

Supporting Information

Swelling and surface interactions of end-grafted poly(2-vinyl pyridine) layers in acidic solution: influence of grafting density and salt concentration

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1. AFM images of the grafted P2VP layers in dry state

Prior to the force measurements, the grafted P2VP layers were imaged in dry state using the colloidal probe. These images are shown for $\sigma \sim 0.03 \text{ nm}^{-2}$ and $\sigma \sim 0.06 \text{ nm}^{-2}$ in Figure S1. Figure S2 compares cross-sections from the AFM images for all three grafting densities. They were corrected such that the average layer height represents the thickness obtained by ellipsometry.

The layer with $\sigma \sim 0.03 \text{ nm}^{-2}$ (average thickness determined by ellipsometry 2.13 nm) consists of an array of single asperities of about 5 nm height. This is a typical image of a polymer layer in the “mushroom regime”. In contrary, layers with higher grafting densities have a rather smooth surface in dry state with a roughness lower than the layer thickness indicating a “brush regime”.

AFM images of dry grafted P2VP layers of comparable grafting densities but prepared in a slightly different way are published elsewhere¹. They show a closed layer with an average thickness of 2.1 nm and small holes at $\sigma \sim 0.03 \text{ nm}^{-2}$. This layer is assumed to be in a mushroom-to brush transition regime. At grafting densities of 0.06 nm^{-2} and 0.12 nm^{-2} , AFM images of the dry layer show a closed film with height variations smaller than its thickness. Thus a brush regime is assumed for these higher grafting densities.

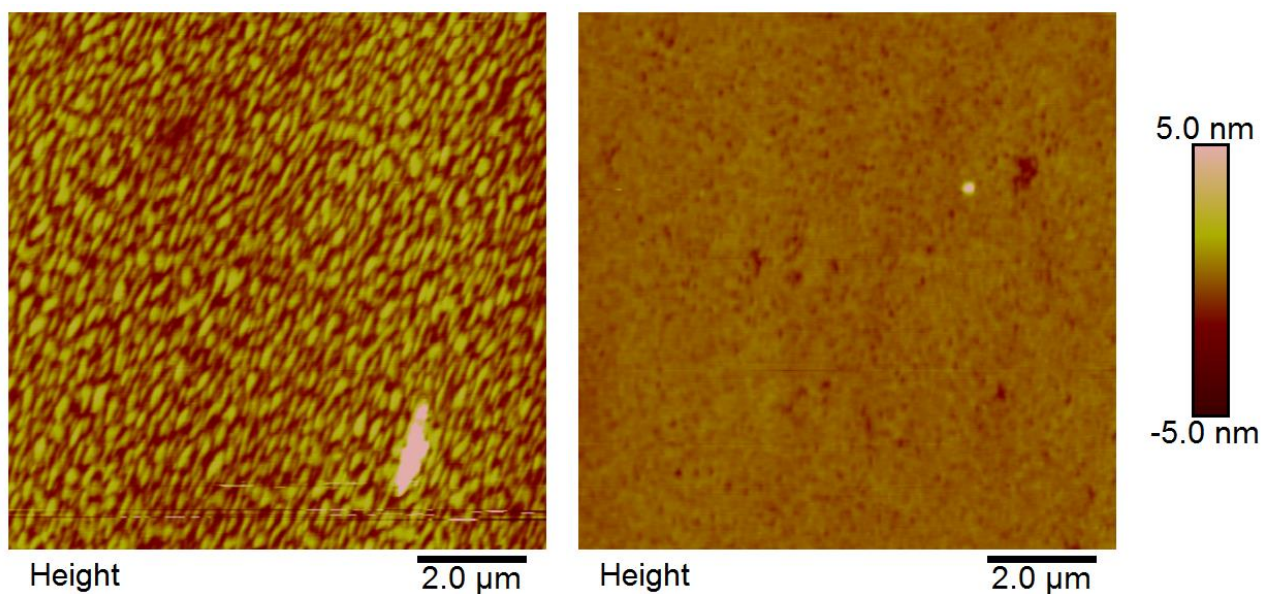


Fig. S1 AFM images of the grafted P2VP layers in dry state taken with the colloidal probe used for force measurements. Left: $\sigma \sim 0.03 \text{ nm}^{-2}$, right: $\sigma \sim 0.06 \text{ nm}^{-2}$. The scale bar is valid for both images.

