Supporting Information

Monolayer Point and Vapor Phase Infiltration

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Section S1 – P2VP Brush Monolayer Formation

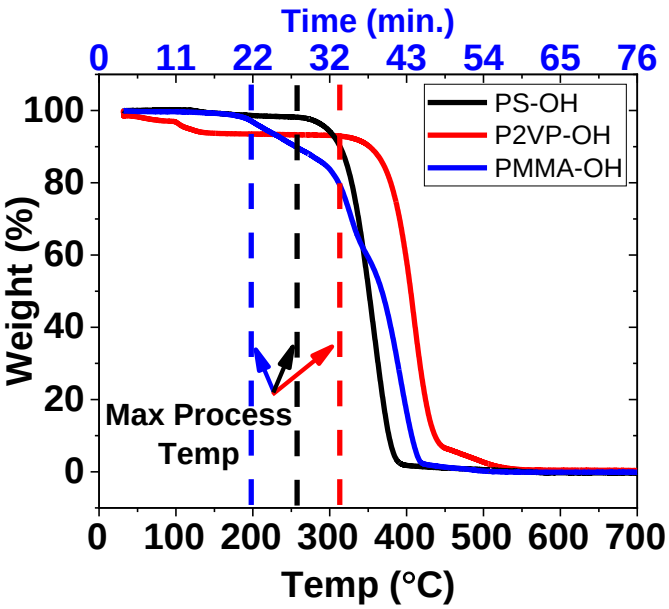

Figure S1 Thermogravimetric data from the 6 kg mol^{-1} functionalized polymers in a temperature range from 25°C - 700°C (samples treated for 90 min). The polymers undergo thermal degradation (PMMA-OH ≈ 195 °C, PS-OH ≈ 260 °C and P2VP-OH ≈ 320 °C) indicating the maximum upper threshold for the grafting process. Note that water loss occurs up to ≈ 120-130 °C.

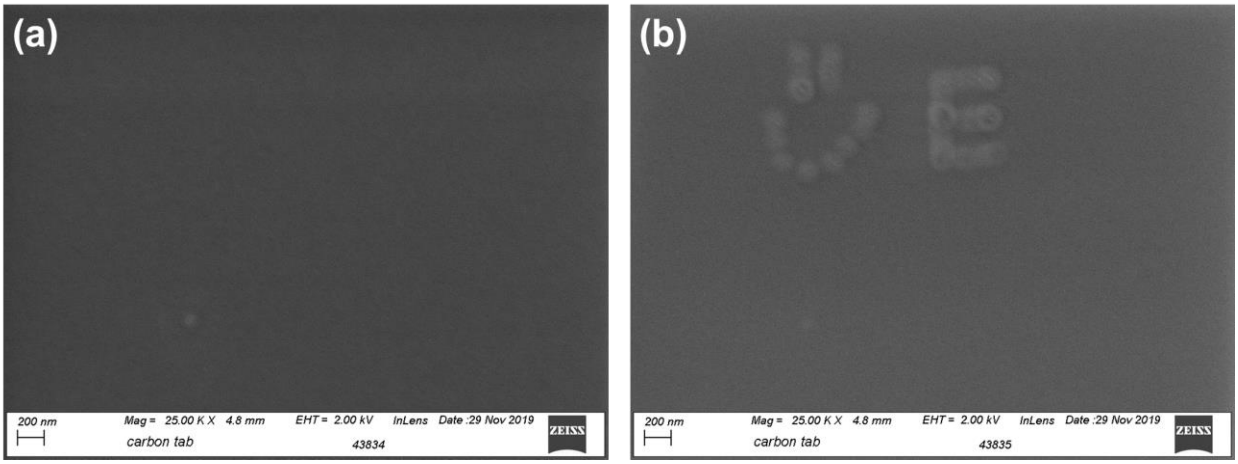

Figure S2 SEM images (a) and (b) of the 6 kg mol^{-1} P2VP-OH (0.2 wt. %) monolayer. Focusing the electron beam at specific points induces swelling in the polymer film (b).

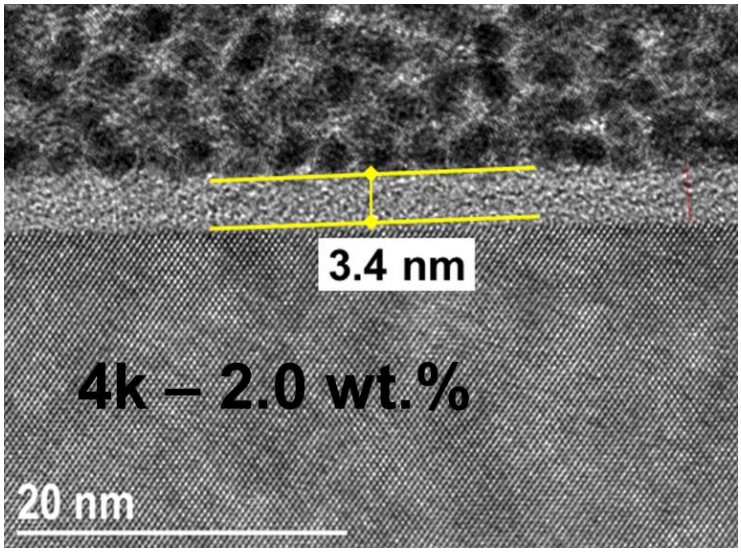

Figure S3 Bright-field TEM image of the 4 kg mol^{-1} P2VP-OH grafted from a 2.0 wt. % casting solution

