

Abstract Submitted
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Molecular Bottlebrushes as Tensile Machines for Probing Specific Bonds under Tension YUANCHAO LI, Department of Chemistry, UNC at Chapel Hill, ALPER NESE, Department of Chemistry, Carnegie Mellon University, NATALIA LEBEDEVA, TYLER DAVIS, Department of Chemistry, UNC at Chapel Hill, KRZYSZTOF MATYJASZEWSKI, Department of Chemistry, Carnegie Mellon University, SERGEI SHEIKO, Department of Chemistry, UNC at Chapel Hill — Significant tension on the order of 1 nN is self-generated along the backbone of bottlebrush macromolecules due to steric repulsion between densely grafted side chains. The intrinsic tension is amplified upon adsorption of bottlebrush molecules onto a substrate and increases with grafting density, side chain length, and strength of adhesion of the substrate. This allows us to employ these molecular bottlebrushes as miniature tensile machines to probe the mechanochemistry of specific bonds. For this purpose, bottlebrush macromolecules with a disulfide linker in the middle of the backbone were synthesized by atom transfer radical polymerization (ATRP). Two processes, (i) homolytic cleavage of disulfide and (ii) scission of disulfide due to reduction by dithiothreitol were monitored through molecular imaging by atomic force microscope (AFM). In both cases, the corresponding rate constants increase exponentially with mechanical tension along the disulfide bond. Moreover, the reduction rate at zero force is found to be significantly lower than that in bulk solution, which suggests an acidic composition of the water surface with $\text{pH}=3.7$. This opens a new application of brush-like macromolecules as surface pH sensors.

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