



Redox Responsive Poly(ferrocenylsilane) (PFS) Interfaces Studied by Atomic Force Microscopy

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Abstract – Atomic force microscopy (AFM) was used to study force interactions between tip and grafted, redox responsive organometallic poly(ferrocenylsilane) (PFS) surface under potential control in electrochemical redox cycles. The role of the electrostatic component in the diffused double layer (DL) in NaClO₄ electrolyte environment was considered for a “grafted to” PFS, which dominated the interplay between the tip and sample surface. The effects of redox voltage, tip-surface contact time, and experimental protocol (contacting and voltage application sequence) were investigated. Reversible friction and adhesion variations at the graft surface at different redox potentials were elucidated.

PFS is composed of alternating ferrocene and alkylsilane units in the main chain and possesses interesting and potentially useful chemical, optical, and electrochemical characteristics in combination with typical good processibility of polymers.¹ In our previous study, external electrochemical stimulus was used to induce reversible elasticity changes of individual PFS chains by altering the redox states of PFS in electrolyte environment.² In-depth understanding of the electrochemically responsive PFS is vital for further realization of single molecule devices. Moreover, the influences of additional parameters in the subtle aqueous electrolyte environment still need further clarifications. In this context, our objective is to further discuss the possible presence and interplay of both physical adsorption and charge generated electrostatic forces at the tip–PFS interface.³ The oxidation of PFS involves the conversion of ferrocenyl group to ferrocenium form. By examining the force data collected between the tip and neutral/positively charged PFS interface, two different scenarios were presented. If the tip is loaded onto the charged PFS surfaces, electrostatic components will dominate the total interaction force. When the PFS surface is subjected to external positive potential, incomplete charge compensation within the polymer system created a diffusive DL. The Si₃N₄ tip with isoelectric point at pH 4.5 is considered as a negatively charged component in the pH ~ 6.7 NaClO₄ electrolyte. Due to the higher positive potential of oxidized PFS over Si₃N₄ tip (+0.5V), the tip is attracted to the surface. In contrary, the DL repulsion dominates the tip-reduced PFS interaction and sometime hinders possible physisorption of PFS onto the tip. In another approach, once the tip has penetrated into the polymer before the electrochemical process, physisorption of PFS chains takes place. The adhesion component, F_{ad} represents the overall non-specific bridging at the tip–PFS interface. The strength of interactions also depends on the tip–surface contact time, t_c . Furthermore, the interaction of AFM tip with annealed gold (Au) surfaces in the identical oxidation/reduction environment was studied. Under such circumstances, the effect of Au charging during the electrochemical cycle is negligible on the force measurement.

If electrostatic forces play a dominant role between tip and PFS grafts, it would offer interesting applications for adhesion and friction control, e.g. for MEMS, by utilizing redox stimuli. In this presentation we discuss reversible variations of friction coefficients obtained by friction force microscopy spanning a range between 0.47 and 0.3 for oxidized and reduced graft layers, respectively. This friction coefficient variation was accompanied by an increase of average adherence forces as obtained from AFM force curve experiments. The results of this presentation illustrate the use of PFS grafts as redox responsive polymer platforms in surface engineering.

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