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AFM Imaging of Single Polycation Molecules Contrasted with Cyanide-Bridged Compounds

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ABSTRACT: We developed the simple contrasting procedure to improve AFM visualization of single positively charged polymer chains via counterion exchange between Cl^- anions and bulky hexacyanoferrate anions or negatively charged nanoclusters of Prussian Blue. This method allowed us to increase thickness of the resulting structures up to 10 nm and, consequently, to provide visualization of isolated polymer chains deposited on a glass surface (root-mean-square roughness about 1 nm). In contrast, the contrasting with relatively large PB clusters (more than 10 nm in size) distorts conformations of the molecules and even eventually leads to a fragmentation of polymer chains.

Introduction

Atomic force microscopy (AFM) is broadly used for the characterization of polymer surfaces[1] as well as for the investigation of isolated (single) polymer molecules.[2] In contrast to conventional physical and chemical methods which provide information refereed to an ensemble of molecules, an AFM visualization of individual members provides a direct information about properties of individual members as well as on a distribution function. Most of experiments were performed with relatively "thick" macromolecules if diameter of chains was larger then 1 nm: dendronized polymers,[3] "molecular brushes",[4] and some naturally occurring polymers.[5] However, most of the synthetic polymers and many natural polymers have much thinner chains.[6] Recently, we succeeded to visualize several synthetic polycations (PC) and block copolymers of different architectures with AFM operating in the tapping mode (TM).[7] These polymers were deposited onto an atomically flat mica surface (root-mean-square roughness, rms, less than 0.05 nm). However, they were very poorly recognized on Si wafers due to the larger roughness of the substrate surface (rms = 0.2 nm). Several methods to improve detection of polymer chains via chemical modification of a tip[8] or by applying special AFM modes[9] have been proposed. Nevertheless, the development of new approaches for the investigations of isolated chains with molecular resolution on rough surfaces is still a challenging task.

We suggest that a selective deposition of appropriate materials along PC molecules (such as bulky counterions or nanoclusters) could be a very promising method to increase the thickness of the PC chains and thus to increase contrast even on rough surfaces. Such a staining strategy is schematically represented in Figure 1. For a successful visualization the grain size of the contrasting agent should be larger than the mean size of surface features.

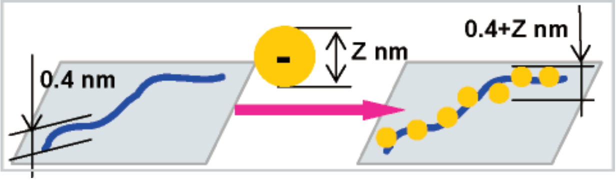

Figure 1. Schematic representation of the contrasting of adsorbed PC: 0.4 nm thick polymer chain becomes AFM visible onto the rough surface due to the deposition of bulky HCF anions or nanoclusters with the grain size of *Z* nm.

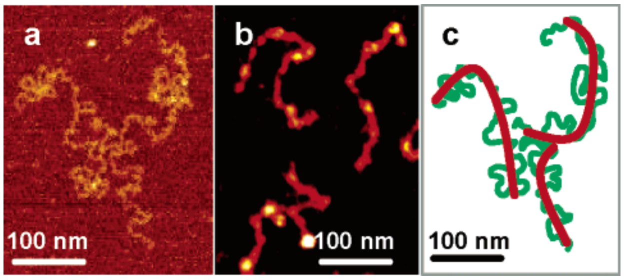

Figure 2. AFM topography images of poly(2-vinylpyridine) (P2VP) molecules (a) and P2VP chains decorated with Pd clusters (b). Schematic representation of a possible change of conformation of P2VP molecules affected by the deposition of Pd clusters (c).

Recently, we have described an approach to produce wire-shaped Pd nanoparticles via metallization of flexible synthetic PC.[10] The metallized molecules are nicely resolved on the Si wafer with the TM AFM, and the location of the Pd clusters clearly reflects the contours of the underlying PC chains (Figure 2). The length of the structures is linearly proportional to the molecular weight of the polymer.[10] Nevertheless, the interaction of PC molecules with bivalent $PdCl_4^{2-}$ anions causes a strong contraction of polymer chains even if the chains are trapped by the surface. The observed worm-shaped metallized PC molecules can be considered as structures reflecting the substantially alternated PC conformations due to the formation of the PC−Pd molecular composite (Figure 2c).

