

Distributions of Functional Groups in Plasma Polymerized Allylamine Films by Scanning Force Microscopy Using Functionalized Probe Tips

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Thin films of poly(allylamine) on silicon were prepared by polymerization of allylamine in a pulsed glow-discharge plasma reactor. The films were characterized by surface plasmon spectroscopy (SPS) and waveguide mode spectroscopy (WaMS), as well as by X-ray photoelectron spectroscopy (XPS) and FT-IR spectroscopy. It was shown that by variation of the duty cycle the film thickness as well as the content of amino and nitrile groups could be controlled. Scanning force microscopy (SFM) measurements with chemically functionalized tips led to a qualitative correlation of adhesion forces with the content of amino groups. Laterally resolved adhesion force measurements indicated the presence of a heterogeneous local environment of the amino groups, with patches exhibiting differences in hydrophobicity on a sub-50-nm scale.

Introduction

Plasma treatments are versatile methods to modify and functionalize polymer surfaces.¹ In addition to a broad range of surface characteristics which can be obtained by introducing different functional groups (by changing the type of monomer hydrophilic and hydrophobic surfaces can be achieved),^{2,3} deposition of polymers,⁴ immobilization of, e.g., surfactant molecules,⁵ or etching of the specimen surface⁶ can be utilized to tailor surface properties by this technique. The formation of polymer films by plasma deposition is a very attractive approach to obtain thin coatings prepared in a “clean” process. Precursor molecules, which are often introduced into a low-pressure glow discharge chamber using a carrier gas, are activated in the plasma. Activation refers to dissociation and radical formation. Polymeri-

zation reactions initiated by these radicals can lead to reactions with monomers and monomer fragments present in the chamber. The reactions take place in the plasma, as well as at the surface of the substrate. If suitable monomers and reaction conditions are chosen, a more or less cross-linked film can be deposited. Plasma polymerized films have been reported to show interesting properties, such as improved adhesion⁷ or improved blood compatibility.⁸

In biomedical applications for instance, the homogeneous distribution of functional groups in, e.g., plasma modified or plasma polymerized materials is desirable to obtain biocompatible polymeric coatings.⁹ In this paper, a surface study of poly(allylamine) films, prepared by polymerization of allylamine^{1,10} in a pulsed plasma,¹¹ is described. Due to the high density of amino functionalities, thin films of poly(allylamine) are potential candidates as substrates for studies involving the growth of cells on surfaces. The film composition and structure can be successfully analyzed by a combination of spectroscopic techniques. These techniques, including FT-IR, surface plasmon spectroscopy, and waveguide

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(11) Radio frequency (13.56 MHz).

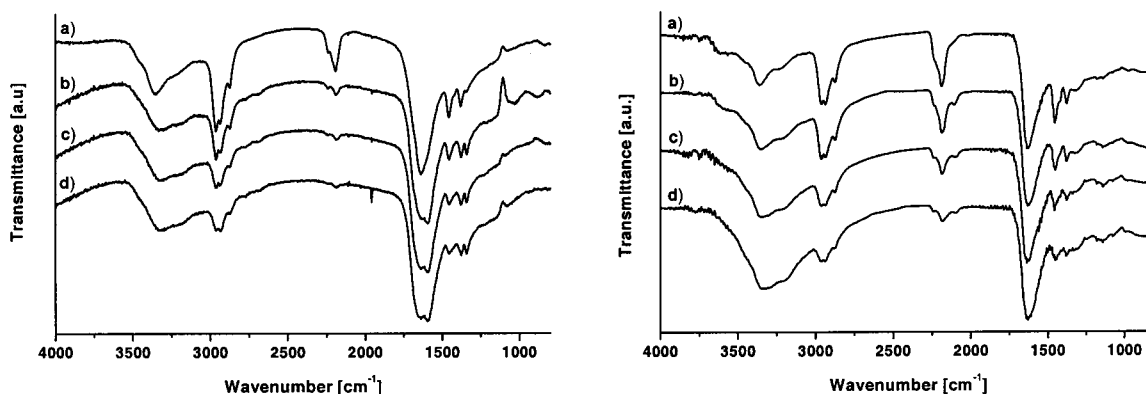


Figure 1. Transmission FT-IR spectra for plasma polymerized allylamine films as a function of the duty cycle. The films were deposited at a peak power of 50 W (left) and 200 W (right). The plasma on time was kept constant at 10 ms, while the plasma off time was varied from (a) 0 ms (CW), (b) 40 ms, (c) 90 ms to (d) 240 ms.

