Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

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Experimental

- **Sample preparation**

Poly(vinylidene fluoride-trifluoroethylene) P(VDF-TrFE) random copolymer with a VDF/TrFE molar ratio of 75/25 obtained from Solvay Solexis was dissolved in dimethylformamide (DMF) and spin-coated on pre-cleaned sapphire substrates at about 45°C using a heat-controlled spin-coating (HCSC) setup as described elsewhere.[1] After that, a capping layer of tetramethyl bisphenol-A polycarbonate (TMPC) was spin-coated from toluene solution. All P(VDF-TrFE) films were spin coated with 3000rpm for 45s from 4.5 wt% solutions with the thickness of approximately 165 nm and the TMPC capping layer had a thickness of ~70nm. The reference sample had only a TMPC capping layer of ~70nm on a sapphire substrate without a P(VDF-TrFE) film underneath. Thin metal lines (3nm Cr/50 nm Au) were patterned using shadow-masking and deposited simultaneously on both the reference and samples using a thermal evaporator (Angstrom Engineering). The resultant metal lines were ~40µm in width.

- **Characterization**

Differential scanning calorimetry (DSC, TA Instruments) was used to measure thermal transitions of bulk P(VDF-TrFE) and TMPC. The melting transition temperature, T_m, of bulk P(VDF-TrFE) was 421K, and Curie temperatures for the ferroelectric-to-paraelectric phase transformation upon heating and the paraelectric-to-ferroelectric phase transformation upon cooling were 400K and 345K, respectively; the glass transition temperature of bulk TMPC was 473K.

The purpose of the TMPC capping layer was to prevent surface roughening of P(VDF-TrFE) after annealing above its T_m, since a very rough surface may change the thermal boundary resistance.[2] The film thickness was measured by atomic force microscopy (AFM, Asylum Research MFP-3D) on several different areas scratched by a razor blade. The topography images and phase images of the P(VDF-TrFE) thin films were examined in frequency modulation mode and amplitude modulation mode respectively on the same area using Si cantilevers (NCH, 42N/m from NanoWorld) after washing away the TMPC capping layer with toluene. The topography images with TMPC capping layers are shown in Figure S1.

Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet 6700 spectrometer utilizing the grazing angle accessory (Smart SAGA) at a grazing incidence angle of 85° under reflection mode. Thin films on Au are well-known to produce high quality FTIR spectra, so 50nm Au coated Si wafers with a 3nm Cr adhesive layer were used both as the background and as the substrates for FTIR measurement. FTIR data with a larger spectral bandwidth than what was shown in the manuscript is provided in Figure S2. P(VDF-TrFE) samples without a TMPC capping layer and with TMPC washed off show almost identical spectra.

TEM samples were collected on copper grids from floating as-cast samples on a deionized water bath. The diffraction pattern was performed using JEOL 2010F TEM equipped with a heating stage. The TEM samples were annealed in the heating stage and cooled down to room temperature for diffraction measurement. The characterization done on different substrates is still representative of the nature of P(VDF-TrFE) films since the morphology of P(VDF-TrFE) is not very sensitive to the substrate.[3,4]

