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 randomly 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) (M₆ = 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 PSBBB₇-P2VP₇MMM₇ 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-Chemtronics), 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 NH₄OH and H₂O₂ at 60°C for one hour.

Sample preparation. PMB, PSBBB₇-P2VP MMM₇ or P2VP were deposited onto the respective substrate from the 0.0005 g/l acid water (pH 2, HCI, 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 10 000 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 investigation of the trapped polymer chains. For example, the coil-globular transition in solvent can be very precisely investigated with AFM.

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 improve 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.

Acknowledgements. The authors acknowledge the contribution of Dr. Werner Jaeger and Dr. P. Stepanec as well as the financial support of Institute for Polymer research Dresden and Center for Advanced Materials Processing, Clarkson University.