Mixed Polyelectrolyte Brush from Oppositely Charged Polymers for Switching of Surface Charge and Composition in Aqueous Environment

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Introduction. Polymer brushes refer to an assembly of polymer chains that are attached by one end to a surface at a high grafting density when the chains are stretched away from the substrate due to the excluded-volume effect.[1] A particular case of the polymer brushes is represented by polyelectrolyte (PE) brushes, consisting of electrically charged polymers.[2] Recently, PE attached to a surface, and formed brushlike layers have attracted great interest because the structure and properties of the layers are strongly modified by electrostatic interactions of the charged chains and by the osmotic pressure of counterions. Swelling of PE brushes and chain conformation in the brushes strongly depend on external environment, ionic strength, valence of counterions, and pH,[3,4] demonstrating very pronounced responsive properties of the thin films.

Mixed polymer brushes constituted from two incompatible polymers grafted to the same substrate represent another example of responsive surfaces. In this case the microphase segregation of the polymers in the mixed brush results in the change of structure and surface chemical composition, depending on external environment.[1g,5] Here we report the combination of these two approaches to fabricate mixed brushes composed of two polyelectrolytes grafted onto the same solid substrate and carrying opposite electrical charges. Such materials are promising to tune wetting behavior and surface charge of the film, which is important to regulate adsorption of proteins, cells, and colloidal particles.

Mixed PE oppositely charged brushes were studied theoretically.[6] Theory predicts that in contrast to equally charged homopolymer brush, when the intra- and interchain Coulomb repulsion leads to a stretching of the chains, the oppositely charged mixed brush has other possibilities to reduce the electrostatic repulsion, depending on charge ratio (degree of compensation of the total charge of the homopolymer A consisting of N_A segments by the total opposite charge of the homopolymer B consisting of N_B segments). At $N_A > N_B$ polymer A chains are coiled due to the electrostatic attraction between A and B, while at $N_A = N_B$ both chains form a compact brush. Addition of salt leads to screening of this attraction, and the brush expands. At a low charge ratio further increase of salt concentration causes a decrease of brush thickness due to screening of the repulsion between equally charged segments, thus exhibiting a maximum. Consequently, the larger variety of combinations of electrostatic and short-range interactions leads to much more complex response as compared to mono-PE brushes.

Here we present the first attempt to synthesize and experimentally investigate such brushes.

Experimental Section. a. Materials. Carboxy-terminated poly(*tert*-butyl acrylate) (PBA-COOH, $M_n = 42\,000$, $M_w = 47\,000$) and poly(2-vinylpyridine) (P2VP-COOH, $M_n = 39\,200$, $M_w = 41\,500$) were obtained from Polymer Source, Inc, Canada. 3-Glycidoxypropyltrimethoxysilane (GPS) (Aldrich) was used as received.

Silicon wafers (100) with ca. 1.5 nm native SiO_2 layer thickness were obtained from Wacker-Chemitronics. The Si wafers were rinsed several times in dichloromethane in an ultrasonic bath and afterward placed in a cleaning solution of NH_4OH and H_2O_2 for 2 h at 60 °C. The cleaned wafers were exposed to 1% GPS solution in toluene for 16 h. The thickness of the rinsed and dried layer of the chemisorbed GPS was 1.3 ± 0.2 nm.

b. Grafting of the Polymers and Hydrolysis of PBA. The mixed brush was synthesized with a two-step procedure. PBA-COOH was selected to be the first grafted polymer. P2VP-COOH was grafted in the second step. The opposite order of grafting gave no reproducible results because of the high affinity of P2VP-COOH chains to the substrate, which suppressed essentially penetration of the second polymer through P2VP brush. The first grafted layer of PBA-COOH was prepared via a deposition of the polymer film on the GPS modified Si wafer by spin-coating from 1% methanol solution and following annealing in a vacuum oven at 150 °C for 20 min. After the grafting procedure, the ungrafted polymer was removed by a Soxhlet extraction in methanol for 3 h. The second polymer P2VP-COOH was then grafted using the same procedure, when a thin film of P2VP-COOH was spin-coated on top of the PBA-COOH brush. The grafting time was 15 h. Afterward, the ungrafted polymers were removed by Soxhlet extraction in THF. PBA component of the mixed brush was then hydrolyzed by treatment in benzene saturated with *p*-toluenesulfonic acid monohydrate at 55 °C for 1 h.

