Visualization of Single Polyelectrolyte Molecules

Sergiy Minko[1], Ganna Gorodyska[1], Anton Kiriy[1], Werner Jaeger[2] and Manfred Stamm[1]

[1]*Department of Polymer Interfaces, Institute für Polymerforschung Dresden. Hohe Strasse 6, Dresden, 01069, Germany*

[2]*Fraunhofer- Institut für Angewandte Polymerforschung, Geiselbergstr. 69, 14476 Golm, Germany*

INTRODUCTION

The field of single molecule research offers possibilities to study physico-chemical processes at a level of single molecules and single molecule events, and to design surfaces and devices operating with single molecules. Most of our knowledge was collected from the study of ensembles of molecules when properties are averaged over large number of molecules. Single molecule study allows to prove our knowledge and to address problems which can not be solved with investigations of ensembles of molecules. Particular, it concerns conformations of individual macromolecules in solvent and adsorbed on a flat surface, conformational transitions, analytic, mechanical properties, polymer-polymer, polymer-biomolecules, polymer – colloid interactions, etc. Manipulating single molecules we get "unlimited" possibilities to design surface properties of materials.

We use recent advances of atomic force microscopy (AFM) to study polymers at the scale of single molecules.[1,2] We study conformations and conformational transitions for single polyelectrolyte molecules deposited on flat surfaces. We try to obtain the information about conformations of the molecules in solution and changes of the conformation introduced when the molecules adsorb on flat substrates.

Polyelectrolytes (PE) attract continuously enhanced interest due to their importance in industry and nature.[3] Gelation of PE in water and a reversible swelling or shrinking of PE gels responding on external stimuli is considered to be one of the most promising properties of PE.[4] At the heart of this phenomenon lies the coil-to-globule transition (CGT). It is well known that in good solvent PE chains display an extended coil conformation due to the Coulomb repulsion between charged units. A decrease of the charge density results in a collapse transition of PE chains to a globule conformation due to the short range van der Waals interactions. Theoretical analysis[5] predict intermediate necklace-like conformations of PE chains, when a weakly charged PE chain adopts a conformation resembling a sequence of polymer beads interconnected by narrow strings. The theory suggests that a decrease of the charge density leads to a cascade of abrupt transitions between necklaces with different numbers of beads. There are numerous attempts to confirm experimentally this prediction. However, it has been difficult to obtain fully conclusive results about mechanism of CGT in a single PE chain, because the competition between single-chain events and an aggregation of several chains was always present under experimental conditions. In addition, conventional methods, such as laser light and neutron scattering, sedimentation and conductivity provide the information referring to the ensemble average over many polymer chains.

EXPERIMENTAL

Materials. In this study we used PE molecules of poly(2-vinylpyridine) (P2VP) and poly(methacryloyloxyethyl dimethylbenzyl ammonium chloride) (PMB)[6] which allowed us to obtain very good resolution for AFM investigations and to identify some particular details of necklace globule structures deposited on mica. P2VP was purchased from Polymer Source Inc (Canada) (anionic polymerization) of different molecular weights ranging from 50 kg/mol to 800 kg/mol Polycation PMB (M_w= 720 000, M_w/M_n=1.5, GPC data) was synthesized by free radical polymerization in water solution.[6]

Sample Preparation. Freshly cleaved mica plates were exposed to acid aqueous solution (pH=3, HCl) for 2 minutes to compensate native negative charges on the surface. Afterward the plates were cleaned two times by rinsing in water. We set a drop of 0.0005 mg/ml of PE aqueous solution on the surface of the mica substrate for 20 sec and afterward removed the rest of the drop with centrifugal force.

Sample Characterization. The adsorbed PE molecules were investigated in a dry state with a Multimode AFM (Digital Instruments, Santa Barbara) operating in the tapping mode[7]. Silicon tips with a radius of 16-25 nm, a spring constant of 0.3 N/m and a resonance frequency of 250-300 kHz were used after calibration with gold nanoparticles (of 5 nm in diameter). The dimensions of structures obtained from AFM images were corrected by the tip radius.

RESULTS AND DISCUSSION

AFM images of P2VP and PMB molecules of different conformations are present in Figure 1 and Figure 2. At pH=2.0 in aqueous solution P2VP is highly charged and adsorbed molecules appear in AFM images as worm-like chains with the average thickness of about 0.2 nm. The number-average contour lengths of the chains are slightly smaller than values calculated from molecular weight. That difference can be explained by error in the evaluation of the experimental contour length caused by bends and knots on the chain. The number of bends increases with molecular weight of P2VP. Mean-square end-to-end distance is proportional to the molecular weight of P2VP. These results suggest that we observe unfolded adsorbed single P2VP chains.

