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Mineralization of Single Flexible Polyelectrolyte Molecules

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Abstract: Conformation of a single flexible polyelectrolyte molecule with a hydrophobic backbone in aqueous solution is effected by the interplay of the short-range intramolecular attraction and the long-range Coulomb repulsion. The conformation can be frozen if the molecule is trapped by a solid substrate. With this approach, we prepared the range of single molecule templates from poly(2-vinylpyridine) (P2VP) deposited on the surface of Si-wafer or mica in different conformations from an elongated wormlike coil to compact globule. Pd(+2) was coordinated by P2VP via an ion exchange reaction exposing the samples to palladium acetate acidic aqueous solution. In the next step, Pd(+2) was reduced by dimethylamine borane. This route results in wire-shaped metallic nanoparticle assembles of about 2−5 nm in diameter and 50−700 nm in length. The conformation and size of the underlaying polyelectrolyte molecules determine the dimensions of nanoparticles.

Introduction

Nanoparticles of a various shape from spherical clusters to nanowires attract great interest because of their importance for the further miniaturization of electronic devices,[1−3] unique optical,[4] magnetic,[5] and catalytic[6] properties. Several routes have been developed for the synthesis of metallic nanowires, including the template synthesis.[7] The ultimate limit of the fabrication of nanoparticles via the template synthesis is determined by the use of polymer micelles,[8] microphases in block copolymers,[9] and single molecules as templates.[10] Recently, DNA molecules were used as biotemplates for the deposition of metal clusters and fabrication of nanowires.[11] Here, we further advanced in the miniaturization of nanowires by templating single synthetic flexible polyelectrolyte molecules of a diameter which is substantially smaller than the diameter of DNA molecules.

DNA represents semiflexible polyelectrolytes (PE), the rigidity of which is affected by both bare and effective electrostatic persistent length. The bare rigidity originates from secondary structures stabilized by hydrogen bonds, while electrostatic rigidity is affected by the Coulomb repulsion, which gives the sum of the persistent length of 50 nm in aqueous environment.[12] Because of this rigidity, DNA exhibits a highly elongated coil conformation in the absence of condensation agents. Polymers, surfactants, metal ions, and organic solvents may cause a first-order coil-compact globule transition of DNA molecules. Nevertheless, the bare rigidity predominates the shape persistence of DNA molecules to the condensation agents to some extent. Particularly, this stability allows one to template DNA in salt solution and obtain wire-shaped metallic nanoparticles.[11]

Flexible synthetic PE molecules express rather different behavior. A flexible backbone rapidly responds to the change of a charge density resulting in a continuous cascade of coil-globule transitions in the presence of condensation agents.[13] Recently, we reported the visualization of different conformations of single flexible PE molecules of poly(2-vinylpyridine) (P2VP) with atomic force microscopy (AFM) and conditions

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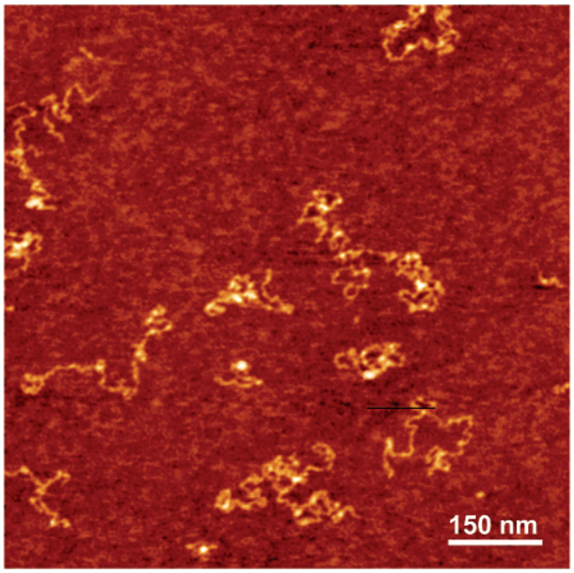

Figure 1. AFM images (1 × 1 μm^2, Z-range 2 nm) of P2VP chains deposited on mica surface from aqueous solution at pH 2.

to deposit fully stretched polyelectrolyte chains on the mica substrate.[14] Solid substrates trap the PE molecules in elongated conformations which appear to be kinetically stable for a relatively long period of time even in the presence of condensation agents. In this work, we employ this possibility to fix the conformation of flexible PE deposited onto solid substrate and perform mineralization of PE in the frozen conformation.

