Supplementary Information

The pH and salt response of mixed brushes made of oppositely charged polyelectrolytes studied by in-situ AFM force measurements and imaging

Astrid Drechsler,[1,] Mahdy M. Elmahdy,[2] Petra Uhlmann,[1,3] and Manfred Stamm[1,4]*

[1]Leibniz Institute of Polymer Research Dresden, Hohe Str. 6, 01069 Dresden, Germany

[2]Department of Physics, Mansoura University, Mansoura 35516, Egypt

[3]Department of Chemistry, University of Nebraska-Lincoln, United States

[4]Technische Universität Dresden, Physical Chemistry of Polymer Materials, 01062 Dresden, Germany

*Corresponding author, e-mail drechsler@ipfdd.de

1. AFM scratch tests

The thickness of the brushes in dry state and in KCl solutions of varying pH values was determined by AFM scratch tests. As an example, a scratch test image made in tapping mode with a sharp tip and the corresponding profile along the white line are presented in Figure SI1. At the left side of the profile, the wavy brush surface is visible, at the right side the scratch with remainders of the PGMA anchor layer. As marked in Figure SI1, the distance between the top of the PGMA layer and the averaged brush surface is taken as average brush thickness.

To adjust the position of the force-distance curves relative to the distance axis, i.e. to determine the distance D' between the substrate surface and the nearest point of the silica sphere for a defined force F', scratch tests were performed in KCl solutions using the same silica sphere (diameter 4.8 µm) as in the force measurements applying the given force F'. These tests gave a higher thickness for swollen brushes than scratch tests with sharp tips. Figure SI1 shows a scratch test image and the profile of the rim of the scratch taken at pH 8. As a result of the large sphere diameter, the rim appears rounded and cannot be defined exactly. The brush height had to be determined from areas that are 1-2 µm away. This led to an error of the brush thickness determination of 3-5 nm. Therefore the height of the compressed brush at pH 4 was with sharp tips. The height of the compressed brush as marked in Figure SI2 was used as offset distance D' to adjust the distance in the force-distance curves.

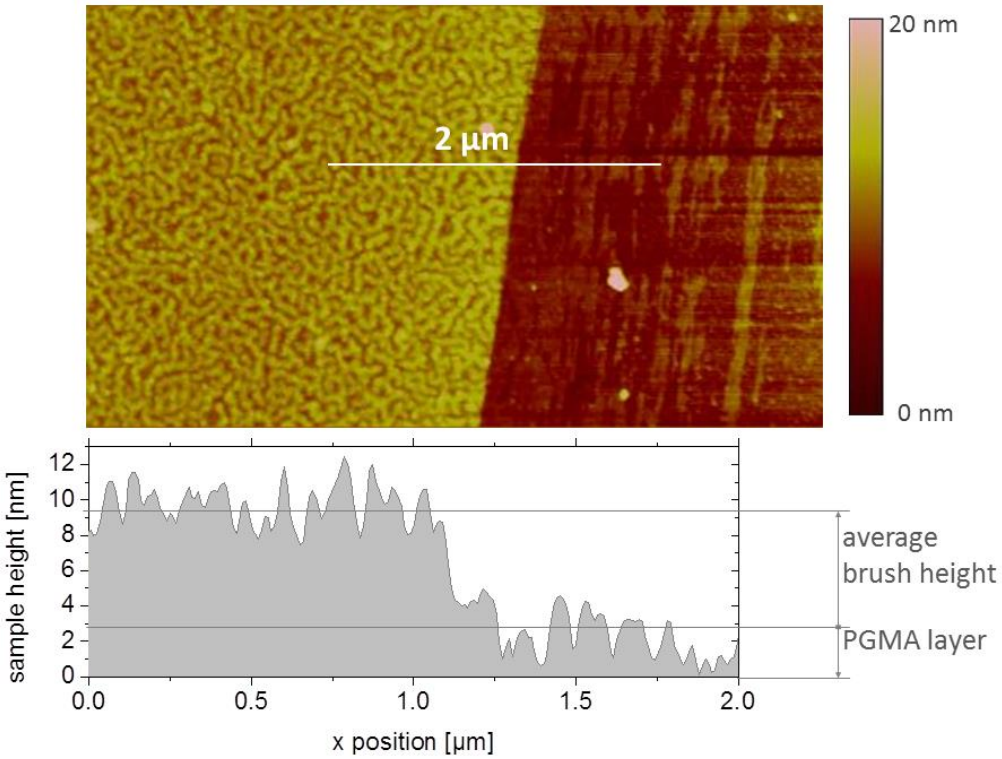

Figure SI1. Top: *Example of an AFM Scratch Test image taken with a standard silicon nitride tip (tapping mode in solution; pH 6, 10^{-3} M KCl).* ***Bottom:*** *Sample profile along the white line with average thickness of PGMA layer and brush.*

