

## P3 – Dynamic Force Spectroscopy of Covalent Bonds

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In chemical and material sciences, as well as for many practical applications, the strength of covalent bonds is of great importance. Because bond dissociation under external force is a thermally activated process, the bond strength is not just controlled by the structural parameters of the binding potential, like potential depth and width, but is also affected by the timescale of the experiment, i.e. the rate at which the force is applied.

In this study we have investigated the dynamic strength of the Si-C bond, by stretching individual carboxymethylated amylose polymers which were attached between an amino activated AFM tip and an amino activated glass substrate. The loading force was continuously increased until the link between AFM tip and substrate surface was lost.

As the weakest bond in this system is the Si-C bond, a failure of the connection between AFM tip and substrate can be attributed to the failure of this bond. To assess the dynamics of this bond rupture process, as well as the structural parameters of the Si-C binding potential, we have varied the force loading rate  $df/dt$  by more than three orders of magnitude.

As expected, we found a logarithmic increase of the observed bond rupture force with the force loading rate.

### Acknowledgement

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### References

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Beyer, M. K. And Clausen-Schaumann, H.: Mechanochemistry: The Mechanical Activation of Covalent Bonds, *Chem. Rev.* 2005, 105 (8), 2921.

# Dynamic Force Spectroscopy of Covalent Bonds

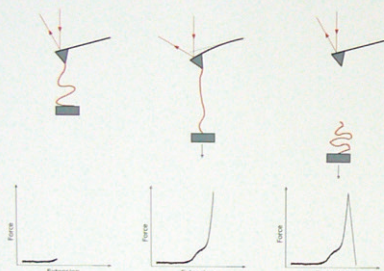
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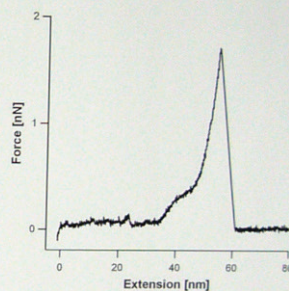
## Abstract

In chemical and material sciences, as well as for many practical applications, the strength of covalent bonds is of great importance. Because bond dissociation under external force is a thermally activated process, the bond strength is not just controlled by the structural parameters of the binding potential, like potential depth and width, but is also affected by the timescale of the experiment, i.e. the rate at which the force is applied. In this study we have investigated the dynamic strength of the Si-C bond, by stretching individual carboxymethylated amylose polymers which were attached between an amino activated AFM tip and an amino activated glass substrate. The loading force was continuously increased until the link

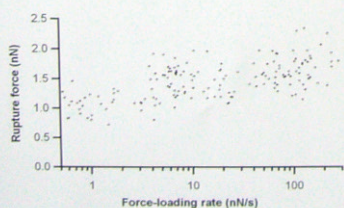
between AFM tip and substrate surface was lost. As the weakest bond in this system is the Si-C bond, a failure of the connection between AFM tip and substrate can be attributed to the failure of this bond. To assess the dynamics of this bond rupture process, as well as the structural parameters of the Si-C binding potential, we have varied the force loading rate  $df/dt$  by more than three orders of magnitude. As expected, we found a logarithmic increase of the observed bond rupture force with the force loading rate. The observed trend was corroborated by density functional theory calculations.



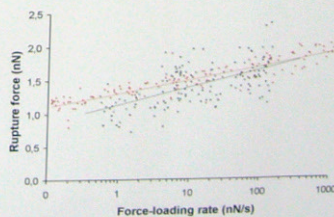
**Fig. 1** Schematic setup of an AFM-based force spectroscopy experiment (top) and of the corresponding force versus extension curve (bottom) of a single-molecular bond attached to a polymer tether (left). The cantilever is displaced by a distance  $d$ , which is proportional to the exerted force, and the displacement is detected with a laser beam (middle). When the tensile strength of the bond is exceeded, the molecular bond ruptures and the cantilever snaps back to its equilibrium position. The relaxation of the cantilever is proportional to the bond-rupture force (right).



**Fig. 2** Typical force versus extension curve of an individual carboxymethylated amylose polymer covalently bound between an amino functionalized AFM tip and an amino functionalized silicon oxide substrate. As the weakest bond in this system is the Si-C bond, a failure of the connection between AFM tip and substrate can be attributed to the failure of this bond. This force versus extension curve was measured at a force loading rate of 100 nN/s resulting in a rupture force of 1.7 nN. All the observed rupture forces at varied force-loading rates were plotted in a scatter plot as shown in Fig. 3.



**Fig. 3** Observed rupture forces at force-loading rates varied by more than three orders of magnitude. The bond rupture force increases logarithmically with the force-loading rate  $df/dt$ . To avoid nonspecific interactions the indentation force was kept below 300 pN for each approach.



**Fig. 4** Simulated rupture forces at various force-loading rates based on density functional theory (red) compared to measured values (black). According to a simplified analytical model, the rupture force  $f^*$  at a given force-loading rate  $df/dt$  is given by:

$$f^* = \frac{k_B T}{\Delta x} \ln \frac{df/dt}{k_0 k_B T}$$

where  $\Delta x$  is the width of the binding potential, and  $k_0$  the thermal off-rate at zero force.

The solid lines in Fig. 4 represent fits of this model to our data, with the fit parameters  $\Delta x = 0.035$  nm and  $k_0 = 3.85 \cdot 10^{-4}$  s<sup>-1</sup> for the experimental data and  $\Delta x = 0.045$  nm and  $k_0 = 3.54 \cdot 10^{-4}$  s<sup>-1</sup> for the theoretical data points.

## References

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