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Single Flexible Hydrophobic Polyelectrolyte Molecules Adsorbed on Solid Substrate: Transition between a Stretched Chain, Necklace-like Conformation and a Globule

Sergiy Minko,* Anton Kiriy, Ganna Gorodyska, and Manfred Stamm
Institut für Polymerforschung Dresden, Hohe Strasse 6, 01069 Dresden, Germany

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Polyelectrolytes are widely used in industry, everyday applications, and lively nature. That generated great permanent interest to theoretical and experimental investigations of polyelectrolytes. Hydrophobic polyelectrolytes (HP) are soluble in water due to the charged monomer units which increase entropy of polyelectrolyte solution via releasing of counterions. An increase of the fraction of uncharged monomers results in a collapse transition of HP chains to a globule conformation due to the short-range interactions between hydrophobic monomers, while an increase of the fraction of charged monomers affects the globule expansion due to the Coulomb repulsion. Khokhlov has suggested a cylindrical conformation for the deformed weakly charged HP globule.[1] Later Dobrynin, Rubinstein, and Obuchov (DRO-theory),[2] then Solis and Cruz,[3] and very recently Lyulin et al. and Mica et al.[4] have predicted that the globule undergoes phase transformation forming a necklace-type structure, in which collapsed segments form beads separated by narrow strings.

Most of applications of polyelectrolytes are connected with their adsorption on solid surfaces. Adsorbed polyelectrolyte chains can be additionally deformed on the surface.[5] Adsorption kinetics in some particular cases shows very pronounced evidence of a large change in conformation of adsorbed polyelectrolyte chains.[6] There is great interest in studying the conformation of single adsorbed polyelectrolyte molecules based on the possibilities offered by atomic force microscopy (AFM).[7] In many reports adsorbed polyelectrolyte molecules appear in a coiled conformation.[8] For shape-persistent cylindrical brush-like polymer molecules the coil-globule transition was visualized and studied with AFM.[9] Here we report on the direct experimental evidence of the transition between a globule and a stretched necklace-like globule for the single flexible HP adsorbed on solid substrate.

In this study we use poly(2-vinylpyridine) (P2VP) purchased from Polymer Source Inc. (Canada) (anionic polymerization) of different molecular weights ranging from 50 to 800 kg/mol as a HP in very diluted (0.0005 mg/mL of P2VP, which is far below the critical overlap concentration) acidic (HCl) aqueous solution. We set a drop of the solution on the surface of freshly cleaved mica (isoelectric point at pH 3.0) for 1 min and afterward removed the rest of the drop with centrifugal force. All experiments were performed at pH values near the isoelecrtic point of mica and/or with adding NaCl to arrange a poor electrostatic interaction between the polymer and the substrate, which allowed a decrease in the effect of the substrate on chain conformations. Nevertheless, we omit any detailed analysis of chain statistics because it is difficult in this work to distinguish between intrinsic conformations of the PVP molecules and those induced by the adsorption.[10] The adsorbed P2VP molecules are investigated in the dry state with a Multimode AFM instrument (Digital Instruments, Santa Barbara) operating in the tapping mode. 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 diameter 5 nm) to evaluate the tip radius. The dimensions of structures obtained from AFM images were corrected by the tip radius.

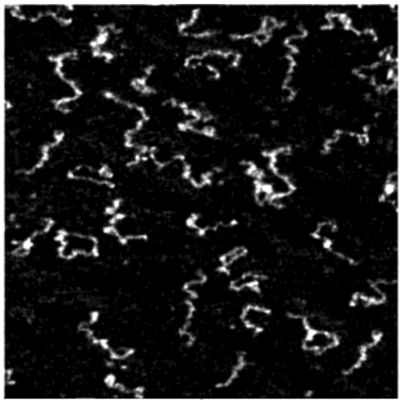

Figure 1. AFM image (500 × 500 nm^2; Z range 2 nm) of P2VP, $M_n = 59$ kg/mol adsorbed on mica at pH 2.0.

