

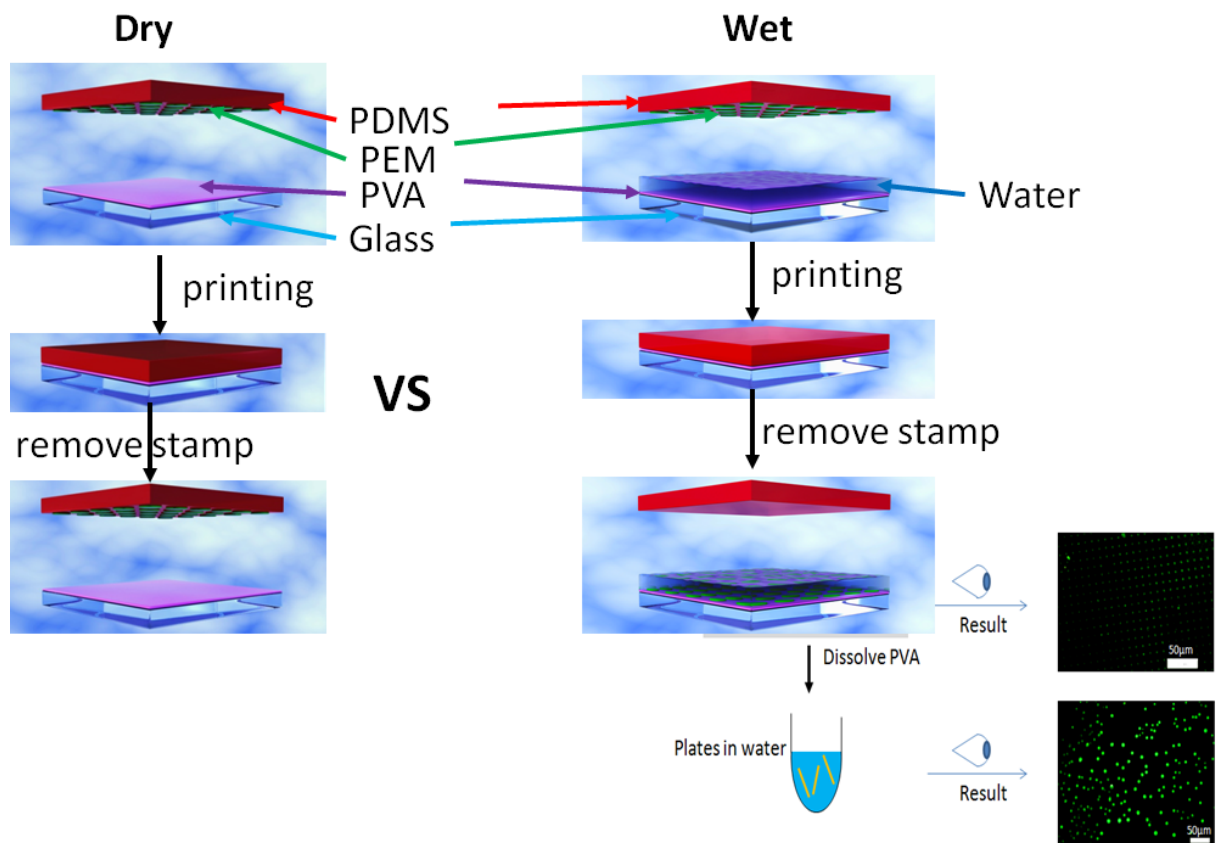
Micro-Contact Printing of PEM Thin Films: Effect of Line Tension and Surface Energies

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Scheme S 1 Preparation mechanism of free standing films. The dry printing approach is not successful, while the wet printing approach allows for pattern transfer. The plates can be released after printing on a sacrificial layer and dissolving the sacrificial layer. Images show fluorescence micrographs of sample 3 on PVA and in solution.