¹ Neubauer, N.; Winkler, R.; Tress, M.; Uhlmann, P.; Reiche, M. Kipnusu, W. K, Kremer, F. Glassy dynamics of poly(2-vinyl-pyridine) brushes with varying grafting density, *Soft Matter* **2015**, 11, 3062-3066.

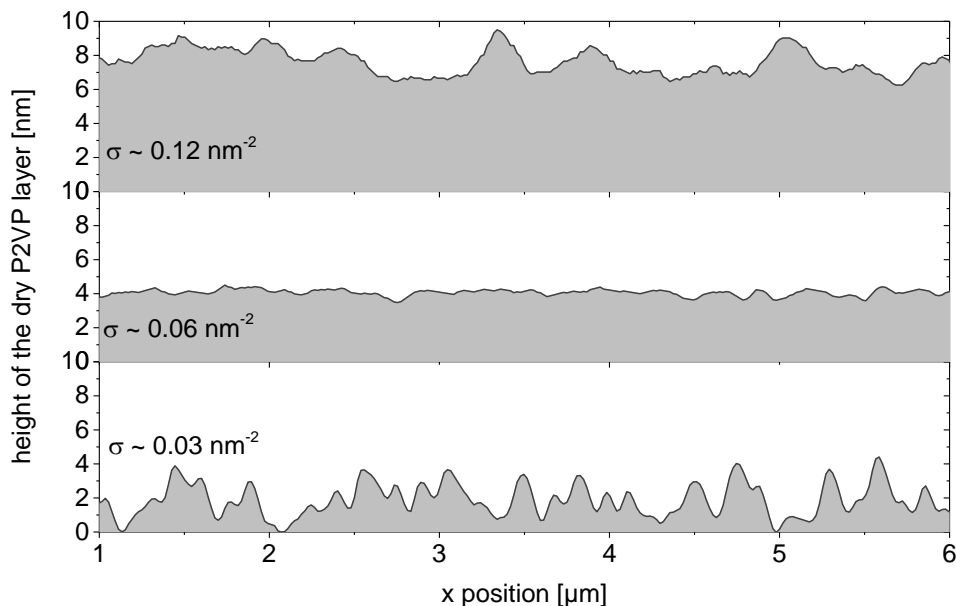


Fig. S2 Profiles of the grafted P2VP layers in dry state (cross-sections of AFM images + average thickness obtained by ellipsometry).

2. Detailed results of the Alexander-de Gennes fits

To obtain satisfactory fits of the interaction energy-distance curves using the Alexander-de Gennes formalism (Equation 2 in the main paper), in most cases the inner and outer part of the curves had to be fitted separately using different fit parameters. All parameters are summarized in Table S1. This reflects the non-parabolic segment density profile of these polyelectrolyte brushes. For the calculation of the brush height and the corresponding pseudotail distance, the fits of the outer part of the Interaction-distance curves were used. The fits of the inner part of the curves yield lower values of the “pseudotail distance” s indicating a higher segment density than in the outer part. The low values of s result from an interplay of steric and electrostatic repulsion and do not represent the true interchain distance within the brush.

For some curves, no fitting could be performed due to a differing shape of the curve or to attractive interactions on approach. In this case the steep decay of the interaction energy at the rim of the layer was used to estimate the brush height independent of a theoretical model. For this purpose, we extrapolated the energy-distance curve to an energy of $1 \times 10^{-4} \text{ mJ/m}^2$ and estimated the corresponding distance. In this case, not “pseudotail distance” s could be determined.

Table S1 Fit parameters used for approximating the interaction-distance curves in Figure S3 according to the Alexander-de Gennes model (equation 2 in the main manuscript).

	$\sigma \sim 0.12 \text{ nm}^{-2}$		$\sigma \sim 0.06 \text{ nm}^{-2}$		$\sigma \sim 0.03 \text{ nm}^{-2}$	
c_{Cl}^- [M]	s [nm]	L [nm]	s [nm]	L [nm]	s [nm]	L [nm]
4×10^{-3}	5^{in} 9^{out}	87^{in} 106^{out}	4^{in} 7.5^{out}	36^{in} 52^{out}	4.1^{in} 9^{out}	26^{in} 47^{out}
1.3×10^{-2}	5^{in} 8^{out}	73^{in} 87^{out}	3.2^{in} 5^{out}	27^{in} 31.8^{out}	4.2^{in} 5^{out}	25^{in} 29.5^{out}
0.1	6	64	3^{in} 4.8^{out}	23^{in} 27^{out}	3^{in} 6^{out}	18^{in} 24^{out}
0.3	8.5	71	5^{in} 7^{out}	35.5^{in} 45^{out}	2.2^{in} 5^{out}	14^{in} 18.5^{out}
1	- ^a	80 ^a	7.5	55	- ^b	35 ^b
3	- ^a	80 ^a	7.5	54	- ^b	33 ^b