Thus, an improvement of the staining procedure would be very important for the further development

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of AFM single polymer molecule experimental methods. The list of the characteristics to be improved for the staining method is as follows: (a) high density of deposited contrasting clusters along the polymer chain; (b) high selectivity of the staining material deposition; (c) persistence of the polymer conformation in the staining procedure (upon reaction with the contrasting agents); (d) reversible binding of the contrasting substances (a possibility to remove the staining material with no distortion of the polymer chain conformation). In our recent communication,[11] we reported on a chemical approach to improve the AFM contrast for imaging of individual PC molecules which matches this list of requirements. Specifically, we found that bulky hexacyanoferrate (HCF) anions can be selectively deposited along PC chains without a distortion of the polymer chain conformations. Afterward, the HCF anions could be easily removed. This paper is an extended report on the study. We report on the synthesis of water-soluble Prussian Blue nanoclusters and conditions to selectively deposit them along PC molecules. We present the direct experimental evidence that the deposition of HCF anions as well as small PB clusters (mean diameter up to 5 nm) introduces virtually no changes into the morphology of adsorbed PC chains, whereas the deposition of the larger PB clusters (diameter more than 10 nm) strongly affects the chain conformation. For the first time, we demonstrate that the isolated PC molecules can be successfully contrasted and imaged on the surface of microscope glass slides (rms about 1 nm).

Experimental Section

Materials. Samples of poly(methacryloyloxyethyl dimethylbenzylammonium chloride) (PMB) (M_w = 6130 kg/mol, polydispersity index (PDI) = 1.6) were obtained from Dr. Werner Jaeger (Fraunhofer-Institut für Angewandte Polymerforschung, Golm, Germany). The synthesis is described elsewhere.[12] Poly(2-vinylpyridine) (P2VP)[2b] of molecular weight 385 kg/mol was purchased from Polymer Sources Inc. (synthesized by anionic polymerization, PDI of about 1.1).

Substrates. In this study we used the following substrates: the freshly cleaved mica, the Si wafers (obtained from Wacker-Chemitronics), the Si wafers with the deposited (using lithography) gold stripes (electrodes), or the microscope glass slides (Menzel-Glaser, Nr. 01 1101). Before experiments the substrates were first cleaned in an ultrasonic bath initially three times for 5 min with dichloromethane (DCM) and then in the cleaning solution prepared from NH_4OH and H_2O_2 at 60 °C for 1 h. (*Note: the 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).

Samples Preparation. PMB or P2VP was deposited onto a substrate from the 0.0005 g/L acid water (pH 2, HCl, Aldrich) solutions by dipping of the substrates into the solution (or by drop-casting). To deposit a PC chain in the stretched conformation, we used a spin-coater rotating at 10 000 rpm. The dry samples were investigated with AFM.

Contrasting with Pd Clusters. The substrate with deposited PC was then dipped into Na_2PdCl_4 solution (0.005 g/L) in acidic (HCl, pH 2.0) water for 1 min at ambient temperature and afterward rinsed in water. In the final step Pd(+2) was reduced by treatment with a 1.0 mg/mL aqueous solution of dimethylamine borane (DMB, Aldrich). Finally, the substrate was cleaned with water and dried with argon.[10]

Contrasting with HCF Anions. The substrate with deposited PC was dipped into either $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ (Aldrich) solution (5 g/L) in acidic (HCl, pH 2.0) water for 3 min at ambient temperature and afterward rinsed in water. Finally, the substrate was dried with argon.