mode spectroscopy, allow one to identify and analyze the functional groups present in the polymer films and to determine the thickness of the films. Furthermore, scanning force microscopy (SFM) with chemically functionalized tips^{12,13} was utilized in order to study the spatial distribution of functional groups and characterize their local environment in pH-dependent pull-off force measurements on a sub-50-nm level.

Experimental Section

Materials. Details on the preparation, characterization, and swelling behavior of the allylamine films can be found in refs 10 and 14. The films for the SFM studies were extracted in cold ethanol for 24 h.

Scanning Force Microscopy and Tip Modification. Triangular shaped silicon nitride cantilevers with silicon nitride tips (Digital Instruments (DI), Santa Barbara, CA), which were coated with 2 nm of Ti and 75 nm of Au in high vacuum (Balzers), were functionalized with 11-mercaptopundecanoic acid (–COOH) or 11-hydroxyundecanol (–OH) following the procedures described previously.¹⁵ The force–distance data were acquired by using a NanoScope III multimode SFM (DI). Measurements were performed with 11-mercaptopundecanoic acid modified tips in ethanol (p.a., Merck) or 11-hydroxyundecanol modified tips in buffered aqueous solutions of constant ionic strength utilizing a liquid cell (DI).¹⁶ The force–distance curves were obtained on at least 10 different positions of each sample, and the pull-off forces of the corresponding single events were plotted in a histogram. The values of at least two independent

Table 1. Process Parameters^a and Thickness Data²⁹ of Plasma Polymerized Allylamine Films Studied

film	duty cycle, ms/ms	equiv power, W	deposition time, min	film thickness, nm
1	CW	50	30	1180
2	10/40	10	30	160
3	10/90	5	30	60
4	10/240	2	30	24

^a Pressure, 0.20 mbar; gas flow, 8 sccm; peak power, 50 W.

tip–sample combinations were averaged. For laterally resolved pull-off force measurements the force microscope was operated in the force volume (FV, DI) mode. Only identical images acquired in subsequent up and down scans were considered.

Results and Discussion

Allylamine was polymerized in a pulsed glow-discharge plasma reactor as described previously.^{10,14} The films were characterized by SPS and WaMS, as well as by XPS and FT-IR spectroscopy. The duty cycle¹⁷ employed during the pulsed plasma experiments has an effect both on the film thickness and on the content of amino groups. In Table 1 the corresponding thickness data are shown.

As is evident from the transmission FT-IR spectra shown in Figure 1, the carbon-to-nitrogen ratio decreases with increasing off times. The broad absorbance for the amino groups (ca. 3200–3500 cm^{−1}) increases with increasing off times, while simultaneously the aliphatic C–H stretching vibrations (ca. 2800–2900 cm^{−1}) and the typical nitrile band at ca. 2200 cm^{−1} are drastically reduced in absorbance.

The nitrogen/carbon ratio as measured in XPS experiments rises steadily from 0.22 for films prepared at continuous wave to 0.32 for low duty cycles. The latter value is almost identical to the N/C ratio of the monomer (0.33). Thus, the films can be expected to present significant numbers of hydrophilic amino groups at the surface in addition to hydrocarbon segments.

The interfacial properties, i.e., the exposed amino groups, were characterized by SFM force–distance measurements using carboxylic acid functionalized SFM tips in ethanol.¹⁸ The pull-off forces measured between

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(16) The data presented here was acquired at an ionic strength of 1.87×10^{-3} . Phosphate and acetate buffers were used. It should be noted that the force titration curves and the corresponding inflection points were found to be independent of the ionic strength (in the range (2×10^{-4}) – (2×10^{-4})).