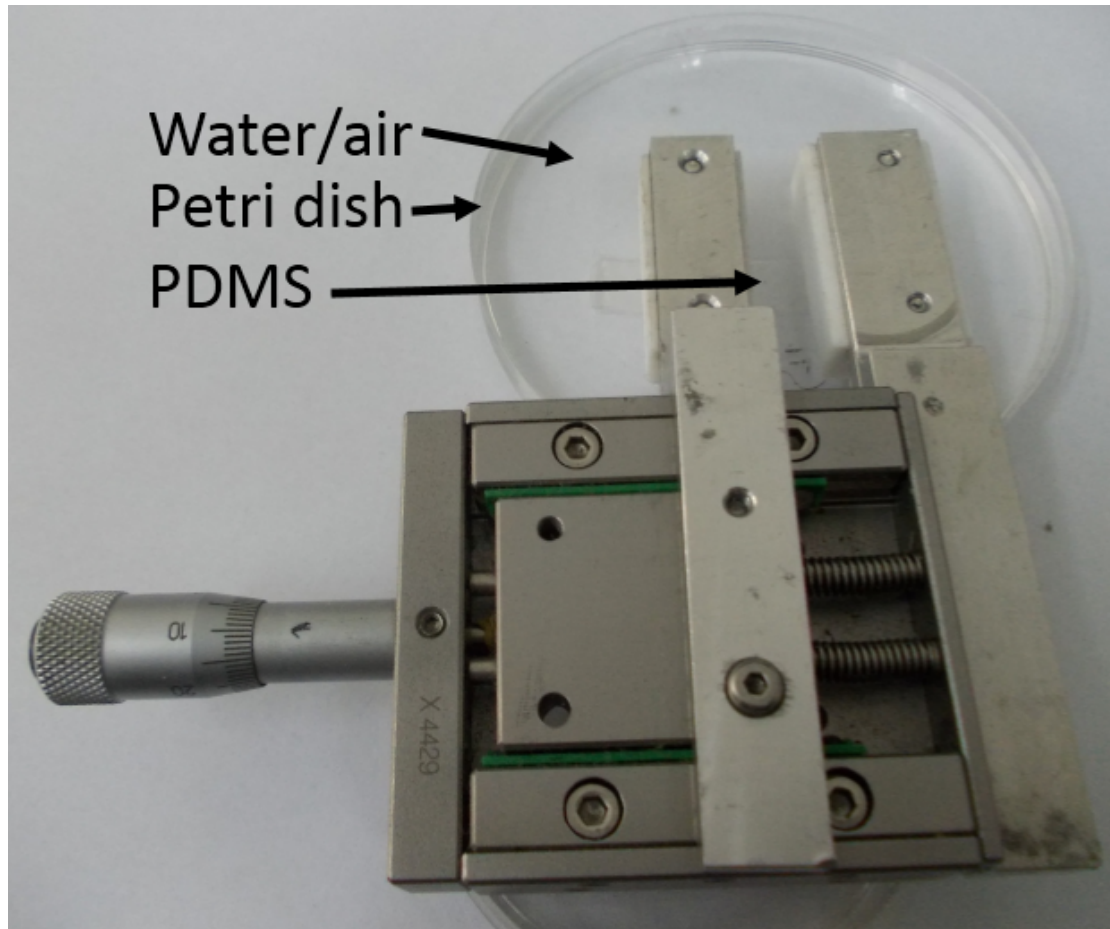


Fig. S 1 Utilized stretching device. PEM was elongated in water and air media.

Energy in mN/m ²	Dispersion surface energy	Ionic surface energy	Polar surface energy	Good surface energy	Van Oss surface energy
PSS	34.5	34	6.1	40.6	74.6
PAH	25.1	102	11.4	36.5	138.5
PAA	25.1	85	11.4	36.5	121.5
PDDA	44.4	68	18	62.4	130.4
SiO ₂	86	153	90	176	329
PEI	35.7	51	11.4	47.1	98.1
PolyS	34.5	0	6.1	40.6	40.6
PolyE	35.7	0	0	35.7	35.7
PTFE	18.4	0	1.6	20	20
Polyetherketone	36.2	0	5.9	42.1	42.1
Polyethylenoxide	30.9	0	12	42.9	42.9
Polyvinylacetate	25.1	0	11.4	36.5	36.5
PDMS	19	0	0.8	19.8	19.8

Table S 1 Used values for the calculation of Fig 2 in the main article. The surface energy without ionic interactions is summarized in the column “Good surface energy” which is the surface energy according to Good to allow a comparison of the surface interaction strength without the ionic contributions, containing only the polar and dispersion part. The Van Ott surface energy contains all 3 components.