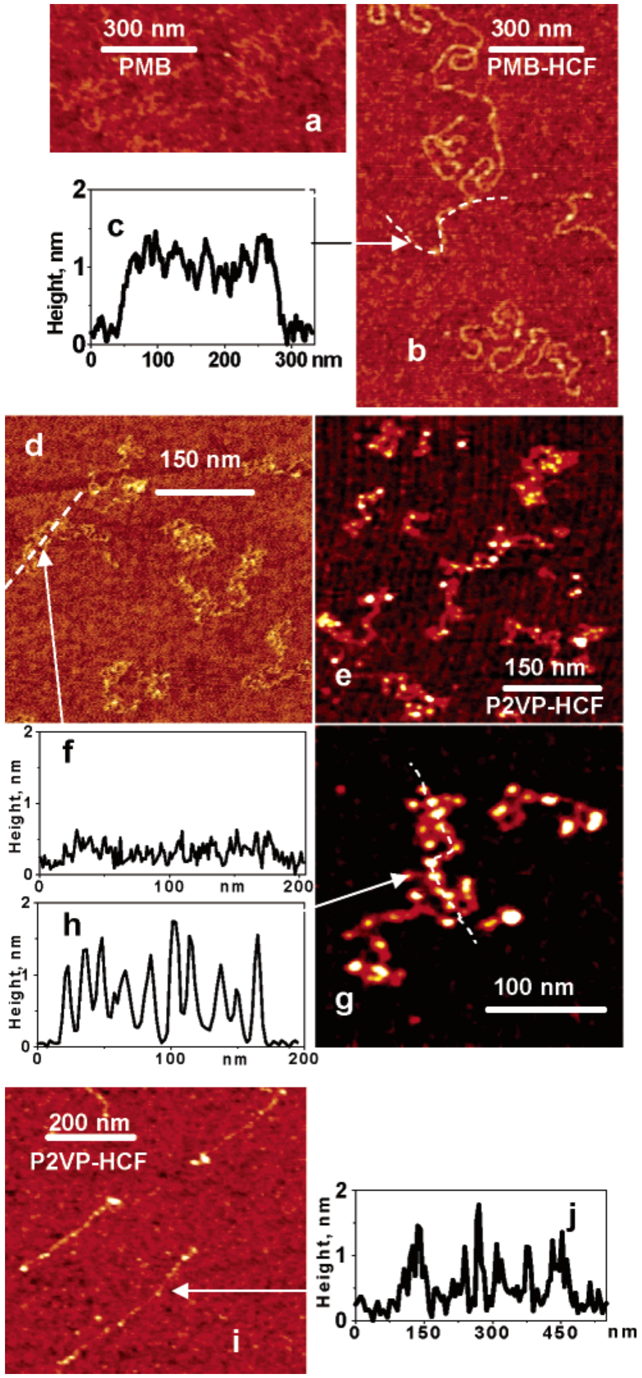

Figure 3. AFM topography images (Z range 5 nm) and a cross sections of PC molecules (bare and contrasted with HCF). PMB molecules adsorbed on the Si wafer before (a) and after (b) contrasting with HCF; the cross sections are made along the chain axis marked by the arrow (c). P2VP molecules adsorbed on mica before (d) and after (e, g) contrasting with HCF and the cross section (f, h). P2VP molecules deposited onto the Si wafer and contrasted with HCF (i) (cross sections (j)).

Contrasting with PB Clusters. To prepare a dispersion of Prussian Blue nanoclusters, a solution of $K_4Fe(CN)_6 \cdot 3H_2O$ (0.5 g/L, 1.18 mmol/L) in acid water (HCl, pH 2.0) and an equal volume of $FeCl_3$ solution in acid water (HCl, pH 2.0) were intensively mixed together for several minutes. We used three different concentrations of $FeCl_3$—0.024 g/L (0.148 mmol/L), 0.048 g/L (0.296 mmol/L), and 0.127 g/L (0.79 mmol/L)—for the preparation of three samples PB1, PB2, and PB3, respectively. The substrate with deposited PC was then dipped into the freshly prepared dispersion of PB clusters for 3 min at ambient temperature and afterward rinsed in water. Finally, the substrate was dried with argon.