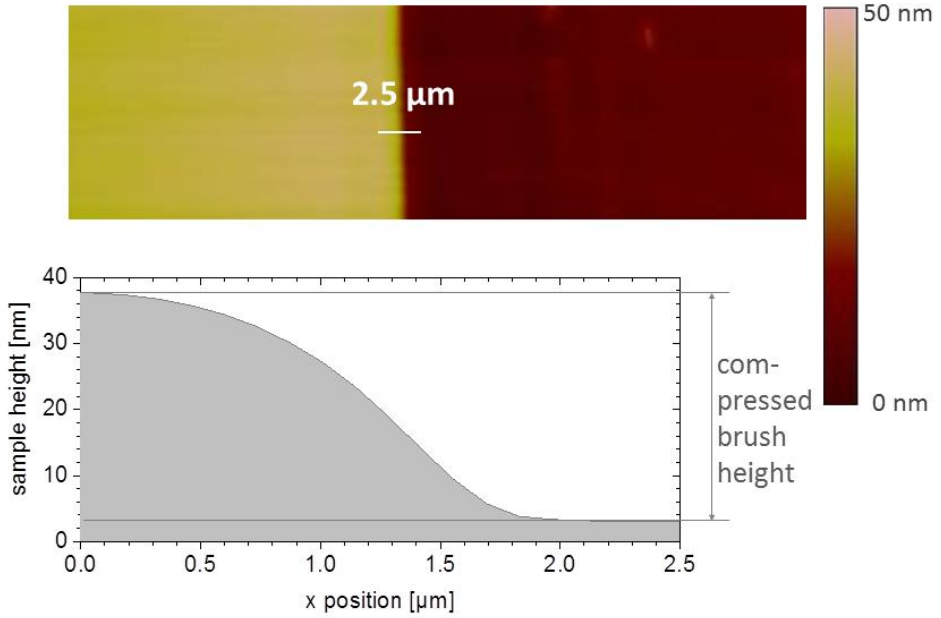

Figure SI2. Top: *Example of an AFM Scratch Test image taken with a silica sphere (contact mode in solution; pH 8, 10^{-3} M KCl).* ***Bottom:*** *Sample profile along the white line with thickness of the brush.*

2. Modelling of the interaction-distance curves

The measured energy-distance curves have been fitted according to Alexander and de Gennes:

$$E_{\text{asymm}}(D) = \frac{2k_B TL}{35s^3}\left[7\left(\frac{L}{D}\right)^{\frac{5}{4}} + 5\left(\frac{D}{L}\right)^{\frac{7}{4}} - 12\right] \qquad (1)$$

To obtain good fits, both the brush height L and the chain distance s had to be adjusted. For uncharged brushes, s is determined by the grafting density $\sigma_g = s^{-2}$. In the case of charged PE brushes, modelling using the true grafting density yields much too high forces. Liberelle and Giasson[1] solved this problem by introducing an additional prefactor (0.02 without salt, 0.1 in 10 mM NaCl) into equation 1 which was interpreted as effect of electrostatic interactions. We tried to model our interaction-distance data in the same way using the right part of equation 1 multiplied by a prefactor A. The resulting values of A (cf. Table SI1) varied between 0.006 and 0.11. Since the KCl concentration is nearly the same in all measurements, it is unlikely that such a strong variation is solely due to electrostatic interactions. In mixed brushes, the chain density in the outer part of the brush is affected strongly by complex formation of a part of the PE chains. Therefore we decided to omit the prefactor A and adjust s in analogy to Block and Helm[2] by an "effective chain distance" s_{eff} in equation 1. From s_{eff} we calculated an "effective chain density" $\sigma_{eff} = s_{eff}^{-2}$ that is assumed to reflect qualitatively the density of extended chains.

