

SUPPORTING INFORMATION

FOR

Single molecule experiments visualizing adsorbed polyelectrolyte molecules in full range of mono- and di-valent counterions concentrations

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Materials

Poly(2-vinylpyridine) (P2VP) of Mw 159 000 and PI=Mw/Mn=1.05 (secondary chromatography standard, Aldrich, MO) was used in the experiments. Acids used for preparing P2VP solutions and adjusting pH: hydrochloric acid (36.5–38%, EM Science, NJ) and sulfuric acid (96%, Fisher Scientific A300-212, NJ). Inorganic salts for adjustments of ionic strength: sodium chloride (crystalline, Fisher Scientific S271, US-NJ) and sodium sulfate (anhydrous – granular, Mallinckrodt 8024-03, US-KY). Water was purified with a Millipore system (18.3 MΩ·cm). V-1 grade muscovite mica, KAl₂(AlSi₃)O₁₀(OH)₂, (Structure Probe, PA) was used as a substrate (discs of 15 mm in diameter) for the AFM experiments.

Preparation of working solutions

A stock P2VP solution (0.025 g/L) was prepared in Millipore water at pH 3 or 4.8 (HCl). Salt solutions were prepared in Millipore water. Solutions of P2VP for the experiments (working solutions) were prepared by diluting the stock solution with salt solutions. The concentration of P2VP was adjusted to 10⁻³ g/L or 10⁻⁴ g/L (monomer unit concentration in range from [P2VP] = 9.51 × 10⁻⁶ mol/L to 9.51 × 10⁻⁷ mol/L) by mixing the P2VP solution with salt solution. The working solutions' pH values (pH meter 345, Corning Incorporated, Corning, NY) were measured after the completion of the AFM experiments (to avoid contact of the working solutions with the glass electrode). We excluded glass instruments and containers (mainly polyethylene materials were used) from all preparation steps to avoid the adsorption of polymer molecules on the containers. The adsorption could change the solution concentrations in this range of polymer concentrations. All solutions were filtered using a Millex-LCR 0.45 μm filter (Millipore, MA). We used the acids with the same anion as in the salt to adjust pH. Ionic strength was estimated based on the concentrations of salts and acids.

Visualization of adsorbed molecules

AFM images were recorded using a MultiMode scanning probe microscope (Veeco Instruments, NY) operating in tapping mode. The samples were scanned using SNL-10 silicon nitride probes (Veeco Instruments, NY) with a tip radius of 2 nm, a spring constant of 0.32 N/m or 0.06N/m, and a resonance frequency in aqueous media of 9 kHz at an amplitude set point in the range from 0.6 to 2.5 V and a tapping force of approximately 98% of the set point at 1–2 Hz at 28 °C (temperature of the fluid cell in the MultiMode microscope was measured by a calibrated thermistor mounted in the fluid cell).

Polymer solutions were injected directly into the fluid cell with the mica substrate. We started scanning the samples in about 20 min after the injection of polymer solutions (because of the sequence of the

steps: adjustment of laser beam reflection; first manual resonant frequency search; first "rough" approach of the tip to the surface; tip withdrawal; second adjustment of the resonant frequency near the surface; second "fine" approach to the surface). We did not observe changes in the conformation of the adsorbed molecules with incubation time. Molecules approached the adsorbed chain conformation immediately upon contact with the substrate and remained unchanged in this conformation for hours.

Image analysis

Our self-developed software was used to analyze the images. Coordinates of the chains were recorded by dragging a cursor along the chain contour. The recorded coordinates were used to estimate the experimental values of rms end-to-end distance $\langle r^2 \rangle^{1/2}$ and rms radii of gyration $\langle s^2 \rangle^{1/2}$. The radii of gyration were calculated drawing the most probable path accounting for the visible fragments. End-to-end distances were recorded if both ends of the molecule were clearly distinguishable. The dimensions of the coils were estimated from measurements of 200 chains.

Equilibration of adsorbed coils

The adsorbed chains may occupy either conformation of 2D-equilibrated or 3D-projected coil.