c. Ellipsometric Measurements. Null ellipsometry was applied to determine the thickness of chemisorbed GPS and grafted polymers. All the measurements were carried out using a null-ellipsometer in a polarizer−compensator−sample analyzer (Multiscope, Optrel Berlin) mode. As a light source, a He−Ne laser with $\lambda = 632.8$ nm was applied, and the angle of incident was set to 70°. A multilayer model for a flat film has been used for the calculation of thickness of chemisorbed GPS and grafted polymer layers from the experimentally measured ellipsometric angles ψ and Δ. The refractive indices used for the calculations were $N = 3.858\text{-}i0.018$ and 1.4598 for the silicon substrate and native silica layer, respectively, $n = 1.4598$ for GPS, $n = 1.466$ for PBA, and $n = 1.595$ for P2VP. After hydrolysis of PBA, a refractive index of 1.527 for PAA was used.[13,15] The roughness of the films measured with AFM and X-ray reflectivity methods was found to be in the range from 1 to 2 nm. This range of roughness did not influence ellipsometric measurements.

For the mixed brush we used a three-layer model, when SiO_2 and GPS layers were considered as an effective optical layer with $n = 1.445$. We found (com-

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paring ellipsometry, AFM scratch test, and X-ray reflectivity data[5e]) that this approach results in the error no larger than 5%. From the obtained values, we calculated the grafting amount of each polymer $A = d\rho$, and the grafting density $\Sigma = AN_A/M_w$, where d is the ellipsometric thickness, ρ is the density (for simplicity we took always $\rho = 1$ g/cm^3), N_A is Avogadro's number, and M_w is the molecular weight.

"In situ" ellipsometric measurements were performed to examine the swelling behavior of the binary polyelectrolyte brush in pH variable aqueous media. An ellipsometric cell with thin glass walls fixed at a known angle (68°) from the sample plane was used. The angle of incidence of the light was settled so that its path was normal to the window. Both swollen layer thickness and refractive index of the swollen layer were extracted from the fitting of ellipsometric data.

d. Analysis of the brushes was performed with Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) (Bruker IFS 28 FTIR). The same, as described above, procedure was used to graft the mixed brushes onto ATR silicon prism. After each step of the surface treatment and grafting we recorded FTIR spectra.

e. Electrokinetic Study. The isoelectric point (IEP) of the brushes grafted to Si wafers was determined from measurements of streaming potential. All the experiments were carried out in 0.001 mol/L KCl solution using a Centec PAAR Physica apparatus (Austria). The zeta potential was measured as a function of pH, adjusted by 0.1 *m* HCl and 0.1 *m* KOH.

f. Contact Angle Measurements. The technique of contact angle measurements was used to probe the surface energetic state of the grafted polymer films and could provide valuable information directly related to changes in surface properties as a result of a change in the surrounding medium. The water contact angle was determined by the sessile drop method of water (Millipore) drop delivered from a syringe onto the film surface.

Results and Discussion. a. Synthesis of the Mixed Brush. We prepared the mixed PE brushes by the "grafting to" approach using esterification reaction between carboxyl-terminated polymers in thin melted film deposited on the substrate surface modified with epoxy groups.[7] Our route comprises four key steps: (1) chemisorption of GPS on the surface of Si wafer, (2) grafting of carboxyl-terminated poly(*tert*-butyl acrylate, (3) grafting of carboxyl-terminated poly(2-vinylpyridine), and (4) hydrolysis of PBA yielding poly(acrylic acid).[8]

The cleaned silicon wafers were exposed to 1% GPS solution in toluene for 16 h. The thickness of the rinsed and dried layer of the chemisorbed GPS was 1.3 ± 0.2 nm. The first grafted layer of PBA-COOH was prepared via the deposition of the polymer film on the GPS modified Si wafer by spin-coating from 1% methanol solution and following annealing in a vacuum oven at 150 °C for 20 min. Because of the kinetic experiments, time and temperature were optimized to fabricate the PBA brush with the grafting amount of $^1/_2$ of the plateau value on the kinetic plot. (The grafting kinetics obtained at 150 °C is shown in Figure 1a.) After the grafting procedure, the ungrafted polymer was removed by a Soxhlet extraction in methanol for 3 h. The grafting procedure yielded 4 mg/m^2 ($\Sigma = 0.051$ nm^{-2}) of grafted PBA. The second polymer P2VP-COOH was then grafted using the same procedure, but the grafting time was 15 h. (The grafting kinetics of P2VP-COOH on the substrate with grafted in advance 4 mg/m^2 PBA is shown in Figure 1b.) Afterward, the ungrafted polymers were removed by Soxhlet extraction in THF. The amount of the grafted P2VP was measured to be 3.3 mg/m^2 ($\Sigma = 0.048$ nm^{-2}), giving the total grafted amount of both polymers 7.3 mg/m^2 or $\Sigma = 0.1$ nm^{-2}. This grafting density corresponds to the 3 nm distance between grafting points, giving evidence for the brush regime. (Note that the end-to-end distance for the polymer chains in Θ solvent is about 10 nm.)

