Supporting Information

Unveiling the Dynamics of Self-Assembled Layers of Thin Films of PVME by Nanosized Relaxation Spectroscopy

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Atomic force microscopy (AFM)

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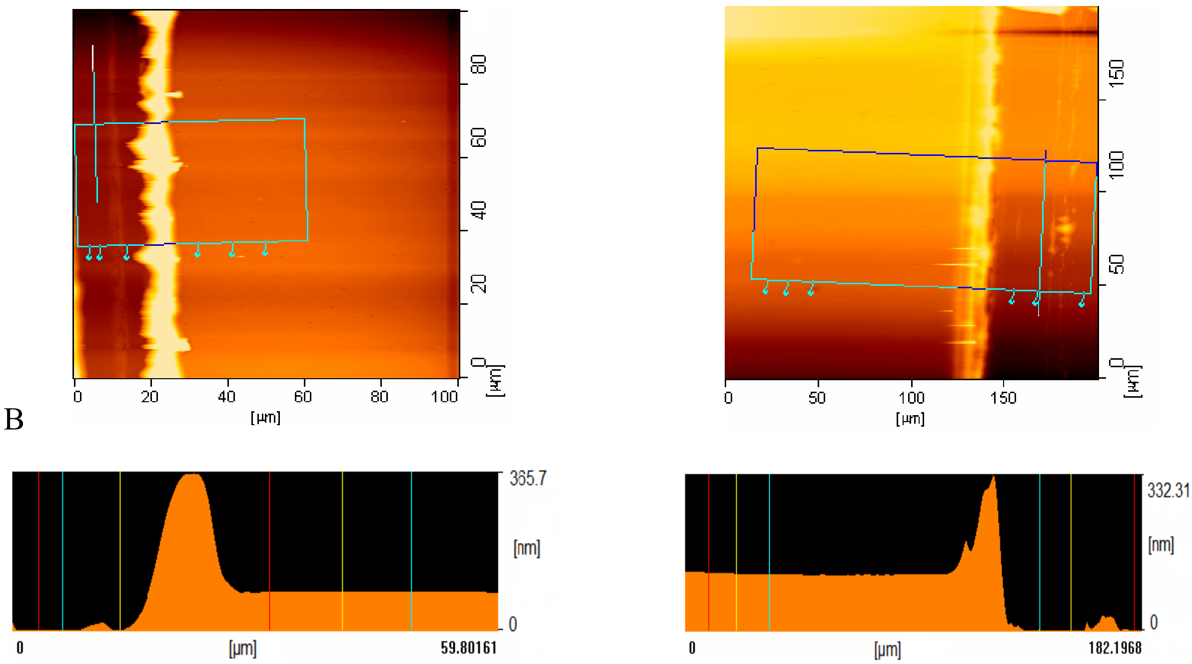

Figure **S1:** AFM image of a scratch across (left) the Al-electrode and (right) PVME film on the same Al-electrode (A), cross section view (B) of the rectangular area indicating that the average thickness of the film in the marked scratch was ca. 50 nm. No sign of dewetting was found.