Experimental Section

Materials. P2VP of molecular weight ranging from 50 to 800 kg/mol was purchased from Polymer Sources Inc. (synthesized by anionic polymerization, polydispersity index of about 1.1). Highly polished silicon (Si) wafers (obtained from Wacker-Chemitronics) were first cleaned three times in a ultrasonic bath for 5 min with dichloromethane (DCM), placed in the cleaning solution (prepared from NH_4OH and H_2O_2) at 60 °C for 1 h (*Note: NH_4OH:H_2O_2 solution reacts* violently *with organic compounds. Caution should be used when handling this solution*). Samples were finally exposed to 50% sulfuric acid for 15 min and then rinsed several times with Millipore water (18 MΩ cm). $Pd(OAc)_2$ (PA), dimethylamine borane (DMAB), and DCM were used as received from Aldrich.

Sample Preparation. We used three different procedures for the mineralization of PE molecules.

Procedure 1. We used after Braun et al.[11a] and Richter et al.[11b] the procedure developed for metallization of DNA. Five milligrams of $Pd(CH_3COO)_2$ in 30 mL of deionized water was placed in an ultrasonic bath for 30 min, and then the mixture was centrifuged for 5 min at 2000*g* to obtain a saturated solution of PA and to settle all unsolved particles. The PA solution was mixed for 2 h with an equal amount of the acidic (pH range from 1 to 3.5) P2VP (0.005 mg/mL) aqueous solution. In the second step, the solution of 1.0 mg/mL of dimethylamine borane, sodium citrate, and lactic acid were added to the PA-P2VP aqueous solution, and immediately afterward the Si-wafer was introduced in the mixture for 30 s to adsorb the resulting products. Finally, Si-wafers were cleaned with water and dried with the argon flux.

Procedure 2. The PA solution was mixed with an equal amount of acidic (pH 2) P2VP (0.0005 mg/mL) aqueous solution for 15 min, and then the Si-wafer was exposed to the solution for 30 s to adsorb P2VPH-1/2($PdCl_4$) composite. Afterward, the Si-wafer was thoroughly rinsed with water and placed for 15 s into the reduction DMAB solution. Finally, the Si-wafer was cleaned with water and dried with the argon flux.

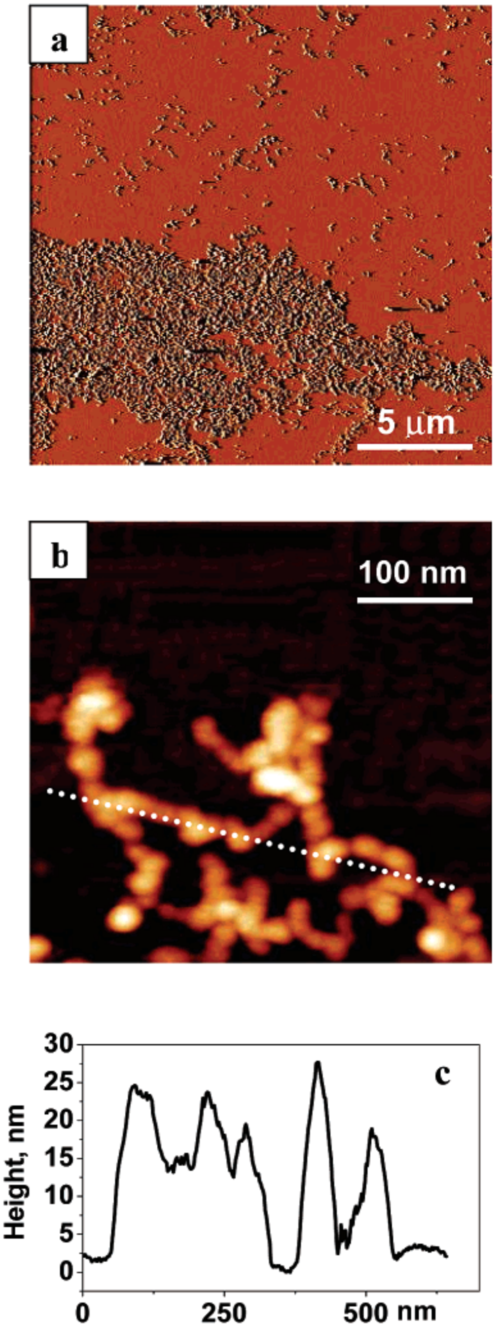

Figure 2. AFM images of Pd particles deposited on Si-wafer by procedure 1: 20 × 20 μm^2 − phase image (a); 0.5 × 0.5 μm^2 − topography image, Z-range 30 nm (b); and its cross section driven along the particle contour (c).