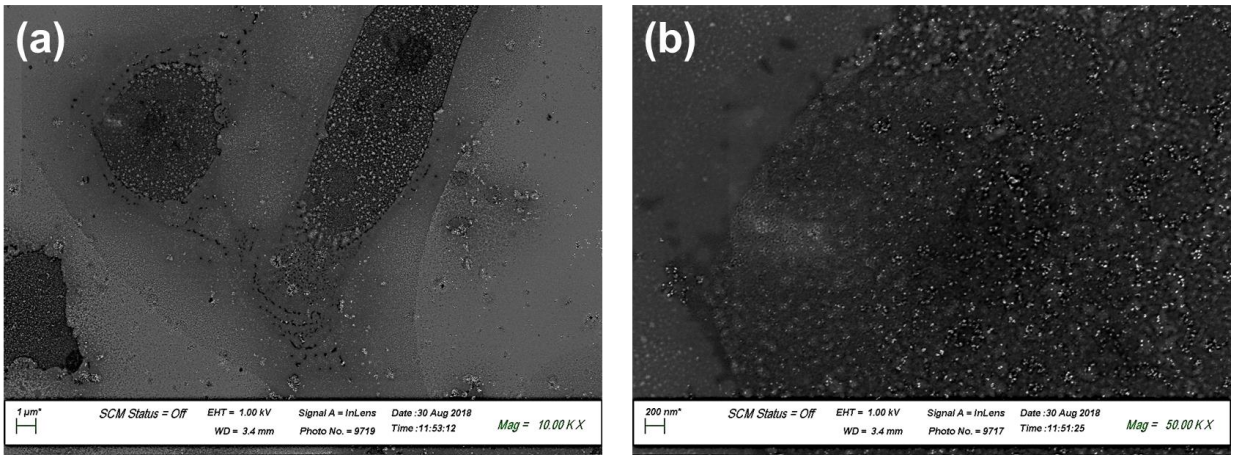

Figure S4 SEM images **(a)** and **(b)** of a 6 kg mol^{-1} P2VP-OH cast and grafted from a 2.0 wt. % solution (i.e. above CAC). Complete uniform monolayers form below the critical agglomeration concentration (< 1 wt. % for 6 kg mol^{-1} P2VP-OH).

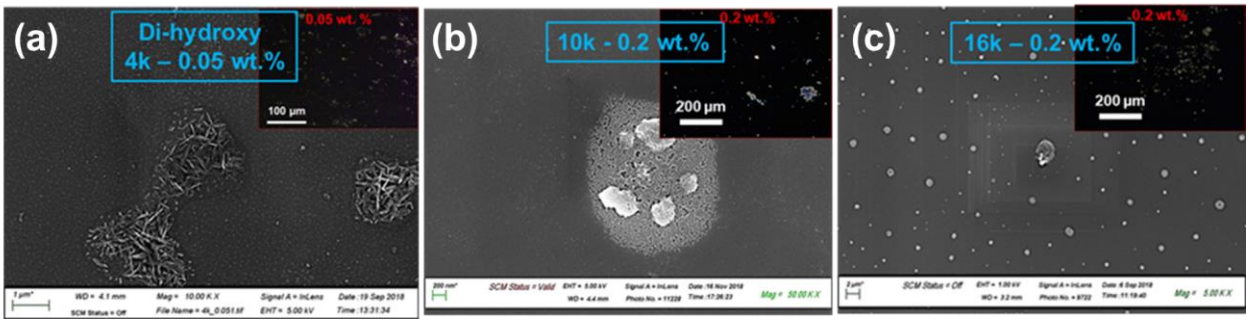

Figure S5 SEM images with darkfield optical microscopy (inset) for P2VP-OH cast and grafted from **(a)** di-hydroxy terminated 4 kg mol^{-1} and **(b)** mono-hydroxy terminated 10 kg mol^{-1} and **(c)** mono-hydroxy terminated 16 kg mol^{-1}.