(17) The duty cycle is defined as the ratio [plasma on time/(on time + off time)].

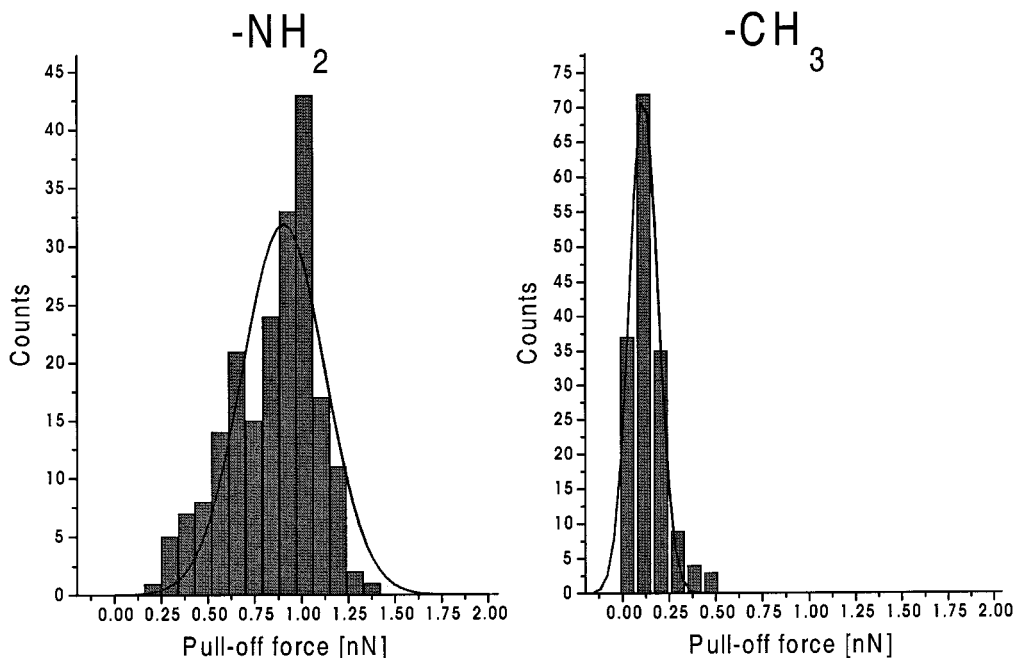


Figure 2. Histograms of pull-off forces measured with a $-\text{COOH}$ tip on $-\text{NH}_2$ (left) and $-\text{CH}_3$ terminated SAMs (right) in ethanol (curves: Gaussian fits).³⁰ The average pull-off forces are 0.90 ± 0.22 nN ($-\text{NH}_2$) and 0.12 ± 0.08 nN ($-\text{CH}_3$).

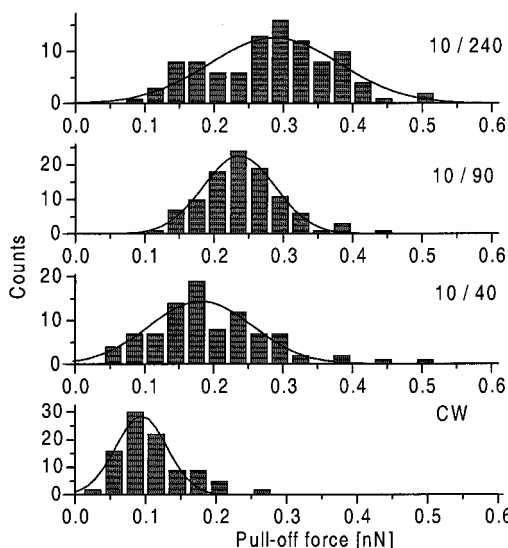


Figure 3. Pull-off force distributions measured with a $-\text{COOH}$ tip in ethanol on allylamine films polymerized with a peak power of 50 W at different duty cycles (ms/ms) (curves: Gaussian fits).