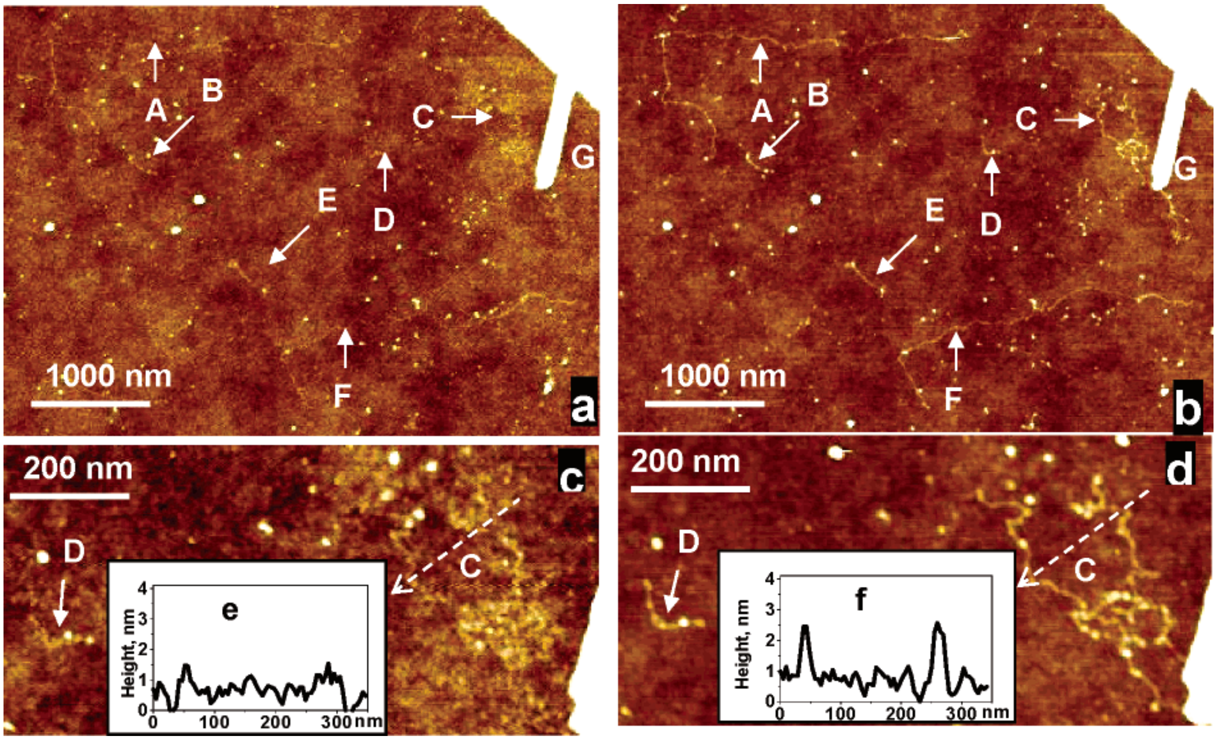

Figure 4. AFM topography images of the PMB molecule deposited on the lithographycally labeled (on the top right corner) Si wafer (rms = 0.6 ± 0.4 nm) before (a, c), and after (b, d) contrasting with HCF (*Z* range 5 nm). The cross sections (e, f) made on the same place of the Si wafer before and after the contrasting reflect the 1 nm increase of the height of PMB molecules. Letters A–F mark several different PMB molecules found on the surface.

AFM Measurements. A Multimode AFM instrument and a NanoScope IV-D3100 (Digital Instruments, Santa Barbara, CA) were operating in the tapping mode. Silicon tips with radius of 10–20 nm, spring constant of 30 N/m, and 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 (decreased) by the tip radius.[13]

UV–vis Measurements. The spectroscopic measurements were carried out using a Perkin-Elmer UV/vis spectrometer Lambda 19.

Result and Discussion

Deposition of Hexacyanoferrate(II) Anions. We found out that negatively charged HCF anions strongly bind to the positively charged PC. A relatively big size of the HCF anion guarantees an efficient improvement of the AFM contrast as schematically shown in Figure 1. AFM images of PMB and P2VP molecules adsorbed onto the Si wafer and then stained with HCF acid solution (pH 2, HCl) are shown in Figure 3.

In all cases we observe an increase of the height of the resulting structures of approximately 0.6–0.7 nm, which is consistent with the dimensions of the HCF anion. To demonstrate that the shape of molecules decorated with HCF reflected the conformation of the adsorbed PC is not changed by the staining procedure, we used two different methods for deposition of P2VP molecules onto the substrate. In the first method, we deposited the protonated P2VP chains in an extended coil conformation onto the mica and the Si wafer by drop-casting. In the second method, P2VP molecules were aligned in stretched conformations using spin-coating at 10 000 rpm. AFM images of PMB molecules (Figure 3) clearly show differences in structures prepared by these two methods. Comparing images a and d with b and e, respectively, demonstrates improvement of the contrast for the molecules deposited by both methods in coiled (Figure 3a–e) and stretched (Figure 3i) conformations. The cross section of the structures as deposited (Figure 3f) and stained (Figure 3c,h,j) explains that the contrast improvement is due to the increase of height of PC molecules decorated with HCF anions.

