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THE INTERACTION OF CATIONIC POLYMERS WITH HUMAN HAIR

Andreas Pfau*, Peter Hössel, Sabine Vogt, Ralf Sander and Wolfgang Schrepp

BASF-AG, D-67056-Ludwigshafen

Abstract: We present a combination of electrochemical methods, i.e. polyelectrolyte titration and streaming potential measurement, and AFM to characterise the adsorption and desorption behaviour and the morphology of a set of polyquaternium polymers on human hair. Specific charge density and molar mass are correlated to the amount of adsorbed polymer and the ease of desorption. Results are in line with a simple model of coulombic interaction between hair and polymer and are interpreted on this basis.

1 INTRODUCTION

Cationic polymers play a key role in the surface modification of human hair by a variety of hair care products such as shampoos, foams, hair treatments and rinses. The main function of the polymers is to adsorb reversibly to the hair surface, which is negatively charged in the relevant pH range, and thereby to protect the hair and to improve its wet-combability. Still successive build-up of the polymers is not desired. Hence for the development of new products and cosmetic formulations the characterisation of the adsorption and desorption properties of these polymers on hair surfaces is crucial.

Here we present a combination of electrochemical methods, i.e. polyelectrolyte titration and streaming potential measurement [1], and AFM to characterise the interaction of cationic polymers with human hair in terms of mean, surface integrated properties (polymer loading, surface charge on the hair) and in terms of locally resolved properties respectively (polymer distribution and morphology).

With the polyelectrolyte titration we determined the adsorption behaviour of the cationic polymers given in Tab. 1. Subsequently the surface properties of hair modified by selected cationic polymers (mainly polyquaternium-16; (PQ-16)) were investigated by streaming potential determination and AFM. From these measurements the desorption behaviour of the

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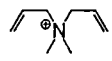
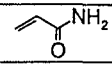
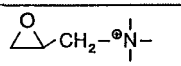
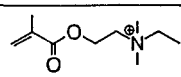
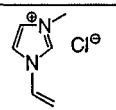
CTFA name Polyquaternium	Monomers: Cationic	Neutral
4		Hydroxyethylcellulose
6		–
7		
10		Hydroxyethylcellulose
11		
16 (four derivatives)	 Vinylimidazolium-chloride (VI)	

Tab. 1: Survey of polymers used in this study

polymers in water and surfactant solution were determined. Finally mica is discussed as an easy to handle and very reproducible model surface for AFM studies of polymer adsorption.

2 EXPERIMENTAL

2.1 Cationic Polymers

Tab. 1 gives a survey of the conditioning polymers used in this study, their CTFA names (polyquaternium) and their chemical nature. Their chemical structure varies in a wide range. Apart from the homopolymer polyquaternium-6 (PQ-6; polydiallyldimethylammonium chloride) these cationic polymers consist of a neutral and a cationic component. PQ-4 and PQ-10 are cationically modified hydroxyethyl celluloses of different composition. PQ-7 includes copolymers consisting of diallyldimethylammonium chloride and acrylamide. PQ-11 and PQ-16 are copolymers with vinylpyrrolidone as the neutral component. PQ-11 contains dimethylaminoethyl methacrylate as the cationic component, quaternized with diethyl sulphate. PQ-16 includes a total of four copolymers with quaternized vinylimidazole (VI) as the cationic monomer. Here, the different cationic activities are determined by the ratios of the monomers [2,3,4]. Because of their different chemical structure, the technical properties of these cationic polymers and their areas of application can differ considerably. In the following, some widely used conditioning polymers are subjected to our test methods.

