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SUPPORTING INFORMATION

Processing of ferroelectric polymers for microelectronics: from morphological analysis to functional devices

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S1 Input parameters for modeling

Input parameters Flory-Huggins model. The Flory-Huggins free energy density for our ternary blend is given by:[1]

$$\frac{f}{kT} = \frac{\phi_P}{N_P} ln\phi_P + \frac{\phi_W}{N_W} ln\phi_P + \frac{\phi_S}{N_S} ln\phi_P + \chi_{PW}\phi_P\phi_W + \chi_{PS}\phi_P\phi_S + \chi_{WS}\phi_W\phi_S \qquad \text{(S1)}$$

We obtain the effective molecular sizes N_i in terms of numbers of lattice sites by normalizing the molar volumes of all components by that of the smallest species in the mixture (here water, so: $N_W = 1$). The polymer is obviously much larger and taken to have an effective degree of polymerization of $N_P = 1000$. The average molecular weight of the experimentally used P(VDF-TrFE) (see Experimental section) even suggests N_P ~7000. We nevertheless take the lower value as it renders more numerical stability while calculating the binodal concentrations, with only very minor changes to the phase diagram and demixing dynamics. We take $N_S = 5$ for cyclohexanone and cyclopentanone and $N_S = 4$ for DMF, with the remark that the exact molecular size of the solvent does not noticeably affect the phase behavior. The binary interaction parameters used in our study are: $\chi_{PW} = 2.8$, $\chi_{PS} = 0.1$ and $\chi_{WS} = 0.89$, 1.67 and 2.3 for DMF, cyclohexanone and cyclopentanone respectively. The value for χ_{PW} is consistent with the literature value for PVDF:water,[2] assuming a comparable interaction for P(VDF-TrFE). The value for χ_{PS} assumes the solvent to be moderate to good in all cases, in line with experimental observations. The values for χ_{WS} for the interaction between water and the various solvents are to some extent a trade-off between approaching physical reality as closely as possible and obtaining numerical stability. The value for $\chi_{water\text{-}DMF}$ assures full miscibility between water and solvent. The values for $\chi_{water\text{-}cyclohexanone}$ and $\chi_{water\text{-}cyclopentanone}$ give water saturation concentrations of

~14% and ~4%, respectively, and somewhat overestimate the water compatibility of both solvents at 20 °C. The former is in fair agreement with tabulated data.[3] The latter is overestimated in comparison to tabulated data,[4] but that does not affect our reasoning. In contrast, it even sketches a "worser case" scenario.

Vapor pressures water and solvents. The vapor pressures relevant to this work have been retrieved from readily accessible tabulated values: $\overset{\circ}{p_W}(20\ ^{\circ}\mathrm{C}) = 2333\ Pa$ (subscript "W" for water), $\overset{\circ}{p}_{cyclohexanone}(20\ ^{\circ}\mathrm{C}) = 667\ Pa$, and $\overset{\circ}{p}_{cyclopentanone}(20\ ^{\circ}\mathrm{C}) = 1467\ Pa$. The polymer (indicated by subscript "P") is non-volatile: $\overset{\circ}{p_P} = 0\ Pa$. The applied partial pressures are assumed constant and taken to be $p_i^{\infty} = 0\ Pa$ for i = S, P (subscripts "S" and "P" for solvent and polymer) and $p_W^{\infty} = \frac{RH}{100} \cdot \overset{\circ}{p_W}(20\ ^{\circ}\mathrm{C})$ for water, with RH the relative humidity given as a percentage of $\overset{\circ}{p}_{H_2O}$.

Mass transfer coefficient. The mass transfer coefficient k is (for all modeled blends) assigned a value of 0.01 $D_S^0 M_S/\rho_S \kappa RT$, with D_S^0, M_S and ρ_S the self-diffusivity, molar weight and mass density of the solvent, κ an effective gradient energy coefficient (see below), R the ideal gas constant and T the absolute temperature (here assumed to be 293 K). The choice for the value of k, which in reality is hard to establish, represents a situation wherein, roughly stated, the typical timescale for evaporation somewhat exceeds that of solvent diffusion. Changing the magnitude of k does affect demixing dynamics, but the general trends in the humidity-dependence of the characteristic time and length scales associated to vapor-induced demixing predicted by our ternary phase field model remains.

