

Direct Measurement of the Strength of Single Ionic Bonds between Hydrated Charges

Supporting Information

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Supporting Figures

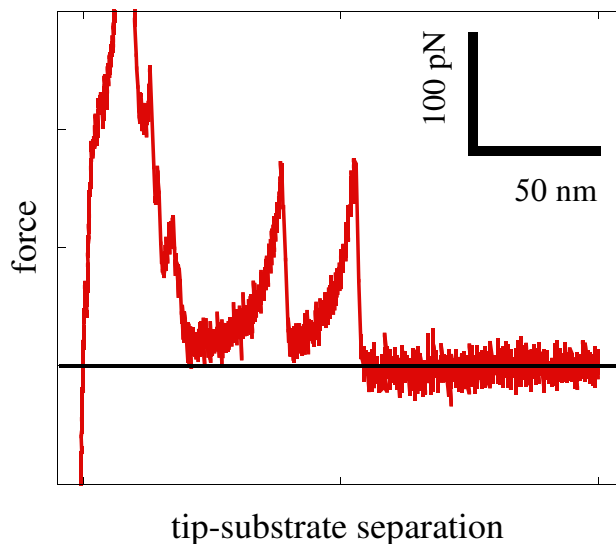


Figure 1: Example force curve at 1.2 M salt with two separated stretching events.

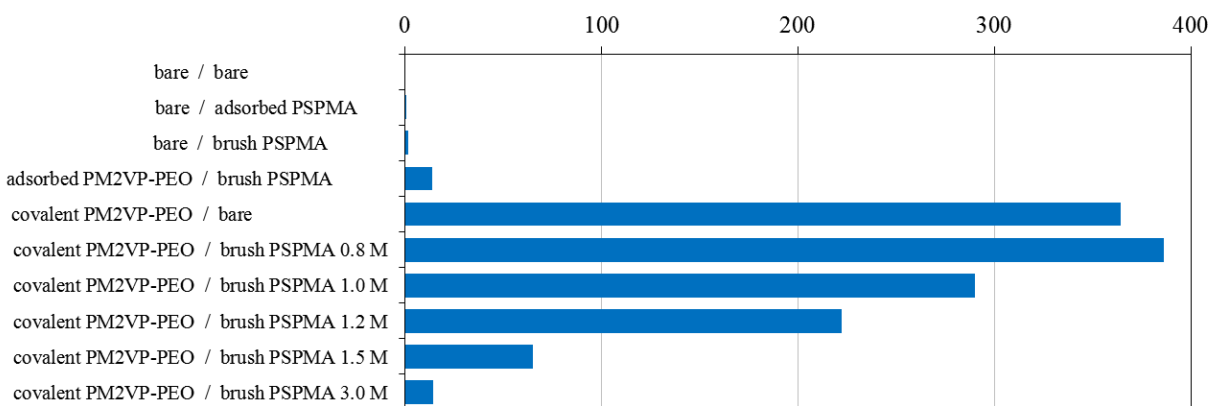


Figure 2: Total number of events recorded per 1,000 F-D curves (with a raw automatic selection of $|\Delta f| > 100$ pN and $h > 50$ nm) for a series of references, with bare tips (blank), tips with adsorbed diblock copolymers, bare surfaces and surfaces with adsorbed PSPMA polymers. The numbers are an indication of the frequency of detection of interactions between tip and substrate, they are not directly related to the frequency of type I or type II events.

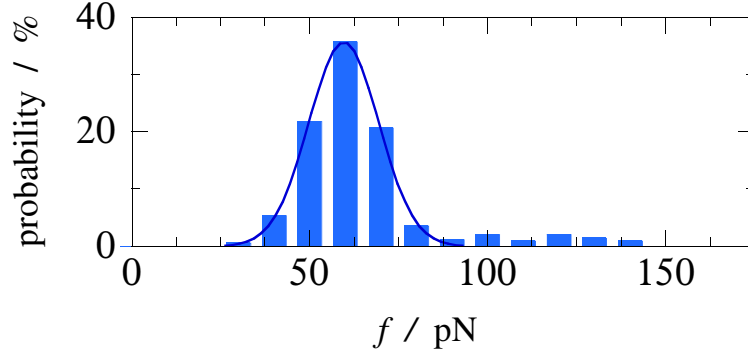


Figure 3: Plateau force histogram of type I events in the force curves of a modified tip and a bare silica surface at 1.0 M salt. A desorption event is observed in 99.4% of all force curves. The histogram does not change when increasing the salt concentration to 3.0 M.