2.2 Polyelectrolyte Titration

Charge density was determined by polyelectrolyte titration using a dual beam method [5,6,7] (photoelectric titrator, type 90, BASF). The cationic polymer is titrated against potassium polyvinyl sulphate in the presence of o-toluidine blue as an indicator. Due to a significantly higher value of the interaction constant of the polyelectrolyte complex formation, polymer dye complexes only form in the presence of excess titrant. As the indicator changes colour from blue to pink when it is complexed by the polyvinyl sulphate the endpoint of titration is determined with a special photometer with two light-emitting diodes as light sources and a photodiode as detector. The maxima of the emission spectra of the light-emitting diodes lie within the absorption band of the free indicator and the polymer indicator complex respectively. The difference between the light intensities of the two diodes after being transmitted through the solution is measured by lock-in technique and is used as the output signal.

2.3 Streaming Potential Measurements

The streaming potential measurements were performed with a Paar EKA electrokinetic analyser. The electrolyte flows through the measuring cell filled with the hair swatches (approx. 4 g) and the resulting streaming potential is measured across the electrodes (Ag/AgCl with fine holes) parallel to the flow of the electrolyte. The electrolyte is circulated in a closed loop system by a microprocessor controlled rotary-vane pump. In the experiments the streaming potential E_S and the pressure drop across the sample Δp is continuously recorded. The ζ potential, i.e. the electrostatic potential at the shear plane [8,9,10], is calculated from the slope in the E_S versus Δp plot [11] following the method of Fairbrother and Mastin [10,12], in which the hair plug is treated as a bundle of capillaries.

2.4 AFM

AFM contact mode and force mode images were recorded on a Topometrix Explorer system with commercially available silicon-nitride tips on levers with a force constant of 0,032 N/m (Park Scientific). Tapping mode pictures were taken with a Nanoscope Dimension 3000 SPM (Digital Instruments) using Si cantilevers (35 N/m, ν_0 approx. 300 kHz, Nanoprobe).

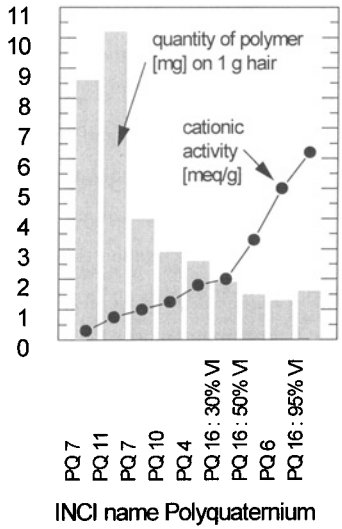


Fig. 1: Adsorption of conditioner polymers to human hair (200 mg/l initial concentration; 10 min contact time); 30%, 50% and 95% VI in the case of PQ-16 denotes the fraction of vinylimidazolium in the polymer.

3 RESULTS AND DISCUSSION

3.1 Polyelectrolyte Titration

As the charge density or ionic activity of the cationic polymers is one of the most important properties determining the adsorption behaviour, in a first step we measured the charge density of a set of polyquaternium polymers (4, 6, 7, 10, 11 and 16, see Tab. 1) by polyelectrolyte titration.

In a second step the absolute amount of polymer adsorption (mg polymer per g hair) upon a definite contact time (10 min) with the polymer solution (200 mg/l) was determined by the decrease of polymer concentration in the solution [13]. Starting concentrations lay between 0,1 and 1,0 g/l. Prior to adsorption the swatches of hair (1,0 to 2,5g) were washed with nonionic surfactant (PEG-40 hydrogenated castor oil, 2ml in 1 l deionized water), rinsed for one minute in distilled water and finally squeezed between filter papers to remove excess liquid.

As Fig. 1 shows, the amount of adsorbed polymer decreases with its charge density. Obviously the higher the specific charge of the polymer, the less is needed to compensate the negative charges on the hair surface. This interpretation is based on the notion that the interaction polymer/hair is predominantly ionic and that after the reaction time of 10 min saturation adsorption is reached.

The molar weight of the polymers shows a pronounced influence on the amount of adsorbed polymer. We found saturation adsorption of PQ-16-LM (M_w=90.000) to be 2,5 mg/g hair, whereas the PQ-16-HM (M_w=430.000) only showed 1,0 mg/g hair, which is most likely due to steric hindrance of the adsorption of the bigger molecules.