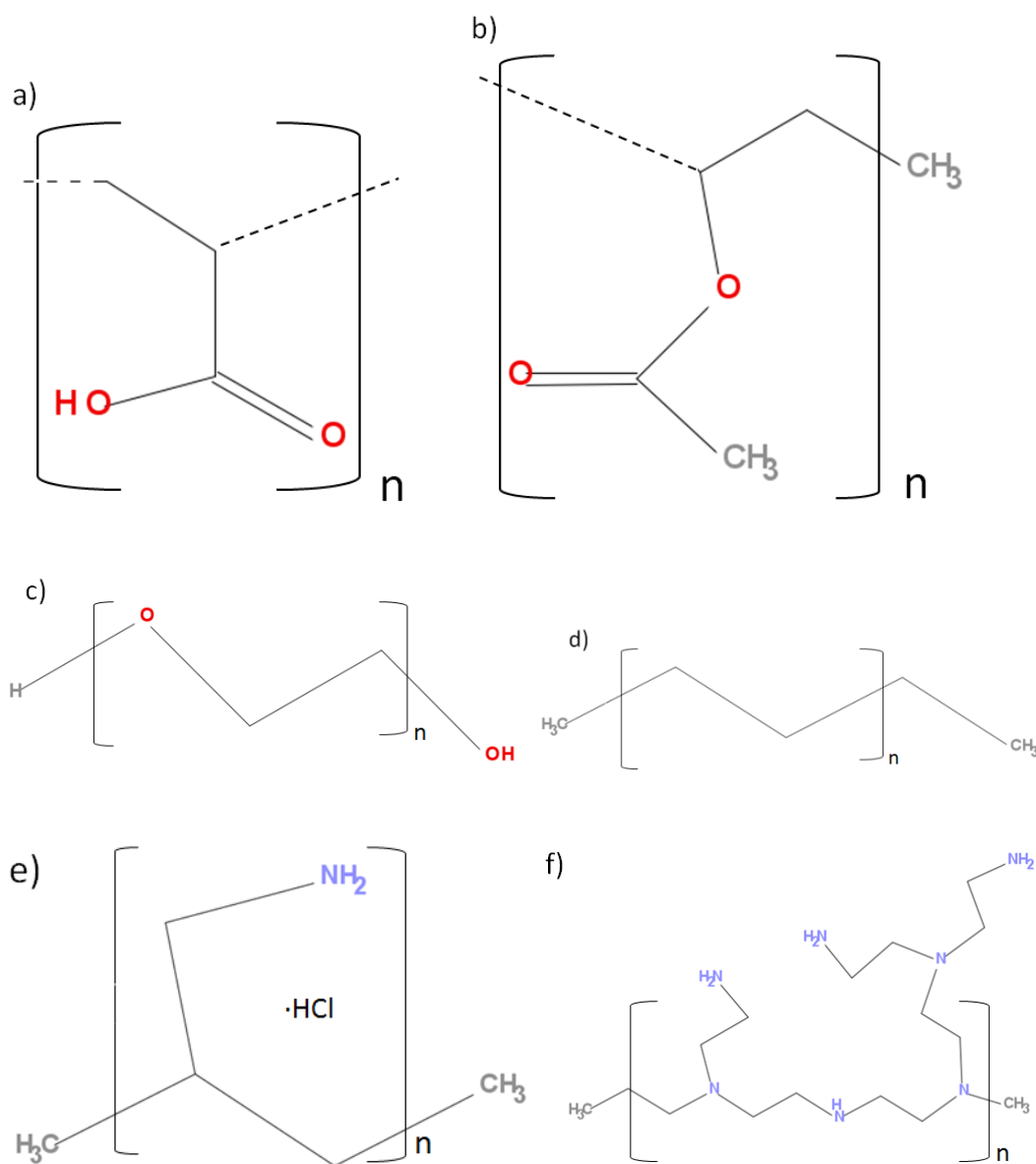
Values for non-polyelectrolyte polymers were obtained from reference^{1,2} which is a reliable online collection of surface energies of chemicals. The Van Oss surface energy of freshly cleaved and the non-ionic contribution SiO₂ was obtained from references^{3,4}, the ionic contribution was calculated from the zeta potential of silica nanoparticles published in reference⁵.