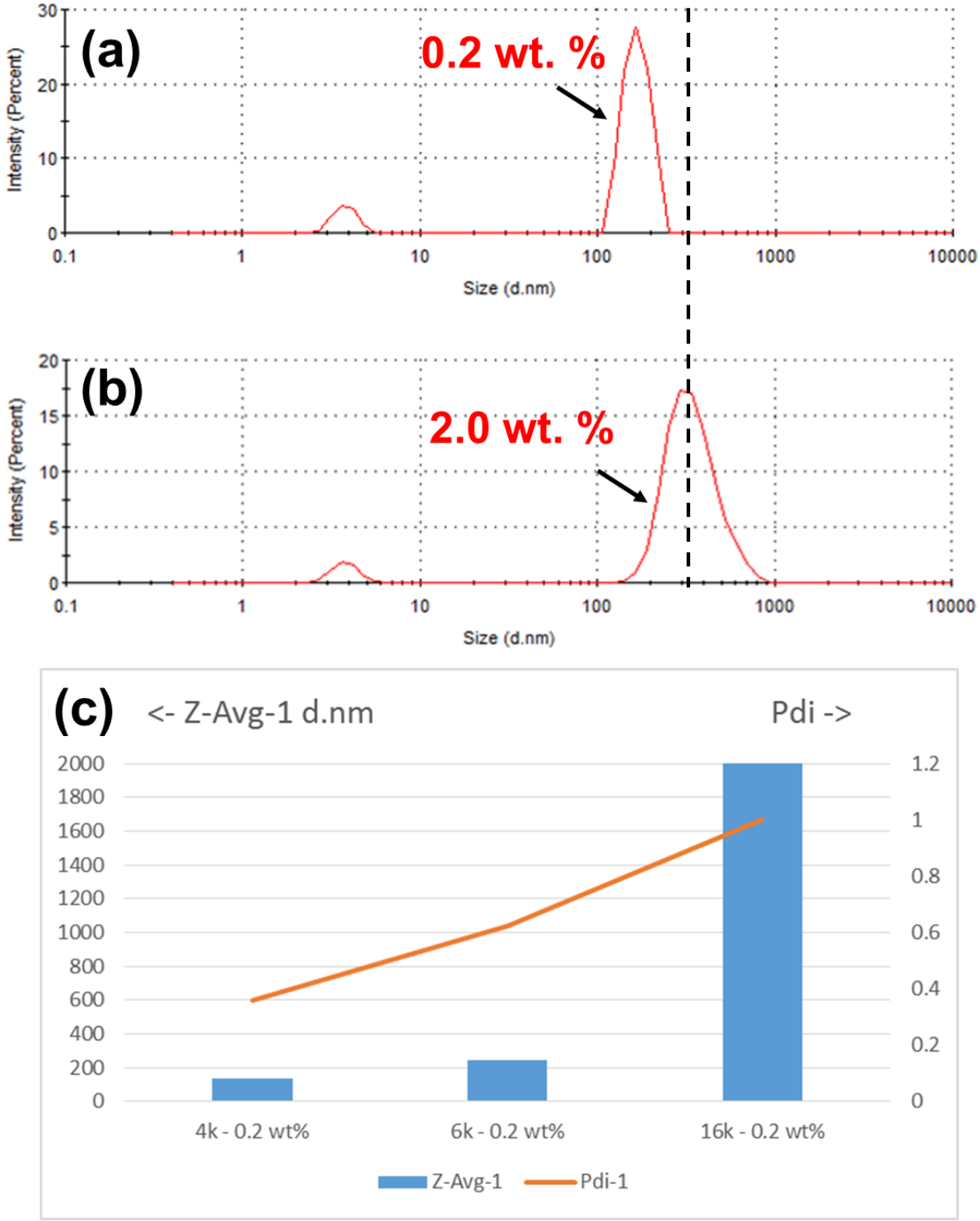

Figure S6 Dynamic light scattering data of P2VP casting solutions for **(a)** 0.2 wt. % (6 kg mol^{-1}) and **(b)** 2.0 wt. % (6 kg mol^{-1}) showing the effect of concentration on agglomeration size. **(c)** Average agglomeration size as a function of molecular weight (4 – 16 kg mol^{-1}) at fixed concentration (0.2 wt. %).

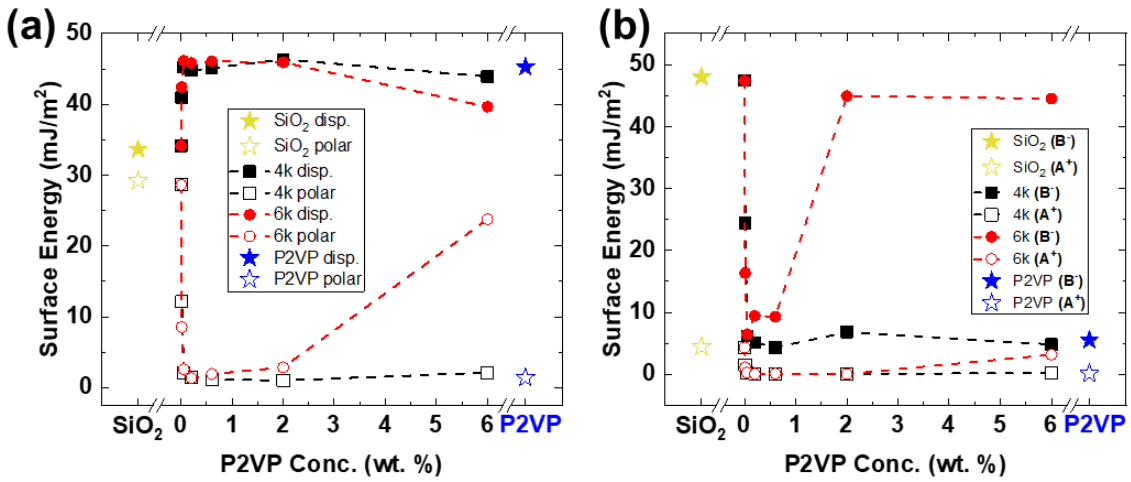

Figure S7 (a) Apolar (dispersive) and polar surface energy and **(b)** Lewis acid (A^+) and Lewis base (B^-) interactions for annealed brush samples over a range of concentrations (0.01 – 6.0 wt. %). The dashed lines are a guide for the eye.