Polymer desorption however can not be determined by polyelectrolyte titration as the desorbed quantities are too small and anionic surfactants interfere with these measurements. So for the desorption experiments additional streaming potential measurements were performed.

3.2 Polymer Adsorption Detected by Streaming Potential Determination

The adsorption and desorption behaviour of a set of vinylpyrrolidone/vinylimidazolium copolymers (quaternium-16) with charge densities ranging from 6.1 meq/g down to 2.1 meq/g was studied with the streaming potential method [11] which gives - for a particular polymer - a semiquantitative parameter for the amount of polymers adsorbed at the surface of the hair.

As one would expect, the change of ζ potential upon adsorption is found to increase with charge density and molar mass of the polymer. This is deduced from the starting values of the ζ potentials in Fig. 2 which gives the evolution of the ζ potential starting from polymer treated hair (4 g hair, stirred for 15 min. in 500 ml of a solution containing 240 mg of polymer and 5 mM of pH 7 buffer) as a function of time under a continuous flow of electrolyte (5 mM of pH 7 buffer). The observed decrease in ζ potential can be correlated to polymer desorption from the hair. However desorption is slow and incomplete, as the ζ potential for untreated hair (-60 mV at pH=7) is not reached even after prolonged rinsing with water. As deduced from Fig. 2, desorption increases with decreasing charge density on the polymer which is perfectly in line with the model of coulombic interaction. The ζ potential is higher for the higher molecular weight polymer - as seen in Fig. 2 - which can be attributed to a different adsorption configuration as compared to the low molecular weight polymer.

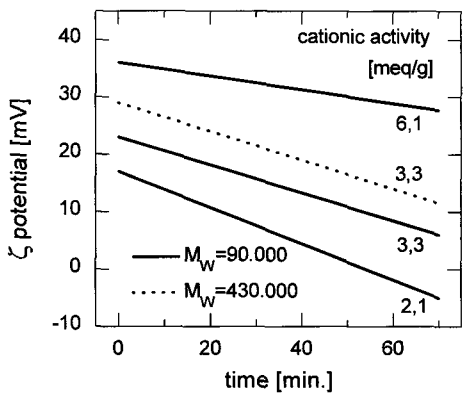


Fig. 2: Adsorption/desorption of PQ-16 polymer as monitored by the evolution of the ζ potential of polymer treated hair (4 g hair, stirred for 15 min. in 500 ml of a solution containing 240 mg of polymer and 5 mM of pH 7 buffer) in a continuous flow of electrolyte (5 mM of pH 7 buffer).

The build-up effect was studied, by repeating the above adsorption and desorption several times. For the first three cycles successive build-up was found, but after the third treatment no change in the streaming potential was observed anymore.

Upon rinsing with anionic surfactants the polyquaternium 16 Polymers could be completely desorbed from the hair. This is shown in Fig. 3. Hair treated with PQ-16 was placed in an electrolyte stream (5 mM of pH 7 buffer) for one minute and then sodium lauryl ether sulphate was added (7,2 g/l). The ζ po-

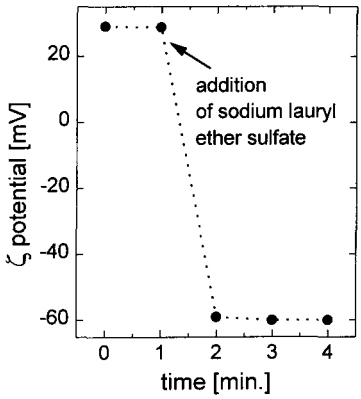


Fig. 3: Evolution of ζ potential for hair first treated with PQ-16 (50% VI, M_W=-90.000) and placed in a stream of pH=7 buffer to which sodium lauryl ether sulphate is added.

tential immeadiately drops to the value of untreated clean hair, which indicates that the polymer has been desorbed completely.