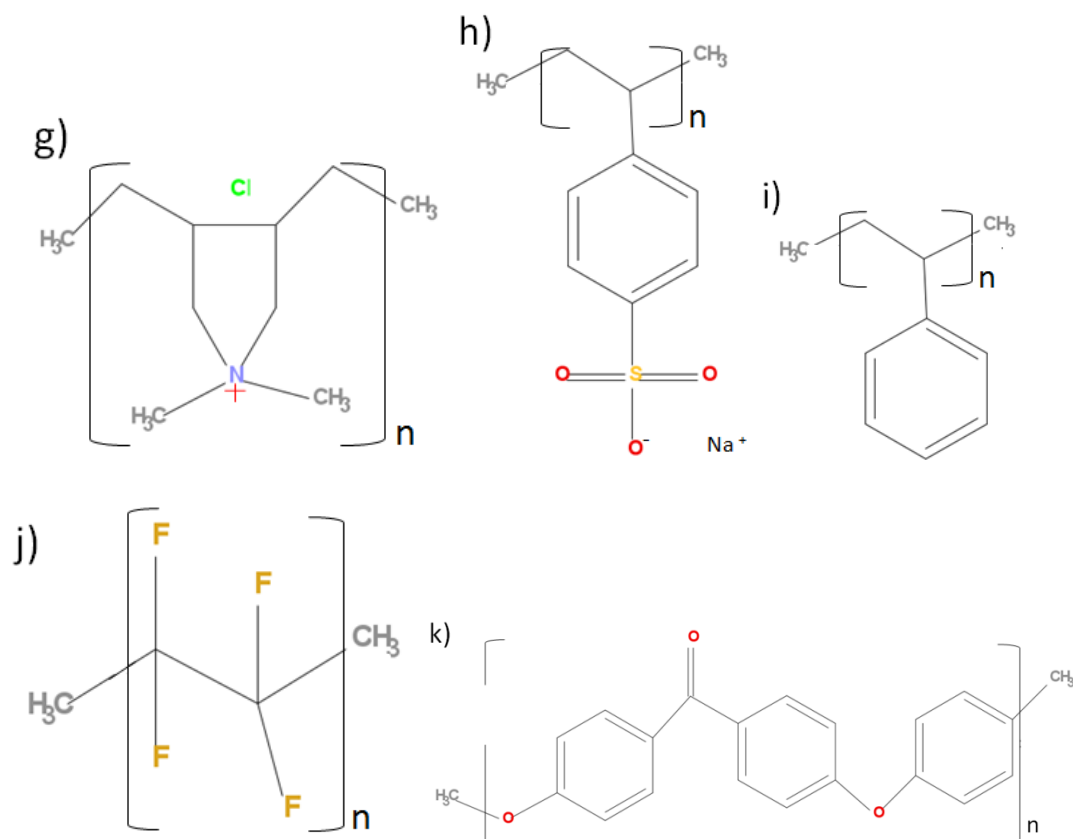
The calculated values fit with the ones published in reference⁴ within 10% (error bars of publications^{3,4}). The unpolar contributions of the polyelectrolytes were taken from their polymeric backbone unit whereas the polar contribution was calculated out of the

zeta potential published in references⁶⁻⁸ as well as own Zeta potential measurements.

the calculated values were compared with the ones published in reference⁹ for PSS and PDDA, which were found to fit within the error of publication⁹, for these two polyelectrolytes the values from reference⁹ were taken into Table S1.

PTFE is poly(tetrafluoroethylene), PolyE poly(ethylene). Structure formulas can be observed in Scheme S2. The calculation method for the molecular ionic surface energy is described in on page 6 of the supporting information.





Scheme S 2 Molecular structures of, a) PAA; b) Poly(vinylacetate); c) Poly(ethylenoxide) (also known as poly(ethyleneglycol)); d) Poly(ethylene) (PolyE); e) PAH; f) PEI; g) PDDA; h) PSS; i) Poly(styrene) (PolyS) which is the backbone of PSS; j) poly(tetrafluoroethylene); k) Poly(etherketone).

Explanation of the values in Table S 1.