Procedure 3. In the first step, single molecules of P2VP were deposited on the cleaned Si-wafer from acidic (pH 2, HCl) aqueous solution of P2VP (0.0005 mg/mL) for 1 min at room temperature. In the second step, the silica wafer was then rinsed several times with water and placed into the PA solution (pH 2) for 1 min for the formation of the P2VPH-1/2($PdCl_4$) composite. In the third step, the silica wafer was thoroughly rinsed with water and placed for 15 s into 1.0 mg/mL DMAB solution. Finally, the Si-wafer was cleaned with water and dried with the argon flux.

Sample Characterization. The adsorbed P2VP molecules before and after Pd deposition were investigated in dry state at ambient

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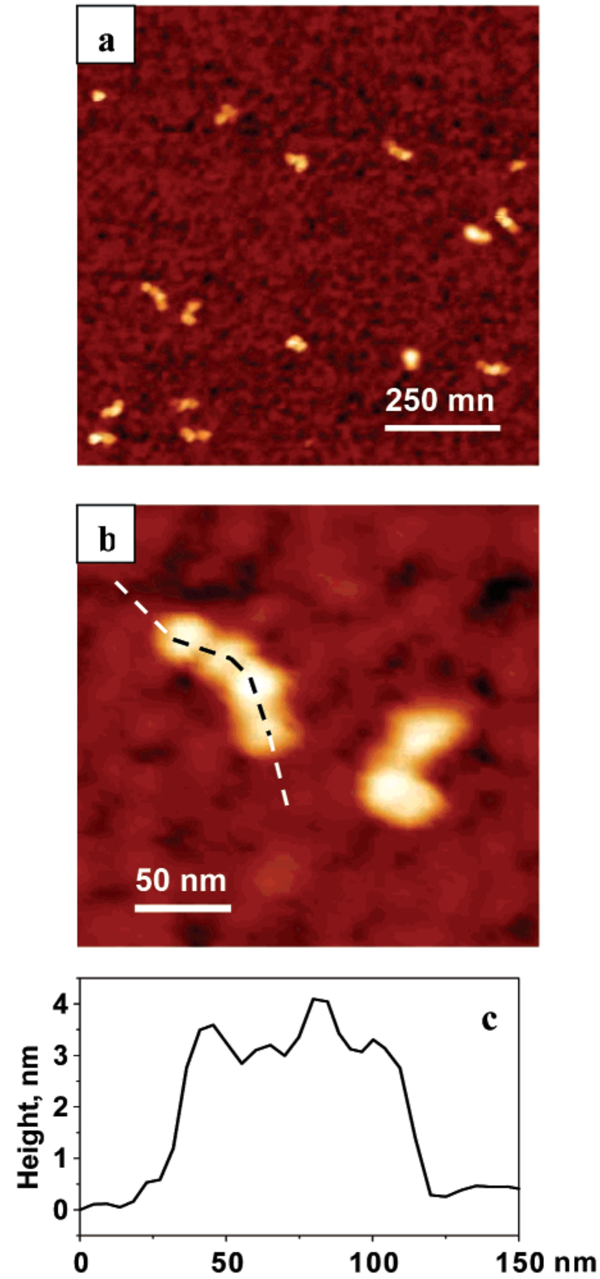

Figure 3. AFM topography images of Pd-P2VP composite deposited on Si-wafer by procedure 2: 1 × 1 μm^2, Z-range 10 nm (a); 0.25 × 0.25 μm^2, Z-range 10 nm (b); and its cross section driven along the particle contour (c).

conditions (we found no effect of humidity on the measurements) with AFM instrument Multimode (Digital Instruments, Santa Barbara) operating with amplitude feedback in "light" tapping mode (amplitude setpoint in the range of 0.99−0.95). Silicon tips with a radius of 10−20 nm, spring constant of 0.3 N/m, and resonance frequency of 250−300 kHz were used after the calibration with gold nanoparticles (diameter of 5.22 nm, Pelco AFM Gold Standard Kit) to evaluate the tip radius. Most measurements were done with the tip radius equal to 14.9 ± 1.9 nm. The dimensions of structures obtained from AFM images were corrected (decreased) by the tip radius according to the standard procedure.

