# Supporting Information

## Multiscale understanding of electric polarization in poly(vinylidene fluoride)-based ferroelectric polymers

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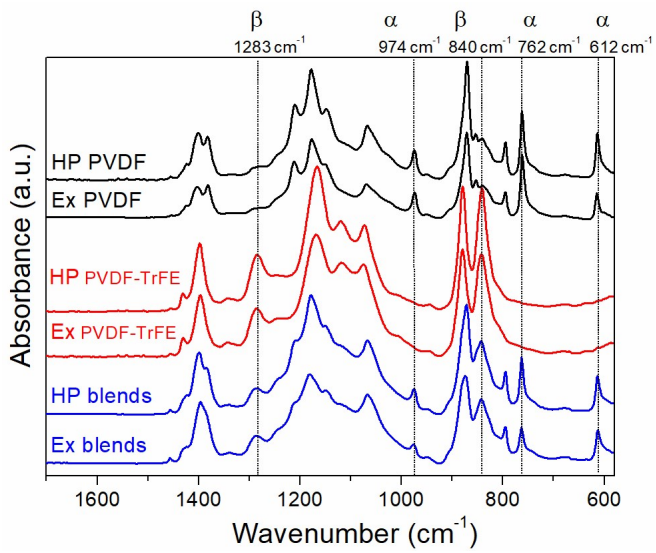


**Figure S1**. FTIR of PVDF, PVDF-TrFE and 50/50 blended films processed via melt-extrusion (Ex) and hot-compression (HP).

The hot pressed and extruded PVDF films show obvious and strong characteristic bands of α-phase, 612 $cm^{-1}$, 762 $cm^{-1}$ and 974 $cm^{-1}$ and weak appearance of β-characteristic bands, 840 $cm^{-1}$ and 1283 $cm^{-1}$, which suggests that the hot pressed and extruded PVDF films mainly crystallized into α-phase. The hot pressed and extruded PVDF-TrFE films contain pure β-phase, concluded from the strong β-characteristic bands (840 $cm^{-1}$ and 1283 $cm^{-1}$) and the absence of α-characteristic bands (612 $cm^{-1}$, 762 $cm^{-1}$ and 974 $cm^{-1}$). The blends show mixed bands of α- and β-phase.

FTIR can also be used to quantitatively determine the volume fraction of β-phase ($F(\beta)$) using the below equation[1] :

$$F(\beta) = \frac{A_\beta}{\frac{K_\beta}{K_\alpha} \times A_\alpha + A_\beta} \times 100\% \qquad (1)$$

where $A_\alpha$ and $A_\beta$ are the absorbance of α- and β-characteristic bands, 762 $cm^{-1}$ and 840 $cm^{-1}$, respectively. $K_\alpha$ and $K_\beta$ are the absorption coefficients of bands at 762 $cm^{-1}$ and 840 $cm^{-1}$, which

are $6.1 \times 10^4$ cm²/mol and $7.7 \times 10^4$ cm²/mol, respectively. The calculated values of $F(\beta)$ are summarized in Table S1, which also includes the DSC characteristic parameters.

**Table S1**. The content of β-phase ($F(\beta)$) and thermal characteristics of melting temperature ($T_m$), Curie transition temperature ($T_c$), fusion enthalpy ($\Delta H_f$) and degree of crystallinity ($\eta$) for pure PVDF, PVDF-TrFE and their blends prepared using melt-extrusion (Ex) and hot compression (HP).

| | HP PVDF | Ex PVDF | HP PVDF-TrFE | Ex PVDF-TrFE | HP blends | Ex blends |
|---|---|---|---|---|---|---|
| F(β) (vol.) | < 10% | < 10% | 100% | 100% | 50-60% | 65-70% |
| $T_m$ (°C) | 157±2 | 157±3 | 152±1 | 150±1 | 158±1 (PVDF) 148±1 (PVDF-TrFE) | 158±2 (PVDF) 148±2 (PVDF-TrFE) |
| $T_c$ (°C) | > $T_m$ | > $T_m$ | 115±3 | 122±2 | 119±3 | 128±2 |
| $\Delta H_f$ | 41±2 | 44±3 | 25±2 | 28±2 | 28±2(PVDF) 21±1(PVDF-TrFE) | 30±2(PVDF) 22±1(PVDF-TrFE) |
| *$\eta$ | 39±2% | 42±3% | 65±6% | 74±4% | 27±2% (PVDF) 55±3% (PVDF-TrFE) | 29±2% (PVDF) 58±3% (PVDF-TrFE) |