3.3 AFM Measurements

In addition to the electrochemical methods AFM was used as a tool to monitor polymer adsorption directly and with high spatial resolution on hair and mica as model system. Besides purely geometric information AFM yields material contrast either by the force spectroscopy (force mode) [18] or by recording the phase contrast in tapping mode. Hence even with the relatively irregular structure of human hair polymer patches can be clearly identified.

3.3.1 Untreated Hair

We used AFM for testing hair batches prior to their use in all experiments to exclude contamination and irregularities often encountered in natural materials. Fig. 4 a shows tapping mode AFM pictures of human hair as received and upon two cleaning steps. The hair as received does not exhibit the typical overlapping tile structure of keratin scales [18]. This structure is largely obscured by fairly structureless material sticking to the hair surface. Nevertheless most

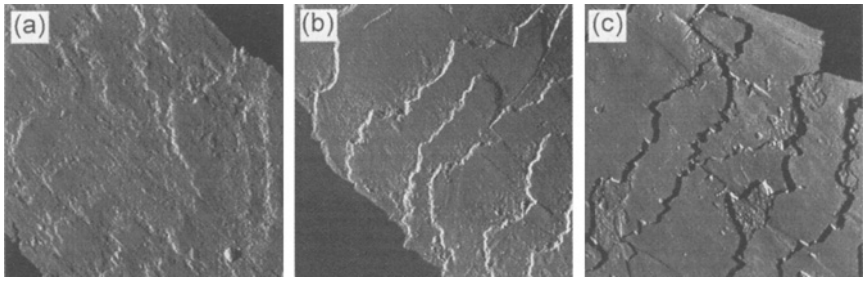


Fig. 4: Tapping mode AFM pictures (topography, 30x30 μm) of hair as received (a), upon rinsing with water (b) and upon rinsing with a surfactant solution (sodium lauryl ether sulphate) (c)

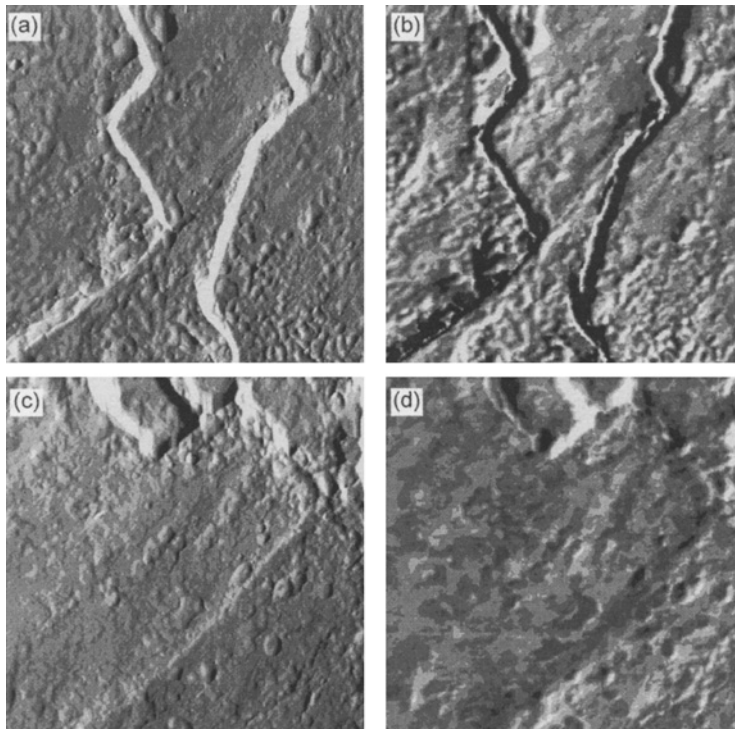


Abb. 5: (a) and (c): Topographical pictures (10x10 µm; contact mode) of hair surfaces treated with PQ-16-LM and PQ-16-HM respectively and rinsed with water
(b) and (d): corresponding force mode pictures reflecting the elasticity of the surfaces; bright areas represent the soft polymer

of it is removed by rinsing with deionized water as depicted in Fig. 4 b. Now the keratin terraces are clearly visible and only close to the steps a contamination film is still detectable. By rinsing the hair with sodium lauryl ether sulphate the clean keratin structures emerge, as shown in Fig. 4 c. Here also defects in the scale structure become visible.

