



Effect of added salt on swelling dynamics of ultrathin films of strong polyelectrolytes



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ABSTRACT

Solvent mass uptake and swelling dynamics of spin coated poly(sodium-4-styrenesulfonate) (NaPSS) films containing different concentration of externally added monovalent salt ions have been performed in presence of water vapor to study the effect of low molecular weight salt ions on the swelling dynamics of charged polymeric chains in confined geometry. Diffusion coefficient of the water molecules within the NaPSS films, as obtained from the solvent mass uptake study, is found to be independent of salt concentration. Swelling dynamics of the chains in presence of water vapor has been studied in-situ using X-ray reflectivity technique. The actual salt concentration and the distribution of salt ions within the films were examined using X-ray Photoelectron Spectroscopy (XPS). The diffusion coefficients of the NaPSS chains show a salt concentration independent behavior and are of same order as that of salt free NaPSS chains. Whereas, the fraction of charged monomers, that determines the strength of the repulsive interaction between the polymer segments, increases with salt concentration when the later becomes comparable to that of already present counterions in the system. The Na and Cl ions show clear tendency to be redistributed within the films instead of forming NaCl salt. The negative Cl ions migrate towards the top surface whereas the positive sodium ions accumulate on the substrate. Counterion condensation process of the polyelectrolyte chains gets inhibited by the internal electric field produced between the top Cl⁻ layer and the bottom Na⁺ layer which increases the effective charge of the polyelectrolyte chains.

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1. Introduction

Over last few decades ultrathin polymeric films are extensively studied not only for their numerous technological applications in areas like coating, membrane etc. but also from a pure scientific interest. Properties of polymer molecules in thin films are very much different from their corresponding bulk properties [1–4] due to various types of energetic and entropic interactions arising at the surfaces and interfaces. These interfacial effects lead to changes in the conformation and mobility of the chains near substrate and the knowledge of bulk properties are not sufficient in this case. When a dry polymer is exposed to a solvent, the solvent molecules enter into the free volume of the polymer. If the solvent is a good solvent for the polymer there is a strong attractive interaction between the polymer and the solvent and the net interaction between the polymer segments become repulsive. As a result, the polymer

molecules start to swell. The understanding of the mobility of the polymer chains and their equilibrium structure close to the substrate or interfaces in presence of solvent vapor are of technological importance in many areas like emulsion, coating and adhesion [5]. The phenomenon of solvent absorption into the pores of polymer has been exploited by several authors to study the diffusion of solvent into the pores [6,7], pore size distribution [8,9], viscoelastic properties [10] etc. Swelling dynamics of the polymeric chains in thin film is very much sensitive to the minute changes in interaction within the system [11–17] and therefore gives an insight about the interaction between the polymer segments in nano-confinement.

Polyelectrolytes are special class of polymers that contain ionizable groups attached to their backbone. In presence of polar solvent, the ionizable groups dissociate releasing low molecular weight counterions to the solution and thus make the polymer chains charged. The effect of long range electrostatic interaction between the charged monomers manifests in several properties of polyelectrolyte chains which are very different from that of neutral polymers. For example it makes the polymer chains more

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elongated than their neutral counterpart, lowers the crossover concentration of the polyelectrolyte solution [18]. Presence of the charged species also increases the osmotic pressure of the polyelectrolyte solution [19].

Presence of low molecular weight salt ions in the polyelectrolyte solution control the electrostatic interaction between the segments by their well-known screening effect and at higher salt concentration polyelectrolyte chains in semidilute solution tend to behave like neutral polymer solution [20]. This screening effect is supported by several experimental studies on polyelectrolyte semidilute solution with added salt. Screening of electrostatic interaction results the destruction of intermolecular ordering present in semidilute polyelectrolyte solution and the peak height of the scattering function diminishes with increasing salt concentration [20]. From the dynamical point of view, addition of salt also changes the fast and slow mode diffusion coefficient of polyelectrolyte chains in semidilute solution of fixed polyelectrolyte concentration [21]. The polyelectrolyte concentration, where the maximum in the reduced viscosity occurs, depends on the ratio of polyelectrolyte and salt concentration [20]. Melting temperature of DNA decreases with decreasing salt concentration which also supports the shielding of polyelectrolyte charge by small ions [22].

If focus is shifted from polyelectrolyte solution towards polyelectrolyte chains under confinement in forms of thin films and multilayers, one can see that the structure and dynamical behaviors of the polyelectrolyte thin films substantially depend on the added salt concentration. Growth and morphology of polyelectrolyte thin films and multilayers prepared by both dip coating and spin coating techniques are quite sensitive to the concentration and valency of the salt in the system [23–25]. Externally added salt ions change the multilayer growth mode from linear to exponential by tuning the interaction between the polyions and controlling the chain conformation [23,24]. McAloney et al. have shown that thickness and roughness of the polyelectrolyte multilayers (PME) increase with salt concentration and the surface morphology of the films can be modified by salt solution of various concentrations [26,27]. Presence of salt also control the polyelectrolyte deposition on functionalized surface and at higher salt concentration reverse deposition is obtained [28]. Asnacios et al. have found that the oscillatory force, present in case of polyelectrolyte liquid films confined between two plates, disappears with increasing salt concentration [29]. Some recent experiments also reveal the impact of salt concentration on the water penetration in the PME [30] and swelling of multilayers by salt [31,32].

