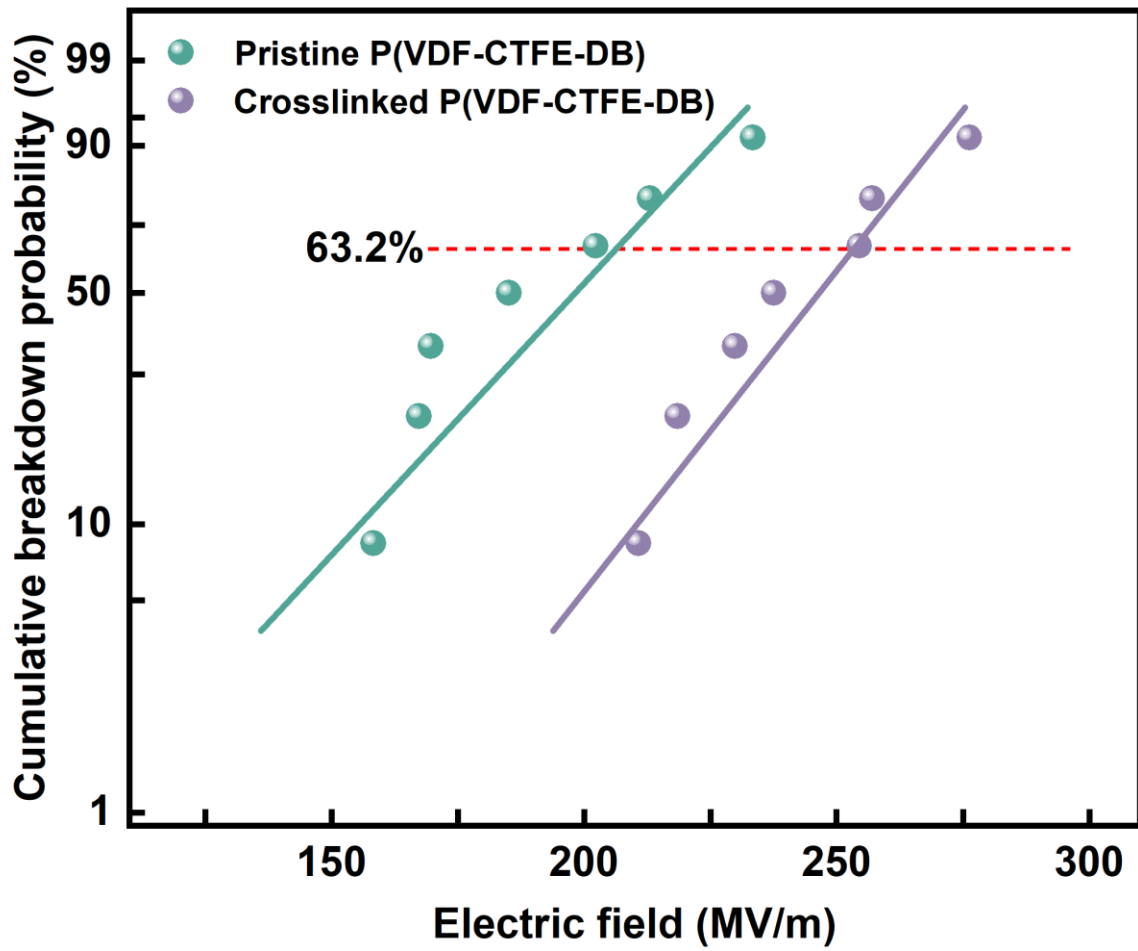
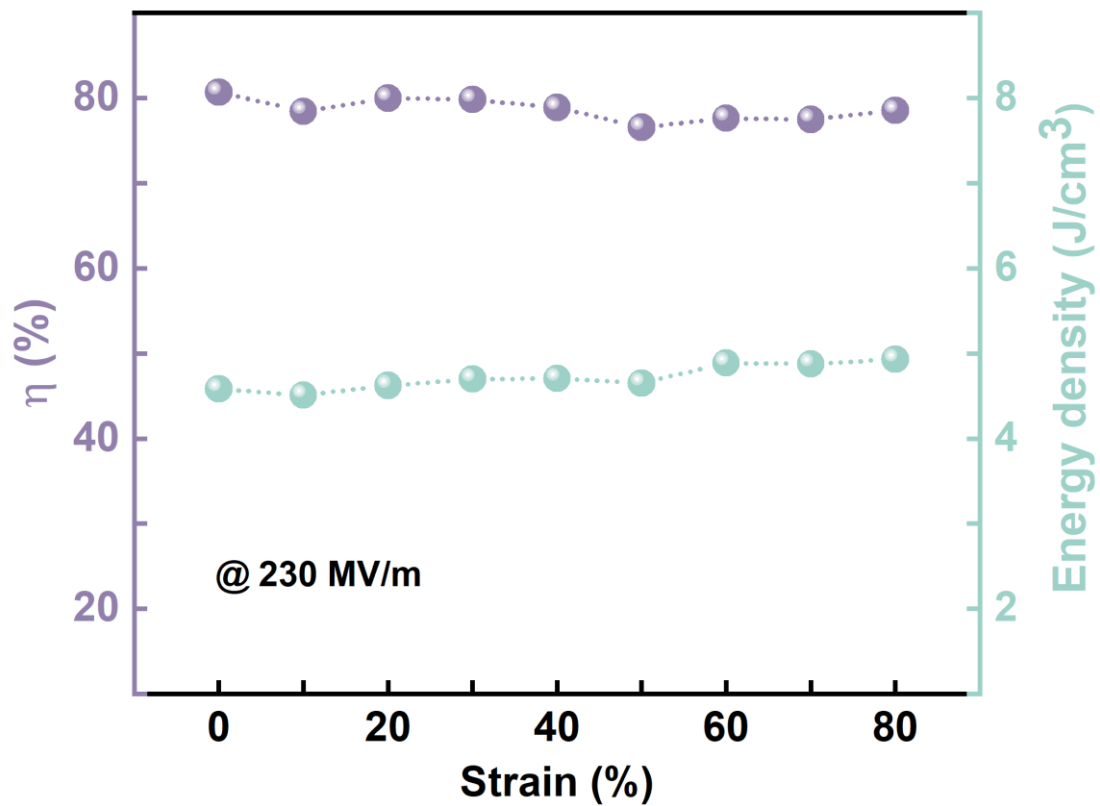**Figure S22.** Weibull distribution of measured breakdown strengths of pristine and crosslinked P(VDF-CTFE-DB).

Figure S23. The energy density and η of crosslinked P(VDF-CTFE-DB) at 230 MV/m.