Section S2 – PS Brush Monolayer Formation

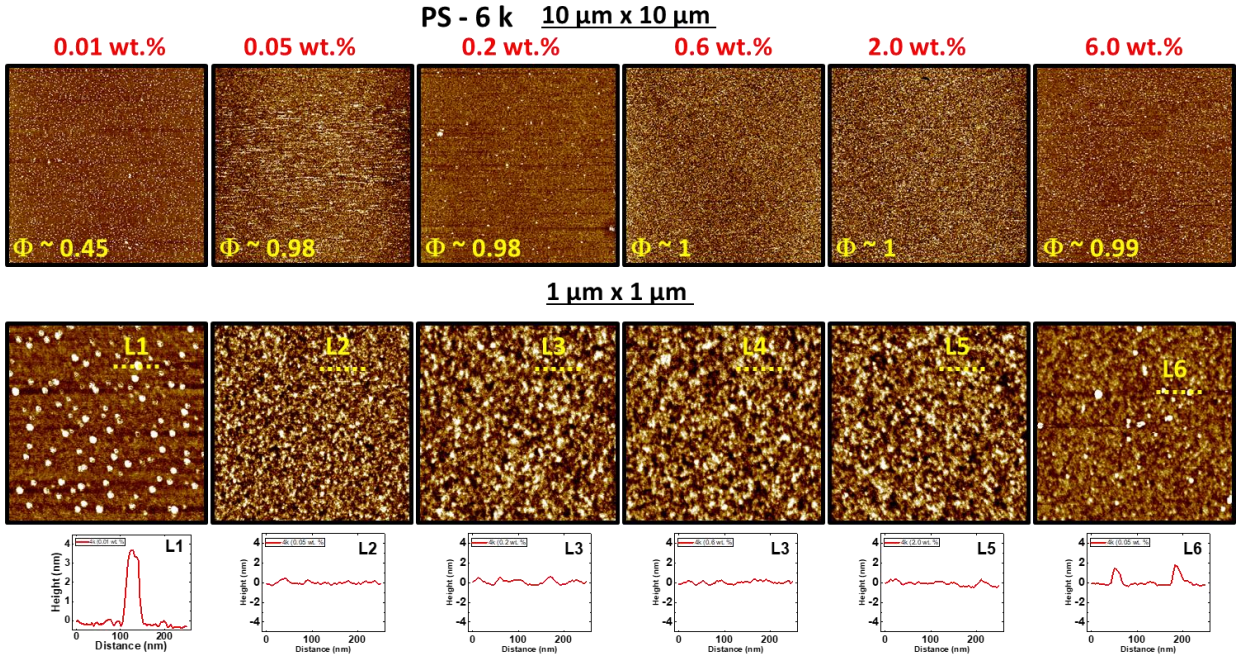

Figure S8 AFM images with roughness profile at L1 – L6 for the **6** kg mol^{-1} PS-OH grafted at various concentration (0.01 – 6.0 wt. %). High coverage monolayer formation is evident even at very high casting concentrations.

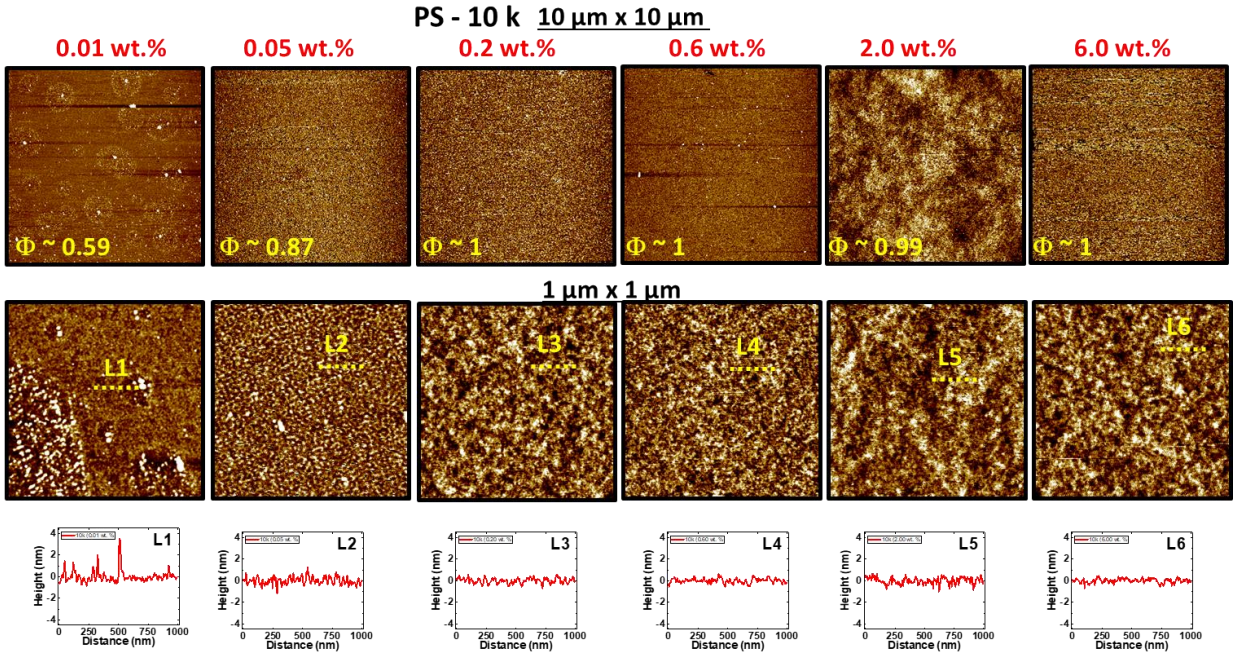

Figure S9 AFM images with roughness profile at L1 – L6 for the **10** kg mol^{-1} PS-OH grafted at various concentration (0.01 – 6.0 wt. %). High coverage monolayer formation is evident even at very high casting concentrations.