At pH=3.5 P2VP (NaCl 0.02 mol/l) molecules appear to be much more strongly coiled chains resembling a deformed globule (Figure 1b) with average height of 0.35 nm. Here and below we consider, as an example, the structures formed by P2VP of M_n=385 kg/mol. The data suggest that a decrease of the fraction of charged monomers affects the transition to necklace-like globular conformation. These globule conformations resemble dumbbell (Figure 1c) and trimbell structures predicted from simulations.[5]

At pH=3.5 and NaCl concentration 1.0 mol/l the chains undergo a transition to the still more compact globule conformation (Figure 1d) with the average height of the structures of 1.4 nm. The average volume of the globule calculated from AFM data is 680 nm^3, which is comparable with the volume of the single P2VP molecule equal to 660 nm^3.

PMB molecules adsorbed from salt-free aqueous solution appear in AFM images as wormlike chains (Figure 2a). It was found that the height of adsorbed worms is independent from their contour lengths and displays a narrow distribution (0.75±0.05 nm). The width of single strands ranges from 2 to 3 nm. Figures 1b and 1c present examples of AFM images for PMB deposited from aqueous solution with added NaCl. The stepwise increasing of NaCl concentration continuously changes the conformation of PE from wormlike (Figure 1a) to patch-like (Figure 1b, 1c) via partially intra-segregated coil structures resembling necklaces with different number of beads. To characterize the size of PMB coils, the apparent size of the coil *L* was measured as the longest dimension of the structures appearing in AFM images. Values of *L* for at least 150 individual structures were obtained for each NaCl concentration. The stepwise increase of ionic strength leads to the decrease of the average long-axis length which displays the continuous collapse in the ensemble of polymer chains. On the single molecule level this collapse transition occurs to be discrete. For an example, even at the high salt concentration (0.2M NaCl, Figure 1b, 1c) the extended wormlike single chains coexist with considerably more compact states

We suppose that chain conformations of PE molecules in solution are dynamically fluctuating, and in this way also the number of beads of the necklace conformations changes with time. The chain conformation is frozen-in during adsorption and drying. From our investigations we can expect to see an ensemble average over space and time when we average over a large number of adsorbed molecules. We thus have evidence of necklace-like conformations with e.g. 1, 2 and 3 beads present, which are coexisting with stretched coil-like and globule conformations. This distribution might be a

consequence of polydispersity and charge distribution as well as dynamic fluctuations of investigated molecules in solution prior to adsorption.

