Supporting information to

Enhanced piezoelectricity of electrospun polyvinylidene fluoride (PVDF) fibers for energy harvesting

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In this supporting data we provided all obtained FTIR spectra (Fig. 1S), Fig. 2s. Wide energy survey scan for PVDF60+ fibers , all deconvoluted WAXS profiles (Fig. 3S), DSC and WAXS crystallinity comparison (Fig. 4S) including details on the crystallinity calculations, XPS spectra used for calculating absolute values (Fig. 5S), D33 coefficient measurements of single PVDF fibers as obtained from PFM (Fig. 6S) and in (Table 1S) we present raw data obtained from XPS spectra used for calculating F/C values.



Fig. 1S. FTIR spectra showing differences in phase composition for a) PVDF30+/- and b) PVDF60+/-.



Fig. 2S. Wide energy survey scan for PVDF60+ fibers. The C 1s and F 1s lines are the main recognizable peaks whereas O 1s signal at 530 eV is almost unnoticeable. The oxygen content calculated from the presented WESS spectra is about 0.6 % at.

Fig. 3S presents deconvoluted WAXS profiles for all samples. Deconvolution was performed using Gauss function, providing area, position and width of the peaks. The profile registered for the pellet sample (Fig. 3S a) shows diffraction peaks of the \mathbb{P} -phase, only, noting that the \mathbb{P} 021 peak required use of two Gaussian peaks. This profile was used as reference in deconvolution of the other profiles (Figs. 3S b-e). In detail, the positions of the \mathbb{P} phase peaks, as obtained for the pellet sample, were fixed in the deconvolution of the profiles of the fibers, allowing determination of the area of the 200/110 \mathbb{P} phase diffraction peak and of the amorphous halo. Thus, the error in the calculation of relative content of the \mathbb{P} and \mathbb{P} phase is assumed negligible.



Fig. 3S. Deconvoluted WAXS profiles showing original data, cumulative fit curve, diffraction peaks related to 2 and 2 phases (labelled) as well as peak representing the amorphous halo for: a) pellet, b) PVDF 30+, c) PVDF 30-, d) PVDF60+ and e) PVDF60-.

$$x_{\alpha} = \frac{I_{\alpha 100} + I_{\alpha 020} + I_{\alpha 110} + I_{\alpha 021}}{\Sigma I},$$

where,

$$\Sigma I = I_{\alpha 100} + I_{\alpha 020} + I_{\alpha 110} + I_{\alpha 021} + I_{\beta 200/110} + I_{am}$$

$$x_{\beta} = \frac{I_{\beta 200/110}}{\Sigma I}$$

$$x_{c} = x_{\alpha} + x_{\beta}$$
(15)

Fig. 4S presents comparison of the content of the $eqistic and equation for the set of the melting peak, and of the melting peak, <math>\Delta H_m$, obtained by DSC. The equations:

$$x_{\alpha} = \left(\frac{\Delta H_{m\beta}^{0}}{\Delta H_{m}} \cdot \frac{x_{\beta}}{x_{\alpha}} + \frac{\Delta H_{m\alpha}^{0}}{\Delta H_{m}}\right)^{-1}$$

$$x_{\beta} = \left(\frac{\Delta H_{m\alpha}^{0}}{\Delta H_{m}} \cdot \frac{x_{\alpha}}{x_{\beta}} + \frac{\Delta H_{m\beta}^{0}}{\Delta H_{m}}\right)^{-1}$$

$$x_{C} = x_{\alpha} + x_{\beta}$$

$$(25)$$

were derived from the relation assuming direct melting of the crystals without recrystallization nor polymorphic transitions, i.e. the measured melting heat, ΔH_m , assumed equal to the sum of the melting heats of the phases:

$$\Delta H_m = \Delta H_{m\alpha}^0 \cdot x_\alpha + \Delta H_{m\beta}^0 \cdot x_\beta \tag{3S}$$

assuming the melting enthalpies the \mathbb{P} and \mathbb{P} phases as $\Delta H^0_{m\alpha}$ =104.5 and $\Delta H^0_{m\beta}$ =220 J/g, respectively⁴⁵ and assuming the ratio $x_{\mathbb{P}}/x_{\mathbb{P}}$ as determined from WAXS analysis.



Fig. 4S. Crystallinity calculated from the melting heat, ΔH_m, as measured by DSC, compared with WAXS crystallinity results (see Table 1 in the main text).



Fig. 5S. XPS spectra for all samples used for distinguishing between carbon and fluorine atoms; a) PVDF30+, b) PVDF30-, c) PVDF60+, d) PVDF60-.



Fig. 6S. PFM data a) d_{33} calibration measurement from LiNbO₃, b) d_{33} coefficient measurements of single PVDF fibers.

Sample	C [at. %]	F [at. %]	F/C
PVDF30+	26.6	23.4	0.88
PVDF30-	27.2	22.8	0.83
PVDF60+	26.4	23.6	0.89
PVDF60-	28.1	22.0	0.78

Table 1S. Grazing angle XPS results of carbon and fluorine groups at the surface ofelectrospun PVDF fibers (measured down to 2 nm from the surface).