In the following the cleaning corresponding to Fig. 4 c, i.e. the rinsing in sodium lauryl ether sulphate solution, was done prior to the conditioning polymer adsorption.

3.3.2 Polymer Adsorption and Desorption

Polymer adsorption and polymer desorption upon rinsing with water and an upon rinsing with 0,2% sodium lauryl ether sulphate was monitored by AFM. In the following the behaviour of

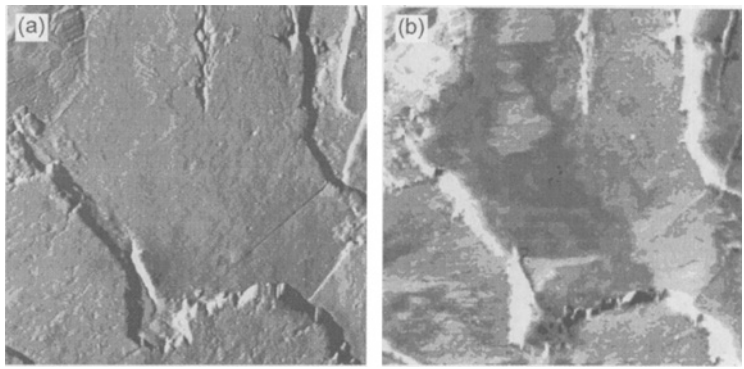


Abb. 6: (a) Topographical picture (10x10 µm; contact mode) of hair surfaces treated with PQ-16-HM and rinsed with anionic surfactant solution (1 min., 0,2% sodium lauryl ether sulphate); (b) corresponding force mode picture

two polyquaternium-16 polymers (PQ-16) of different molar mass (PQ-16-LM: M_W=90.000; PQ-16-HM: M_W=430.000) is compared.

Treatments with PQ-16 polymers, i.e. placing the hair in 3% solution for 30 min. and overnight drying, leaves the hair surface covered with thick layers of polymer that in some cases even obscure the scale structure.

Identically prepared samples of both PQ-16 polymers were rinsed with water. Fig. 5 a and c show topographical pictures recorded in contact mode, whereas b and d show corresponding

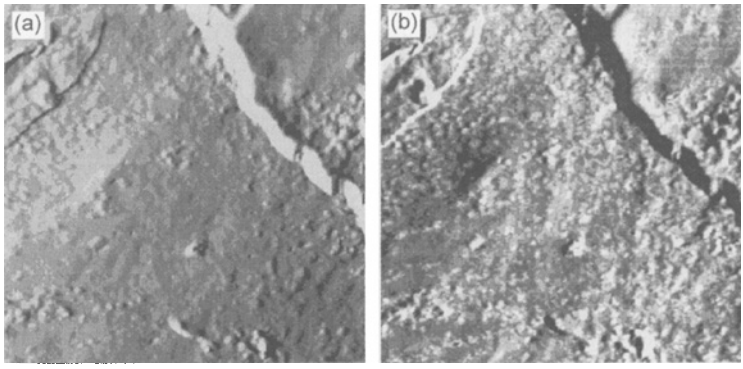


Abb. 7: (a) Topographical picture (10x10 µm; contact mode) of hair surfaces treated with PQ-16- LM and rinsed with anionic surfactant solution (1 min., 0,2% sodium lauryl ether sulphate); (b) corresponding force mode picture

force mode images. Here the topographical information does not allow a clear identification of adsorbed polymer. On the contrary in the force modulation pictures for both polymers (Fig. 5 b and c) bright areas in which only slight variations of height are detectible clearly indicate the presence of soft material, i.e. polymer, at the surface. Hence rinsing with water does not remove all polymer from the surface of the hair.

