Supporting Information

Crystal Orientation and Temperature Effects on Double Hysteresis Loop Behavior in a Poly(vinylidene fluoride-*co*-trifluoroethylene-*co*-chlorotrifluoroethylene)-*graft*-Polystyrene Graft Copolymer

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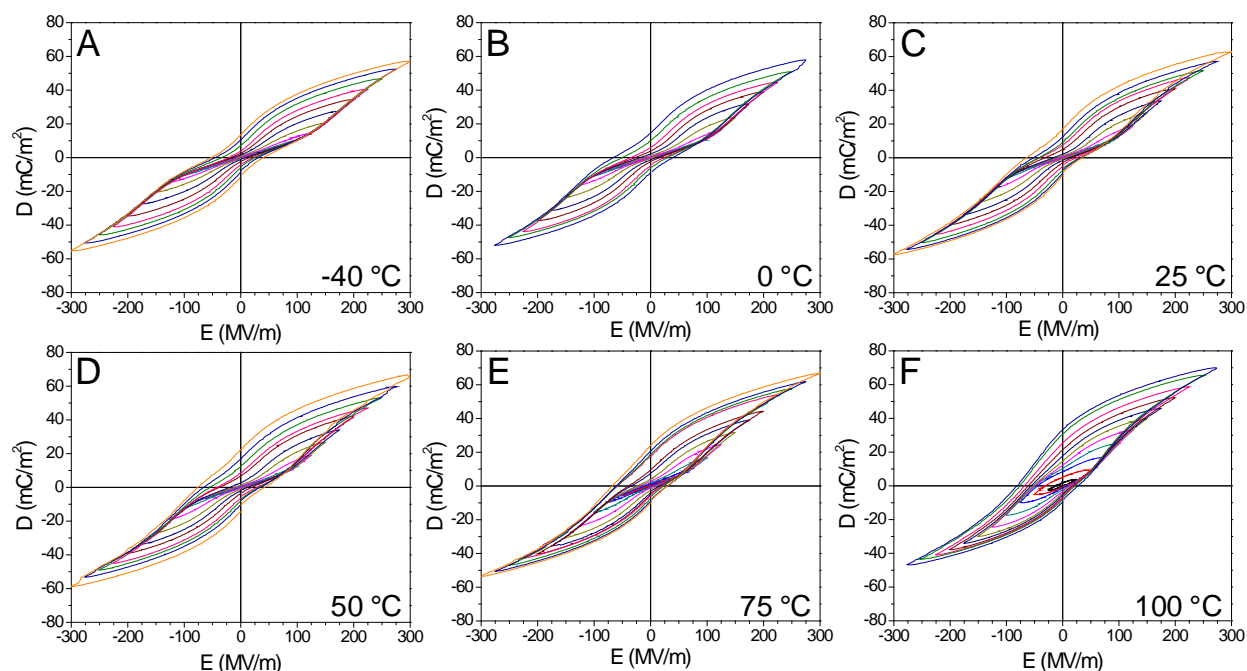## I. Raw Data for D-E Loops of the Stretched P(VDF-TrFE-CTFE)-*g*-PS(14%) at Different Temperatures

Figure S1. Bipolar D-E hysteresis loops for the stretched (extension ratio = 500%) P(VDF-TrFE-CTFE)-*g*-PS(14%) film at different temperatures from -40 °C to 100 °C, plotted from the raw data. The poling frequency is 10 Hz with a triangular waveform. The poling field has increments of 25 MV/m until electric breakdown at each temperature.