Results and Discussion

Figure 1 shows a representative AFM image of P2VP chains deposited on mica from acidic aqueous solution. The contour length of the chains evaluated from the AFM images agrees with the value calculated from the degree of polymerization.[14] At these conditions, more than 50% of 2-vinylpyridine monomers are protonated, and the polymer chains are stretched forming wormlike coils due to the electrostatic repulsion between randomly distributed positive charges along the chain.[13] This conformation is frozen due to the interaction with the solid substrate. We performed several controlled experiments which have shown that the conformation of P2VP molecules on the solid substrates was stable at least for several hours even if they were exposed to NaCl aqueous solutions at pH 7.0. This result assumes a slow kinetics of a conformation change of the trapped PE chains. Consequently, we assumed that flexible PE molecules in the wormlike conformation might be used as templates for mineralization in the same way as it was recently suggested for semiflexible PE, particular for DNA. Below we present different attempts to metallize single molecules of *flexible* PE.

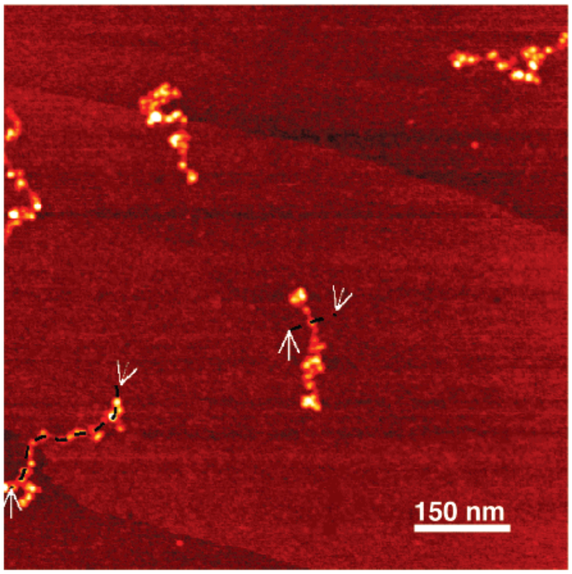

Figure 4. AFM images (1 × 1 μm^2, Z-range 5 nm) of Pd-nanowires prepared from P2VP of M_W = 385 kg/mol on the surface of freshly cleaved mica by procedure 3.

Procedure 1 for the mineralization of PE was copied from the method developed for a decoration of DNA molecules with metal clusters.[11] This approach suggests one to coordinate metal ions with PE and afterward to reduce metal. The product was deposited on the surface of the Si-wafer. The addition of PA to P2VP solution effects a charge compensation due to the ion exchange and mutual attraction.[15] The water insoluble Pd-P2VP complex agglomerates in aqueous medium producing Pd clusters after reduction of metal. The clusters are of a large polydispersity with the size ranging from tens to hundreds of nanometers (Figure 2). Molecular weight of P2VP and pH affects the cluster size only slightly. The cluster size increases with time of exposure of the Si-wafer to the solution.

In contrast, in procedure 2, the Pd-P2VP complex was deposited on the Si-wafer in the first step, and then it was reduced by exposure of the Si-wafer to the DMAB solution. The shape and the size of the obtained particles (Figure 3) are still far from the dimensions of elongated single PE molecules. The