amino groups and carboxylic acid groups in highly ordered model systems (self-assembled monolayers (SAMs) of amino-terminated disulfides)¹⁹ were shown to be much stronger than the interaction between methylene groups and carboxylic acid groups (Figure 2). This qualitative trend can be understood considering dipolar interactions and the strong hydrogen-bonding between carboxylic acid and amino groups.²⁰

The average pull-off forces for the poly(allylamine) films described above were estimated from the corresponding pull-off force distributions (Figure 3). The

(18) The films with the following deposition parameters were investigated: $P_{\text{peak}} = 175$ W; duty cycle = 10 ms/10 ms, 10 ms/40 ms, 10 ms/90 ms. The roughness R_A of these films was 1.0 ± 0.2 nm as determined by tapping mode AFM.

(19) Wolf, H. Diploma thesis, University of Mainz, Germany, 1991.

average data are summarized in Figure 4 as a function of the plasma off time. The trend of increasing average pull-off forces with increasing off times, and its correlation with the increasing N/C ratios as seen in FT-IR and XPS (vide supra) are evident.

It can be concluded at this point that SFM force data obtained with chemically modified tips can be successfully correlated with the amino group content. The homogeneity of the distribution of the amino groups in

(20) According to the JKR theory (Johnson, K. L.; Kendall, K.; Roberts, A. D. *Proc. R. Soc. London A* **1971**, *324*, 301) the pull-off force F_{ad} of a sphere from a planar surface is proportional to the work of adhesion (eq 1), while the work of adhesion is the sum of the surface free energies of the functional groups (tip and sample) in contact with the liquid minus the interfacial free energy (eq 2). For the symmetric cases the work of adhesion is 2 times the surface free energy.

$$F_{\text{ad}} = -\frac{3}{2}\pi RW_{\text{ST}} \quad (1)$$

where W_{ST} is the work of adhesion and R the radius of the tip.

$$W_{\text{ST}} = \gamma_{\text{S}} + \gamma_{\text{T}} - \gamma_{\text{ST}} \quad (2)$$

where γ_{S} and γ_{T} denote the surface free energies of the sample and the tip (in contact with ethanol) and γ_{ST} is the interfacial free energy of the two surfaces in contact. As stated in eq 3, the total surface free energy can be written as the sum of Lifshitz-van der Waals and acid-base contributions:

$$\gamma = \gamma_{\text{S}}^{\text{LW}} + \gamma_{\text{S}}^{\text{AB}} \quad (3)$$

where $\gamma_{\text{S}}^{\text{LW}}$ denotes the contribution of Lifshitz-van der Waals interactions to the surface free energy and $\gamma_{\text{S}}^{\text{AB}}$ the acid-base component of the surface free energy. The acid-base parameters for $-\text{CH}_3$ terminated SAMs are zero. If we assume that in a first rough approximation the Lifshitz-van der Waals surface free energies are similar for $-\text{COOH}$, $-\text{CH}_2\text{NH}_2$, and $-\text{CH}_3$ SAMs, it follows that $\gamma_{\text{COOH}} > \gamma_{\text{CH}_3}$ and $\gamma_{\text{NH}_2} > \gamma_{\text{CH}_3}$. Furthermore, the positive interfacial energy between $-\text{COOH}$ and $-\text{CH}_3$ groups (van Oss, C. J. In *Polymers and Interfaces II*; Feast, W. J., Munro, H. S., Richards, R. W., Eds.; Wiley & Sons: New York, 1993; Chapter 11, pp 267–290) and the negative interfacial energy between $-\text{NH}_2$ and $-\text{COOH}$ groups¹² reduce the work of adhesion for the $-\text{COOH}$ and $-\text{CH}_3$ combination as compared to the combination $-\text{NH}_2$ and $-\text{COOH}$. Thus, the acid-base contributions of the $-\text{NH}_2$ and $-\text{COOH}$ -terminated SAMs are responsible for the observed trends. The trends can also be qualitatively explained by the fact that forces involving dipolar interactions and hydrogen bonding ($-\text{COOH}$ and $-\text{NH}_2$) are stronger than interactions between dipoles and nonpolar molecules ($-\text{COOH}$ and $-\text{CH}_3$) in ethanol.