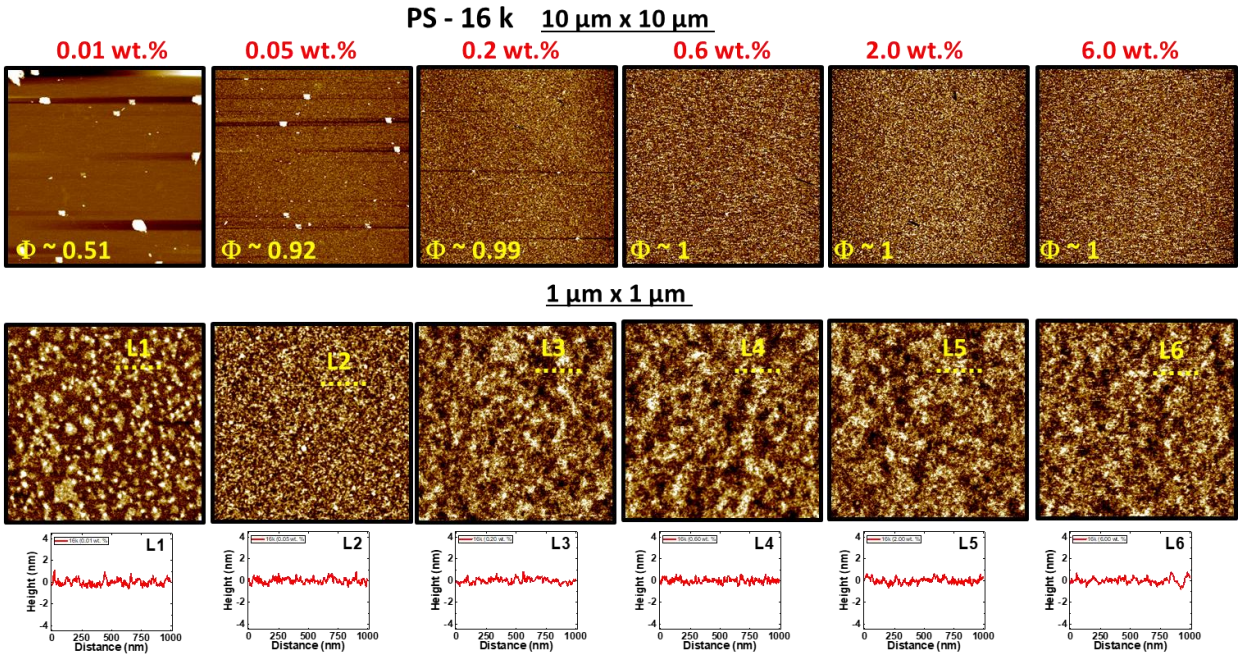

Figure S10 AFM images with roughness profile at L1 – L6 for the **16** kg mol^{-1} PS-OH grafted at various concentration (0.01 – 6.0 wt. %). High coverage monolayer formation is evident even at very high casting concentrations.

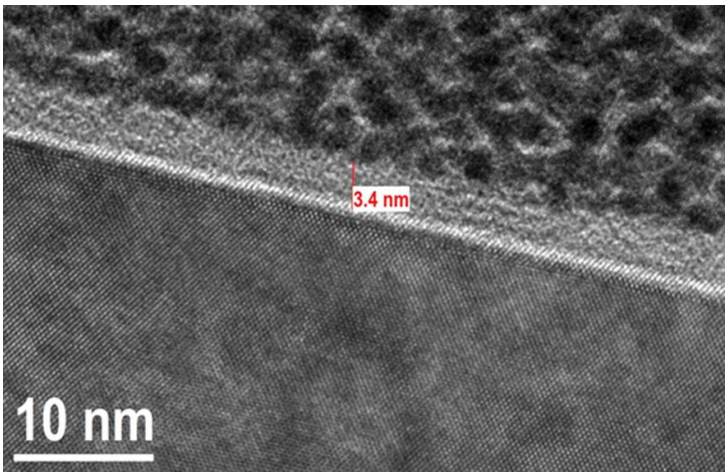

Figure S11 Bright-field TEM image of the 6 kg mol^{-1} PS-OH sample.