ⁱⁿ fit parameters for the inner part of the interaction-distance curve^{out} fit parameters for the outer part of the interaction-distance curve^a no fitting possible due to shape of the interaction-distance curve, brush height estimated from the range of the repulsive interaction^b no fitting possible due to attractive interaction on approach, brush height estimated from the range of the attractive interaction

3. Comparison of interaction-distance curves of P2VP layers with different grafting density at fixed salt concentrations

Figures S3 and S4 compare the force-distance curves from Figures 1-3 in the main paper at constant salinity (4 selected values) and varying grafting density. They clarify the increasing range of the repulsive interaction on approach with increasing grafting density but also the influence of the grafting density on the adhesion force during retraction. For a detailed discussion see the main paper.

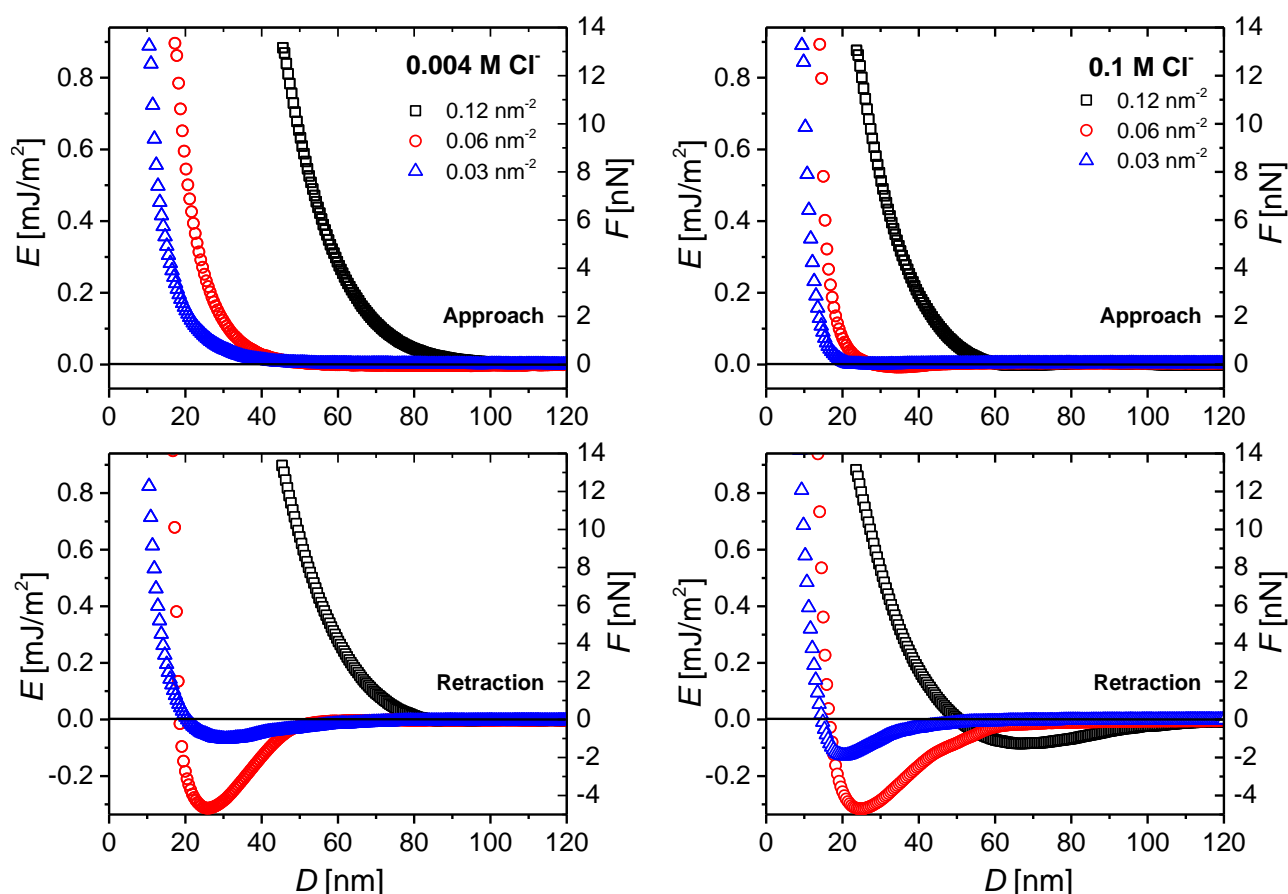


Fig. S3 Energy- and force-distance curves between grafted P2VP layers and a silica sphere at pH 2.5 and Cl⁻ concentration of 0.004 M (left) and 0.1 M (right) at different grafting densities. (top) approach curves; (bottom) retraction curves.