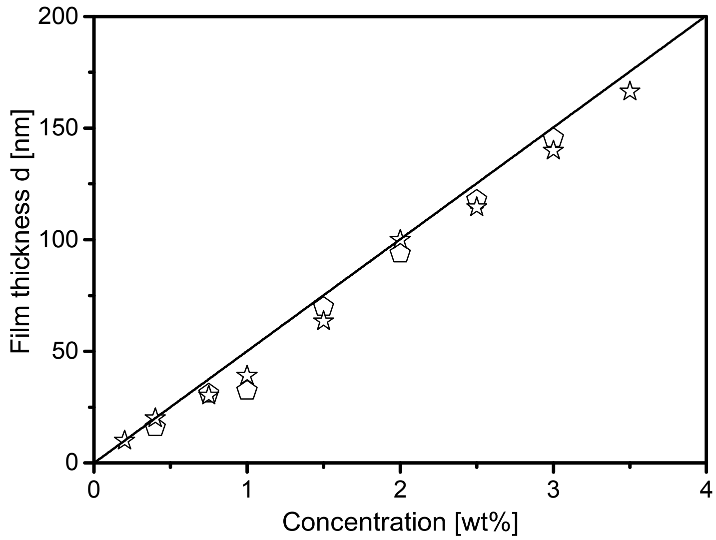

Figure **S2:** Film thickness versus concentration of the polymer solution. Stars - ellipsometry thicknesses of PVME; black circles - thickness values estimated by AFM. The solid red line represents a common linear regression of the data.

Broadband dielectric spectroscopy (BDS)

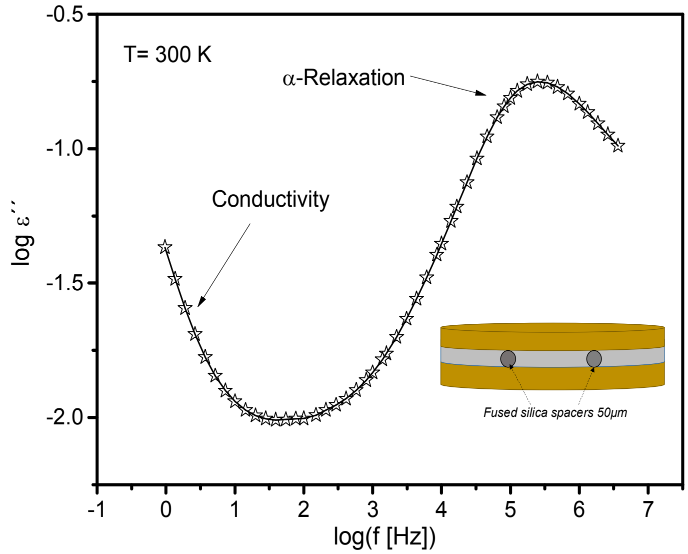

Figure S**3.** Dielectric loss spectra for bulk PVME at 300 K- stars. The solid line is a fit of equation 3 to the data. Inset: Schematic of the sample geometry used to measure bulk PVME.

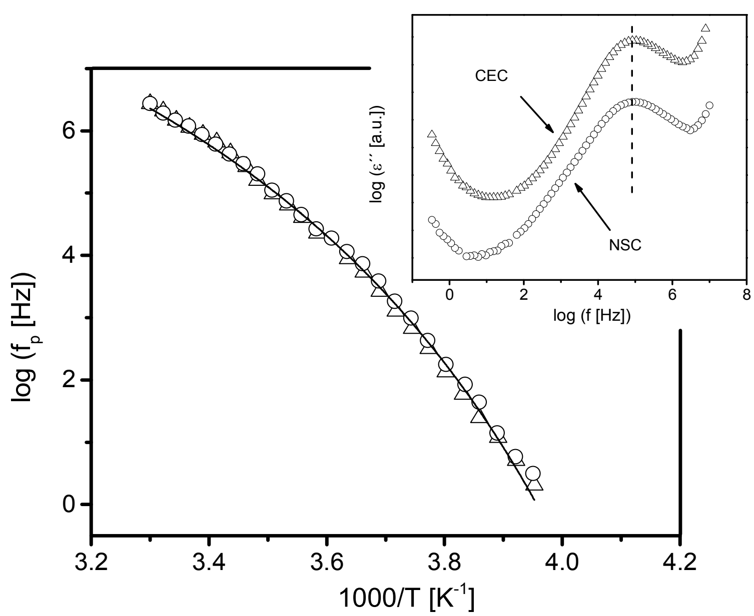

Figure S**4.** Relaxation map of ca. 50 nm PVME films measured by CEC –triangles and NSC –circles. The solid line is a common VFT fit to the data. Inset: Dielectric loss spectra at 293 K for a ca. 50 nm PVME ultrathin film using the CEC - triangles and NSC – circles. The curves are shifted along the y-scale for sake of clearness.