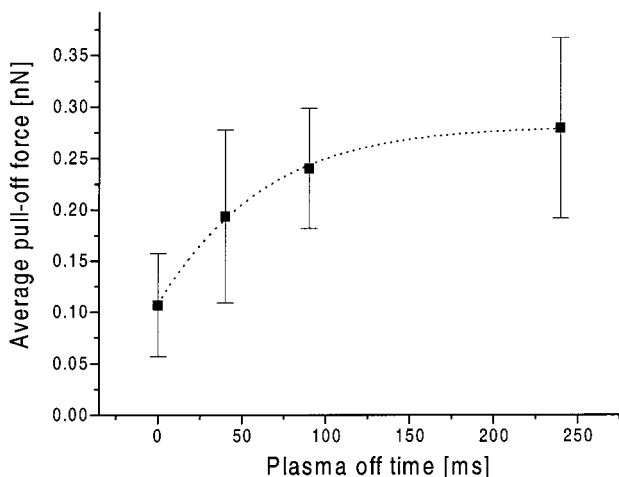


Figure 4. Average pull-off forces measured with $-\text{COOH}$ tip in ethanol on allylamine films prepared at constant on times (10 ms) and varying off times.³¹ The error bars correspond to the standard deviations obtained from the pull-off force distributions shown in Figure 3. The line has been added to guide the eye.

these very flat films¹⁸ was investigated in more detail in aqueous environment.

By performing pH dependent pull-off force measurements the contribution of the ionizable functional groups (amino groups) can be studied separately. In aqueous solutions, the sum of the different attractive forces is counteracted by the electrostatic repulsion of protonated amino groups if the pH is close to or lower than the pK_a of these groups. Thus, in these systems the balance of attractive forces and repulsive electrostatic forces is measured as "pull-off force".

For the pH-dependent SFM experiments, hydroxy-terminated ($-\text{OH}$) tips were used as these do not show any pH dependence in force measurements,¹² while the interaction between these hydrophilic tips and various surfaces is relatively weak in aqueous environment.^{12,13a} By measuring pull-off forces as a function of pH, a corresponding "force titration" curve and a "force pK_a " value can be obtained.²¹

In the *average* pH-dependent force measurements a pronounced dependence of the magnitude of the average pull-off forces on the pH was observed. In Figure 5 a typical force titration curve is shown. Due to the protonation of the amino groups, the pull-off forces decrease significantly for pH values below 5.5. However, there was surprisingly no pronounced difference between films prepared at different pulsed plasma deposition conditions. The data obtained in experiments with six different films were normalized and plotted in one graph (Figure 6). Despite the scatter of the data points one can clearly notice the reduction of the adhesive interactions between pH 6.2 and 5.2.

Typical thermodynamical pK_a values of amines in solution are around 10.5.²² A comparison with the force data presented here indicates that the local environment of the amino groups in the allylamine films is somewhat hydrophobic. Upon lowering the pH, the amino groups will resist protonation since the stabilization of the charge is low in the (hydrophobic) environment. This causes a shift of the thermodynamic pK_a , and thus also of the force pK_a measured by SFM, to lower values. Similar shifts have been previously reported for $-\text{NH}_2$ terminated SAMs.^{12a,23} For disordered SAMs of amino-terminated silanes, a force pK_a of 3.9 was reported previously in the literature.^{12a,23} In general, these shifts are in accordance with simulation results.²⁴

In all allylamine films studied here there seems to be on *average* little difference in hydrophobicity for different films. This is probably related to a possible restructuring of the thin poly(allylamine) films in contact with water. The films consist of a flexible network²⁵ which has been previously shown to facilitate rearrangements of the polymer network and the amino groups.²⁶

Laterally resolved measurements of pull-off forces with OH-terminated SFM tips on plasma polymerized allylamine films at pH 5.2 showed inhomogeneities of adhesive interactions on a sub-50-nm scale. In contrast, the interaction between the SFM tips and the polymer