*The degree of crystallinity was achieved using the experimental values of $\Delta H_f$ divided by the values of fusion enthalpy for 100% crystalline materials ($\Delta H_f^\circ$), which are 104.6 J/g and 38 J/g for PVDF and PVDF-TrFE, respectively.[2]

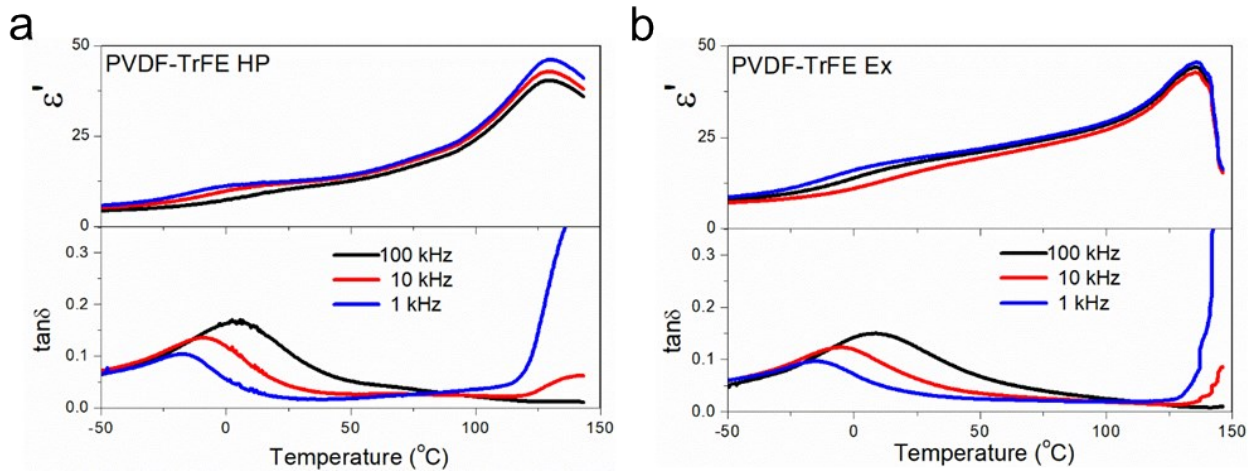


**Figure S2.** The temperature dependence of dielectric permittivity of the (a) hot pressed and (b) extruded PVDF-TrFE films.