These intense controls imposed by the added salt ions on the interaction between the charged species in a polyelectrolyte system motivates us to examine the effect of salt ions on the swelling dynamics of the ultrathin polyelectrolyte films as the latter is extremely sensitive to the minute changes in interaction in the system. In our previous studies, we have shown that the swelling dynamics of the polyelectrolyte films [17] are different from that of neutral polymeric films [11] as repulsive Coulombic interaction plays an important role in their swelling. Since polyelectrolyte chains in solution tend to behave like neutral polymer chains with addition of salt ions, as mentioned in the previous two sections, it is expected that the swelling dynamics of polyelectrolyte films with higher concentration of added salt ions approaches the swelling dynamics of neutral polymeric films. Our main objective in this work is to investigate whether the polyelectrolyte films with added salt behave as neutral polymeric films with respect to their swelling dynamics or the confinement of the chains leads to any different behavior of the system. As the biological polymers like protein, DNA lie within the family of polyelectrolytes and a certain concentration of salt is always present in the physiological condition [33] the knowledge of water absorption and swelling dynamics study of the

prototype system of simple synthetic polyelectrolyte can be exploited to explore the behavior of those complex biological systems in body fluid.

In the present study, swelling dynamics of ultrathin films of a strong polyelectrolyte NaPSS with different concentration of added monovalent salt ions have been examined in presence of water vapor. Thin films of almost similar thickness are prepared from NaPSS solutions with different concentration of added NaCl using spin coating technique and solvent mass uptake and swelling dynamics were studied separately with the same set of films. Increase of salt concentration within the films was crosschecked by XPS technique which is also used to study the distribution of salt ions in the films. Swelling dynamics of the NaPSS thin films are modeled in terms of swelling of polyelectrolyte ellipsoids (prolate), with their major axis parallel to substrate, obeying Katchalsky's free energy expression [34] for intermediate screening. Contribution of salt ions is incorporated in this equation through screening length. Diffusion coefficients of the chains as well as the diffusion coefficient of water within the films are found to be independent of salt concentration. Whereas, effective charge of the chains is found to be increasing with the increase of externally added salt. Results of angle dependent XPS study indicates that both Na^+ and Cl^- ions were redistributed in the films rather than forming NaCl salt crystal. Relative amount of Na is higher towards bottom of the films whereas Cl mainly accumulates on the upper part of the film. Counterion condensation process of the polyelectrolyte chains appears to be affected by the electric field produced between the top Cl^- layer and the bottom Na^+ layer which increases effective charge of the polyelectrolyte chains. This outcome somewhat contradicts the behavior of polyelectrolyte chains in solution where it is expected to behave like neutral polymer chains with addition of salt ions. Contrary to the general belief, our study suggests that polyelectrolyte chains do not act like neutral polymers at higher salt concentration in confined geometry. It may be noted that anomalous behavior at short range has been observed earlier for charged particles or macromolecules in electrolytic environment [35,36].

2. Experimental section

2.1. Sample preparation

NaPSS (30% water solution) was procured from Sigma Aldrich (molecular weight $\sim 2 \times 10^5$ g/mol). Aqueous solution of NaPSS of concentration 24 mg/mL was prepared by diluting the mother solution. According to the phase diagram [37] of the polyelectrolyte solution the concentration lies well within the semidilute regime. Pure sodium chloride crystal (NaCl, 99%) was used as received from Merck to vary the ionic strength of the polyelectrolyte solution. Concentrations of NaCl in the NaPSS solution were varied from 5×10^{-4} to 10^{-1} M by adding different amount of NaCl crystals to the solution. All solutions were sonicated for 10 min for proper mixing of salt crystals so that a homogeneous solution can be achieved. Thin films of NaPSS were prepared on silicon (100) substrate by spin coating technique. Before preparation of films, the substrates were cleaned using RCA cleaning method in which method the wafers were boiled at 100 °C in a solution of water (H_2O), ammonium hydroxide (NH_4OH) and hydrogen peroxide (H_2O_2) ($\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2 = 2:1:1$) for 10 min and rinsed thoroughly with Millipore water. This chemical treatment also enhances the hydrophilicity of the silicon surface by introducing $-\text{OH}$ dangling bonds on the surface which helps in better attachment of the water soluble polymer. It was observed that thickness of the films prepared from solutions of different salt concentrations vary even if they are prepared with same spinning speed. As we are interested to study the effect of salt concentration it was important

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