We performed a special experiment to precisely monitor the effect of the staining on conformations of deposited PC onto the lithography-labeled Si wafer by scanning always the one place and visualizing the one molecule before and after the contrasting. As a representative example, Figure 4 shows images of several PMB molecules taken before and after the staining with HCF anions. Although “as-deposited” PMB molecules are poorly resolved on AFM images (Figure 4a,c), they are clearly observed after the contrasting with $K_4Fe(CN)_6$ (Figure 4b,d). Long molecules (A and F) and short chains (B, D, and E) adapt stretched conformations, and their contour length can be easily measured: $L_A = 3339$ nm, $L_B = 275$ nm, $L_D = 247$ nm, $L_E = 376$ nm, and $L_F = 2727$ nm. The contour length of several molecules (marked “C” in Figure 4) cannot be measured due to the coiled conformation. Careful analysis of the AFM data clearly indicates that the staining results in an increase of the chain thickness from a few tens of nanometers to 1.5 nm (compare parts e and f of Figure 4) upon treatment with $K_4Fe(CN)_6$ occurs virtually without remarkable changes of locations of the molecules, contour length, and visible fine details of the conformations.

Thus, we showed that the deposition of HCF anion (the diameter about 0.7 nm) improved the visualization of PC deposited onto the surfaces with the rms less than 0.5 nm.

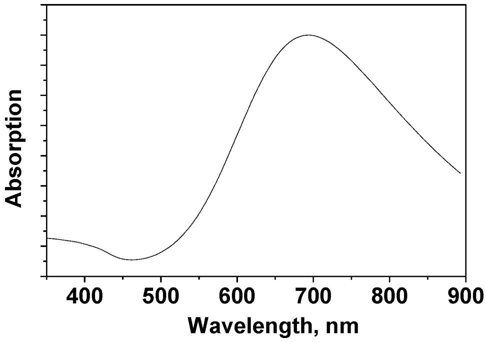

Figure 5. UV−vis spectra of Prussian Blue dispersion (prepared at molar ratio $K_4Fe(CN)_6/FeCl_3$ = 4:1, PB2).

Deposition of Prussian Blue Nanoclusters. It is well-known the mixing of stoichoimetric amounts of $K_4Fe(CN)_6$ and $FeCl_3$ leads to synthesis of microscopic particles of $Fe_4[Fe(CN)_6]_3$ (PB) which precipitates from the solution.[15] Several methods to fabricate well-defined surfactant- or polymer-protected PB nanoclusters have been recently reported.[16] Here we described a simple method to produce surfactant-free water-soluble negatively charged PB nanoclusters stabilized by excess of HCF anions. Specifically, we found out that mixing of diluted solution of $FeCl_3$ with an excess of $K_4Fe(CN)_6$ solution in acid conditions (pH 2) leads to clear deep-blue dispersions stable for several months. The characteristic blue color and the broad signal in the UV−vis spectra at λ_{max} = 695 nm are consistent with the intermetal charge transfer from Fe^{2+} to Fe^{3+} band, and it gives evidence for the formation of PB (Figure 5).[18]

We prepared and studied a range of PB dispersions at different mixing ratios and stirring time. To characterize the PB clusters, we set a drop of the suspension onto the Si wafer with the preadsorbed PMB molecules and washed out excess of the unattached material. PB clusters selectively bind to the PC deposited onto the Si wafer. In the reference experiment we found no adsorption of PB clusters onto bare substrates (without preadsorbed PC molecules) neither at neutral pH nor in acid conditions (as confirmed by AFM and ellipsometry).

Figure 6 shows typical AFM images of PMB−PB nanoparticles with the beads-on-string morphology obtained upon deposition of PB clusters onto the spin-stretched PMB molecules. We made cross sections of all clusters observed on images and defined their height. We collected, at least, three images for each dispersion and analyzed, at least, 150 structures for each sample of different dispersions. Finally, we performed a statistical analysis of the data.