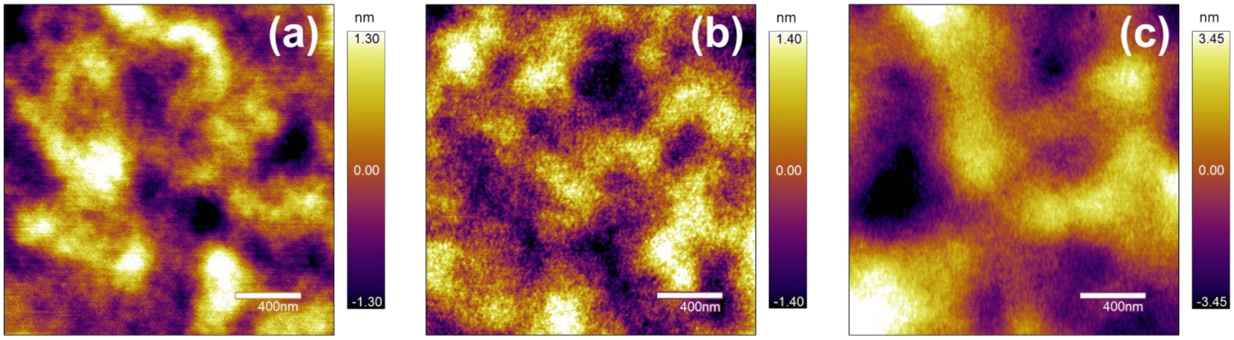

Figure S1. Topography images of P(VDF-TrFE) films ~165nm annealed at different temperatures with TMPC capping layer ~70nm: (a) as-cast, (b) 380K and (c) 440K. The RMS roughnesses for all three films are below 2nm.

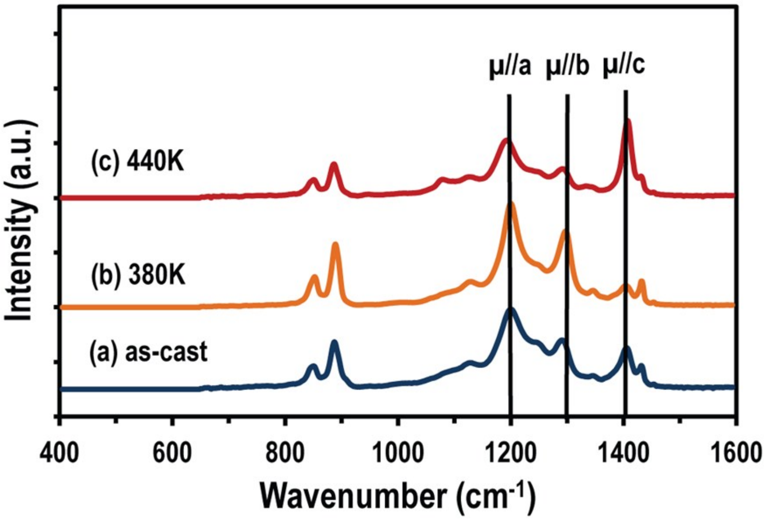

Figure S2. Grazing incidence FTIR spectra of (a) as-cast film and films annealed at (b) 380 K and (c) 440 K.

- **Thermal conductivity measurement using 3ω technique**

The thermal conductivity, κ, of P(VDF-TrFE) thin films was measured using 3ω technique under vacuum conditions. The samples were in-situ annealed at 380K and 440K for 2h in a Janis cryostat chamber and slowly cooled down to specific temperatures at which κ was measured. The as-cast sample was directly measured from 340K. Further details about extrapolation of thin film P(VDF-TrFE) thermal conductivity are provided as follows.

The 3ω method is a well-established technique that has been used to measure the out-of-plane thermal conductivity of thin films.[5] In principle, a resistive metal heater line is deposited onto the film of interest; either a sinusoidal voltage or current is applied to the line at frequency ω. This results in a temperature oscillation at 2ω, $T(t) = T_0 + T_{2\omega}(t)$; and a corresponding fluctuation in the line resistance at the same frequencies, $R(t) = R_0 + R_{2\omega}(t)$. Thus, the potential across the heater line has two oscillation components: $V(t) = I(t)R(t) = I_{1\omega}(t)\left(R_0 + R_{2\omega}(t)\right) = V_{1\omega}(t) + V_{3\omega}(t)$, and provides semi-cylindrical heating to the underlying substrate down to the thermal penetration depth, $r = \sqrt{D/2\omega}$, where D is the thermal diffusivity of the substrate. By measuring the 3ω signal, one can obtain the temperature oscillation at 2ω, $\Delta T_{2\omega}$.

For a single-layer substrate, under the condition that r is much smaller than the thickness of the underlying substrate, $\Delta T_{2\omega}$ can be directly related to the 3ω and 1ω oscillations in voltage across the heater line:[6]

$$\Delta T_{2\omega} = \frac{2V_{3\omega}}{\alpha V_{1\omega}} \qquad (1)$$

where α is the temperature coefficient of electrical resistance of the metal heater line.

