

Investigating Light Gated Folding of Single Chains on Surfaces and the Limits of Grafting Processes via Atomic Force Microscopy (AFM)

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The design of functional interfaces is critical for almost every application as the majority of materials interface with their environment. In particular, interfaces decorated with (functional) macromolecules fulfil important roles in a range of devices and applications, covering areas like medical implants, 3D cell scaffolds, opto-electronics, sensors and coatings. The functionality of the interface and its interactions with the environment are dictated by the type of polymer chains and, importantly, their intra- and intermolecular properties. We herein provide a theoretical and experimental investigation into the properties and behavior of polymer chains attached to surfaces, starting from a single polymer chain up to a polymer brush.

In the case of the single polymer chains, we focus on the light-gated folding behavior of single chain nanoparticles (SCNPs) on surfaces. SCNPs are mimicking the folding of peptides into higher ordered structures.¹ The folding process is triggered by the reversible light-driven folding of SCNPs, containing a poly(methyl methacrylate) (PMMA) backbone and anthracene based folding points, which are attached to a silicon surface. The ex-situ and in-situ characterization of folding and unfolding was investigated by atomic force microscopy (AFM) based single-molecule force spectroscopy (SMFS) in a toluene solvent environment. More specifically, the change in contour length of the folded and unfolded SCNPs was determined.

Within the polymer brush regime, we quantitatively explore limits of physical grafting densities by applying a theoretical model. More importantly however, we examine the three most commonly employed methods for experimentally estimating grafting densities, i.e. dry thickness measurements, gravimetric assessment and swelling experiments. We provide an estimation of the reliability of these determination methods via carefully evaluating their assumptions and assessing the stability of the underpinning equations. We demonstrate that the literature reported grafting densities are beset with a considerable error that can, however, be minimized by selecting the correct experimental assessment.² By performing colloidal probe measurements (with an AFM) on polymer brushes (either PMMA or poly(2-hydroxyethyl methacrylate) (PHEMA) based) with different grafting densities, we introduce an alternative measurement method that leads to a direct determination of grafting densities. As with the SCNPs, these measurements were executed in solvents (in toluene for PMMA or water for PHEMA) in order to examine the polymer brushes in their usual environment.

¹ Blasco E., Tuten B. T., Frisch. H., Lederer A., Barner-Kowollik C., *Polym. Chem.* **2017**, *8*, 5845-5851

² Michalek L., Barner L., Barner-Kowollik C., *Adv. Mater.* **2018**, in press