

P18 – Investigation of the pH-Dependent Hydrolysis in Covalent Mechanochemistry

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Chemical bonds control the strength properties of materials and are therefore of fundamental importance in many practical applications. The scission of individual chemical bonds is a thermally activated process following Arrhenius kinetics, and like in any other chemical reaction, the activation energy has to be provided, e.g. mechanically, in order to overcome barriers in the potential energy surface.

In the present study, the strength of individual bond ruptures was investigated as a function of the force-loading rate df/dt at acidic and nearly neutral pH using an atomic force microscope (AFM) in the dynamic force spectroscopy mode. Therefore, individual carboxymethylated amylose polymers were anchored between an amino-functionalized silicon-nitride AFM tip and an amino-functionalized glass substrate and the tension was continuously increased until the weakest link between AFM tip and substrate surface failed.

To extract the dynamics of these single bond rupture events, as well as the structural parameters of the underlying binding potential, i.e., the bond dissociation energy D_e , the maximum rupture force f_{max} , and the force-dependent Arrhenius A-factor, the results were analyzed with a theoretical model based on Arrhenius kinetics combined with a Morse potential as an analytic representation of the binding potential.

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Investigation of the pH-dependent Hydrolysis in Covalent Mechanochemistry

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Abstract

Chemical bonds control the strength properties of materials and are therefore of fundamental importance in many practical applications. The scission of individual chemical bonds is a thermally activated process following Arrhenius kinetics, and like in any other chemical reaction, the activation energy has to be provided, e.g. mechanically, in order to overcome barriers in the potential energy surface. In the present study, the strength of individual bond ruptures was investigated as a function of the force-loading rate df/dt at acidic and nearly neutral pH using an atomic force microscope (AFM) in the dynamic force spectroscopy mode. Therefore, individual carboxymethylated amylose

polymers were anchored between an amino-functionalized silicon-nitride AFM tip and an amino-functionalized glass substrate and the tension was continuously increased until the weakest link between AFM tip and substrate surface failed.

To extract the dynamics of these single bond rupture events, as well as the structural parameters of the binding potential, i.e. the bond dissociation energy D_0 , the maximum rupture force f_{max} , and the force-dependent Arrhenius A-factor, the results were analyzed with a theoretical model based on Arrhenius kinetics combined with a Morse potential as an analytic representation of the binding potential.

Methods



Figure 1. Amino-functionalized surface (left, A) and covalent linkage of single carboxymethylated amylose polymer tethers between an amino-functionalized AFM tip and an amino-functionalized silicon oxide substrate at pH 7.4 (left, B) and pH 2.0 (left, C). At nearly neutral pH, an amide bond is formed between a carboxylate group of the amylose and an amino-group of the silane layer by addition of carbodiimide (EDC) and *N*-hydroxysuccinimide (NHS). Under acidic conditions, an efficient coupling of carboxymethylated amylose to the amino-functionalized surfaces is possible without the addition of EDC and NHS. This is presumably due to the formation of an acid-catalyzed ester between the carboxylate group of the amylose and a free silanol group in the surface linker (left, C). Single polymers were stretched until the weakest bond in the linker between AFM tip and substrate surface failed (schematically shown on the right). In order to obtain the dynamic strength of the observed rupture process the applied force-loading rate was systematically varied over three orders of magnitude.