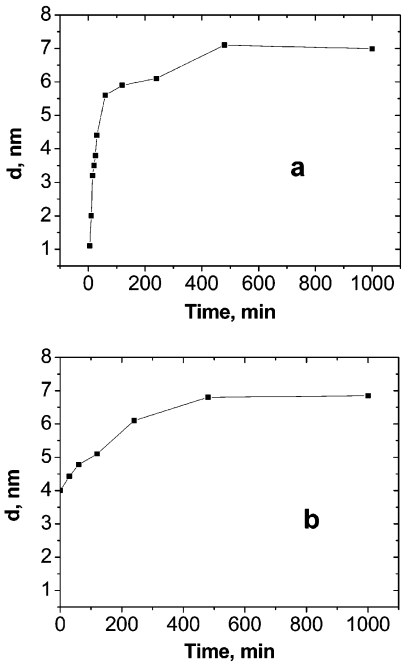

Figure 1. Grafting kinetics on the modified with epoxy groups Si wafer, 150 °C, melt: PBA-COOH (a), P2VP-COOH after grafting of 4 mg/m^2 of PBA-COOH (b).

The PBA component of the mixed brush was then hydrolyzed by treatment in benzene saturated with *p*-toluenesulfonic acid monohydrate at 55 °C for 1 h. After the hydrolysis a nonsignificant decrease (about 5%) of the brush thickness was observed. To prove stability of the formed PAA film, the brush was treated in ethanol by Soxhlet extraction for 5 h. No considerable change in the film thickness was observed.

The structure of the brushlike layers obtained after each step of the synthetic procedure performed on the surface of the silicon ATR prism with a native silica layer was investigated using FTIR-ATR. The spectrum of the chemisorbed GPS was used as a reference (Figure 2a). Spectra b−d in Figure 2 are shown after subtraction of the GPS spectrum. The characteristic bands detected at 1730 cm^{-1} (−C═O) and 1370 cm^{-1} (−C(CH$_3$)$_3$) refer to butyl ester groups of the first grafted PBA (Figure 2b). The grafting of the second polymer P2VP was proved by the characteristic bands at 1568 and 1590 cm^{-1} (Figure 2c). After conversion of PBA to PAA via hydrolysis of the *tert*-butyl ester groups the bands at 1710−1730 cm^{-1} (acid carbonyl) as well as at 1230 and 3200 cm^{-1} (−OH) were found (Figure 1d). Also, a new peak at 1610 cm^{-1} due to the presence of −COO$^-$ groups in the polymer layer was identified. The dramatically decreased intensity of the band at 1370 cm^{-1} proves almost complete hydrolysis of PBA.

b. Responsive/Switching Behavior. The mixed PE brush is capable for a sharp switching of the surface charge upon change of pH. We show in Figure 3 the

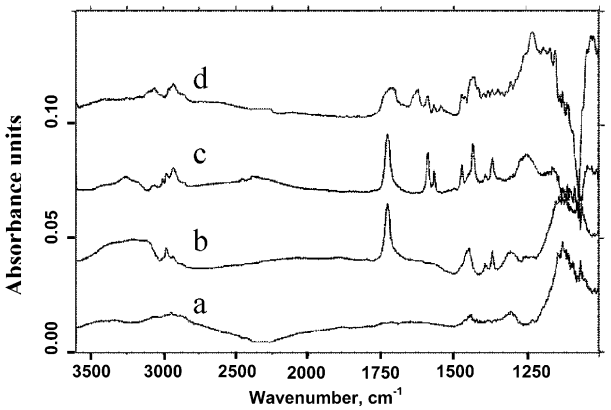

Figure 2. FTIR-ATR spectra of grafted layers on Si prism: GPS (a), PBA brush (b), PBA/P2VP mixed brush (c), PAA/P2VP mixed brush (d). Spectra b−d are plotted after subtraction of spectrum a.