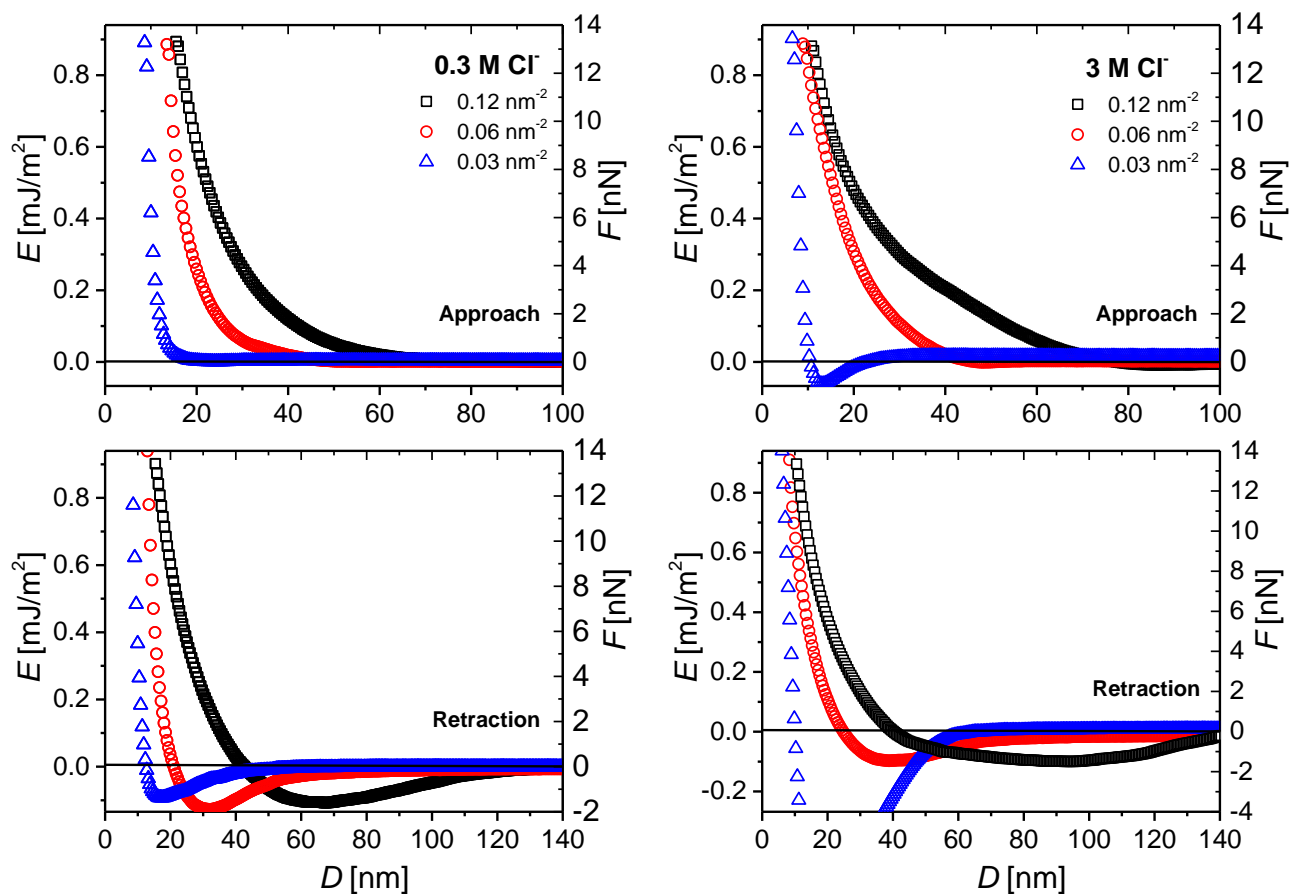


Fig. S4 Energy- and force-distance curves between grafted P2VP layers and a silica sphere at pH 2.5 and Cl^- concentration of 0.3 M (left) and 3 M (right) at different grafting densities. (top) approach curves; (bottom) retraction curves.