S2 Supplementary experimental results

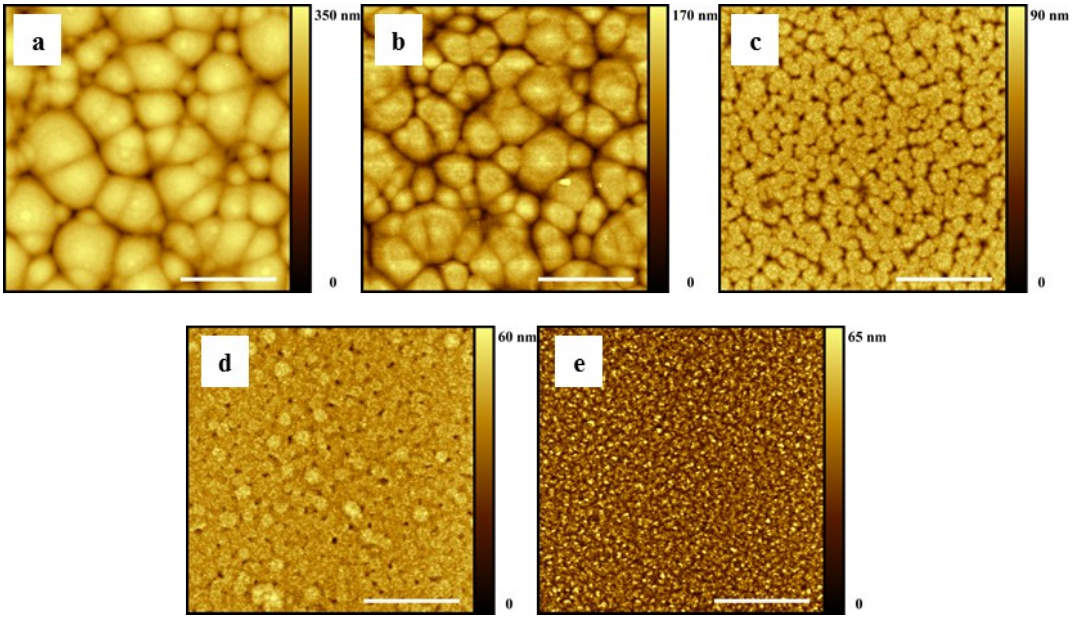


Figure S1. AFM height images of P(VDF-TrFE) thin films coated from solution in DMF at 50% relative humidity and substrates temperature of (a) 20°C, (b) 35°C, (c) 50°C, (d) 65°C and (d) 80°C. The scale bar is 10 µm. The images of (a) and (d) are also given in the main text.

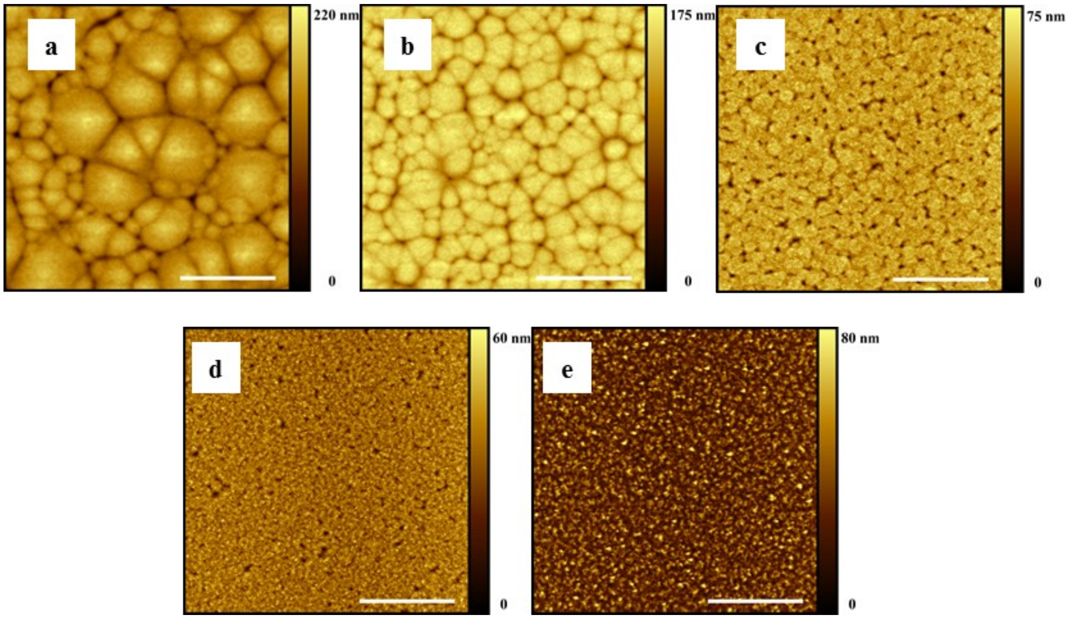


Figure S2. AFM height images of P(VDF-TrFE) thin films coated from solution in a-DMF at 50% relative humidity and substrates temperature of (a) 20°C, (b) 35°C, (c) 50°C, (d) 65°C and (d) 80°C. The scale bar is 10 μm. The image (a) is also given in the main text.

