CONFORMATIONAL TRANSITIONS VISUALIZED IN SINGLE POLYELECTROLYTE MOLECULE AFM EXPERIMENTS

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Introduction

High resolution AFM allows for the visualization of the adsorbed polymer chains. If the chains are rapidly trapped by the substrate the two-dimensional structures visualized with AFM reflect the sample prehistory in solution. In contrast to scattering methods the single molecule AFM experiments allow for the investigation of the molecules deposited from very diluted solutions when the interchain interactions can be neglected. It is of special interest for polyelectrolyte systems if the interchain interactions may cause various technical problems in scattering experiments.

Experimental

Materials. Samples of poly(methacryloyloxyethyl dimethylbenzyl ammonium chloride) (PMB) (M_W = 6130 Kg/mol, polydispersity index (PDI) = 1.6) were obtained from Dr. Werner Jaeger. Poly(2-vinylpyridine) (P2VP) of molecular weight 385 kg/mol was purchased from Polymer Sources Inc. (synthesized by anionic polymerization, PDI of about 1.1). The PSBBB_{7BBB}-P2VPBBB_{7BBB} heteroarm star copolymer constituted of seven polystyrene (PS) and seven P2VP arms was prepared via a three-step sequential "living" anionic polymerization procedure using divinylbenzene linkage

Instrumentation. Multimode AFM instrument and NanoScope IV-D3100 (Digital Instruments, Santa Barbara) were operating in the tapping mode. Silicon tips with radius of 10-20 nm, spring constant of 30 N/m and resonance frequency of 250-300 KHz were used after the calibration with gold nanoparticles (of diameter 5 nm) to evaluate the tip radius. The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius.

Substrates. In this study we used the following substrates: the freshly cleaved mica, the Si-wafers (obtained from Wacker-Chemitronics), the Si-wafers with the deposited using lithography gold stripes (electrodes), or the microscope glass slides (Menzel-Glaser, Nr. 01 1101). Before experiments the substrates were first cleaned in an ultrasonic bath initially three times for 5 min with dichloromethane (DCM), and then in the cleaning solution prepared from NH_4OH and H_2O_2 at 60°C for one hour.

Sample preparation. PMB, PSBBB_{7BBB}-P2VPBBB_{7BBB} or P2VP were deposited onto the respective substrate from the 0.0005 g/l acid water (pH 2, HCl, Aldrich) solutions by dipping of the substrates into corresponding solution or by drop casting. To deposit polyelectrolyte (PE) chains in stretched conformations we used a spin-coater and placed several drops of a PE solution onto the substrate rotating at 10000 rpm. The dry samples were investigated with AFM.

Results and Discussion

Conformations of the trapped polymer molecules reflect in some extend the conformation in solution. Although, the tiny details of the conformation are lost due to the adsorption and solvent evaporation, however some important details of the macroconformation may be extracted from the investigation of the trapped polymer chains. For example, the coil-globular transition in solvent can be very precisely investigated with AFM experiments. This transition is usually observed as dramatic conformational changes when the conformation switches from a coil-, worm-, or rod-like chain conformation to the compact globule conformation when dimensions of the chains change in 10-100 folds. Such substantial conformational alterations are frozen and observed in the trapped chains.

In Figure 1, we present the series of experiments when we study the stepwise coil to globule transition (CGT) of PMB molecules in aqueous solutions by adding Na_3PO_4. In salt-free solutions, the polymer molecules appear as extended coils (Figure 1, left). Added salt dramatically changes molecular conformations and the fine morphology of the PE chains. Images in Figure 1(middle and right) clearly show intramolecular segregated areas. Two pronounced differences from salt-free solution can be found on the images: the polymer coil starts to segregate into small beads, the beads segregate in big clusters. The height of the beads is several times larger than the height of the backbone. We assume according to the DRO model that the beads are formed due to the PE intrachain segregation induced by the screening effect of the added salt and due to the enhanced attraction induced by condensed salt ions. Each step of adding salt results in the increase of the size of beads and the decrease of their number, as well as the decrease of the necklace length.

The changes of macroconformations in solution can be successfully reconstructed and used for the investigations of the polymer molecules of a complicated architecture. The experiments with heteroarm star-like block-copolymer PS_7-$P2VP_7$ give the convinced evidence for that.

It was previously shown that at a relatively high concentration (0.3 g/L) PS_7-$P2VP_7$ undergoes intermolecular micellization in acid water (pH 1-2) with the aggregation number equal to 8. In contrast, at extremely low concentrations (0.005 g/L of PS_7-$P2VP_7$) micellization occurs as an intramolecular process. In these conditions the PS_7-$P2VP_7$ star copolymer survives in the nonassociated state and forms stable unimolecular micelles. AFM images reflect uniform star-shaped core-shell structures formed upon dilution of PS_7-$P2VP_7$/THF solution with acid water (pH 2). Such a morphology gives evidence for very pronounced intrasegregation of the star copolymer in acid water. PS chains collapse due to hydrophobic interactions and form a compact core whereas protonated P2VP arms adopt an extended conformation due to the Coulomb repulsion and form a shell. We may conclude that the AFM image represents an "off print" of the solution conformation when the molecules were adsorbed and trapped by the substrate. After the rapid evaporation of water the structure was formed due to the collapse in the *Z*-direction. The experimental value of the collapsed PS core volume is about 219 nm^3, which again corresponds to the calculated value (245 nm^3).

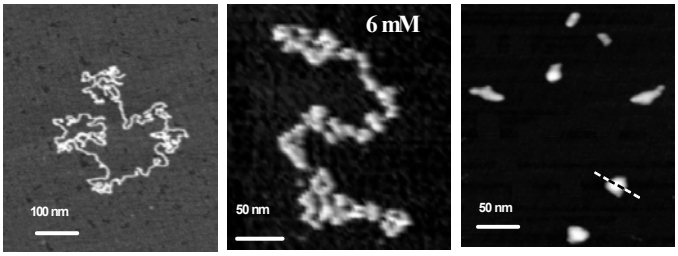

Figure 1. Coil-to-globule transition of poly(methacryloyloxyethyl dimethyl-benzylammonium chloride)

We developed the contrasting procedure which allows us to improve substantially the resolution of a single molecule experiment with no changes of the conformation of adsorbed polymer molecules. In our approach, we use the deposition of either hexacyanoferrate anions or negatively charged clusters of cyanide-bridged complexes as contrasting agents. This method allowed us to increase the thickness of the resulting structures up (for example, for P2VP chains) to 3 nm and, consequently, to provide visualization of polymer chains on Si-wafers and glass slides. After AFM-measurements, the contrasting agents were then removed also without distortion of the molecule conformation.

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