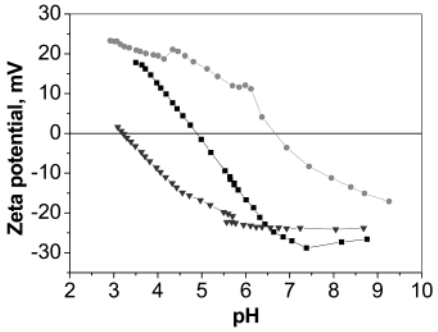

Figure 3. Zeta-potential plotted as a function of pH for the PE brushes: homopolymer P2VP brush (circles), homopolymer PAA brush (triangles), mixed PAA/P2VP brush (squares).

results of electrokinetic investigations of the mixed brush on the surface of Si wafers in 0.001 mol/L KCl aqueous solution. Homopolymer P2VP and PAA brushes were used as a reference. Isoelectric points at pH 6.7, 3.2, and 4.9 were determined for P2VP, PAA, and the mixed P2VP/PAA brushes, respectively. The data demonstrate amphiphilic properties of the mixed brush when the isoelectric point is located in between the values corresponding to each of homopolymer brushes. A small shift of pH away from the isoelectric point results in a sharp linear change of surface charge in the wide range of pH. The change of surface charge is accompanied by a U-shaped change of the swollen film thickness (Figure 4). We measured the thickness of the swollen brush in situ in aqueous environment using a liquid ellipsometric cell. In this experiment the thickness and the refractive index of the layer were obtained from the fitting procedure.

The mechanism of the switching behavior of the mixed PE brush is schematically explained in Figure 5. Each homopolymer in the mixed brush is a weak PE. The charge density of the weak PE depends on pH. At pH < 6.7 P2VP is protonated, and a further decrease of pH results in the increase of density of positive charges on P2VP chains. The inverse scenario may be assigned to PAA chains. PAA is negatively charged at pH > 3.2. In the range of 3.2 < pH < 6.7 the charged P2VP and PAA interact so that at pH = 4.9 the charges are completely compensated, resulting in the neutral surface. The thickness of the brush in the isoelectric point was 7 nm, which was close to the thickness of the dry film. Outside this region at a small pH PAA chains

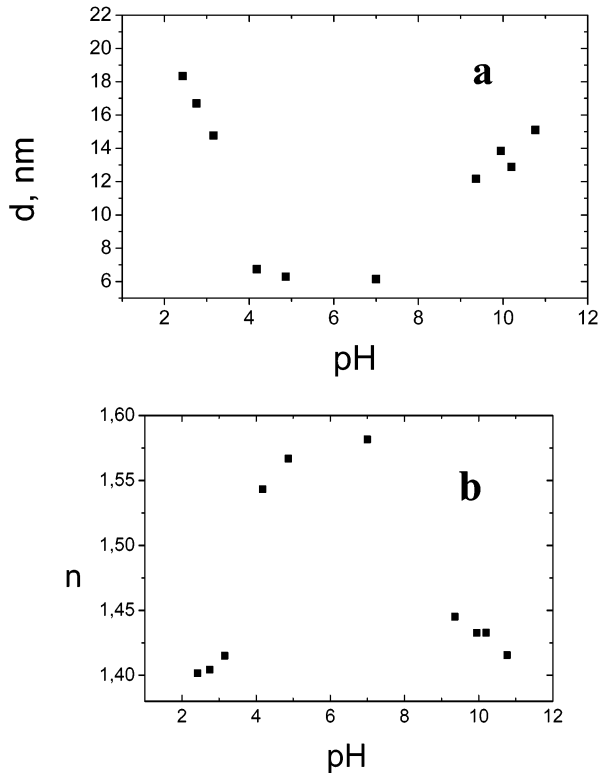

Figure 4. Influence of pH on the (a) thickness (*d*) and (b) refractive index (*n*) of the swollen PAA-P2VP brush. The thickness in dry state was measured to be 6.4 nm.