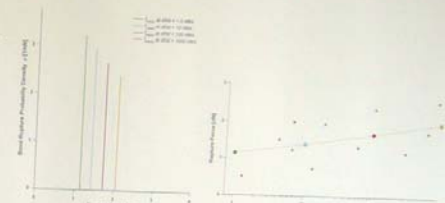


Figure 2. To extract the structural parameters of the binding potential, i.e. the bond dissociation energy D_0 , the maximum rupture force f_{max} , and the Arrhenius A-factor, the resulting scatter plots at pH 7.4 and pH 2.0 were individually analyzed with a theoretical model based on the combination of the Arrhenius rate equation and a Morse potential. Therefore, mean rupture forces f_{max} were extracted from numerically calculated force-loading rate dependent probability density histograms (left) and the root-mean-square deviation between mean forces and experimental results was calculated (schematically shown on the right). The parameters D_0 , f_{max} and the Arrhenius pre-factor A were generated with a random number generator and optimized with a genetic algorithm until a minimum root-mean-square deviation was found. All rupture events recorded at pH 7.4 and pH 2.0 are shown together with the corresponding fit functions in a scatter plot in Fig. 3. Experiments were conducted at room temperature.

Results

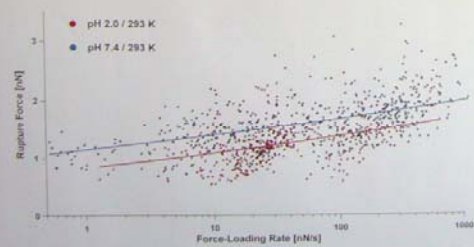


Figure 3. Experimental data recorded at nearly neutral pH (blue dots) and acidic pH (red dots) together with the corresponding fit functions. Here, the rupture forces is plotted versus the force-loading rate. The fit function for the obtained data at pH 7.4 (blue line) was achieved with the parameter set $f_{max} = 5.29$ nN and $D_0 = 79.2$ kJ/mol, with the force-dependent Arrhenius pre-factor A covering $2.5 \times 10^9 \cdot 1.2 \times 10^{10} \cdot s^{-1}$. The red line represents the fit function for the data measured at pH 2.0. Here, the parameters $f_{max} = 3.53$ nN, $D_0 = 36.0$ kJ/mol, and $A = 8.6 \times 10^9 \cdot 4.2 \times 10^{10} \cdot s^{-1}$ were found. If one compares the obtained results to gas-phase DFT-calculations for a homolytic bond-rupture mechanism of the weakest bond, i.e. the Si-C bond at pH 7.4 and the Si-O bond at pH 2.0, respectively, it can be noticed that the bond dissociation energy D_0 is lowered by 4-5 times of magnitude (cf. Table 1). This may be attributed to a non-homolytic bond-rupture mechanism, i.e. bond hydrolysis at pH 7.4 and acid-catalyzed ester cleavage at pH 2.0.

Table 1. Experimentally Found Parameters Sets and Values Obtained from DFT-Calculations for the Weakest Bond, i.e. the Si-C bond

Experimental Data	Experimental Data	DFT-Calculations
pH 7.4	pH 2.0	Si-C Bond
D_0 [kJ/mol]	79.2	107.4
f_{max} [nN]	5.29	4.98
A [s ⁻¹]	$2.5 \times 10^9 \cdot 1.2 \times 10^{10}$	$8.6 \times 10^9 \cdot 4.2 \times 10^{10}$

Conclusion

It has been shown that there are two alternative coupling linkages of carboxymethylated amylose to amino-functionalized surfaces depending on the pH value. The fact that a connection is formed under acidic conditions without the addition of NHS and EDC is presumably due to the formation of an acid-catalyzed formation of an ester. The described fit procedure based on the numerical calculation of bond rupture probability densities allows for the direct extraction of the parameters D_0 , f_{max} and the A-factor from the experimental data and reproduces the experimental data quite well. Comparing the obtained structural parameters

to the results for the Si-C bond determined from DFT calculations in the gas-phase, shows that the experimentally observed dissociation energy is almost a factor of five smaller than theoretically expected. This may be attributed to ancillary effects on the bond rupture process induced by the solvent. Bond hydrolysis at pH 7.4 may most likely occur on the amide bond, and at pH 2.0 an acid-catalyzed ester cleavage on the Si-O bond in the surface linker may be a reasonable scenario. However, accompanying DFT-calculations may provide a deeper insight into the investigated bond rupture mechanism.

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