The measured data and fits are presented in figure SI3 in logarithmic scale. Table SI1 shows the brush height L, the prefactor A, the effective chain distance s_{eff} and the effective chain density σ_{eff} for each pH value. Especially at pH 8 the model curves show a noticeable deviation from the experimental ones at low interaction energies. This is a shortcoming of the Alexander – de Gennes model that assumes a box-shaped brush profile. Better results have been obtained using the Milner-Witten-Cates model basing on a parabolic density profile[2]. Due to an experimental error (damaged fluid cell) we obtained curves at pH 7 that could not be fitted satisfactorily as a whole. Therefore we did two fits: one for distances $d < 50$ nm (marked grey in Fig. SI3 and Table SI1) and one for distances $d > 50$ nm, but only the second fit gave physically reasonable results. Thus the obtained brush height L for pH 7 may of

[1] Liberelle, B.; Giasson, S. Friction and normal interaction forces between irreversibly attached weakly charged polymer brushes. *Langmuir* **2008**, *24*, 1550-1559

[2] Block, S.; Helm, C: A. The conformation of PSS layers physisorbed from high salt solution studied by force measurements on two different length scales. *J. Phys. Chem. B* **2008**, *112*, 9318-9327

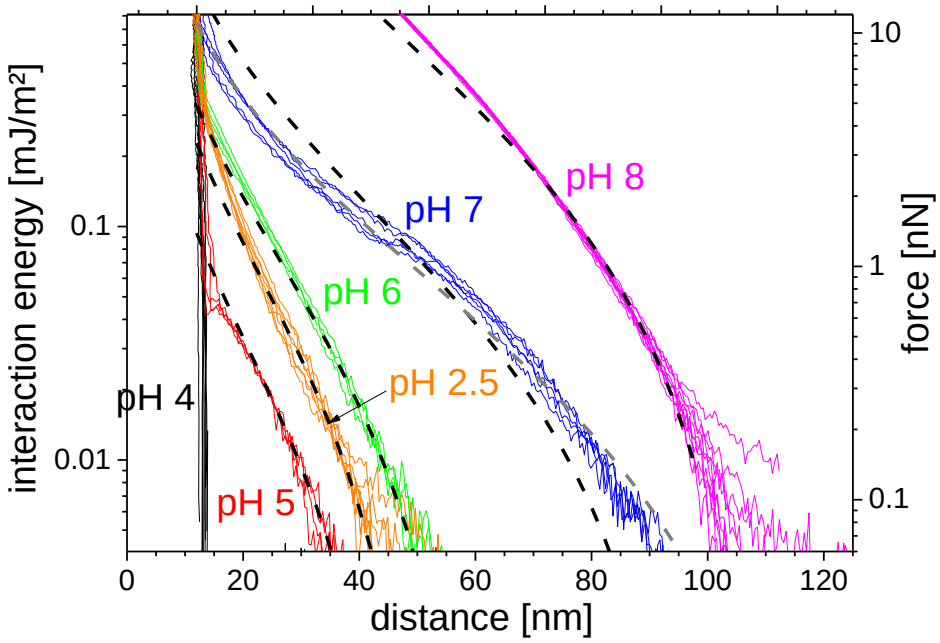

Figure SI3. *Selected force-distance curves measured in 10^{-3} M KCl at different pH values. The left scale gives the geometry-independent free interaction energy, the right scale the measured force. Dashed lines mark the fits according to eq. 1.*