If the polymer treated hair surfaces are rinsed with anionic surfactant solution (1 min., 0,2% sodium lauryl ether sulphate) instead of pure water the situation changes for the high molar mass PQ-16-HM. As Fig. 6 shows, neither the topography (a) nor the elasticity map (b) attained by force modulation yields appreciable contrast on the keratin steps. The force modulation picture shown in (b) is practically identical to corresponding pictures of untreated hair which we used as reference. From this we conclude that by rinsing with the anionic surfactant the PQ-16-HM polymer is completely removed from the surface of the hair.

The low molecular mass polymer (PQ-16-LM) on the contrary, does not fully desorb even upon an identical treatment of rinsing with anionic surfactant. This is deduced from the bright patches or spots in the force modulation picture (Fig. 7 b) which correspond to featureless zones in the topographical image (Fig. 7 a). Only rinsing with anionic surfactant solutions of higher concentration (7,2 g/l), completely removes the PQ-16-LM from the hair surface (compare Fig. 3). This is in perfect agreement with the streaming potential measurements.

3.3.3 Mica Model Surfaces as Reference Systems

As a standard reference we adsorbed the conditioning polymers on mica. We chose mica mainly for three reasons:

1. It exposes atomically flat cleavage surfaces with extremely high reproducibility [15, 16]. So tracking polymeric structures down to the sub-nm level is feasible. In this regime data evaluation for polymers on hair becomes extremely difficult due to the intrinsic structure of the keratin scales. This is made clear in Fig. 8 which shows a linescan on a keratin terrace and one on mica both upon rinsing with water.

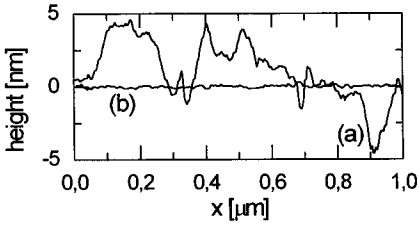


Fig. 8: Linescans on a keratin scale (a) and on a cleavage plain of muscovite mica (b) upon rinsing with water and drying. The scans were recorded in tapping mode.

2. When immersed in water a negative surface charge builds up on the mica surface

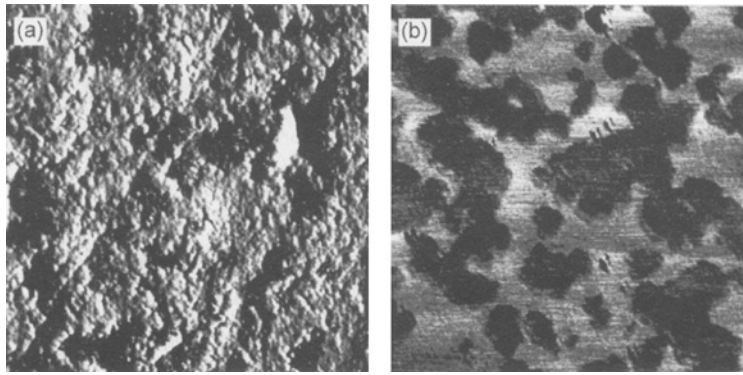


Fig. 9: Phase contrast images (1x1 μm) recorded in tapping mode of a typical conditioning polymer on (a) hair and (b) mica. The bright patches represent polymer domains. The hair and the mica were treated identically with 1% polymer/14% surfactant solution (sodium lauryl ether sulphate) and rinsed with water afterwards.

due to the partial loss of potassium ions [17]. This mimics the negative surface charge human hair shows in water due to the surplus acidic groups in the amino acids it is made up of [19]. So on both surfaces, hair and mica, coulombic binding sites for cationic polymers do exist. As the polyelectrolyte titration results imply (Fig. 1) that the polymer/hair interaction is predominantly ionic, mica should be a reasonable model for hair in the respect of polyelectrolyte adsorption, although both materials differ chemically.