We assume (postulate) a near spherical geometry of PB clusters, and hence, their height is taken as diameter of the spherical clusters. It should be noted that lateral dimensions of the clusters extracted from cross sections of AFM images are overestimated due to the well-known tip-broadening effect. Therefore, only height of the clusters was analyzed. As seen in Figure 6i,j, all PB clusters have relatively narrow distribution on sizes (PDI = 1.15). We found that stabilization of the size of the PB clusters was approached in 10 min for the mixture of $K_4Fe(CN)_6$ and $FeCl_3$ solutions at molar ratio 8:1. The diameter of PB particles was 3.7 nm (PB1, Figure 6a−d), whereas mixing at molar ratio 4:1 leads to the PB2 clusters with the diameter of about 4.8 nm (Figure 6e−h). Obviously, the stability of the PB clusters is due to negative charges provided by the excess of HCF anions located on the clusters surface. That explains

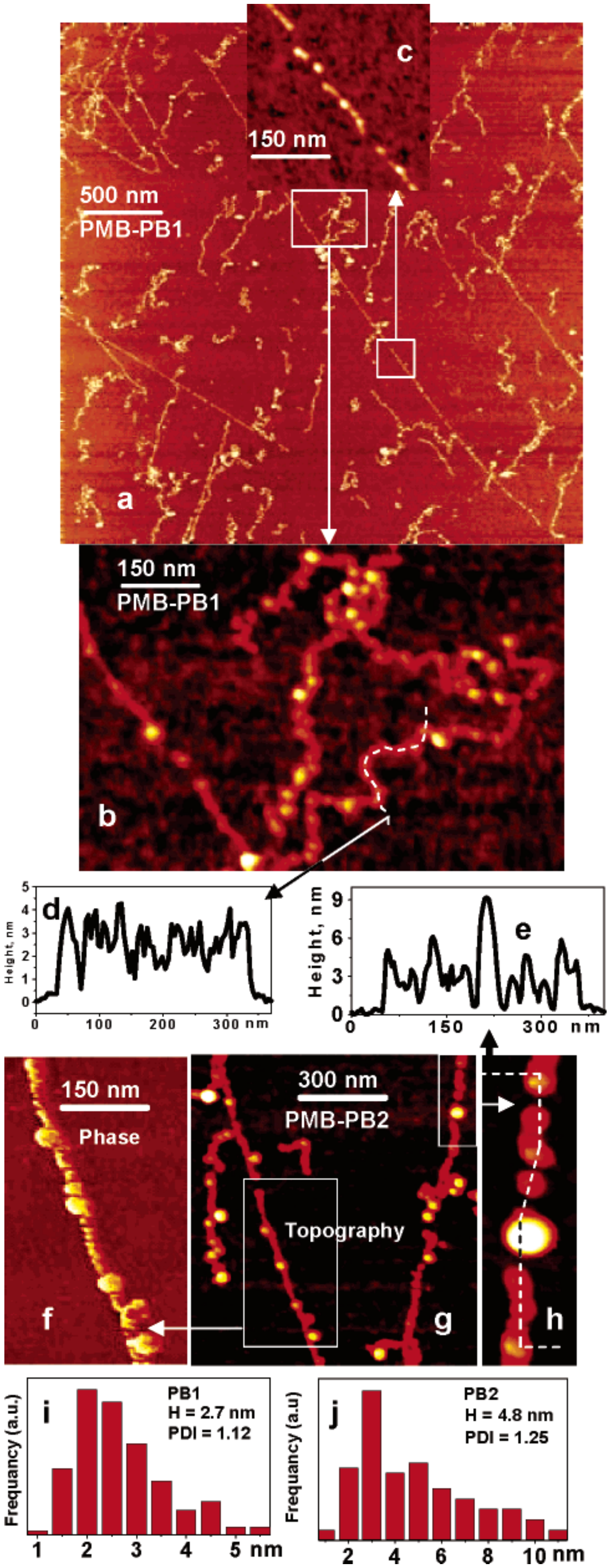

Figure 6. AFM topography (a−c, g, h) (*Z* range 10 nm) and phase (f) images of the PMB molecules deposited onto the Si wafer by spin-coating and then contrasted with PB nanoparticles (prepared at molar ratio ($K_4Fe(CN)_6/FeCl_3$ = 8:1 (PB1) for images (a−c) and 4:1 (PB2) for images (f−h). The dash line in (c, h) indicates the locus of the cross sections (d and e, respectively). Histograms (i, j) present the size distribution for the PB clusters.