Table 1. Molecular Dimensions of Adsorbed P2VP Chains at pH 2.0

M_n (kg/mol)/ polydispersity index	calcd no. av. contour length, nm	exptl no. av. contour length (nm)/ polydispersity index	exptl end-to-end distance, R, nm
59/1.05	143	130/1.04	52 ± 5
176/1.2	425	325/1.10	78 ± 28
385/1.08	931	845/1.05	153 ± 35

At pH 2.0 in aqueous solution P2VP is highly charged[11] and adsorbed molecules appear in AFM images as wormlike chains with the average thickness of about 0.2 nm (Figure 1). The number-average contour lengths of the chains are slightly smaller than values calculated from the molecular weight (Table 1). That difference can be explained by the error in the evaluation of the experimental contour length caused by bends and knots on the chain. The number of bends increases with the molecular weight of P2VP (Figure 2a). The mean-square end-to-end distance is proportional to the molecular weight of P2VP (Figure 3). The error of the measured end-to-end distance increases with the molecular weight of the polymers because of the difficulty in identifying the ends of the coiled chains. 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 2b) with an average height of 0.35 nm. Here and below we consider,

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* Address correspondence to this author. E-mail: minko@ipfdd.de.

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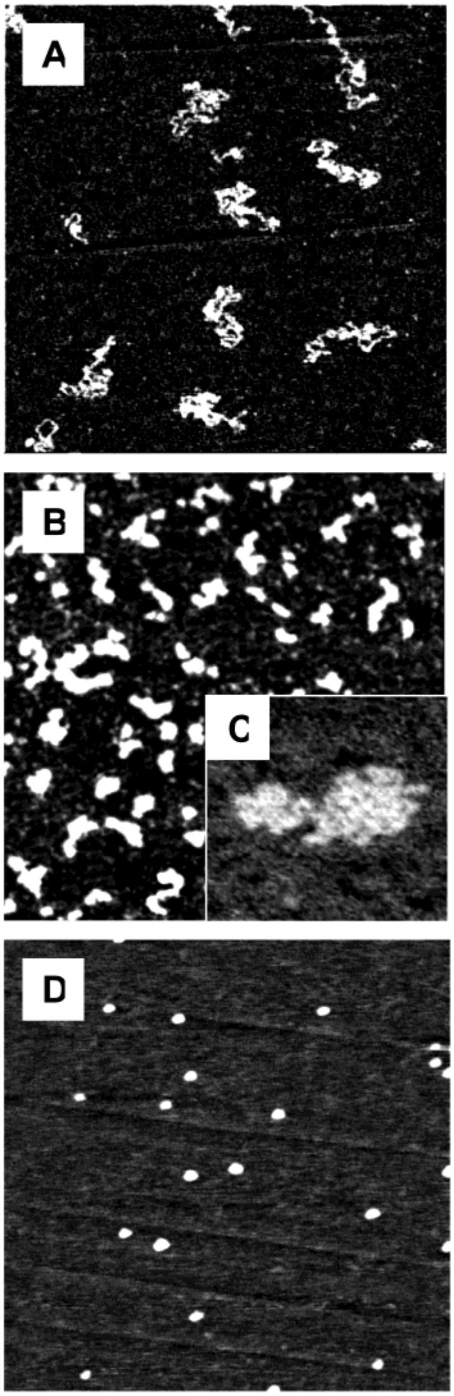

Figure 2. AFM images of P2VP, $M_n = 385$ kg/mol adsorbed on mica (Z range 2 nm): (A) 1 × 1 μm^2 at pH 2.0; (B) 500 × 500 nm^2 at pH 3.5 and NaCl 0.02 mol/L; (C) inset, 100 × 100 nm^2, zoom of the image B; (D) 1 × 1 μm^2 at pH 3.5, NaCl 1.0 mol/L.

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 2c) and trimbell structures predicted from simulations.[4]

At pH 3.5 and a NaCl concentration 1.0 mol/L the chains undergo a transition to the still more compact globule conformation (Figure 2d) 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.