The surface energy is made out of at least 3 parts. The dispersion force, which stems from induced dipoles and holds together mainly unpolar units, the polar interaction forces, which stems from permanent dipoles ((in other literature called in a wider sense Lewis acid/base interactions) e.g. ketone, alcohol, or aldehyde groups) and from ionic units (e.g. sulfate groups).¹⁰ Investigating the surface energy of solids is tricky, since the energy cannot directly be measured like in case of liquids. Therefore reference

liquids are used to determine the surface energy. To determine the respective (polar, dispersion and ionic) content different liquids are usually used and the contributions are calculated using equation S 1 and S 2 which are the definitions from Good and van Oss.¹¹⁻¹³

$$\sigma_{SL} = \sigma_S + \sigma_L - 2\sqrt{\sigma_L^D \cdot \sigma_S^D} - 2\sqrt{\sigma_L^P \cdot \sigma_S^P} \quad (S 1)$$

$$\sigma_{12} = (\sqrt{\sigma_1^D} - \sqrt{\sigma_2^D})^2 + \sigma_2^{AB} - 2\sqrt{\sigma_1^- \cdot \sigma_2^+} \quad (S 2)$$

In equation S1 the σ denotes the surface energy, whereby the denominators S and L symbolize the solid and liquid energies, whereby SL is the solid-liquid interaction. The superscript P and D stand for the polar and dispersion contribution. In equation 2 the denominator 1 and 2 stand for component respective solid liquid interaction. The AB stands for Lewis acid-base. Using the Young's equation, with different solvents one can determine the respective surface energies^{11,12}:

$$\sigma_S = \sigma_{SL} + \sigma_L \cdot \cos\theta \quad (S3)$$

In equation S3 the cos stands for cosine and θ is the contact angle of the sessile droplet. In case of combinations of liquids, not the air-liquid or air-liquid-solid interaction but the liquid 1 - solid and liquid 1 - liquid 2 and liquid 1 - liquid 2 – solid as well as liquid 2 - solid interactions need to be considered, as stated in reference 12.

The expression in equation S 2 is close to the Hamaker constant which applies to the sum of all 3 electrodynamic interactions (dispersion, orientation, induction and coupling terms).¹³

$$A = A^D + A^O + A^I + \text{coupling terms} \quad (S4)$$

Here the superscripts O stand for orientation and I for induction terms.

In our case we used for the calculation references and values from polymers with similar backbone units like the utilized PE. Therefore the poly(vinylacetate) dispersion and polar values are used for PAA, since it resembles PAA except for the ionic part. These values are taken also for PEI, and PAH for 2 reasons, first the measurement method of using liquids in a oil environment¹⁰ for high energy surfaces like silicon, PAH, PEI, PAA and PSS is very error prone. Since our error bars were larger than those in literature, literature values were taken for these units and only the ionic contribution was calculated from own measurements (zeta potential) as well as literature. Our own zeta potential measurements achieved similar values like reported in literature. The ionic contribution of the surface energy was calculated out of the zeta potential using the approach for close surfaces stated in reference 13 where the zeta potential can be used directly for surfaces close to each other instead of psi, due to low decay of the wave function (see equation S 5). In addition also a direct comparison with the surface energy using the zeta potential was done, and results compared with reference ^{14,15}.

$$\Delta F_{el} = \varepsilon R \psi_0^2 \ln[1 + \exp(-\kappa l)] \quad (\text{S } 5)$$

Here ΔF is the free energy, el stands for electric energy, ε is the dielectric constant, ψ , is the electrostatic interaction, but for the low distances and direct contact applied here, the zeta potential can be used, see reference 13. Interestingly, our results fit very well with reference 14 when using either the direct zeta potential (which is also a force unit per area) or using equation S 5 with ψ instead of ψ^2 . This can be easily explained by the fact, that reference 13 states already that in some systems the ionic interaction can be explained using the zeta potential directly, which are however usually exceptions. Since

we used a low ionic strength in our experiment and press strongly charged units in direct contact with each other, we conclude that the higher field intensities cause the deviation from equation S 5 in our case. We therefore conclude that our system is one of these special cases where the zeta potential is directly linked to the ionic interaction of the surface energy. Another reason for our system deviating from equation 5 is due to the fact that the ionic contribution of this surface is larger than the van der Waals contribution, which is true in case of a linear ψ component in equation S5 but not for an exponential term, when using standard SI (here SI is International system of units) units.

Additional note: In Table S1 the poly(etherketone) is used as a reference for comparing the polarity of a system containing polar but not ionic groups of aromatic ring containing polymers. This is because the backbone unit of PSS which is PolyS has no polar group, and it is suspected that the sulphate group is also having a polar and not just ionic component.