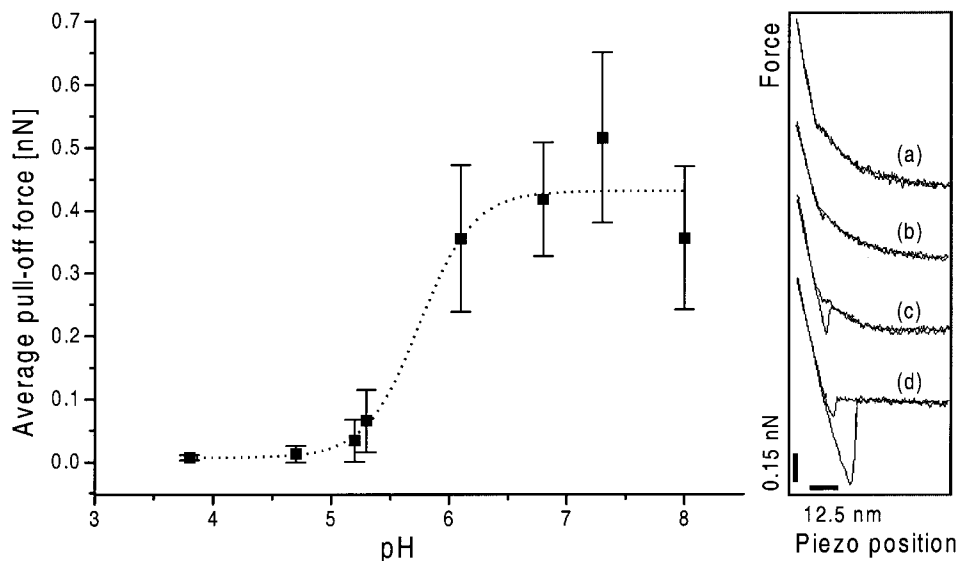


Figure 5. Force titration of plasma polymerized allylamine film (left, the dotted line has been added to guide the eye).³² On the right, corresponding force-distance curves which display (depending on the pH of the buffered aqueous solution) (a) exclusively repulsive (pH 4.7), (b) and (c) repulsive and attractive (pH 5.3 and 6.2, respectively), or (d) exclusively adhesive interactions (pH 6.8).¹⁶

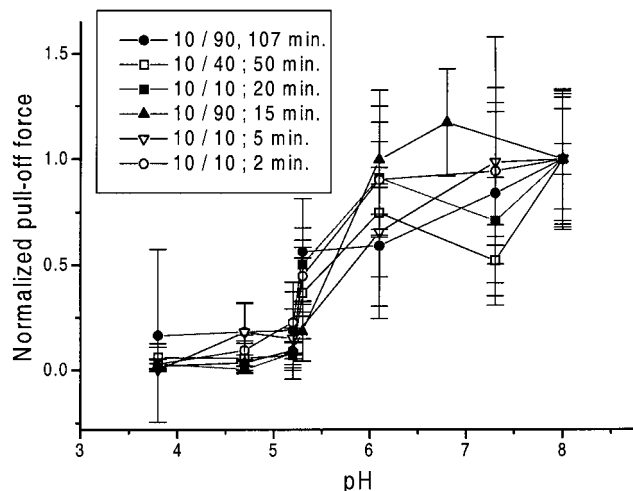


Figure 6. Normalized force titration curves of six different plasma polymerized allylamine films deposited at a peak power of 175 W (deposition parameters are indicated).¹⁸ The data were normalized to the pull-off force measured at pH 8.0. The individual data points were connected by lines to guide the eye.

surface became almost exclusively repulsive at pH 3.8 (Figure 7). In the plasma polymerized allylamine films coupling of topography into the force images can be

neglected due to the featureless, flat surface of these films.¹⁸ An inhomogeneous coverage of the surface, i.e., areas covered with polymer and areas without film coverage, can also be excluded since the observations were fully reproducible after changing the pH.²⁷