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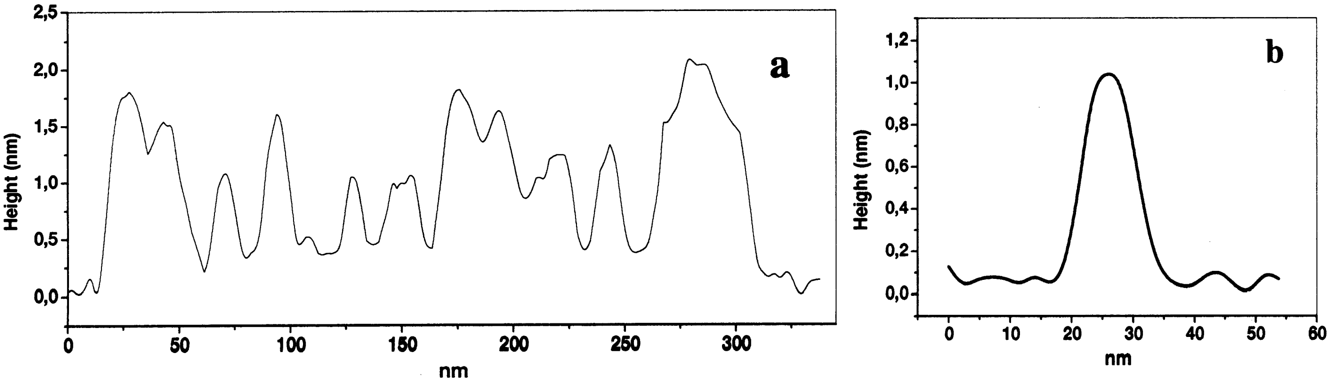

Figure 5. Cross-section profiles (original AFM-data; no deconvolution was performed) of Pd-nanowires drawn parallel (a) and perpendicular (b) to the contour.

Scheme 1. Schematic Representation of the Route To Metallize a Single Polyelectrolyte Molecule via Multistep Procedure: Dissolution of PE in Acidic Water When PE Chains Adopt Wormlike Conformation Because of the Electrostatic Repulsion between Positive Charges, Deposition of the Wormlike Chain on the Substrate, Attachment of Metal Ions via Ion Exchange Reaction, and Reduction of the Metal

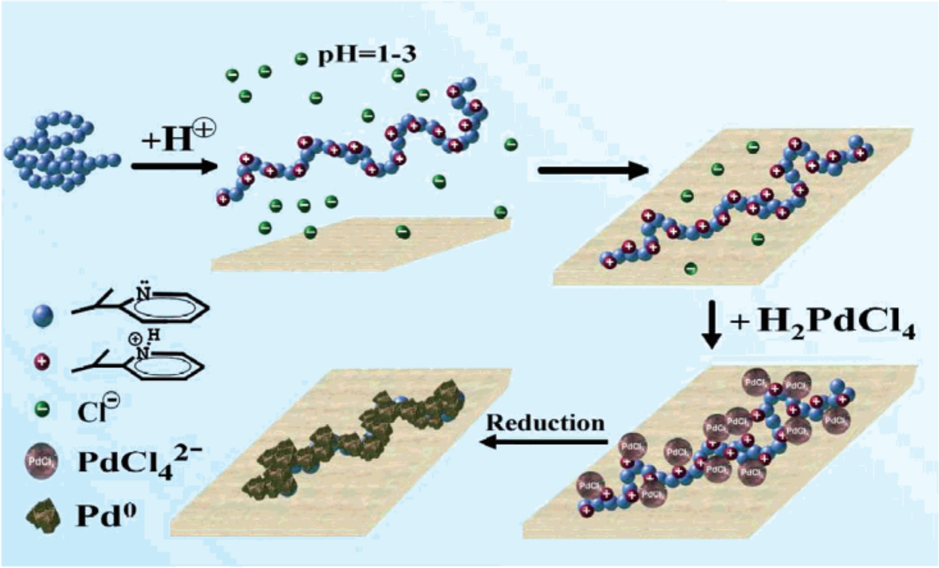

Table 1. Average Sizes of P2VP Molecules, Metallic Nanowires, and Pd-Clusters Deposited on the P2VP Single Molecules[a]

		average dimensions of nanowires		average size of Pd-clusters	
M_n (kg/mol)/ polydispersity index of P2VP	contour length of P2VP, nm	contour length, nm/polydispersity index	end-to-end distance, nm	height, nm	width, nm
59/1.05	143	55/1.08	44	2.5	5.1
176/1.4	425	132/1.2	79	2.4	5.0
385/1.08	931	346/1.03	109	2.6	5.4
735/ 1.23	1778	630/1.03	161	2.0	5.6

[a] The polydispersity index was calculated as a ratio between the second and the first moments of the Gauss distribution function.

height of clusters equals 3 nm and has a narrow distribution. A long axis length is about 100 nm, and the width is about 50 nm. This result suggests that we mineralize collapsed PE coils. This collapse is caused by the interaction with PA.