We used the ideal random walk (IRW) model to estimate changes in dimensions of the adsorbed PE chains using experimental values of the contour length (L) and the persistence length. The values of rms end-to-end distance estimated using the IRW model were compared with the experimental $\langle r^2 \rangle^{1/2}$ values to judge whether molecules are projected from 3D conformation onto 2D plane or equilibrated on the surface. The IRW model is the simplest approximation and does not reflect intrachain interactions. However, this model provides a useful analysis of relative changes in the coil behavior upon changes in salt concentration. That can be justified by the following data: (1) in the condensed states (I= 0.1-0.3M) the dimension of the P2VP chains corresponds to the size of coil measured in light-scattering experiments (see Ref. 21 and Beer, M.; Schmidt, M.; Muthukumar, M. *Macromolecules* **1997**, *30*, 8375–8385). This result verifies the conclusion that the coil occupies 3D-project conformation; (2) for elongated conformations of the adsorbed chains, we have demonstrated earlier that the coil dimensions are well described by the self-avoiding random walk (SAW) model for 2D equilibrated coil (Ref 19a). Surprisingly, the experimental dimensions of the coils are in good agreement with the IRW model, while the scaling factor corresponds to the SAW model. Thus, it is important that the IRW model provides simple and useful guidelines for the analysis of changes of the coil conformation between two limiting cases, 2D-equilibrated and 3D-projected conformations, upon changes in salt concentration.

Standard deviations (StD) of the molecular dimensions

Standard deviation bars in Fig. 2 for the root mean square (rms) radius of gyration ($\langle s^2 \rangle^{1/2}$) and rms end-to-end distance ($\langle r^2 \rangle^{1/2}$) values reflect combined contributions of StD from AFM experiment, polymer polydispersity, and distribution function of end-to-end distances (that depends on the interaction with solvent and substrate). For random coil $\text{StD} = \langle r^2 \rangle^{1/2}$.

The StD for the contour length of P2VP chains, that was measured with AFM, was 4% (as estimated from multiple measurements of the same polymer chain in different conformations).

The StD of the contour length due to polydispersity for the P2VP sample with PI=1.05 was estimated as: $100\%(\text{PI}-1)^{1/2}=22\%$.

Thus, the error bars in Fig. 2 reflect the combined StD which is a function of conformation of the PE chains and their polydispersity by molecular weight. The contribution of the error from AFM measurements is much lower than those two contributions.

Typically, distribution function of end-to-end distances becomes broader in conditions of phase transition. However, in case of a combined distribution function, changes in the distribution function may be screened by a number of factors. In Fig. SII, we demonstrate the StD as a function of salt concentrations for MC and BC. The broadening of the distribution function in the presence of both salts was observed only for the second transition – reexpansion of polymer coils.

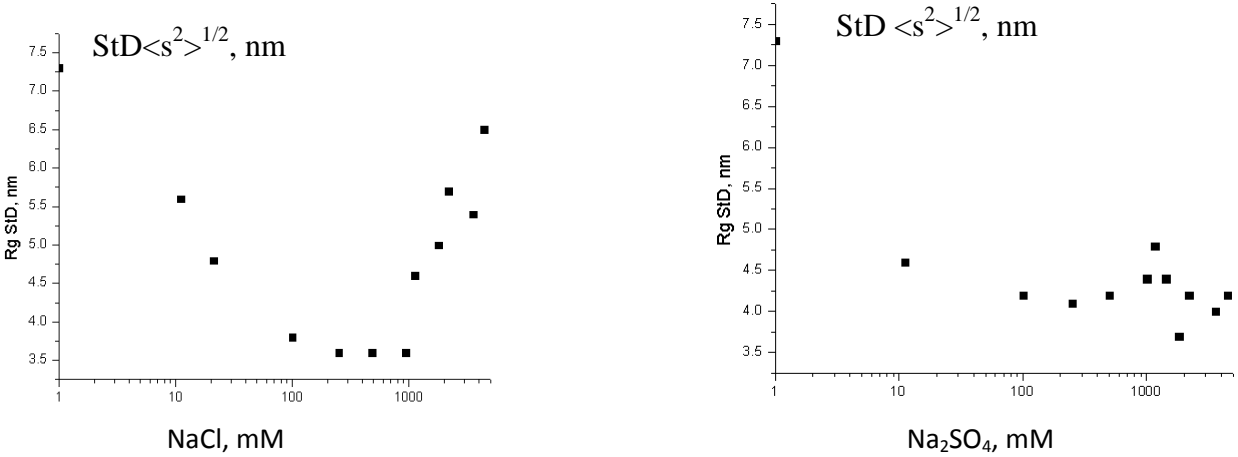


Fig. SI 1. StD of experimental rms radius of gyration ($\langle s^2 \rangle^{1/2}$) vs. salt concentration.