3. It is easy to handle, very reproducible and cheap.

In most cases polymers adsorbed on mica show similar distributions as on human hair. Fig. 9 shows a typical conditioning polymer, adsorbed from a 1% polymer/14% surfactant solution (sodium lauryl ether sulphate) and rinsed with water, on hair (a, phase contrast) and on mica (b, phase contrast). On both surfaces the polymer resides in a patchwork of interconnected islands corresponding to the bright areas in the phase pictures. As deduced from topographical images of the polymers on mica these islands exhibit heights on the order of several angstroms (≈ 0,2 nm). This implies that this particular polymer resides mainly as trains, i.e. in a very flat configuration, on the surfaces.

Besides a purely qualitative assessment of polymer adsorption in terms of island or layer by layer growth it is desirable to quantify the amount of adsorbed polymer. With the use of mica, i.e. its flat surface, numerical treatment in terms of bearing analysis [20] becomes possible. As Fig. 10 depicts islands of conditioning polymer on mica can be quantified in terms of height

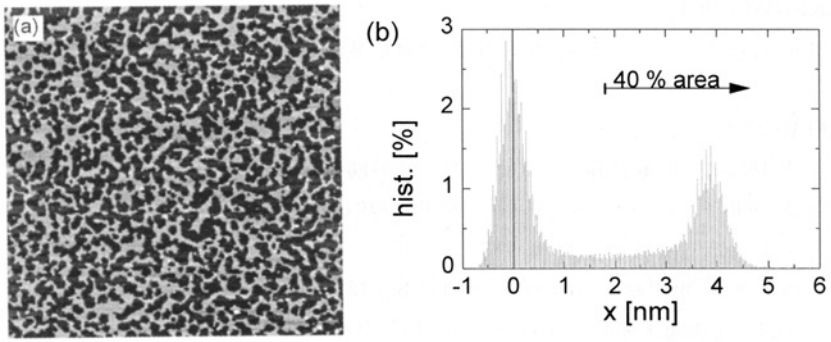


Fig. 10: 5x5 µm scan (tapping mode, topography) of a conditioning polymer adsorbed on mica (a) with a corresponding histogram for the height distribution (b). The peak around the origin corresponds to the roughness of the substrate and the noise level. The peak at 4 nm correspond to the bright islands in (a) and it corresponds to approx. 40 % of the surface.

or height distributions and covered area. Here in this particular case 40 % of the surface are covered by polymer patches with the height of approx. 4 nm.

4 CONCLUSION

The combination of electrochemical methods, i.e. polyelectrolyte titration and streaming potential measurement, and AFM is apt to characterise the adsorption and desorption behaviour of conditioning polymers on human hair. With polyelectrolyte titration we show that the amount of adsorbed polymer decreases with increasing charge density which can be rationalised on the basis that the higher the specific charge of the polymer, the less is needed to fully compensate the negative charges on the hair surface. On the other hand the adsorbed amount of polymer decreases with increasing molar mass, as adsorption is hindered by steric effects. In addition polymer adsorption on hair was directly monitored by AFM using its spectroscopic modes, i.e. force mode or phase detection in tapping mode.

By streaming potential measurements and AFM we showed that polymer desorption from hair depends on specific charge density and also on molar mass of the polymer. The cationic polymers PQ-16 could be desorbed from the hair completely by means of anionic surfactants.

As a standard reference we also adsorbed the polymers on mica. In all cases the surface structures of the polymers adsorbed on hair closely resembled the structures observed on mica, so that these systems can be used as easy to handle model systems for AFM investigations.

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