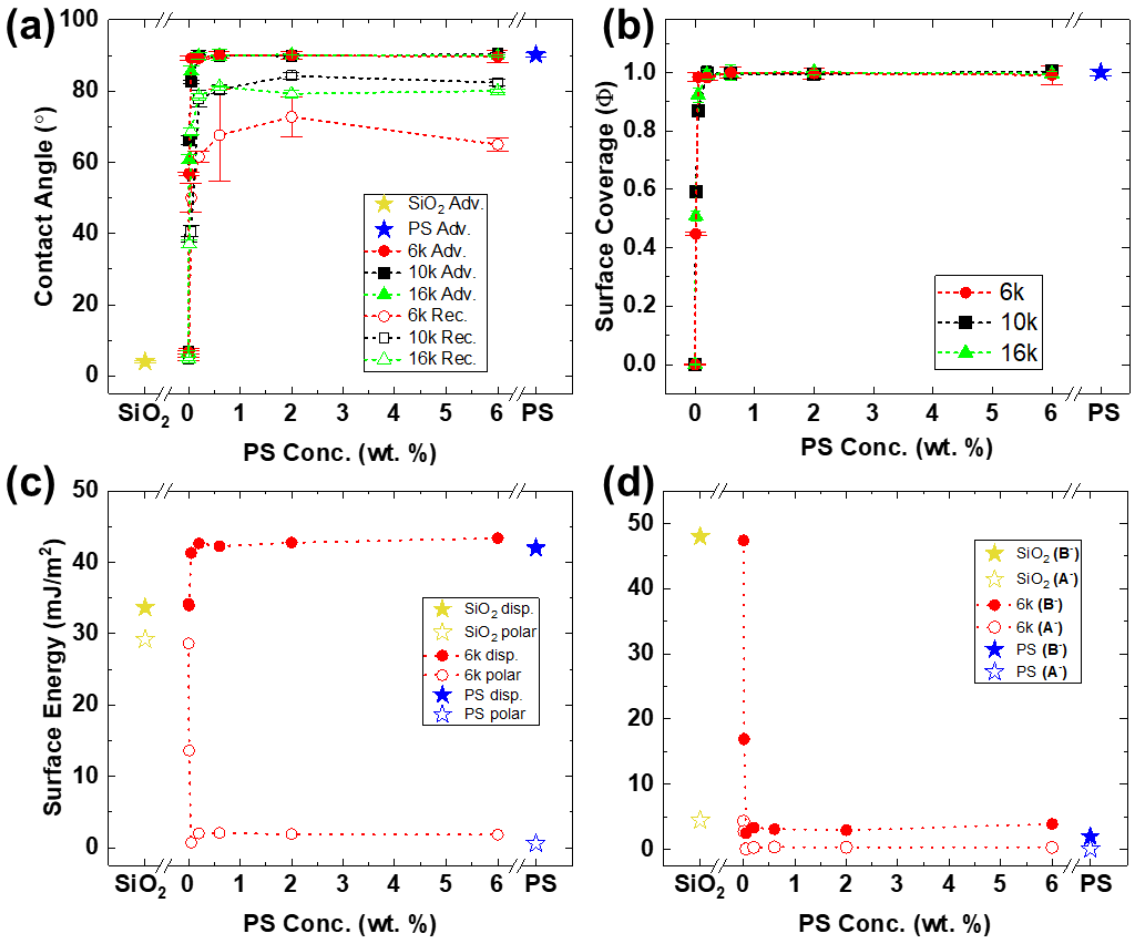

Figure S12 (a) Water contact angles of the PS-OH brush samples (6 – 16 kg mol^{-1}) annealed over a range of concentrations (0.01 – 6.0 wt. %) with corresponding coverage (**b**). **(c)** Apolar (dispersive) and polar surface energy and **(d)** Lewis acid (A^+) and Lewis base (B^-) interactions for the 6 kg mol^{-1} annealed brush. The dashed lines are a guide for the eye.

Section S3 – PMMA Brush Monolayer Formation

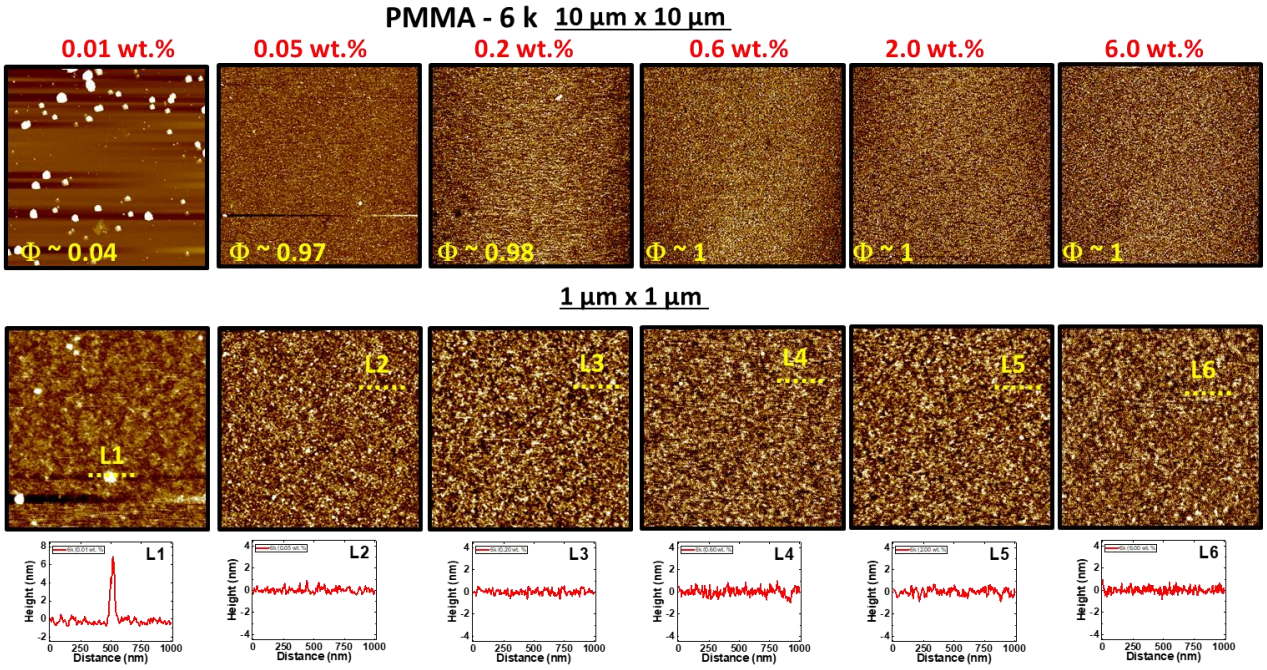

Figure S13 AFM images with roughness profile at L1 – L6 for the **6** kg mol^{-1} PMMA-OH grafted at various concentrations (0.01 – 6.0 wt. %). High coverage monolayer formation is evident even at very high casting concentrations.

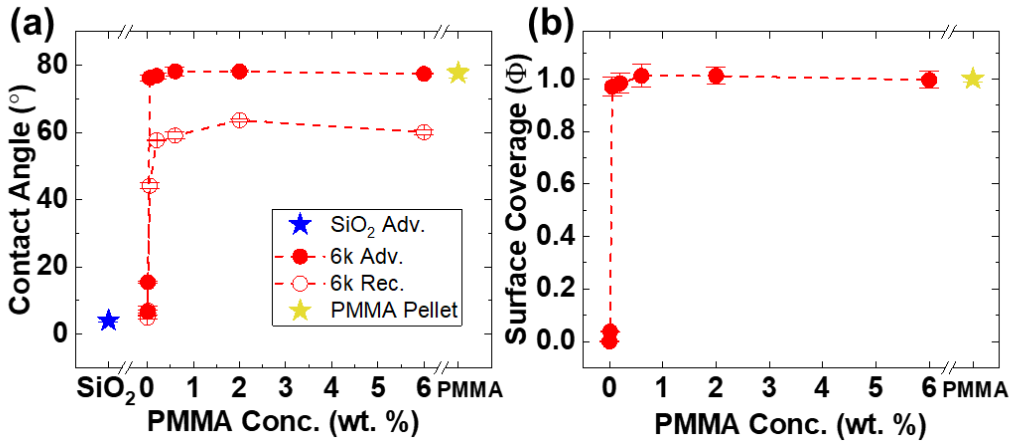

Figure S14 (a) Water contact angles of the PS-OH brush samples (6 – 16 kg mol^{-1}) annealed over a range of concentrations (0.01 – 6.0 wt. %) with corresponding coverage (**b**). The dashed lines are a guide for the eye.