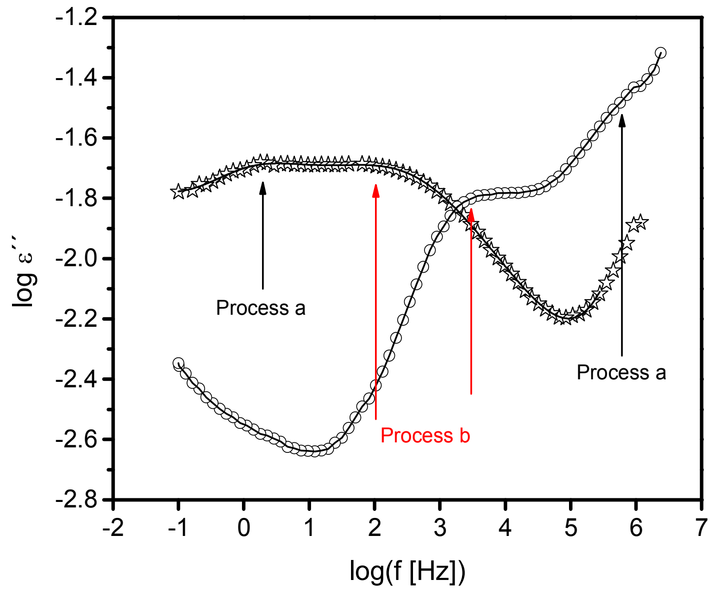

Figure S**5.** Dielectric loss spectra at 305 K -circles and 253 K -stars for a ca. 7 nm PVME thin film using the NSC. The solid lines are fits for the data using equation 3. Process (a) α-relaxation of PVME and process (b) the relaxation of the segments within the part of the adsorbed layer with logarithmic time dependence.

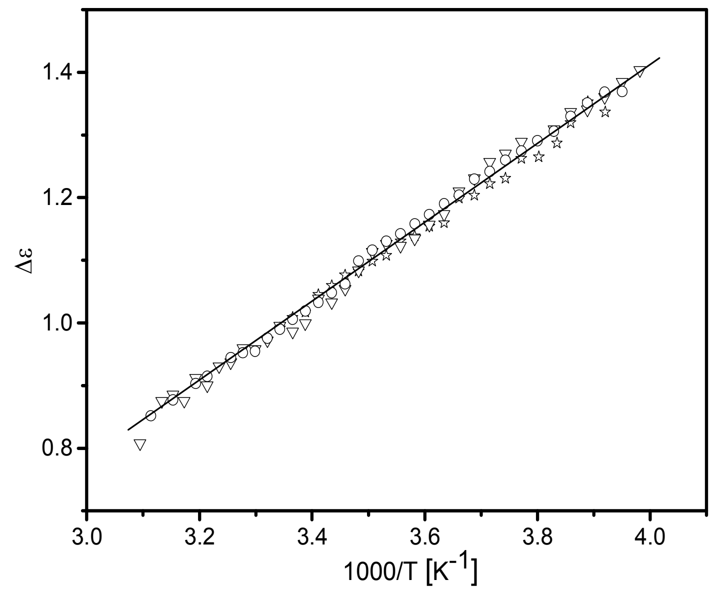

Figure S**6.** Dielectric strength for PVME ultrathin films in CEC with thicknesses of 160 nm– circles, 110 nm-upside triangles and 50 nm – stars. The solid lines are linear fits to the data.