II. Deduction of the Current Density
II.1. Ionic Current
The ionic current is a sum of the positive and negative currents:

$$I_{ionic}/S = j_{ionic}(x,t) = qj_+(x,t) - qj_-(x,t) \qquad (1)$$

Here, $j_+(x,t)$ and $j_-(x,t)$ are ion fluxes, whereas $qj_+(x,t)$ and $(-q)j_-(x,t)$ are ionic current densities. For simplicity, the current densities are short as currents in the following discussion. The continuity equation for all ions reads:

$$\frac{\partial j_+(x,t)}{\partial x} = -\frac{\partial n_+}{\partial t}$$

$$\frac{\partial j_-(x,t)}{\partial x} = -\frac{\partial n_-}{\partial t} \qquad (2)$$

The currents obeys the Nernst-Planck equation:

$$j_+(x,t) = -D_i \frac{\partial n_+(x,t)}{\partial x} + \mu n_+(x,t) E_i(x,t)$$

$$j_-(x,t) = -D_i \frac{\partial n_-(x,t)}{\partial x} - \mu n_-(x,t) E_i(x,t) \qquad (3)$$

Here, $n_+(x,t)$ and $n_-(x,t)$ are the distribution of ionic concentrations in the film, and $E_i(x,t)$ is the electric field inside the film at point x and time t. The ion mobility μ is related to ion diffusion D_i through the Einstein equation:

$$D_i = \frac{\mu q}{k_B T} \qquad (4)$$

Here, k_B is Boltzmann constant. Ion concentrations $n_+(x,t)$, $n_-(x,t)$, and the internal electric field $E(x,t)$ obey macroscopic Poisson equation:

$$-\partial E_i(x,t)\partial x = -\frac{q}{\varepsilon\varepsilon_0}\left(n_+(x,t) - n_-(x,t) + \rho_0\right) \qquad (5)$$

where ρ_0 is related to source charges, which are assumed to be zero in our set-up. For simplicity, in Eqn.(5) it is assumed that the + and - ions have the same valency q. We put Eqn.(2) into Eqn.(3) and obtain:

$$\frac{\partial j_+(x,t)}{\partial x} = -D_i \frac{\partial^2 n_+}{\partial x^2} + \mu E_i(x,t)\frac{\partial n_+}{\partial x} + \mu n_+ \frac{\partial E_i}{\partial x} = -\frac{\partial n_+}{\partial t}$$

$$\frac{\partial j_-(x,t)}{\partial x} = -D_i \frac{\partial^2 n_-}{\partial x^2} - \mu E_i(x,t)\frac{\partial n_-}{\partial x} - \mu n_- \frac{\partial E_i}{\partial x} = -\frac{\partial n_-}{\partial t} \qquad (6)$$

For solving these second order differential equations, we make the following approximation: Ion densities under external field deviate not too much from the equilibrium values.

$$n_+ = n_0 + \delta_+(x,t),\ \delta_+(x,t) = \eta_+(x)e^{i\omega t}$$

$$n_- = n_0 + \delta_-(x,t),\ \delta_-(x,t) = \eta_-(x)e^{i\omega t} \qquad (7)$$

Periodicity over time in Eqn.(8) means also the same time periodicity of the internal electric field E_i, $E_i(x,t) = E_0 e^{i\omega t}$. Putting Eqn.(7) into Eqn.(3) leads to:

$$j_+(x,t) = -D_i \frac{\partial \eta_+}{\partial x}e^{i\omega t} + \mu n_0 E_i(x)e^{i\omega t}$$

$$j_-(x,t) = -D_i \frac{\partial \eta_-}{\partial x}e^{i\omega t} - \mu n_0 E_i(x)e^{i\omega t} \qquad (8)$$

Also, the Eqn.(6) with the help of Eqn.(7) now transfers to:

$$\frac{\partial j_+(x,t)}{\partial x} = -D_i \frac{\partial^2 \eta_+}{\partial x^2} e^{i\omega t} + \mu n_0 \frac{\partial E_i(x)}{\partial x} e^{i\omega t} = -\eta_+(x) i\omega e^{i\omega t}$$

$$\frac{\partial j_-(x,t)}{\partial x} = -D_i \frac{\partial^2 \eta_-}{\partial x^2} e^{i\omega t} - \mu n_0 \frac{\partial E_i(x)}{\partial x} e^{i\omega t} = -\eta_-(x) i\omega e^{i\omega t} \qquad (9)$$