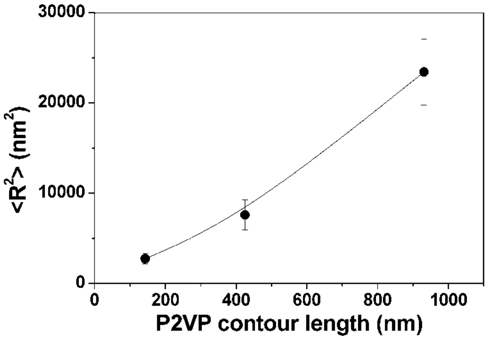

Figure 3. Mean-square end-to-end distance $\langle R^2 \rangle$ for the adsorbed P2VP molecules at pH 2.0 plotted as a function of the contour length.

The AFM images obtained for P2VP of $M_n = 735$ kg/mol show very coiled conformations and were not used for statistical analysis of structures in the whole pH range.

In conclusion, we present in this report the first direct observation of the polyelectrolyte chain conformations representing the transition between different conformations of single flexible HP molecules adsorbed on solid substrates from aqueous solution affected by different environments. The HP molecules undergo conformational transitions from stretched wormlike coil to necklace-like globule, and to compact globule as the fraction of charged monomers decreases with an increase of pH and ionic strength. These results are in good agreement with recently developed DRO theory for weakly charged flexible polyelectrolytes in poor solvent.

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References

(1) Khokhlov, A. R. *J. Phys. A* **1980**, *13*, 979−987.

(2) Dobrynin, A. V.; Rubinstein, M.; Obukhov, S. P. *Macromolecules* **1996**, *29*, 2974−2979.

(3) Solis, F. J.; de la Cruz, M. O. *Macromolecules* **1998**, *31*, 5502−5506.

(4) (a) Lyulin, A. V.; Dünweg, B.; Borisov, O. V.; Darinskii, A. A. *Macromolecules* **1999**, *32*, 3264−3278. (b) Mica, U.; Holm, C.; Kremer, K. *Langmuir* **1999**, *15*, 4033−4044.

(5) Netz, R. R.; Joanny, J.-F. *Macromolecules* **1999**, *32*, 9013−9025.

(6) (a) Voronov, A.; Pefferkorn, E.; Minko, S. *Macromolecules* **1998**, *31*, 6387−6389. (b) Voronov, A.; Pefferkorn, E.; Minko, S. *Macromol. Rapid Commun.* **1999**, *20*, 85−87. Minko, S.; Voronov, A.; Pefferkorn, E. *Langmuir* **2000**, *16*, 7876−7878.

(7) Thang, Q.; Ihhiss, D.; Kjoller, K.; Elings, V. B. *Surf. Sci.* **1993**, *290*, L688-L692.

(8) (a) Stipp, S. L. *Langmuir* **1996**, *12*, 1884−1891. (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) Ibn-Elhaj, M.; Ouali, L.; Papastavrou, G.; Möhwald, H. *Langmuir* **1999**, *15*, 1528−1533. (e) Zhu, M.; Akari, S.; Möhwald, H. *NanoLett.* **2001**, *1*, 569−573. (f) Zhu, M.; Schneider, M.; Papastavrou, G.; Akari, S.; Möhwald, H. *Langmuir* **2001**, *17*, 6471−6476.

(9) (a) Dziezok, P.; Sheiko, S. S.; Fisher, K.; Schmidt, M.; Möller, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2812. (b). Börner, H. G.; Beers, K.; Matyjaszewski, K.; Sheiko, S. S.; Möller, M. *Macromolecules* **2001**, *34*, 4375−4383. (c) Sheiko, S. S.; Prokhorova, S. A.; Beers, K. L.; Matyjaszewski, K.; Potemkin, I. I.; Khokhlov, A. R.; Möller, M. *Macromolecules* **2001**, *34*, 8354−8360.

(10) Rivetti, C.; Guthold, M.; Bustamante, C. *J. Mol. Biol.* **1996**, *264*, 919−932.

(11) Pefferkorn, E.; Elaissari, A. *J. Colloid Interface Sci.* **1990**, *138*, 187.

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