Finally, procedure 3 (Scheme 1) consists of the P2VP deposition (step 1) from very dilute acidic (HCl, pH 2.0) aqueous solution on the surface of the Si-wafer or freshly cleaved mica. The substrate with deposited P2VP was exposed to the PA solution (step 2) to perform the ion exchange reaction. In step 3, Pd(II) was reduced by the treatment with DMAB. AFM images (Figures 4, 5) document mineralization of elongated PE coils. The chemical reactions involved in this process are listed below:

$$\mathrm{P2VP} + n\mathrm{HCl} \rightleftharpoons \mathrm{P2VP{\cdot}}n\mathrm{HCl} \quad (1)$$

$$\mathrm{Pd(OAc)_2} + 4\mathrm{HCl} \rightleftharpoons \mathrm{H_2PdCl_4} + 2\mathrm{HOAc} \quad (2)$$

$$\mathrm{P2VP{\cdot}}n\mathrm{HCl} + (n/2)\mathrm{H_2PdCl_4} \rightarrow \mathrm{P2VP{\cdot}}(n/2)\mathrm{H_2PdCl_4} + n\mathrm{HCl} \quad (3)$$

$$2(\mathrm{P2VP{\cdot}}(n/2)\mathrm{H_2PdCl_4}) + n(\mathrm{CH_3})_2\mathrm{NH{\cdot}BH_3} + 3n\mathrm{H_2O} \rightarrow 2(\mathrm{P2VP{\cdot}}n\mathrm{HCl}) + n\mathrm{Pd^0} + n\mathrm{B(OH)_3} + n(\mathrm{CH_3})_2\mathrm{NH{\cdot}HCl} + n\mathrm{HCl} + 2n\mathrm{H_2} \quad (4)$$

The obtained wire-shaped nanoparticles appear in AFM images as a 1-D sequence of the interconnected Pd clusters. This structure resembles a necklacelike morphology nicely observed in the profile of the AFM image as beads (undulations) separated by narrow strings (Figure 5). The length of the nanowires is proportional to the molecular weight of P2VP (Figure 6). We performed the statistical analysis of parameters extracted from the AFM images and their profiles: height, width, contour length, and end-to-end distance (Table 1).

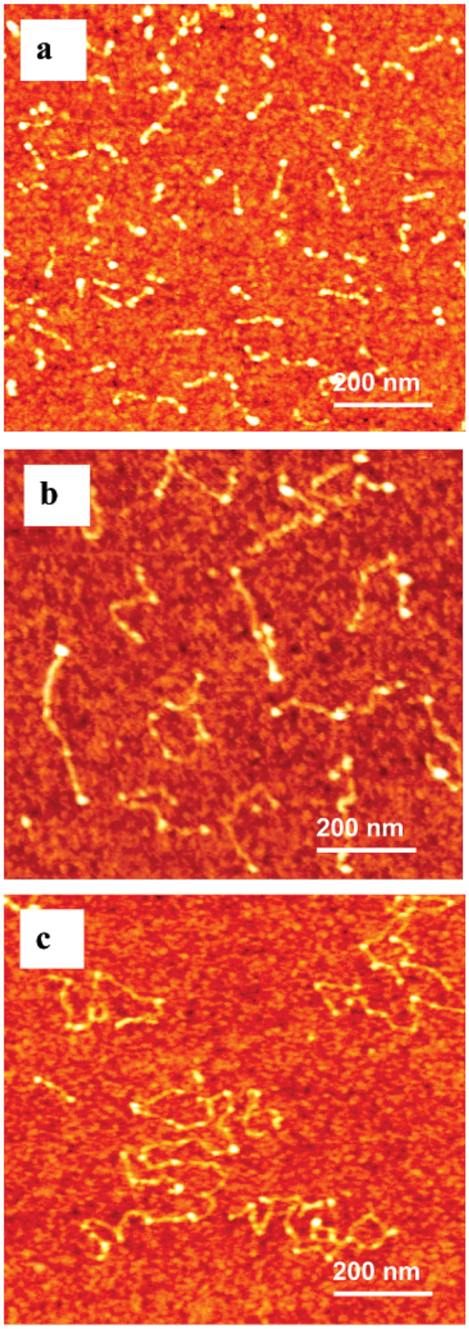

Figure 6. AFM images (1 × 1 μm^2, Z-range 5 nm) of Pd-nanowires prepared on the surface of Si-wafers from P2VP of different molecular weights: 59 (a), 385 (b), and 735 kg/mol (c).