Eq.(9) can be rewritten as:

$$-D_i \frac{\partial^2 \eta_+}{\partial x^2} + \mu n_0 \frac{\partial E_i(x)}{\partial x} = -\eta_+(x) i\omega$$

$$-D_i \frac{\partial^2 \eta_-}{\partial x^2} - \mu n_0 \frac{\partial E_i(x)}{\partial x} = -\eta_-(x) i\omega \qquad (10)$$

Here, term $\dfrac{\partial E_i(x)}{\partial x}$ can be taken from the PB equation, Eqn.(5), which is now rewritten as:

$$-\partial E_i(x,t) \partial x = \frac{e}{\varepsilon \varepsilon_0} \left(\eta_+(x) - \eta_-(x) \right) \qquad (11)$$

Finally, the Eqn.(10) takes the form:

$$-D_i \frac{\partial^2 \eta_+}{\partial x^2} + \mu n_0 \frac{q}{\varepsilon \varepsilon_0} \left(\eta_+(x) - \eta_-(x) \right) + \eta_+(x) i\omega$$

$$-D_i \frac{\partial^2 \eta_-}{\partial x^2} - \mu n_0 \frac{q}{\varepsilon \varepsilon_0} \left(\eta_+(x) - \eta_-(x) \right) + \eta_-(x) i\omega \qquad (12)$$

Putting Eqn.(4) into Eqn.(12), and introducing Debye screening length $\lambda^2 = \varepsilon \varepsilon_0 k_B T / (2 n_o q^2 e^2)$, we have:

$$\frac{\partial^2 \eta_+}{\partial x^2} - \left(\frac{1}{2\lambda^2} + \frac{i\omega}{D_i} \right) \eta_+(x) + \frac{1}{2\lambda^2} \eta_- = 0$$

$$\frac{\partial^2 \eta_-}{\partial x^2} - \left(\frac{1}{2\lambda^2} + \frac{i\omega}{D_i} \right) \eta_-(x) + \frac{1}{2\lambda^2} \eta_+ = 0 \qquad (13)$$

The solution of this equation is sought in the form:

$$\eta_+(x) = A_1 e^{\alpha_1} + A_2 e^{-\alpha_1} + A_3 e^{\alpha_2} + A_4 e^{-\alpha_2}$$

$$\eta_-(x) = B_1 e^{\beta_1} + B_2 e^{-\beta_1} + B_3 e^{\beta_2} + B_4 e^{-\beta_2} \qquad (14)$$

Putting Eqn.(14) into Eqn.(13), and after simple mathematical manipulations we arrive at the following analytical formula for the density profiles using blocking electrodes condition (there is no ion exchange between the polymer layer and the electrodes):

$$\eta_+(x)/n_0 = -A_0 \frac{\sinh(Bx)}{\sinh(Ba) + i \dfrac{\omega \lambda^2}{D_i} Ba \cosh(Ba)}$$

$$\eta_-(x)/n_0 = A_0 \frac{\sinh(Bx)}{\sinh(Ba) + i \dfrac{\omega \lambda^2}{D_i} Ba \cosh(Ba)} \qquad (15)$$

Here, $B\lambda = \sqrt{1 + i\omega\lambda^2/D_i}$ and $A_0 = qV_0 (B\lambda)^2)/(2k_B T)$.