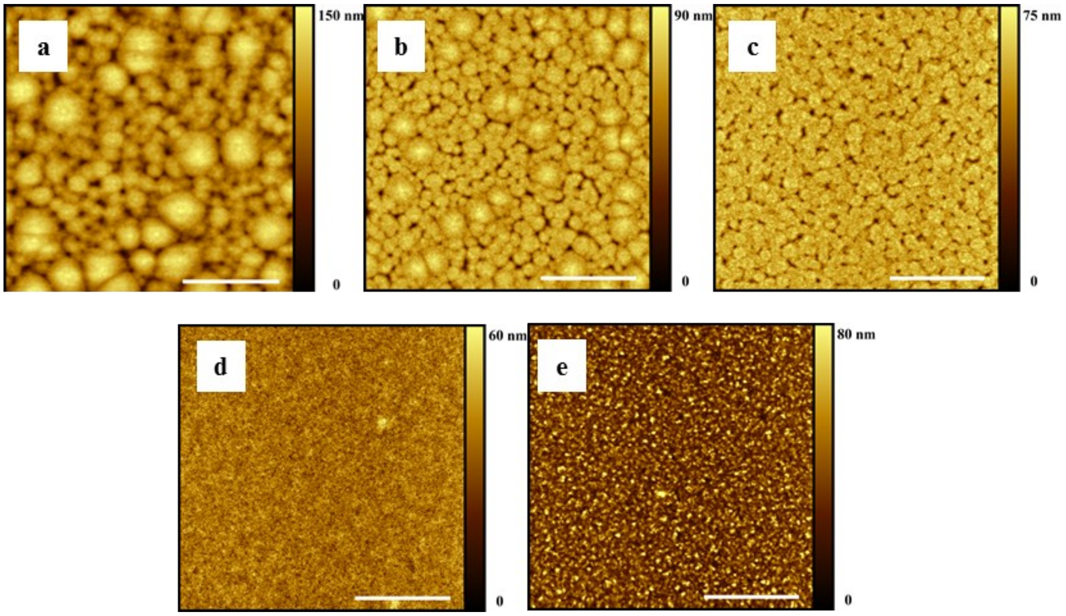


Figure S3. AFM height images of P(VDF-TrFE) thin films coated from solution in a-DMF at 10% relative humidity and substrates temperature of (a) 20°C, (b) 35°C, (c) 50°C, (d) 65°C and (d) 80°C. The scale bar is 10 μm.

