Physical properties of grafted polymer monolayers studied by scanning force microscopy
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Summary & Conclusions

Grafted polymer monolayers play an important role in colloidal stabilization, chromatography, adhesion, lubrication, microelectronics and biocompatibility of artificial organs in medicine. The subject of this thesis is to study the morphology, friction and elasticity of these monolayers in the nanoscale.

Scanning probe microscopies (SPM’s), which are based on piezoelectric transducers and sharp probing tips that scan a surface while a feedback loop regulates the distance between the probing tip and sample, have revolutionized the field of surface microscopy. The scanning force microscope (SFM) senses forces between the tip and sample. Spatial and force resolution in the order of angstroms and nanonewtons, respectively, can be routinely obtained. Being a real space analytical tool is ideal for investigating the nanostructure of amorphous surfaces like polymer monolayers.

In chapter 2, the principles of (the first SPM) the scanning tunneling microscope (STM) and the basic theory of SFM are outlined. STM combines the sensitivity of tunneling current with lateral scanning to obtain atomic-scale images of conducting surfaces. However the SPM techniques are not simple imaging instruments, spectroscopic measurements (eg. force-distance profiles) and a variety of different modes of operation (eg. lateral force images) can reveal a wealth of information for the probed sample.

SFM images suffer from tip effects and many a time their interpretation is not straightforward. In chapter 3, we deal with the SFM artefacts. Using a simple computer simulation for AFM imaging in the contact mode, the convolution effect was demonstrated in the atomic scale. An atomic vacancy was imaged by a single-atom tip and a polyatomic tip producing true and false atomic resolution, respectively. Artefacts having the size of the effective tip are reported. The convolution effect occurs also in larger scales resulting in an effective broadening of sample’s features. In order to accurately measure the sizes of adsorbed particles, one should use flat substrates, apply low loads and measure independently the tip shape. We have shown an experimental method, based on imaging edges of gold crystals, that one can employ to determine the tip’s radius of curvature. Avoiding normal deformations (low loads) and for known tip radii the features of the sample can be approximately recovered.

In chapter 4, we study the polymer conformation of chemically end-grafted polymer chains in bad-solvent conditions. The samples were prepared by exposing a gold substrate in a (good) solution of thiol-terminated polystyrene (PS-SH) and were imaged in water (bad solvent for PS). It is well known that thiol-terminated polymer chains chemisorb onto gold surfaces via a gold thiolate bond. For short incubation times and dilute solutions we observed individual globular chains weakly adsorbed on the gold substrate. For higher surface coverages microphase separation of the polymer monolayer into ordered globular clusters was observed. Using different molecular weights of PS-SH, arrays of polymer microclusters of different dimensions were formed. These clusters spread better than the single chain globules and their sizes satisfy the scaling laws that were predicted for pinned
micelles. In addition, we showed that the experimental data for the isolated chains and the pinned micelles fit well in a diagram of states that can be deduced from scaling arguments. The chemisorption of PS-SH molecules to gold from poor-solvent conditions produced a qualitatively different result; although microphase separation still occurs, the polymer monolayer organizes itself in the form of semi-continuous dimples. This result is, to some extend, expected since the chemisorption process from poor-solvent conditions results in a high density brush and probably constitutes an additional regime in the diagram of states.

In chapter 5, we describe a system of mixed self-assembled monolayers (SAM) of alkanethiols and thiol-terminated polystyrene (PS-SH) chemisorbed on a gold surface from mixed toluene solutions. Topography and friction images were obtained in bad-solvent conditions. The simultaneous chemisorption of the two species (alkanethiol and PS-SH) resulted in an adsorbate containing isolated polymer chains randomly distributed in a SAM of alkanethiols. The majority of the collapsed chains exhibited structural stability, although some of them were deformed and/or dragged by the tip during imaging. This effect can be attributed partly to the topographical change and partly to the high local friction coefficient of single PS globules, which was measured to be in the range of that of bulk polystyrene.

In chapter 6 we investigate the frictional properties of the pinned-micelle monolayers using friction force microscopy. We found a linear dependence upon the applied load and the shear velocity, implying multiasperity contact and solid-state structure, respectively. The friction coefficient while it was found to compare well with the friction coefficient of bulk polystyrene that has been reported in the literature, is 33% higher than the local friction coefficient $\mu_0$ for PS globules that was found in the previous chapter. We showed that a model incorporating the surface roughness is not adequate to account for this increase. We argue that the discrepancy is due to differences in adhesive force and contact area induced by the corrugation.

In chapter 7, we examine the polymer elastic properties in good-solvent conditions. As a model system we chose the Poly(methacrylic acid) PMAA which is water soluble. Using mixed monolayers (to attain low polymer grafting densities), we covalently attached individual polymer chains to a SFM tip and substrate. Taking reverse force-distance curves, we observed sharp attractive forces in the nanonewton range. These forces are associated with the rupture of single covalent bonds and polymer elasticity. For a polymer alone end-grafted monolayer (relatively high grafting densities), the forward force-distance curves show the distinctive repulsive force associated with brushlike configurations. We found that Alexander-de Gennes theory is partly inadequate to describe brush compression via a SFM tip probably due to the bending of the chains at the edge of the tip-apex. During the reverse force-distance curve we observed long range attractive forces. We have shown that these forces appear because of the stretching of individual chains or parts of chains that have adhered to the tip probably due to physisorption. The single chain elastic force was found to agree with the entropic force predicted by the freely jointed chain model.