On a number of different films similar observations were reproduced. Analogous to oxyfluorinated iPP films studied previously,²⁸ it can be concluded that the distribution of the functional groups is inhomogeneous. Differences in the local hydrophobicity and charge density can be assumed to cause a shift of the local pK_a . In general, a more hydrophobic local environment of the amino groups corresponds to a lower pK_a . Thus, at pH 5.2, areas with high adhesion correspond to the more hydrophobic regions. The origin of the inhomogeneous distribution of functional groups is not known at present. An inhomogeneous temperature distribution in the plane of the film during the polymerization or different reaction pathways due to inhomogeneous *initial* coverage or *initially* deposited reaction products may lead to an inhomogeneous distribution of functional groups and film structure. This may lead to a heterogeneous restructuring of the polymer and the reorientation of the amino groups upon initial aging of the films in air similar to the processes observed previously.²⁶

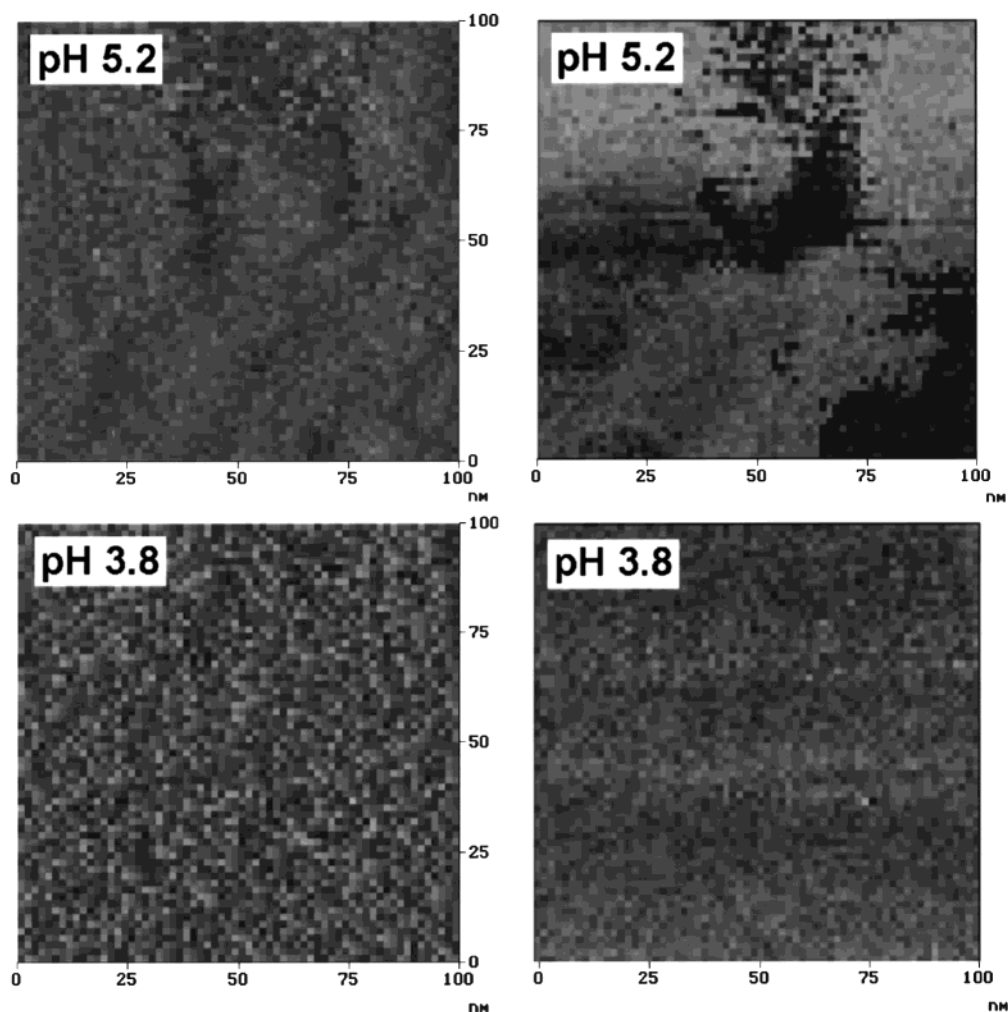


Figure 7. Height (left) and pull-off force (right) images of a plasma polymerized allylamine film (175 W, 10/40 ms/ms) obtained with OH-terminated tips at different pH. In the height image, the color scales range from dark (0 nm) to bright (25 nm). In the force images dark color indicates high adhesion (≈ 0 and -2.0 nN for pH 3.8 and 5.2, respectively), bright color indicates low adhesion (≈ 0 and -0.1 nN for pH 3.8 and 5.2, respectively).