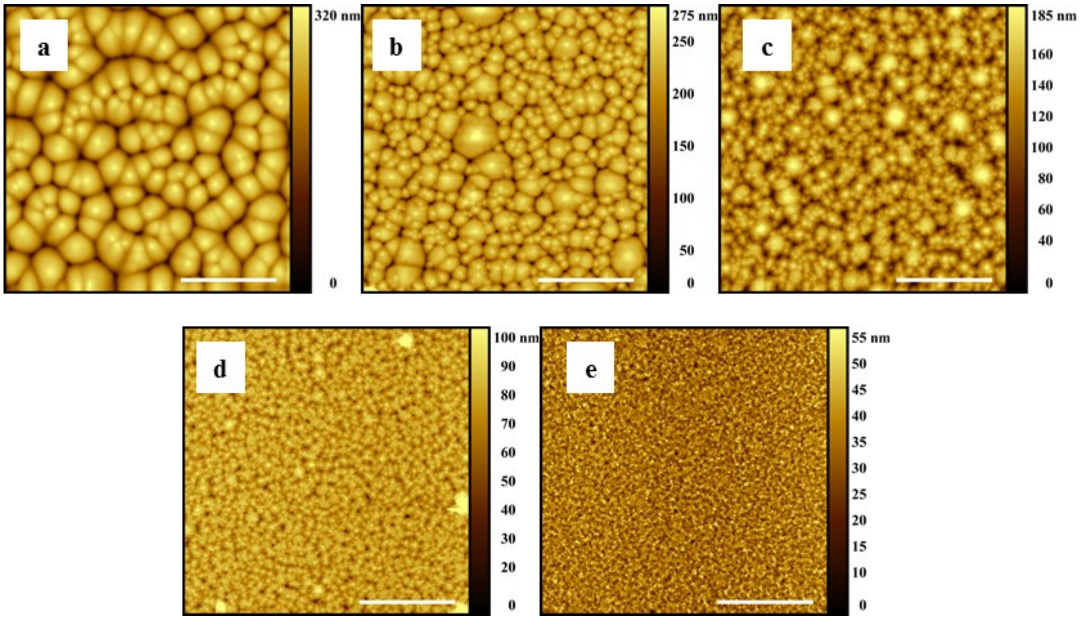


Figure S4. AFM height images of P(VDF-TrFE) thin films coated from solution in cyclohexanone at 50% relative humidity and substrates temperature of (a) 20°C, (b) 35°C, (c) 50°C, (d) 65°C and (d) 80°C. The scale bar is 10 μm. The image (a) is also given in the main text.

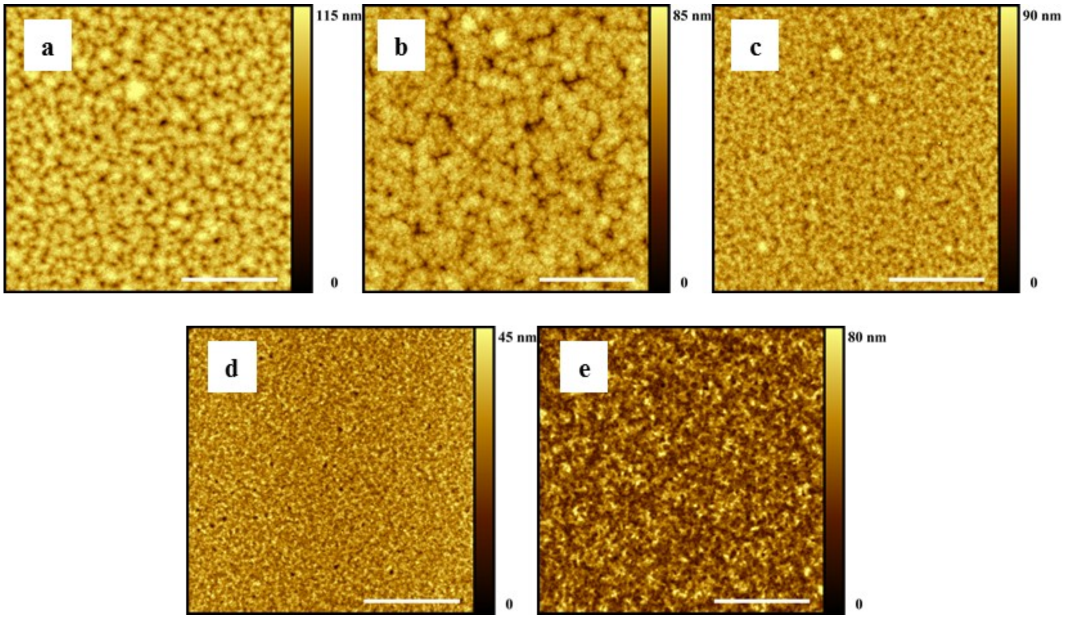


Figure S5. AFM height images of P(VDF-TrFE) thin films coated from solution in cyclopentanone at 50% relative humidity and substrates temperature of (a) 20°C, (b) 35°C, (c) 50°C, (d) 65°C and (d) 80°C. The scale bar is 10 μm. The image (a) is also given in the main text.