For the derivative of ion profiles we get:

$$\frac{1}{n_0}\frac{\partial \eta_+}{\partial x} = -A_0 B \frac{\cosh(Bx)}{\sinh(Ba)+i\frac{\omega\lambda^2}{D_i}Ba\cosh(Ba)}$$

$$\frac{1}{n_0}\frac{\partial \eta_-}{\partial x} = A_0 B \frac{\cosh(Bx)}{\sinh(Ba)+i\frac{\omega\lambda^2}{D_i}Ba\cosh(Ba)} \quad (16)$$

For the electrical potential, the following relation is obtained:

$$\frac{q\phi(x)}{k_B T} = \frac{1}{(B\lambda)^2}\frac{\eta_+(x)}{n_o} + \frac{q}{k_B T}Cx \quad (17)$$

where

$$C = \frac{i\omega B\lambda^2 V_0}{2D_i}\frac{\cosh(Ba)}{\sinh(Ba)+i\frac{\omega\lambda^2}{D_i}Ba\cosh(Ba)} \quad (18)$$

The derivative for the potential is:

$$\frac{q\phi^{'}(x)}{k_B T} = \frac{1}{(B\lambda)^2}\frac{\eta_+^{'}(x)}{n_o} + \frac{q}{k_B T}C \quad (19)$$

Now, we go back to Eqn.(3), put in Eqns.(17-19), and calculate $j_+(x,t)$ and $j_-(x,t)$. Then we use Eqn.(1) to get j_{ionic}.

II.2. Displacement Current

The displacement current density is defined as:

$$I_{disp}/S = j_{disp}(x,t) = \frac{\partial \varepsilon\varepsilon_0 E_i}{\partial t} = -\varepsilon\varepsilon_0 \frac{\partial \phi(x)}{\partial x}i\omega e^{i\omega t} \quad (20)$$

Here $\phi^{'}_x$ is from Eqn. (19).

II.3. Total Charge on Plates

Total charge density on the plate surface is:

$$Q(t)/S = \sigma(t) = \int_0^t j_{tot}(x=a,\tau)d\tau = (1/i\omega)e^{i\omega t}\left(j_{ionic}(x=a,t)+j_{disp}(x=a,t)\right) \quad (21)$$

Here, for the set-up used in the main text, we use

$$j_{ionic}(x=a,t) = qj_+(x=a,t) \quad (22)$$

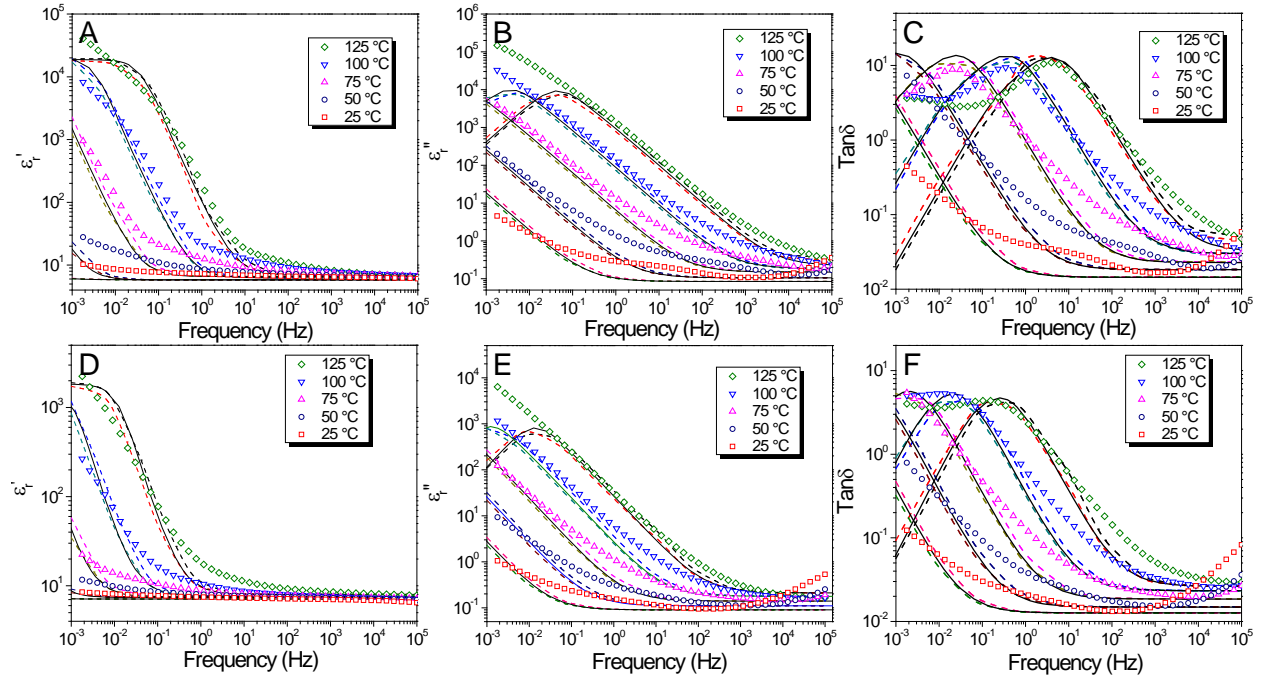## III. Estimation of Errors in Sawada Model-Fit BDS Results