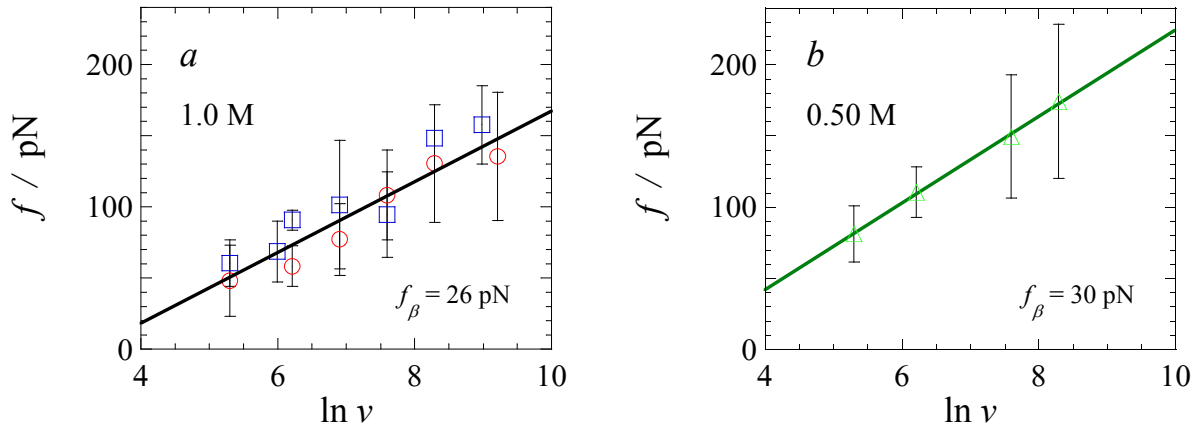


Figure 4: Plateau force versus the logarithm of the scan rate in nm/s for type I events. (a) Results for two independent tips at 1.0 M salt. The slope of the linear fit is indicated in the figure. (b) Results for a single tip at 0.5 M salt. The slope of the linear fit is indicated in the figure.

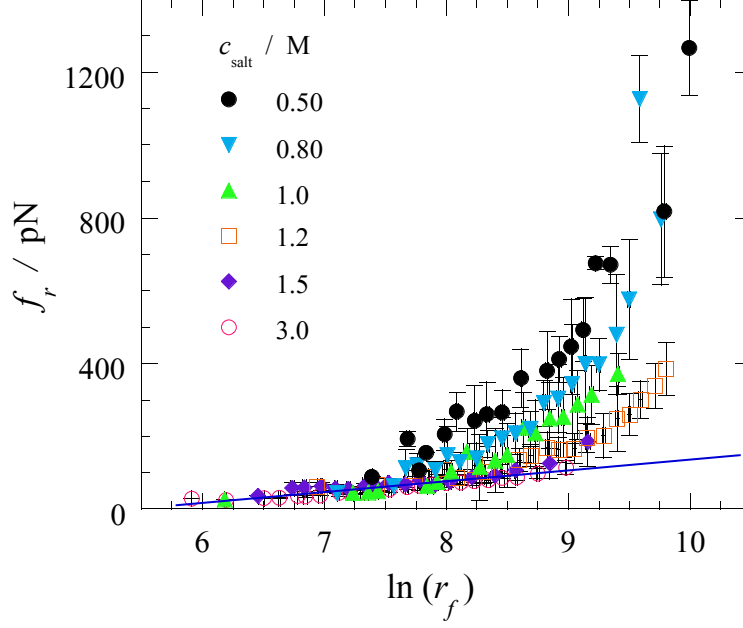


Figure 5: Rupture force versus the logarithm of the loading rate in pN/s for type II stretching events. The loading rates are determined from the slope of the F-D curve at the point of rupture (EFJC fit). Symbols represent different salt concentrations. The solid line is drawn as a guide to the eye.

Distribution of Ionic Bonds

The number of ionic bonds (N) formed when the tip-bound polymer penetrates into the brush is not constant. Sequences of ion pairs alternate with more loosely arranged parts of the chain. We presume that the maximum rupture force measured in experiments is determined by the longest sequence of consecutive ion pairs. For a given probability of ion pair formation, the probability distribution of this longest sequence converges to the same distribution as the longest run of heads in a series of coin flips: a Gumbel extreme value distribution, with a tail at large N :

$$p_G(N) = \frac{1}{\sigma} \exp \left[-\frac{x - \mu}{\sigma} - \exp \left(-\frac{x - \mu}{\sigma} \right) \right] \quad (1)$$

where μ is the mean and σ is the width of the distribution. The rupture force distribution is a weighted sum of all possible complex sizes (N):

$$p(f) = \sum_{N=1}^{N_{\max}} p_G(N) \frac{1}{r_f} k_{N \rightarrow 0}(f) \exp \left[- \int_0^f \frac{1}{r_f} k_{N \rightarrow 0}(f') \, df' \right] \quad (2)$$

where $k_{N \rightarrow 0}(f)$ is given by Equation (5) in the main text for shear loaded bonds. We solve the above expression for the rupture force distributions numerically to obtain the mean rupture force as a function of salt concentration. In Figures 2 and 4, we use $\mu = 6$, $\sigma = 2.3$ and a cut-off $N_{\max} = 20$, in combination with the previously determined parameters a and B to fit our data. Alternatively, the rupture force distributions can be approximated by a Gumbel distribution themselves for large enough μ . For our distribution of ionic bonds, the error in the mean rupture force is less than 20% for all salt concentrations.

Effect of brush erosion

As a result of the shear loading of multiple ionic bonds, the mean rupture forces of ionic bonds can become very large at low salt concentrations (see main text, Figure 4). This makes measurement of their strength impossible at low salt concentration, as failure of the covalent bonds between tip and linker, within the linker or between the brush and the substrate starts to occur more frequently and such failure is catastrophic for the system. Indeed, we find a decrease of the rupture force for some measurement series after longer time. However, we can only speculate that this decrease results from erosion of the PSPMA brush. We do not use these F-D curves in our analysis.