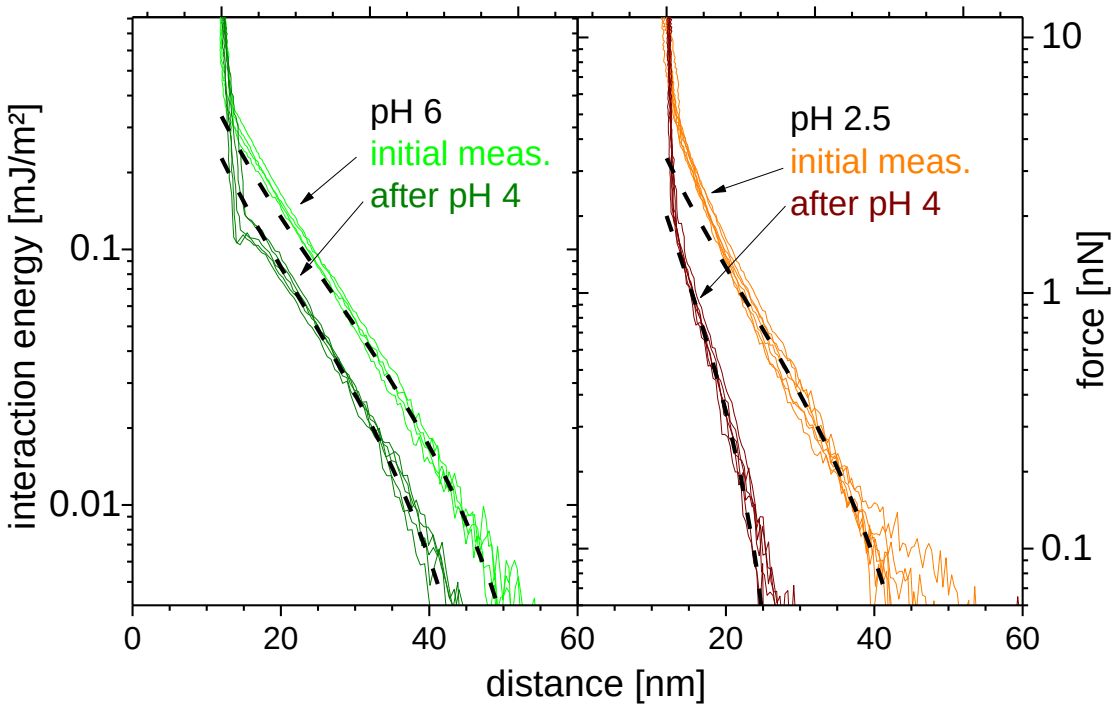

Figure SI4. *Selected force-distance curves measured in 10^{-3} M KCl at pH 6 and pH 2.5 after preparation and after force measurement at pH 4.*

course be slightly erroneous but it confirms the general tendency and is therefore included in Figure 2 in the main paper.

Figure SI4 shows the interaction at pH 2.5 and pH 6 after preparation and after a force measurement a pH 4 on a logarithmic scale. In the first measurement after preparation of the brush a stronger repulsive force, i.e. more pronounced swelling has been observed than in measurements after exposure to pH 4. Modelling of the interaction-distance-curves according to equation 1 showed that at pH 6 the effective chain density remained constant while the brush height decreased. At pH 2.5 the brush height is reduced significantly. This is accompanied by an increase of the effective chain density indicating compression of the brush (cf. Table SI1).

Table SI1. *Parameters inserted in equation 1 to create the fits shown in Figure SI3 and SI4.*

pH	2.5	2.5 after pH 4	5	6	6 after pH 4	7 d>50 nm	7 d<50 nm	8
L [nm]	52	29	48	60	52	97	120	108
A	0.014	0.055	0.0065	0.014	0.014	0.015	0.006	0.07
s_{eff} [nm]	12	8	15	12	12	12	16	7
σ_{eff} [nm^{-2}]	0.007	0.015	0.004	0.007	0.007	0.006	0.004	0.020

Table SI2. *Parameters inserted in equation 1 to create the fits shown in Figures 2-4 in the main paper.*

pH:	2.5	2.5	6	6	6	6	8	8	8	8
c_{KCl} **[M]:**	10^{-3}	10^{-2}	10^{-3}	10^{-2}	0.1	1	10^{-3}	10^{-2}	0.1	1
L [nm]	39	21	55	46	55	30.5	109	100	77	55
s_{eff} [nm]	9	6	12	5	4	3	7	5.5	5	4
σ_{eff} [nm^{-2}]	0.012	0.028	0.007	0.04	0.062	0.11	0.020	0.033	0.04	0.062

3. Influence of the maximum load on the adhesion

Additional force measurements were performed with varying maximum load (maximum cantilever deflection) to study how the pressure between the silica sphere and the brush affects the adhesion force. In measurements at pH 2.5, this influence was very low at all KCl concentration – just as found before for monocomponent P2VP brushes a pH 2.5[3].

At pH 6 we found a significant influence of the maximum load on the adhesion force. In Figure SI5 selected retraction curves are shown for loads between 1.3 nN (the minimum load necessary to ensure contact between sphere and brush) and 15 nN and two different KCl concentrations. The maximum adhesion increases with the load but does not go to zero if the load becaomes very small. Beyond the force minimum (i.e. the maximum adhesion) many single rupture events are visible in the retraction curves. They represent the rupture of adhesive bonds between the sphere and single brush molecules and are much more pronounced at high ionic strength (1 M KCl). We never observed adhesive interactions between a silica sphere and PAA brushes but a strong adhesion to P2VP brushes, especially at intermediate pH values and high ionic strength[4]. Therefore we assumed that these bonds are formed between the sphere and P2VP molecules that extend to the surface of the brush and interact with the sphere. While monocomponent P2VP brushes are collapsed at pH 6 [3,4], P2VP molecules in the mixed brush still seem to be swollen at pH 6 – very likely as part of a swollen PAA-P2VP complex.

At pH 8 a significant adhesion was observed only in 1 M KCl. A similar dependency of the adhesion on the applied load as at pH 6 is visible (Figure SI6) but at pH 8 the adhesion vanishes if the load goes to zero. Obviously the sphere may interact with P2VP molecules but only after compression of the brush. It seems that some P2VP molecules are still stretched at pH 8 but they do not reach the very surface of the brush. At high load (15 nN), however, the retraction curves show a noticeable attractive interaction between the sphere and single (P2VP) molecules.