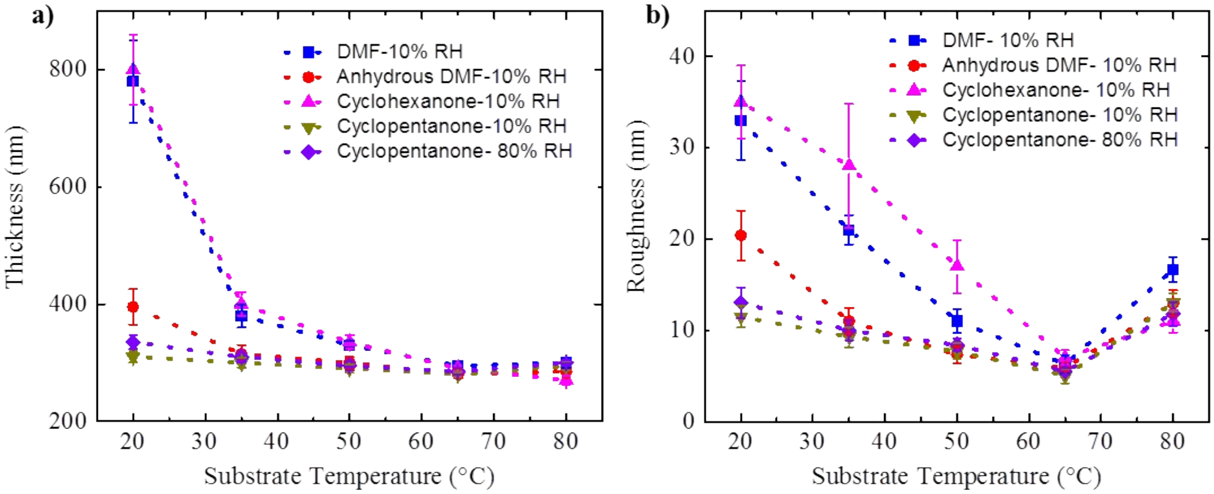


Figure S6. (a) Layer thickness and (b) rms roughness plotted as a function of substrate temperature measured for films prepared films at a fixed relative humidity of 50% (80% only for cyclopentanone).

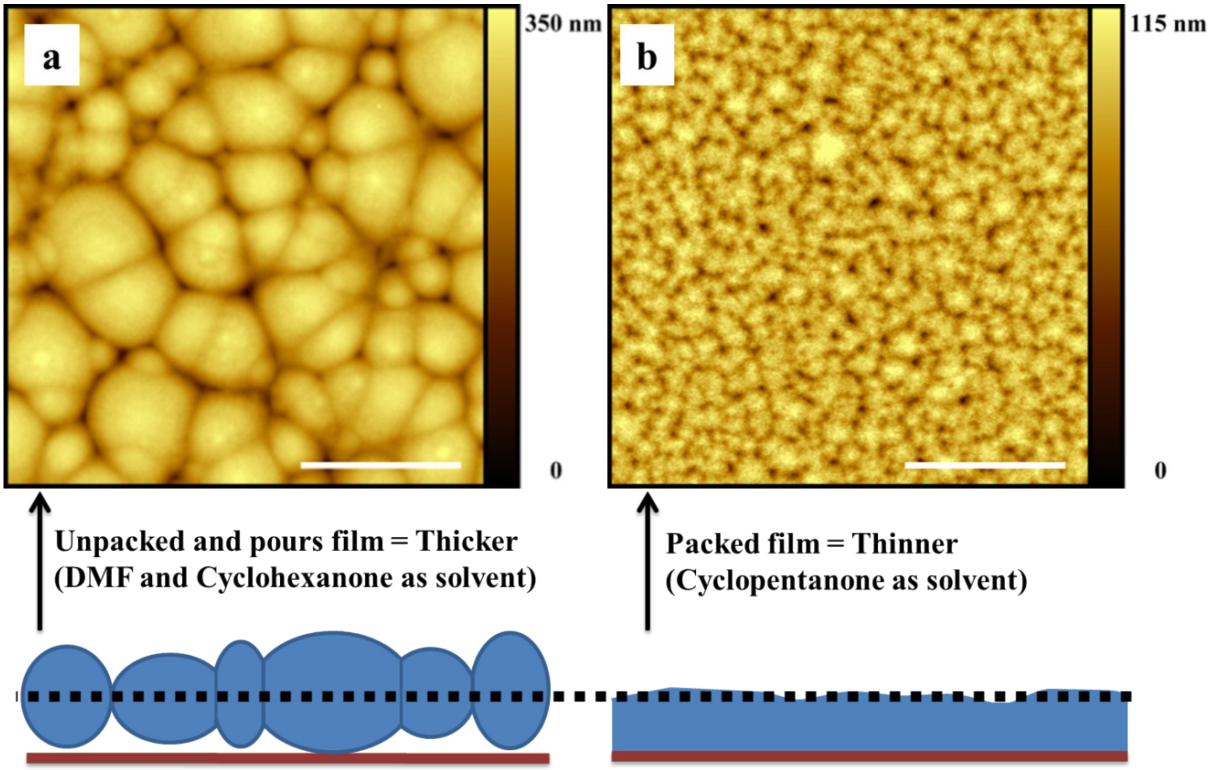
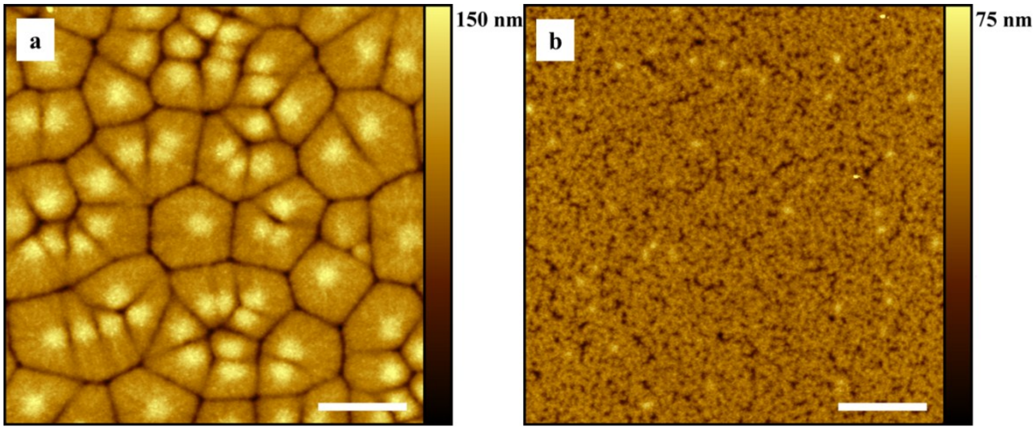
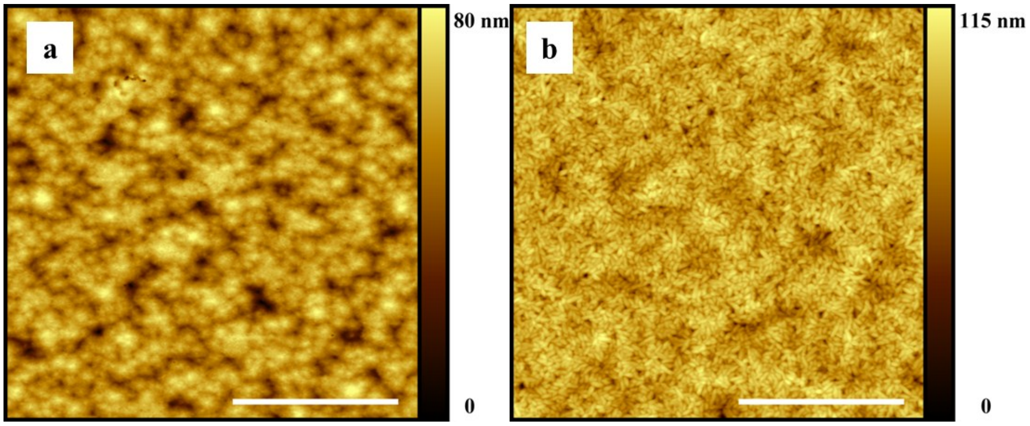