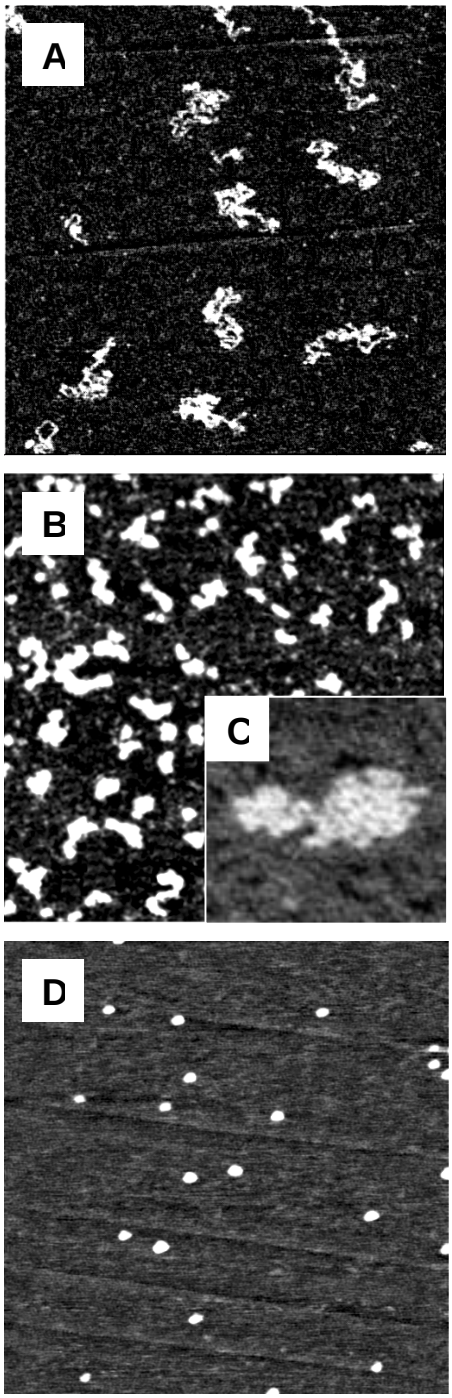

Figure 1. AFM images of P2VP, M_n= 385 kg/mol adsorbed on mica (Z- range 2 nm): (A) 1×1 μm^2 at pH=2.0; (B) 500 × 500 nm^2 at pH=3.5 and NaCl 0.02 mol/l; (C) inset 100×100 nm^2- zoom of the image B; (D) 1×1 μm^2 at pH=3.5, NaCl 1.0 mol/l.

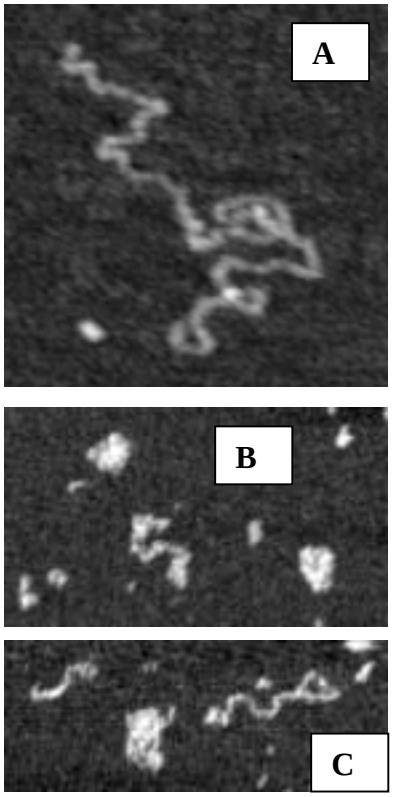

Figure 2. Representative AFM images (Zoom) of PMB adsorbed on mica (Z-range 2nm): in salt-free conditions 0.2 × 0.2 μm^2 (a); 0.2M NaCl, 0.6 × 0.2 μm^2 (b and c).

REFERENCES

1. (a) Kumaki, J.; Nishikawa, Y.; Hashimoto, T. *J. Am. Chem. Soc.* **1996**, *118*, 3321-3322. (b) Akari, S.; Schrepp, W.; Horn, D. *Langmuir* **1996**, *12*, 857-860. (c) Pfau, A.; Schrepp, W.; Horn D. *Langmuir* **1999**, *15*, 3219-3225. (d) Zhu, M.; Schneider, M.; Papastavrou, G.; Akari, S.; Möhwald, H. *Langmuir* **2001**, *17*, 6471-6476. (e) Sheiko, S. S.; Möller, M. *Chem. Rev*. **2001**, 101, 4099-4123.
2. (a) Sheiko, S. S.; Prokhorova, S. A.; Beers, K. L.; Matyjaszewski, K.; Potemkin, I. I.; Khokhlov, A. R.; Möller, M. *Macromolecules* **2001**, *34*, 8354-8360. (b) Ernstsson, M.; Neumann, R. D.; Claesson, P. M. *Langmuir.* **2002**, *18*, 1604-1612.
3. Dautzenberg, H.; Jaeger, W.; Kötz, B. P. J.; Seidel, C.; Stscherbina D. *Polyelectroytes: Formation, characterization and application.* Hanser Publishers: Munich, Vienna, New York, 1994.
4. Tanaka, T. *Phys Rev. Lett*. **1978**, *40*, 820-823.
5. (a) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974-2979. (b) Solis, F. J.; de la Cruz, M. O. *Macromolecules* **1998**, *31*, 5502-5506. (c) Lyulin, A. V.; Dünweg, B.; Borisov, O. V.; Darinskii, A. A. *Macromolecules* **1999**, *32*, 3264-3278. (d) Mica, U.; Holm, C.; Kremer, K. *Langmuir* **1999**, *15*, 4033-4044
6. (a) Zimmermann, A., Jaeger, W., Reichert, K.-H. *Polymer News* **1997**, 390-392. (b) Jaeger, W.; Paulke, B.-R.; Zimmermann, A.; Lieske, A.; Wendler, U.; Bohrisch, J. *Polymer Prepr.* **1999**, *40*, 980-981.
7. Minko, S.; Kiriy, A.; Gorodyska, G.; Stamm M. *J. Am. Chem. Soc.* **2002**, *124*, 3218-3219.