Mechanical Properties of Single "Folded" Polymers: From Defined Supramolecular Oligomers to Collapsed Brush Molecules

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Oligomers of calix[4]arene-catenanes were synthesized and investigated by means of single molecule force spectroscopy in conjunction with stochastic modelling and dynamic force field simulations.
Employing pulling speed dependent force spectroscopy we were able to monitor the rupture processes of bis-loop tetraurea-calix[4]arene-catenanes. These experiments allowed us to determine the dynamic strength of hydrogen bonds and to explore the mechanism of bond breakage in host-guest complexes. Tunable reversibility of bond rupture was achieved synthetically by employing and adjustable loop length, which limits separation of the two capsules. A characteristic sawtooth pattern was observed for both bond rupture and recombination.
In an attempt to understand the experimental findings we used various stochastic models of forced bond rupture combined with Monte Carlo simulation. The rupture force distribution strongly indicates the existence of bond heterogeneities. Including these, the experimental rupture data could be modelled almost quantitatively by Bell approximation of the escape rates, while the experimental rebinding data, however, is not yet fully understood.
In order to gain some microscopic understanding of the hydrogen bond breaking in the systems investigated, we present theoretical results from force field simulations. We find strong correlations in the dynamics of the bond breaking.

Single molecule stretching experiments of polymer brushes with poly-N-isopropyl-acrylamide (PNIPAM) side chains were carried as a function of temperature. Under good solvent conditions we report on persistence lengths that display contour length dependence due to the impact of side chains on the stretching behaviour. A force plateau was found for the collapsed state as predicted theoretically for a first order phase transition between the collapsed and unwound polymer chain. The hysteresis between approach and retraction curve disappears after several extension-relaxation cycles indicative of striving towards equilibrium, which is further confirmed by the absence of load rate dependence.