Section S4 – Brush Exposure to Titanium Isopropoxide

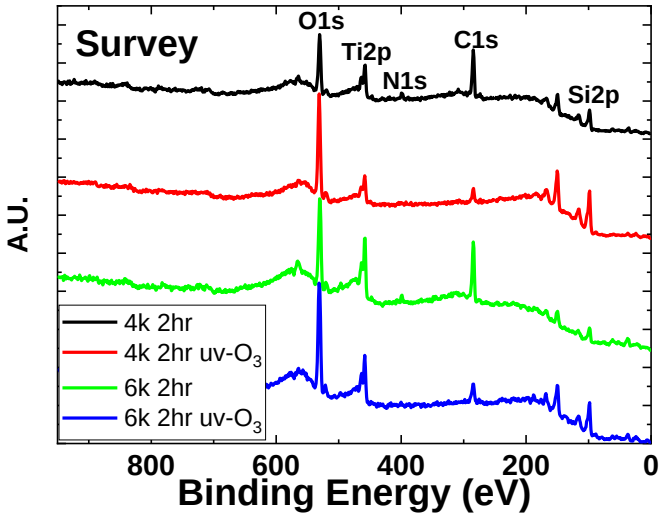

Figure S15 XPS survey spectra of grafted 4 and 6 kg mol^{-1} P2VP sample exposed to TTIP and after subsequent uv/ozone treatment.

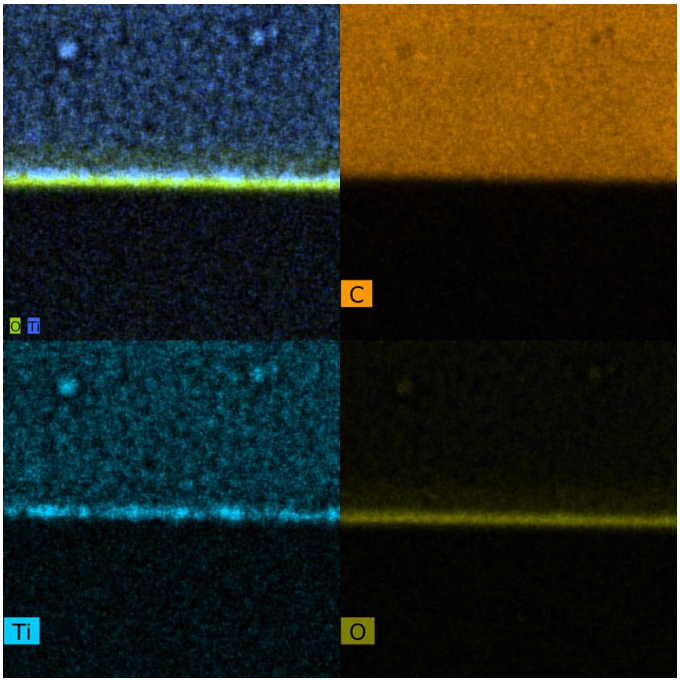

Figure S16 EDX maps (C, Ti, O) of the 6 kg mol^{-1} P2VP brush sample exposed to TTIP (before UV/ozone treatment)

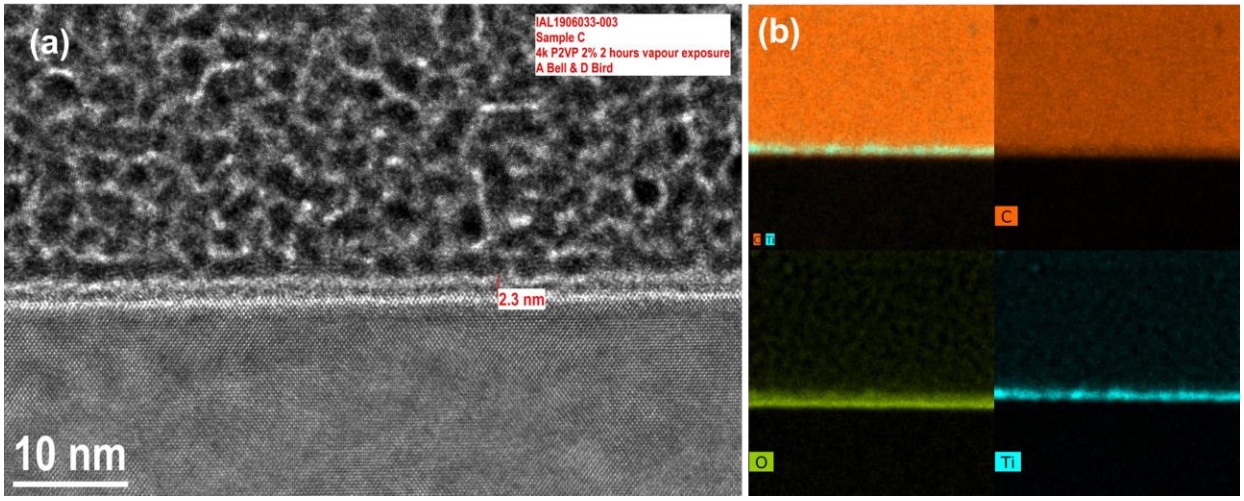

Figure S17 (a) Bright-field TEM image of the 4 kg mol^{-1} P2VP brush sample exposed to TTIP (before uv/ozone treatment) and **(b)** the corresponding EDX maps (Ti, C, O).