[3] Drechsler, A.; Synytska, A.; Uhlmann, P.; Stamm, M.; Kremer, F. Tuning the adhesion of silica microparticles to a poly(2-vinyl pyridine) brush – an AFM force study. *Langmuir* **2012**, *28*, 15555−15565.

[4] Drechsler, A.; Synytska, A.; Uhlmann, P.; Elmahdy, M. M.; Stamm, M.; Kremer, F. Interaction forces between microsized silica particles and annealed polyelectrolyte brushes at varying pH and salt concentration. *Langmuir* **2010**, *26*, 6400–6410.

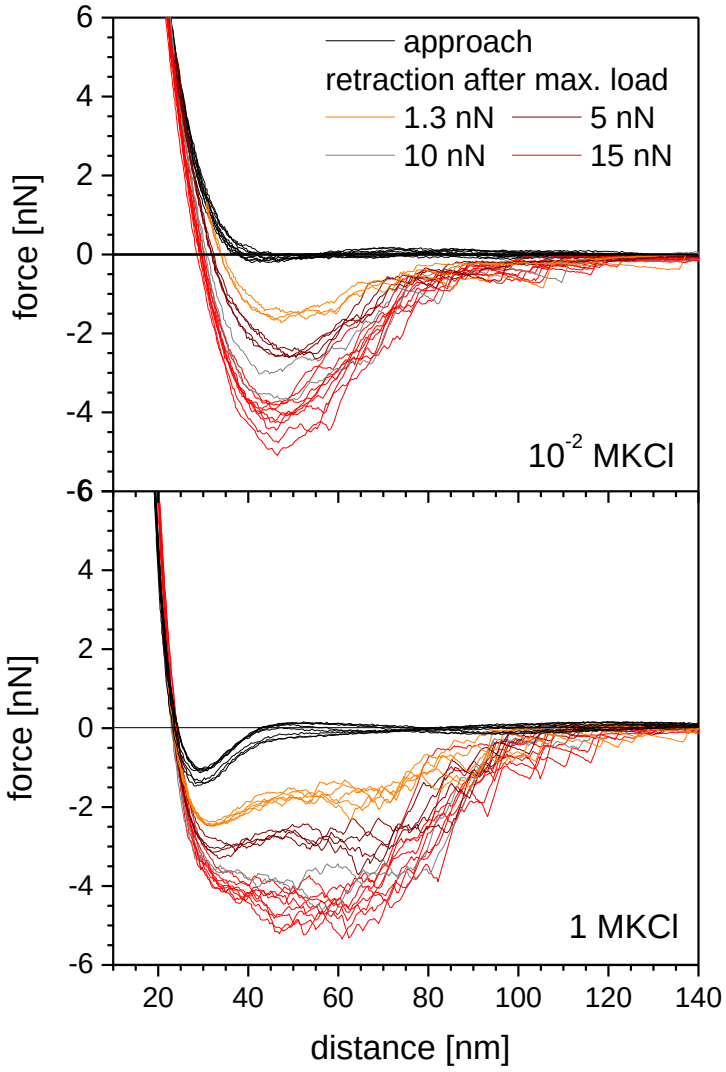

Figure SI5. *Approach and retraction force-distance curves measured at pH 6 at two KCl concentrations with varying maximum load.*

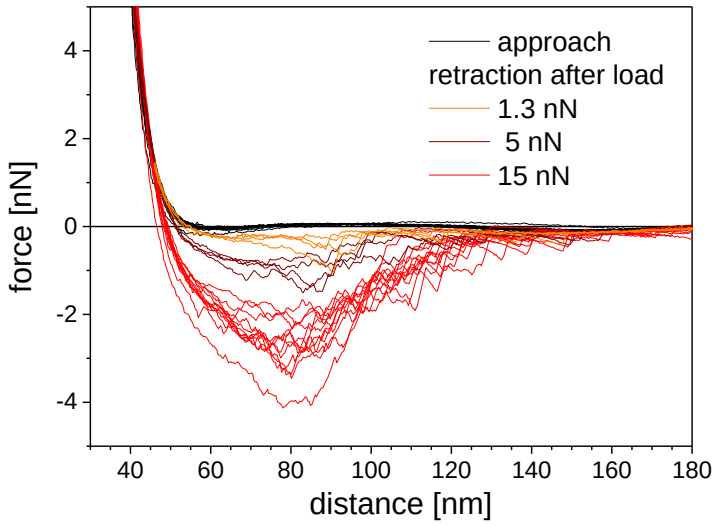

Figure SI6. *Approach and retraction force-distance curves measured at pH 8 in 1 M KCl with varying maximum load.*