Figure S7. Schematic cross-sectional images explaining why the mean thickness of VIPS-influenced films is overestimated due to the high roughness. Films cast under under ambient conditions (20°C and 50% RH) from (a) Cyclohexanone and (b) cyclopentanone. The scale bar is 10 µm.



rms roughness = 22 ± 2.5 nm **rms roughness = 6.2 ± 0.6 nm**

Figure S8. AFM height image of P(VDF-TrFE) thin films with the thickness of 150 ± 20 nm coated from the solution in (a) cyclohexanone and (b) cyclopentanone under ambient conditions. The scale bar is 5 μm.



rms roughness = 9.8 ± 1.2 nm **rms roughness = 10.7 ± 1.3 nm**

Figure S9. AFM height images of P(VDF-TrFE) thin films coated from solution in cyclopentanone at 50% relative humidity and substrates temperature of 20°C (a) before and (b) after annealing. The scale bar is 4 μm.

References

1. P. J. Flory, *Principles of polymer chemistry*, Cornell University Press, 1953.
2. A. Ghodsi, H. Fashandi, M. Zarrebini, M. M. Abolhasani and M. Gorji, *RSC Adv.*, 2015, **5**, 92234-92253.
3. PubChem Compound Database, https://pubchem.ncbi.nlm.nih.gov/compound/7967, (accessed March 30, 2017).
4. PubChem Compound Database, https://pubchem.ncbi.nlm.nih.gov/compound/8452. (accessed March 30, 2017).