The data shown here confirm earlier results on laterally resolved imaging of functional group distributions on polymers on a *sub*-50-nm level using scanning force microscopy with chemically modified tips ("chemi-

cal force microscopy").²⁸ The inhomogeneous forces observed can be related to variations of local " pK_a " values and different local hydrophobicity and thus to inhomogeneous distribution of the polar functional groups introduced by aging of the films or the plasma polymerization process.

(21) The force pK_a is related to the thermodynamic pK_a . However, the relation is very difficult to analyze quantitatively. The interactions in our experiments are probed on a noncontinuum level using a rather ill-defined geometry (tip covered with granular gold vs rough polymer surfaces). A theory which would allow one to relate forces measured with this geometry to surface charge is currently not available. Different methods for the determination of surface pK_a values have been discussed in the literature. These include: (a) An, S. W.; Thomas, R. K. *Langmuir* **1997**, *13*, 6881 (combined surface tension and neutron reflection measurements). (b) Holmes-Farley, S. R.; Reamey, R. H.; McCarthy, T. J.; Deutch, J.; Whitesides, G. M. *Langmuir* **1985**, *1*, 725 (contact angle titration). (c) Smith, C. P.; White, H. S. *Langmuir* **1993**, *9*, 1 (electrochemical determination of interfacial capacitance). For the determination of a surface pK_a by force microscopy using a well-defined tip geometry (micrometer-sized spherical particles), see: Hu, K.; Bard, A. J. *Langmuir* **1997**, *13*, 5114.

(22) Typical pK_a values measured for amines in solution are methylamine (10.6), dimethylamine (10.7), ethylamine (10.7), and propylamine (10.6) (Risch, K.; Seitz, H. *Organische Chemie*; Schroedel: Hannover, 1981; p 115).

(23) The extraordinarily low pK_a which was confirmed by independent contact angle titrations (4.3) was explained by the conformational disorder of the silane SAM. The disorder leads to an exposition of hydrophobic methylene groups.

(24) Smart, J. L.; McCammon, J. A. *J. Am. Chem. Soc.* **1996**, *118*, 2283.

(25) Due to the presence of highly reactive species in the plasma, cross-linking of the deposited polymer films occurs. The cross-linking is seen in swelling experiments.

(26) Gengenbach, T. R.; Vasic, Z. R.; Li, S.; Chatelier, R. C.; Griesser, H. J. *Plasma Polym.* **1997**, *2*, 91.

(27) Further support is the observation of practically pH independent pull-off forces measured on a bare Si wafer used as substrate for polymer deposition. Here the adhesion was homogeneous.

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(29) Thicknesses and refractive indices were measured by surface plasmon resonance spectroscopy and waveguide spectroscopy (a) Aust, E. F.; Sawodny, M.; Ito, S.; Knoll, W. *Scanning* **1994**, *16*, 353. (b) Ramsden, J. J. *J. Stat. Phys.* **1993**, *73*, 853.

(30) Monolayers were prepared by self-assembly of 11-mercaptoundecanoic acid (-COOH) and bis(12-aminododecyl) disulfide¹⁹ onto Au(111) substrates as described in: Schönherr, H.; Ringsdorf, H. *Langmuir* **1996**, *12*, 3891.

(31) The increase in pull-off forces with increasing amino group content can be rationalized by taking the hydrogen bonding between carboxylic acid and amino groups into account.²⁰ The interfacial free energy for similar combinations of functional groups was shown to be negative and quite large, which results in large pull-off forces.^{12c}

(32) Peak power 175 W, duty cycle 10 ms/10 ms.