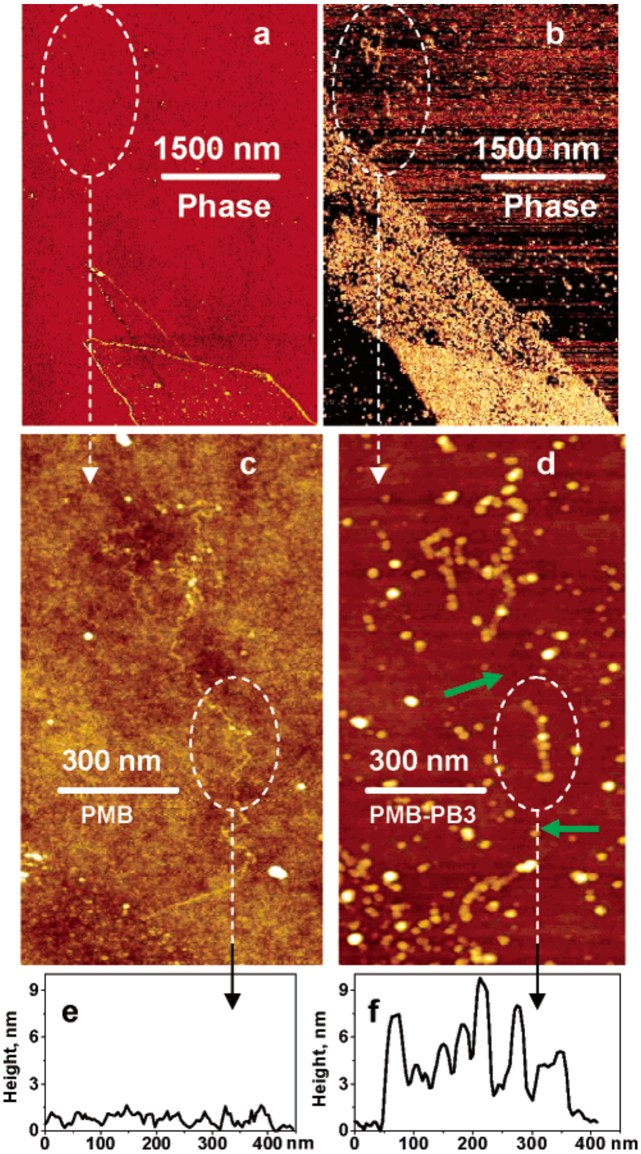

Figure 7. AFM phase (a, b) and topography (c, d) images (*Z* range 20 nm) of the PMB molecules deposited onto the Si wafer before (a, c) and after (b, d) contrasting with PB clusters (prepared at molar ratio $K_4Fe(CN)_6/FeCl_3 = 3:1$). Cross sections (e, f) are made on the same place of the Si wafer before and after the contrasting.

why PB clusters of a smaller diameter are formed from solutions with a higher $K_4Fe(CN)_6$ concentration.

The PB clusters bind PC selectively and homogeneously along PC chains. This modification significantly improves both the topography (Figure 6a–c,g,h) and the phase contrast in AFM images (Figure 6f). The distance between adjacent clusters depends on the diameter of PB clusters, and it is in the range from 10 to 20 nm. The high binding density of the PB clusters is sufficient for the visualization of molecular details of PC conformations on rough surfaces. In the experiments we found that the number of particles per units length (particle density) was unchanged at the concentration range of PB from 0.5 to 5 g/L. Also, we observed no substantial effect of ionic strength on the particle density in the range of NaCl concentrations from 0.01 to 1 M. This poor effect of ionic strength may be at least partially explained by the fact that the last step of the sample preparation includes rinsing the sample with deionized water where all residual salt is removed. Thus, the last step is always independent of ionic strength.