Figure S2. Fitting curves of the real and imaginary permittivity: (A-C) are for the non-stretched film and (D-F) are for the stretched film. The ion concentration is constant at 6.7×10^{19} ions/m^3. Curves with ±20% deviation in diffusion coefficient are calculated at different temperatures and plotted as dashed lines in all figures.

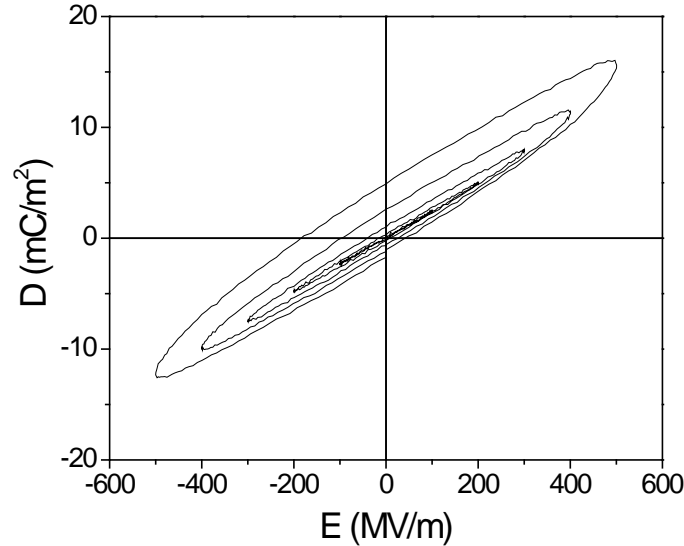## IV. D-E Hysteresis Loops of a Commercial BOPP Film at 100 °C

Figure S3. Continuous D-E loops for a commercial BOPP film (8 μm, SBE, Inc.) at 100 °C. The poling frequency is 10 Hz with a sinusoidal waveform.

V. Comparison of Discharged Energy Densities for P(VDF-TrFE-CTFE)-*g*-PS(14%), e-Beam Irradiated P(VDF-TrFE) 50/50, and P(VDF-TrFE-CFE) Terpolymers
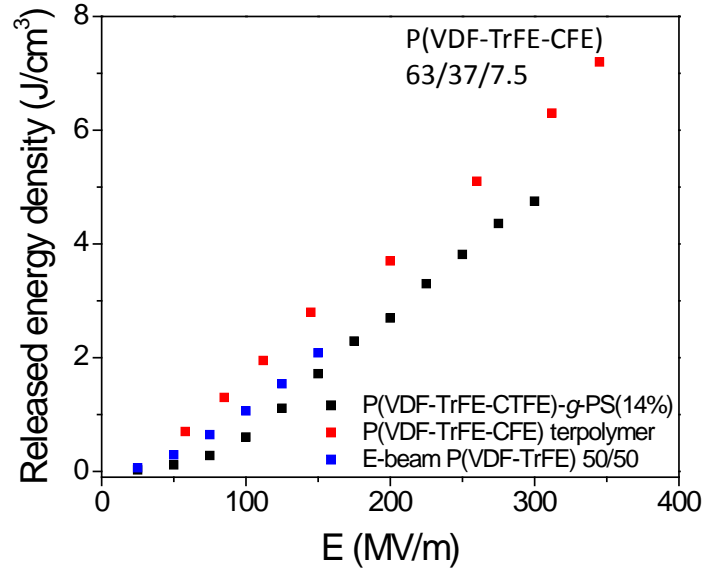