For all P2VP samples of different molecular weights, we obtained the same average values of the height and the width of Pd clusters. The contour length of the nanowires is about 3 times smaller than the contour length of the original P2VP chains (calculated from molecular weight) for all samples. We may explain this fact by conformational changes introduced by the interaction of PE with PA. The resulting product is insoluble in water because of a decreased charge density as compared to protonated P2VP molecules. The mean square end-to-end distance of the wires is proportional to the molecular weight of P2VP (Figure 7). The size distribution of the Pd clusters is presented in Figure 8.

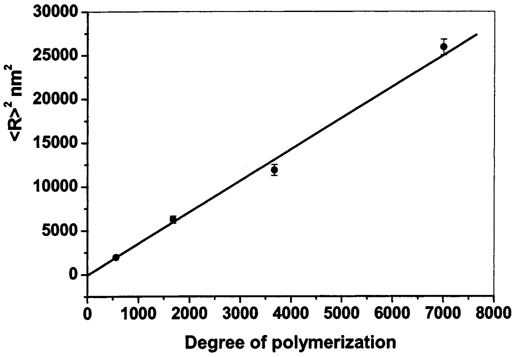

Figure 7. Mean square end-to-end distance of Pd-nanowires plotted as a function of degree of polymerization.

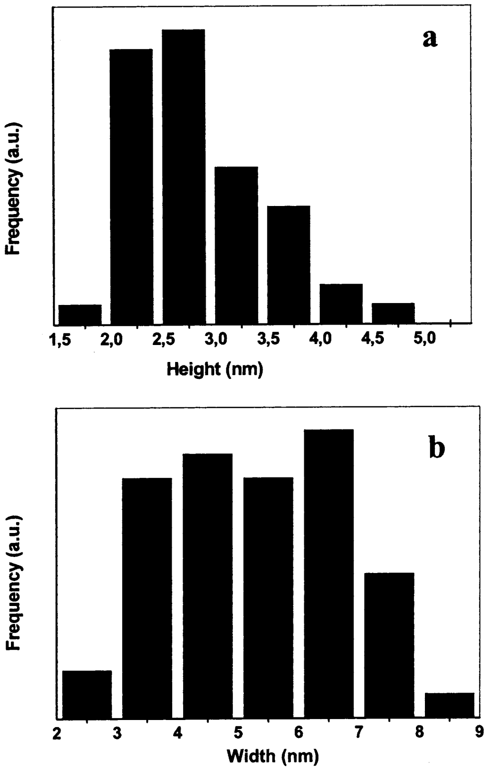

Figure 8. Size distribution of Pd clusters along the polymer chain: (a) height of clusters, (b) width of clusters.

The chemical composition of the nanowires was estimated using X-ray photoemission electron spectra. The atomic ratio between nitrogen of 2-vinylpyridine monomer units and Pd calculated from the XPS spectra was N:Pd = 4:1. We detected separately the charged and uncharged nitrogen with the ratio to be about 50:50 for both P2VP deposited molecules (pH 2) before metallization and for metallized wires. Consequently, we can perform a rough evaluation of size of the Pd clusters assuming that each charged 2-vinylpyridine monomer bonds $^1/_2$ of the Pd atoms (see step 3 in the list of chemical reactions above) and, therefore, P2VP molecules of about 400 kg/mol in average can bond about 1000 Pd atoms. The number of Pd clusters detected with AFM ranges from 10 to 20 per single structure resulting in the number of Pd atoms per cluster ranging from 50 to 100. This number of atoms corresponds to the cluster size of about 1.5−2 nm in diameter which is consistent with the cluster sizes observed in the AFM experiments.