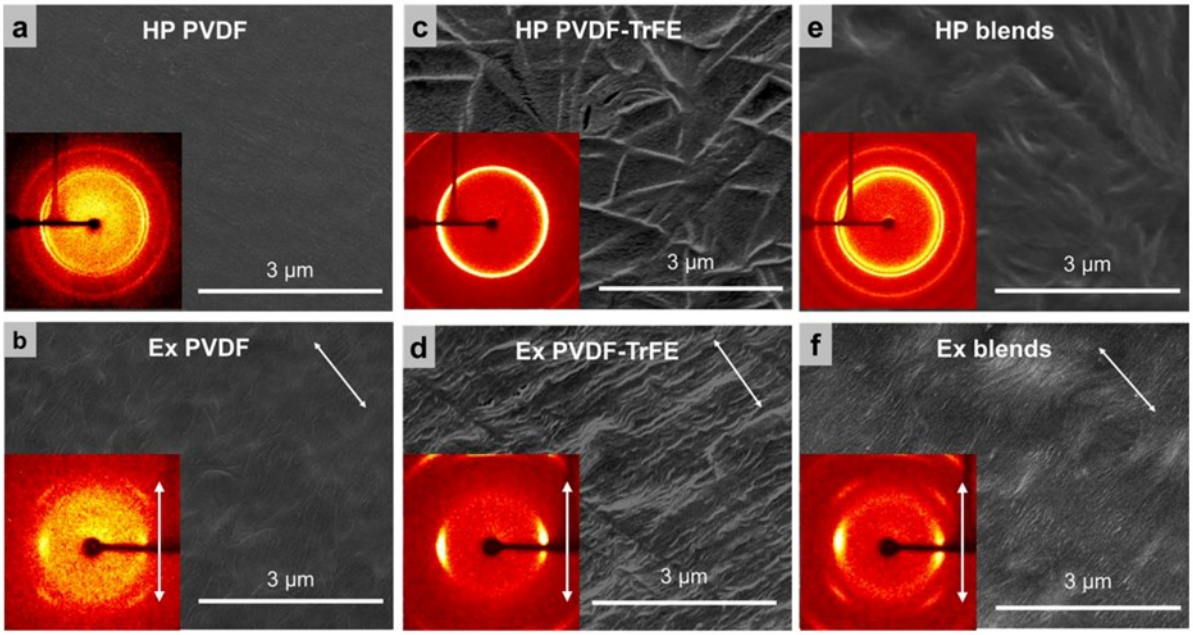


**Figure S3.** Surface SEM morphology images of samples processed using hot-compression (HP) and melt-extrusion (Ex) with the inset images of 2D-XRD ring patterns taken with an incident beam normal to the film surface: (a) HP PVDF; (b) Ex PVDF; (c) HP PVDF-TrFE; (d) Ex PVDF-TrFE; (e) HP blends and (f) Ex blends. The white arrows in SEM images and 2D-XRD ring patterns denote the direction of extrusion.

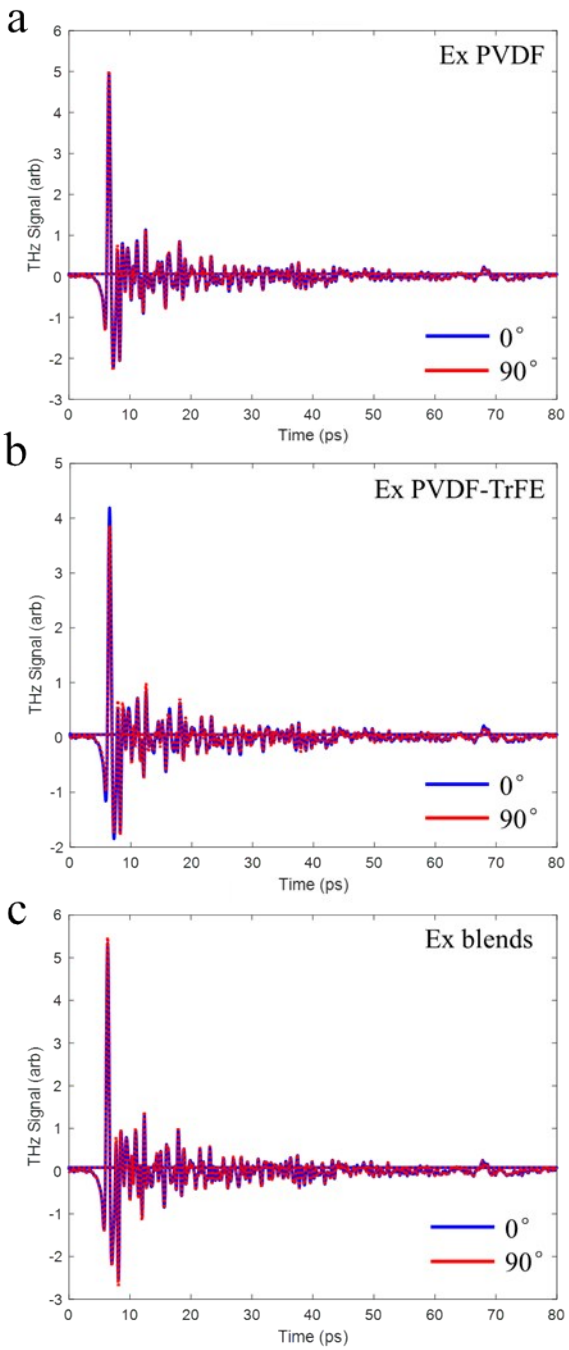


**Figure S4.** The 0°and 90° THz spectroscopy of extruded PVDF, PVDF-TrFE and their blends, which demonstrate that there is no difference in the THz-TDS spectra during the 90° rotation of samples.

**Reference**

1. Jr. R. Gregorio and M. Cestari, *Journal of Polymer Science Part B Polymer Physics*, 1994, **32**, 859-870.
2. P. Martins, A. C. Lopes and S. Lanceros-Mendez, *Progress in Polymer Science*, 2014, **39**, 683-706.