Figure S4. Discharged energy densities for P(VDF-TrFE-CTFE)-*g*-PS(14%) graft copolymer, e-beam irradiated P(VDF-TrFE) 50/50, and P(VDF-TrFE-CFE) terpolymer. The data for the graft copolymer is from this work. The data for the e-beamed P(VDF-TrFE) 50/50 is from ref. 17. The data for P(VDF-TrFE-CFE) 63/37/7.5 is from ref. 23.

VI. D-E Hysteresis Loops for e-Beamed P(VDF-TrFE) and P(VDF-TrFE-CFE) at 75 °C
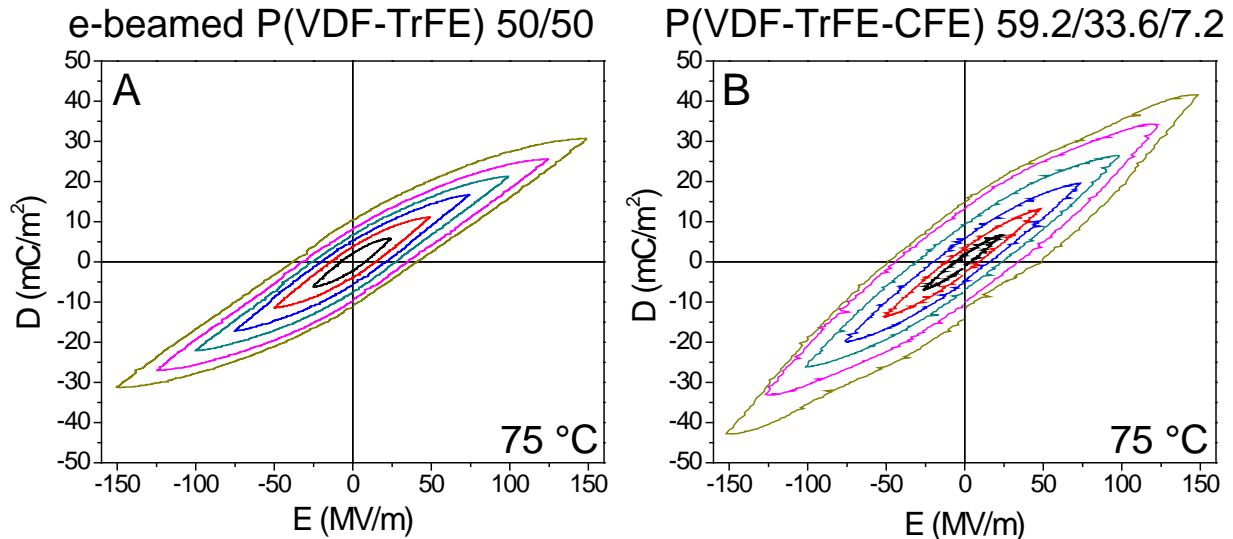

Figure S5. Bipolar hysteresis loops for (A) e-beamed (60 Mrad at 70 °C) P(VDF-TrFE) 50/50 at 1 Hz and (B) P(VDF-TrFE-CFE) 59.2/33.6/7.2 at 1000 Hz. The measurement temperature is 75 °C. The poling frequency is 10 Hz with a triangular waveform.