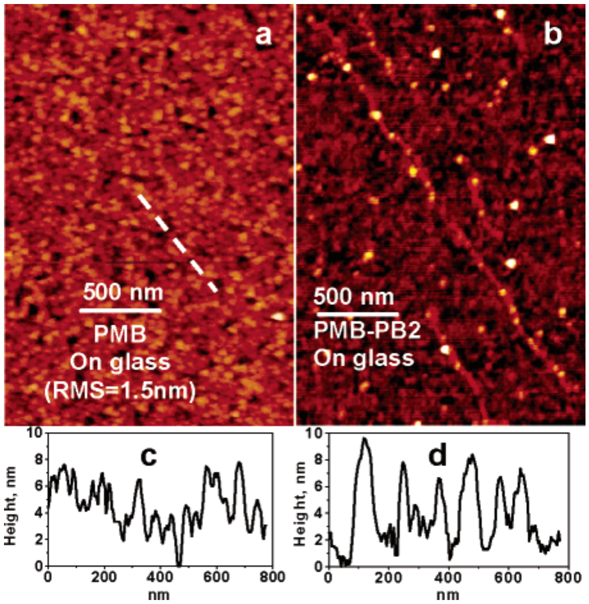

Figure 8. AFM topography images (*Z* range 15 nm) and cross sections (c, d) of the PMB molecules deposited onto the microscope glass slide before (a, c) and after (b, d) the contrasting with PB2 clusters (prepared at molar ratio ($K_4Fe(CN)_6/FeCl_3 = 4:1$).

We again address the question of whether the deposition of the PB nanoclusters can alternate conformations of the PC molecules. Figure 6 presents the PMB molecules deposited on the Si wafer by spin-coating and then stained with PB1 clusters ($D = 3.7$ nm). As seen from the zoom image (Figure 6c, inset), some of stretched PMB chains contain 10–30 nm gaps. It is important that these gaps remain unchanged even upon repeating the staining procedure. These gaps may be explained by fracture of the polymer chains due to the energy released by cluster deposition.

Even larger defects were observed when PMB molecules were decorated with the larger PB clusters. Figure 7 shows PMB chains decorated with PB clusters by the treatment with $K_4Fe(CN)_6/FeCl_3$ solution (molar mixing ratio = 1.5:1, PB3). PMB molecules with attached PB clusters display considerably distorted conformations and contain large gaps (up to 200 nm, marked by arrows).

The selectivity of the binding of HCF anions and PB nanoclusters along PC molecules should be especially emphasized. The AFM images (Figures 3–6) prove that the contrasting materials preferentially bind to PC chains but not to the bare surface of the substrates.[17]

Finally, we demonstrate that the staining procedure allows for the visualization of single polymer molecules deposited onto microscope glass slides with rms about 1 nm. The contrasting of PMB molecules with PB3 clusters results in quite remarkable contrast so that PMB chains can be easily visualized (Figure 8).

In all staining experiments the substrate surfaces were negatively charged. That prevents from nonselective deposition of HCF and PB on the bare surfaces of the substrates. To show the importance of this issue, we performed a model experiment where the surface of the Si wafer was modified with ω-aminosilane molecules. In acidic aqueous solution the surface with the protonated amino groups was positively charged. For this surface we observed a homogeneous nonselective coverage of the surface with PB clusters. However, very strong negative charge of the surface results in strong electrostatic repulsion of PB. At pH 7 we found no deposition of PB on the deposited PMB chains. The results suggest that the preferential pH range depends on the interplay of the electrostatic interactions of the bulky counterions, deposited polyelectrolytes, and the charged surface.

Conclusions

We developed a simple contrasting procedure to improve AFM visualization of positively charged polymer chains deposited on substrates of relatively high roughness. The staining mechanism is based on the counterion exchange between Cl^- counteranions and bulky HCF anions or negatively charged nanoclusters of Prussian Blue. This method allowed us to increase the thickness of the resulting structures up to 10 nm and, consequently, to provide visualization of polymer chains on rough surfaces. In contrast, the deposition of the relatively large PB clusters (more than 10 nm) considerably distorts the initial polymer conformation and even leads to a fragmentation of polymer chains.

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