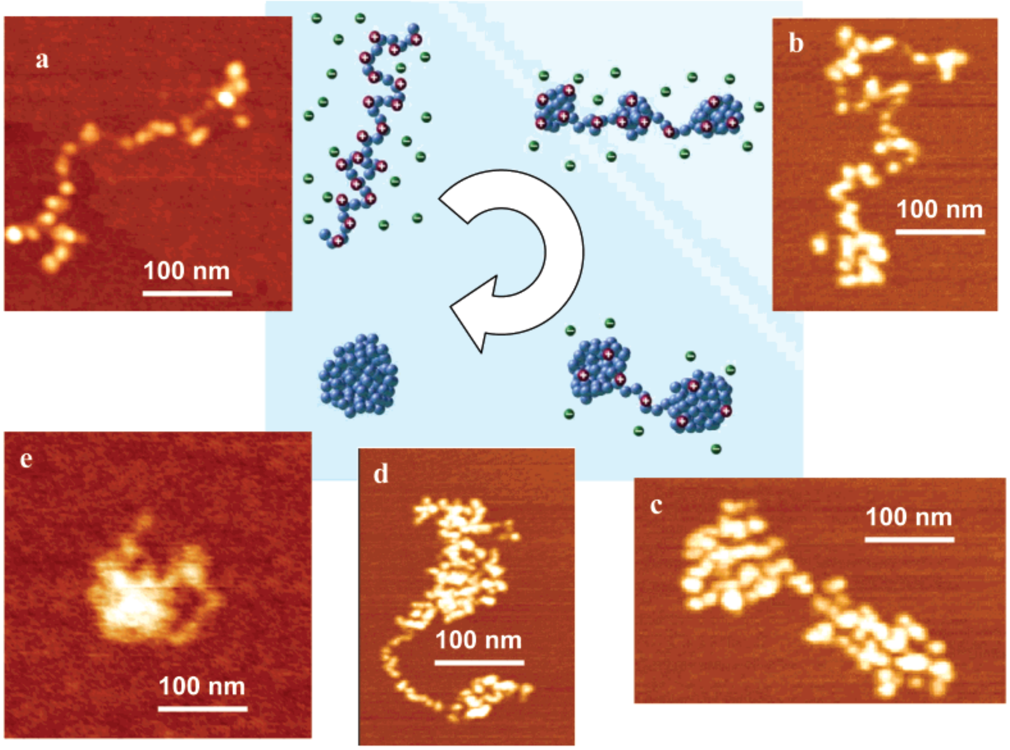

Figure 9. Metallization of P2VP molecules in different conformations. The polymer coils undergo a cascade of transitions from wormlike conformation to necklacelike and compact globule driven by the interplay between attractive short-range and repulsive long-range interactions. The arrow follows an increase of the ionic strength of solution: pH 2, salt free (a); pH 2.5, 0.02 mol/L NaCl (b); pH 3.5, 0.02 mol/L NaCl (c); pH 3.5, 0.1 mol/L NaCl (d); pH 3.5, 1.0 mol/L NaCl (e).

Similar experiments were performed with P2VP chains deposited on Si-wafers from aqueous solutions at different pH values to metallize different conformations of the PE molecules. Figure 9 summarizes these experiments. The increase of pH values and the addition of NaCl result in a decrease of positive charge density of P2VP and consequently to a cascade of coil-globule transitions from wormlike coil to necklacelike coils with a different number of beads and finally to a compact globule. All of these conformations are frozen on the substrate surface and metallized.

Conclusions

As a result, we have shown that molecular details of the adsorbed linear flexible polyelectrolyte molecules determine the dimensions of the nanostructures after metallization and that observed sizes are consistent with the decoration of single molecules with nanoclusters. Those metallized nanoparticles (cluster assembles) thus reflect the conformation of original adsorbed polyelectrolyte molecules. The dimensions of the obtained nanowires are significantly smaller than those previously reported. All of these features are of the potential benefit in applications for nanodevices and permit one to use polyelectrolyte molecules of different architectures to generate metallic nanoobjects of a desired shape. Furthermore, this approach allows for the visualization of single polyelectrolyte molecules via mineralization. The latter is of great importance for the analysis of polar and charged macromolecules. The investigation of morphological details of the nanowires and their electroconductivity is in progress.

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