Contact angle measurements (CAM)

$$(1+\cos\theta_i)\gamma_{L,i} = 2[(\gamma_{PVME}^{LW}\gamma_{L,i}^{LW})^{\frac{1}{2}} + (\gamma_{PVME}^{+}\gamma_{L,i}^{-})^{\frac{1}{2}} + (\gamma_{PVME}^{-}\gamma_{L,i}^{+})^{\frac{1}{2}}] \qquad \text{(S1)}$$

$$a_i\gamma^{PVME} = 2[b_i(\gamma_{PVME}^{LW})^{\frac{1}{2}} + c_i(\gamma_{PVME}^{+})^{\frac{1}{2}} + d_i(\gamma_{PVME}^{-})^{\frac{1}{2}}] \qquad \text{(S2)}$$

$$\frac{(1+cos\ \theta_i)\gamma_{L,i}}{2\sqrt{\gamma_{L,i}^{LW}}} = \sqrt{\gamma_S^P}\frac{\sqrt{\gamma_{L,i}^{p}}}{\sqrt{\gamma_{L,i}^{LW}}} + \sqrt{\gamma_S^{LW}} \qquad \text{(S3)}$$

Test liquids	Contact angle
Glycerol	89.9°
HDEC	13.3°
PEG	64.6°
TDEC	7.4°

Table S**1:** Contact angle values of the test liquids used for poly(vinyl methyl ether).

	γ^{Total} [mJ m^{-2}]	γ^{LW} [mJ m^{-2}]	γ^{P} [mJ m^{-2}]
PVME	27.4	26.01	1.36
AlO_2	30.4	26.5	3.9
SiO_2	47.0	44.6	2.3

Table S**2:** Total surface energies γ^{Total} and their dispersive γ^{LW} and polar γ^{p} components for PVME, SiO_2 and AlO_2 surfaces of the capacitors.

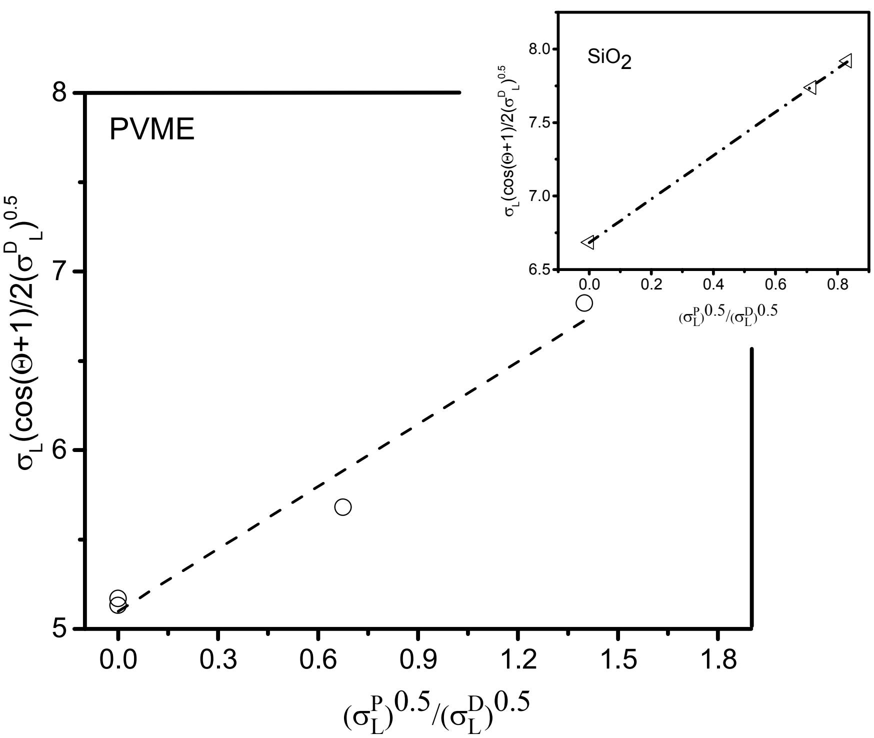

Figure S**7**. Owens/Wendt plot according to Equ. (S3). The polar and dispersive components of the solid surface energy are estimated by linear regression. Results are presented in Table S1.