Film structure	wet	dry
(PSS-PDDA) ₁₆	9 MPa	1 GPa
(PAA-PAH) ₁₆	10 MPa	10 GPa ^{16,17}

Table S 2 Young's modulus of PEM thin films. MPa is Mega Pascal and GPa is Giga Pascal. Measurements from SIEBIMM measurements (details see main article). Wet condition is measured in aqueous conditions (in water), dry refers to measurement in air at 20% relative humidity. Subscripts refer to PEM bilayer repetitions. The references refer to literature which reports properties of similar films with similar Young's modulus.

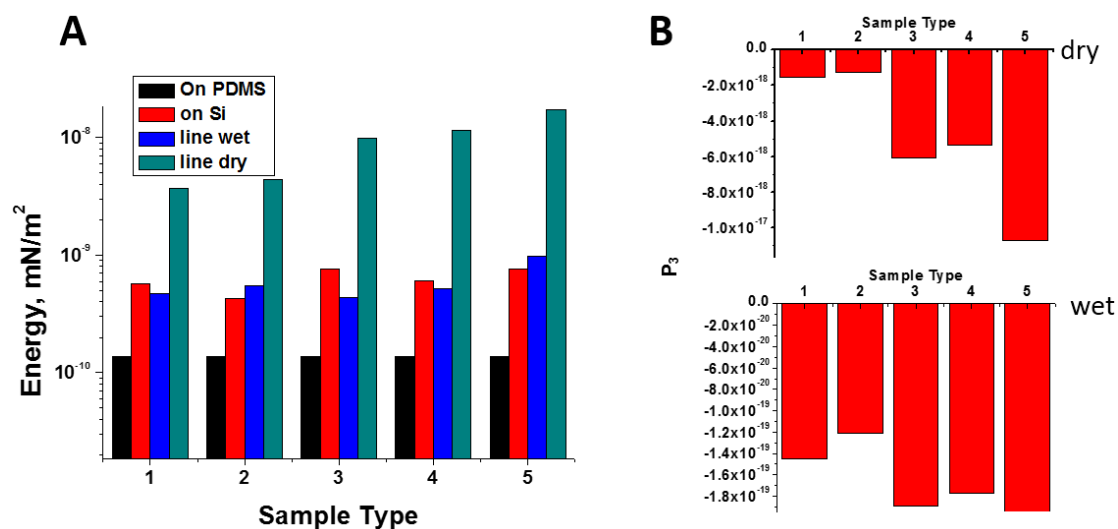


Fig. S 2 Surface Energy (A) and printing parameter (B) of spherical 2.5 μm patterns of samples 1-5. (B) Shows P₃ for dry and wet printing. Values are from Table S 2.

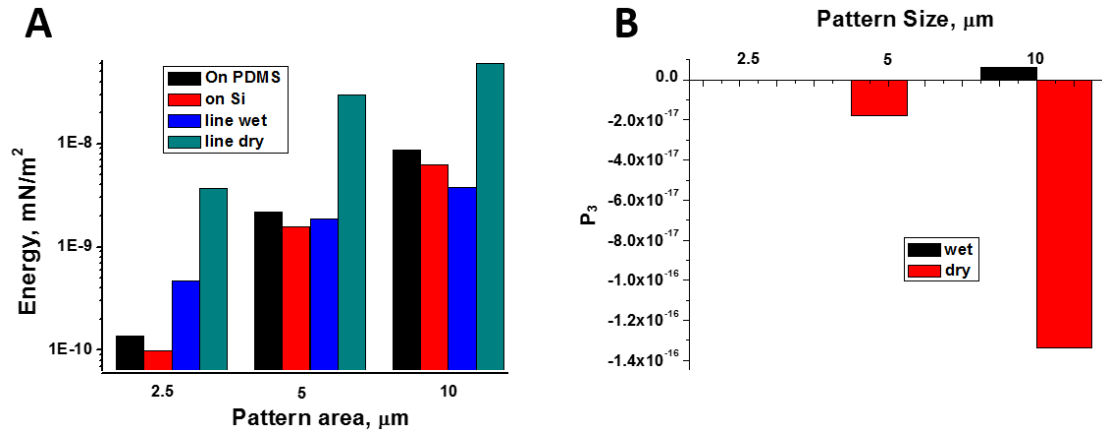


Fig. S 3 Critical size for using a PTFE coated wafer and a PDMS printing stamp. Due to the lower surface energy, printing 5 µm structures is critical (A). Structures of sizes in the range of 10 µm can be printed in wet condition as shown for P₃ in (B). In this figure the line tension values of sample type 3 are used.