The temperature rise, $\Delta T_s(\omega)$, on the sample and the temperature rise, $\Delta T_r(\omega)$, on the reference can be determined by equation (1), the difference of which is the temperature rise ΔT_f across the polymer thin film. In the case where the metal heater line width is much larger than the film thickness, heat flow across the film can be modeled as one-dimensional and thus the κ can be calculated:[5]

$$\kappa = \frac{I_{rms}^2 R \cdot d}{2b \cdot l \cdot \Delta T_f} \qquad (2)$$

where $I_{rms}^2 R$ is the heat power applied to the system, d is the polymer film thickness and $2b$ and l are the width and length of the heater line. It should be noted that $I_{rms}^2 R/\ (2b \cdot l)$ is kept identical for the sample and the reference.

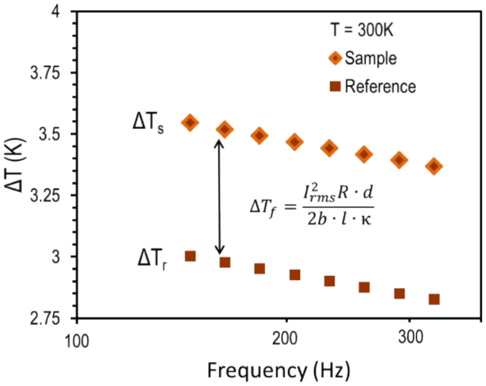

Figure S3. Temperature rise on the sample $\Delta T_s(\omega)$ and temperature rise on the reference $\Delta T_r(\omega)$ at different frequencies, the difference of which is the temperature rise across the polymer film.

- **Solvent Usage for Spin-Casting P(VDF-TrFE) films**

We chose DMF as a solvent because of the excellent quality of the films we were able to create compared to other solvents we tried, for this study. While several studies have had success with forming films using methyl ethyl ketone (MEK) as a solvent[7] (eliminating the need for heat-controlled spin-coating), we were able to achieve the smoothest films using DMF with heat controlled spin-casting. Further, studies have shown that P(VDF-TrFE) films cast from a highly polar solvent like DMF or DMSO tend to have improved chain alignment and higher crystallinity.[8]

Some other important considerations should be noted about the choice of solvent on the as-cast morphology of PVDF-TrFE thin films. Firstly, a volatile solvent such as MEK would result in a higher initial evaporation rate during spin-casting than a high-boiling point solvent (e.g. DMF). Presumably, the fast evaporation rate of a volatile solvent would "freeze" polymer chains into a non-equilibrium state brought about from the high shear stresses present during spin-casting. However, studies have shown that even for volatile solvents, the evaporation rate significantly drops as the film vitrifies; the residual solvent can act as a plasticizing agent that allows for gradual relaxation of chains, similar to the presence of a high-boiling point solvent.[9] This highlights the importance of annealing thin films—not only to remove residual solvent, but also to achieve a relaxed equilibrium state for chains.

A second consideration is the nature of the preferred orientation of crystallites after spin-casting. While a study using MEK as a solvent has shown a preferential edge-on orientation of as-cast PVDF-TrFE[7], a study on P3HT films using chloroform (also a very volatile solvent) exhibited a slightly face-on orientation.[10] However, a report on PVDF (dissolved in DMF) also describes a face-on orientation of chains in the as-cast film.[11] Predicting the nature of the as-cast orientation of a polymer is a complex subject involving several possible parameters including the thermodynamics between the polymer and solvent, polymer and substrate, the spin speed, solution concentration, polymer molecular weight, and the gaseous environment.

Regardless of the initial conformation of chains after spin-casting, a redeeming point is that after annealing a film above the melting temperature, the chains should be mobile enough to form a final equilibrium conformation which is independent of the initial solvent and spin-casting conditions. This is evident in the similar melt-recrystallized morphologies of PVDF-TrFE brought about in our work, when compared to a study that used MEK as a solvent.[7, 12, 13]

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