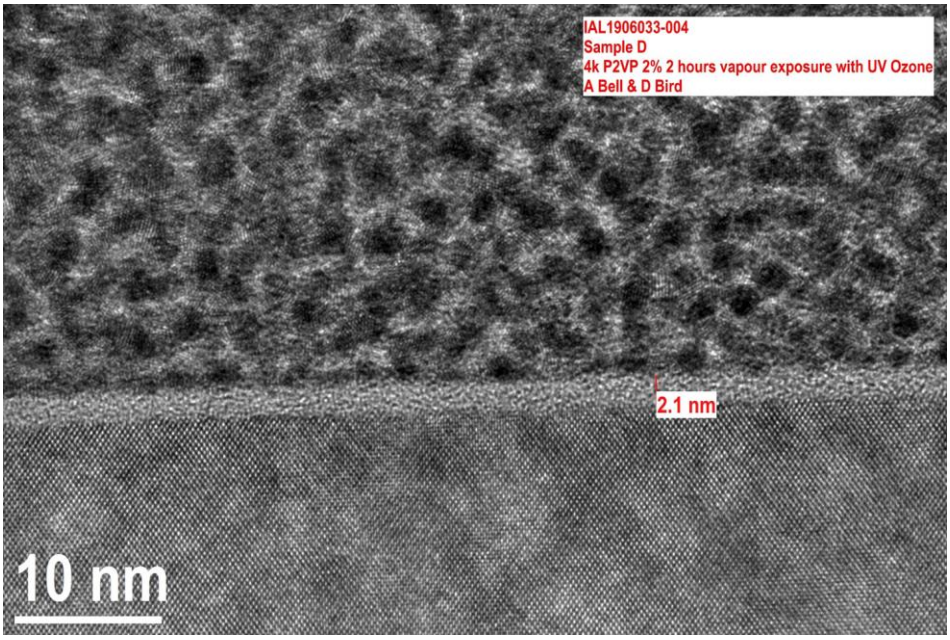

Figure S18 Bright-field TEM image of the titanium dioxide film formed from the 4 kg mol^{-1} P2VP brush sample (after uv/ozone treatment)

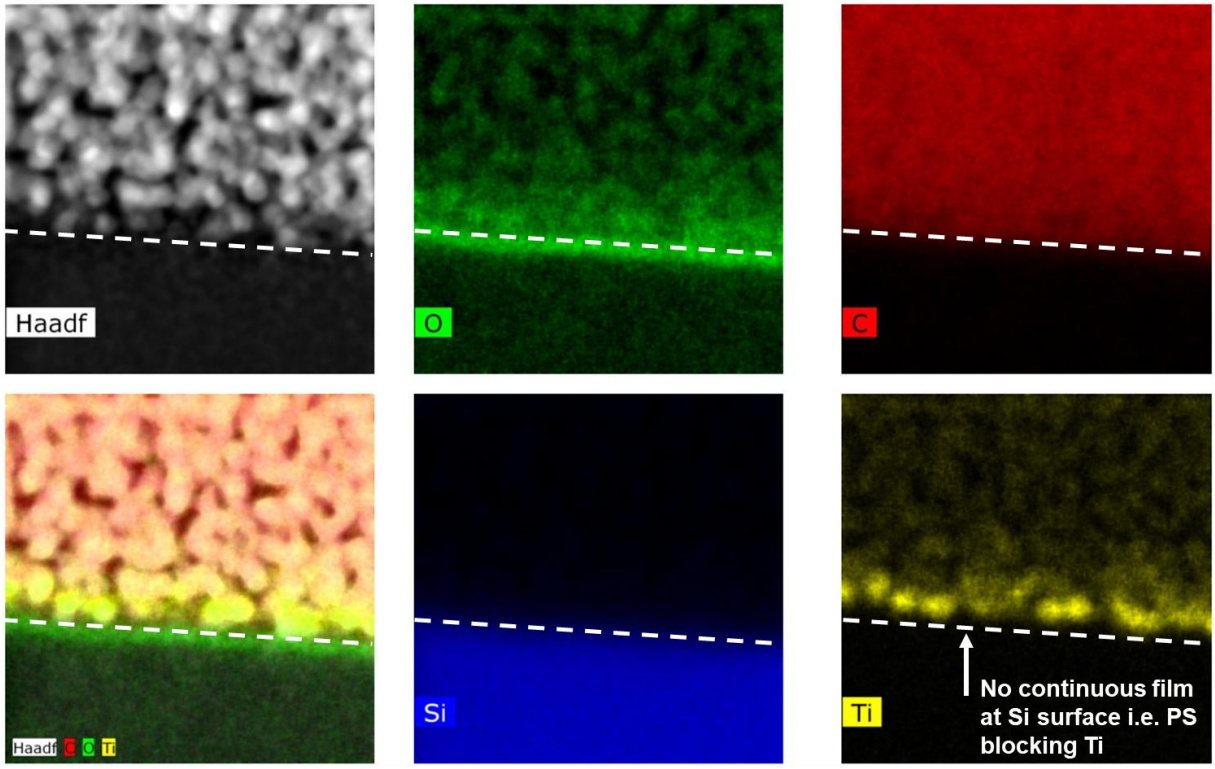

Figure S19 STEM image (HAADF) and EDX maps (O, C, Si, Ti) of the 6 kg mol^{-1} PS grafted polymer after exposure to TTIP.