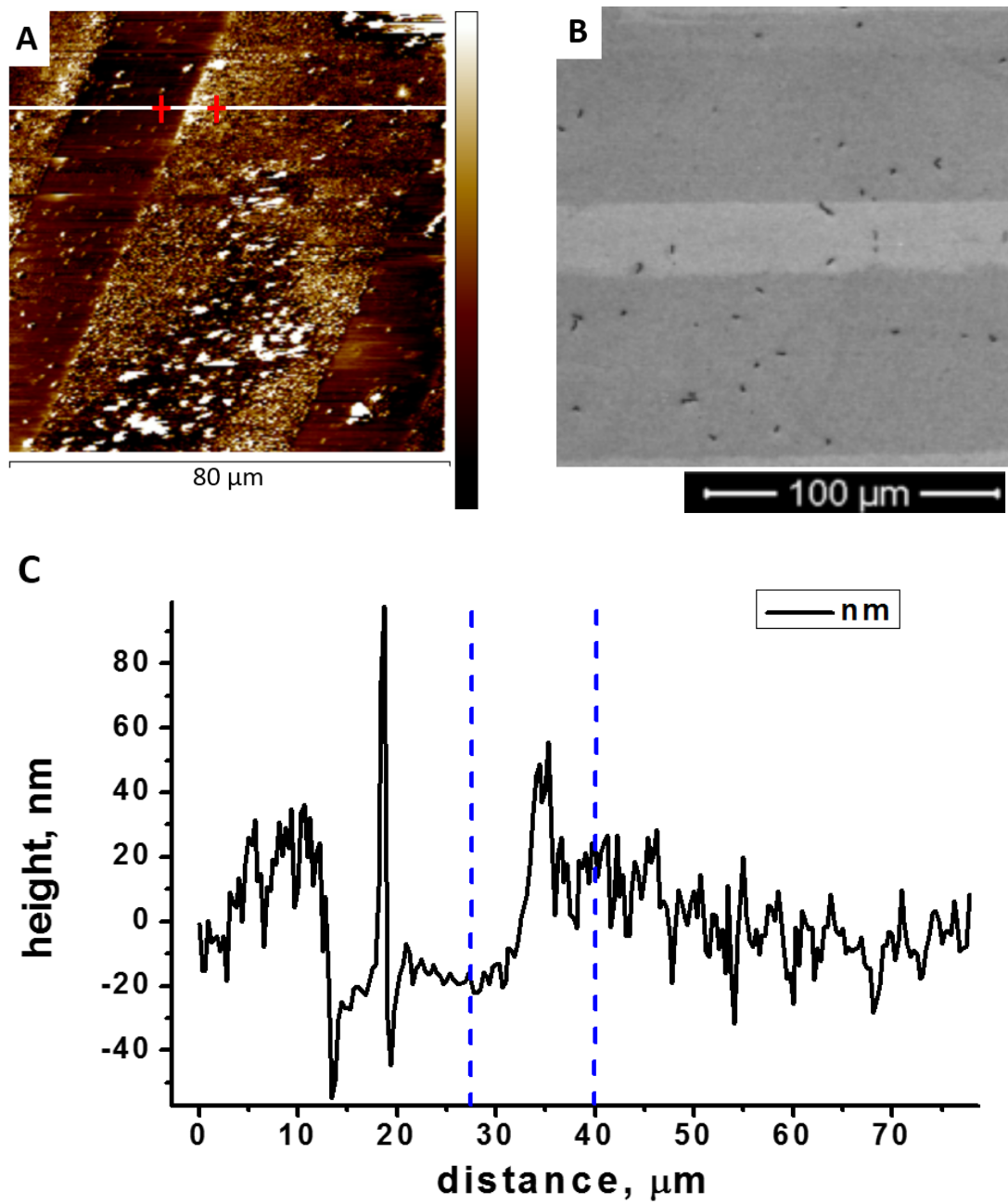


Fig. S 4 Comparison of (A) AFM and (B) SEM micrographs of printed PEM stripes produced with sample 3. (C) Shows the line section scan outlined in (A). The height of a usual printed structure is ~ 35 nm.

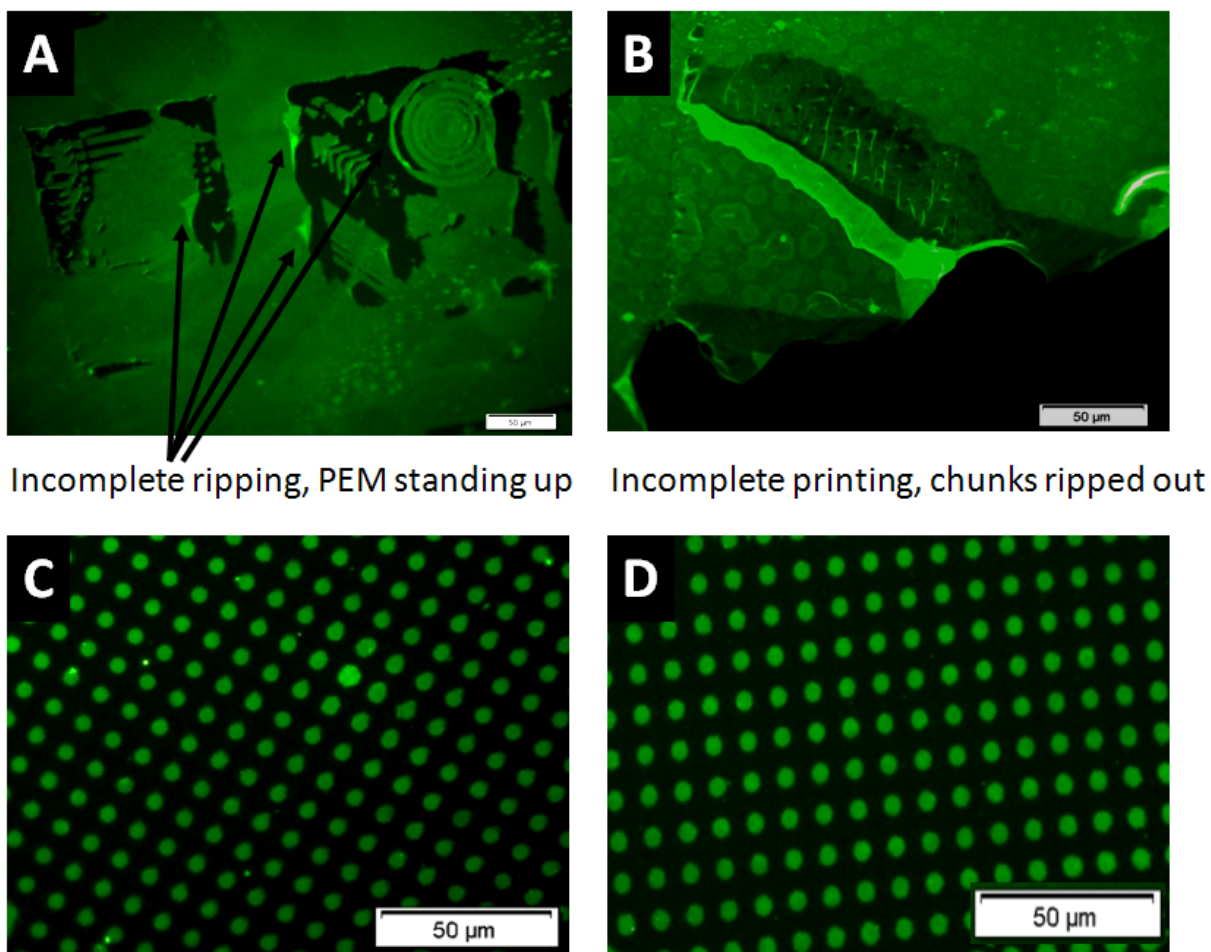


Fig. S 5 Different PEM films under a variety of conditions (all printed in wet condition) and the response in printing quality. (A) Sample 8, scale bar 50 μm . Minimum clear printing pattern size is around 10-15 μm , not repeatable at 5 μm . The borders are not clearly ripped. (B) Sample 6. Only 2 % of the area show patterns at all, which are also not clear. Mostly nothing or chunks ripped out. (C) Sample 3, clear printing (D) Sample 7 (25 $^{\circ}\text{C}$, 20-50 g pressure) mostly nice prints, comparable to C).

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