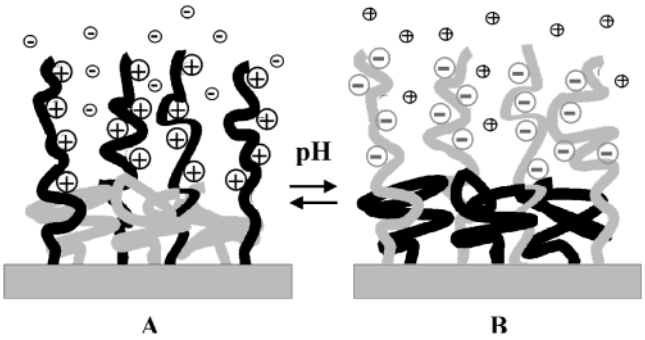

Figure 5. Schematic representation of switching behavior of mixed PE brush upon change of pH: below isoelectric point (A) and above the isoelectric point (B).

adapt a compact conformation on the bottom of the film while P2VP chains are highly protonated and stretched away from the surface. (The thickness of the swollen brush measured at pH 2 was 18 nm.) They preferentially occupy the top of the film. At a large pH value the inverse transformation takes place. P2VP is collapsed on the bottom, while negatively charged PAA chains are on the top. (The thickness of the swollen brush was 15 nm at pH 10.)

The mixed brush allows to approach a much larger range of switching between values of surface charge (from negative to positive surface charge) as compared to the homopolymer brushes (Figure 3). The absolute values of surface charges in acidic and basic pH regions are close to the corresponding values for the P2VP homopolymer brush for acidic pH values and for the PAA homopolymer brush for basic pH values, respectively. That indicates the possibility to switch via a small change of pH in water the surface composition of the brush, when the top layer is enriched with the

charged polymer while the bottom layer is occupied with the uncharged polymer. This possibility demonstrates the substantial difference of the mixed PE brush from the mixed uncharged brush. In the latter case the switching of the surface composition can be approached by the change of solvent,[5] while the layered segregation of two different polymers in the mixed PE brush can be easily approached by a small change of pH. This behavior of the mixed PE brush is promising for the precise regulation of adsorption/desorption processes of charged particles, cells, and protein molecules and controlled release or tunable catalysis in aqueous environment.

Below we demonstrate that pH signal may be used to switch wetting behavior of the mixed PE brush. At low and high pH values the top of the sample is occupied by hydrophilic protonated P2VP and dissociated PAA segments, respectively. Therefore, the brush remains hydrophilic in the entire range of pH, except the neutral region, where a compensation of the charges takes place. If the brush is rapidly removed from the solvent bath and dried, the morphology of the film is frozen. The brush can be easily probed using the contact angle method. Thus, we assume that the ratio between concentrations of different polymers in the top layer of the mixed brush is not much changed during fast collapse, when water is rapidly evaporated. Results of such experiments are presented in Figure 6c, and the same experiments with single polymer brushes are used as reference (Figure 6a,b).

In acidic media, pH 2, P2VP preferentially occupies the top of the substrate, while in basic media, pH 10, PAA replaces P2VP on the top layer. Despite different compositions of the top layer and charge in both cases the mixed PE brush demonstrates very similar wetting behavior with contact angles of 36° for pH 2 and of 39° for pH 10. In contrast, PAA brush is hydrophilic at pH 10 and more hydrophobic at pH 2 (Figure 6a), while P2VP brush demonstrates an inverse behavior (Figure 6b). The values measured for the mixed PE brush in between the limiting points of the range $2 < pH < 10$ represent the stepwise transition, showing a maximum of hydrophobic behavior around the IEP of the brush ($\Theta = 70°$). The reason for that was already explained in the terms of complexation between two oppositely charged PE chains. The stepwise change in contact angle values deals with the weak polyelectrolyte behavior, originating from the dependence of degree of dissociation on pH of the aqueous medium.

Conclusion. In conclusion, we have synthesized the mixed PE brush from two oppositely charged weak PE homopolymers via the "grafting to" approach. The PE brush demonstrates switching behavior when the top of brush is occupied by negatively charged stretched away from the substrate PAA or by positively charged stretched P2VP chains at pH values below and above of the isoelectric point, respectively. At the isoelectric point the mixed brush forms a collapsed PE complex with zeroes charge.

The responsive/switching behavior of the PE brush can be explored to tune surface properties in aqueous environment applying pH signal, which is of potential interest for microfluidic technologies, smart nanodevices, and drug delivery systems.

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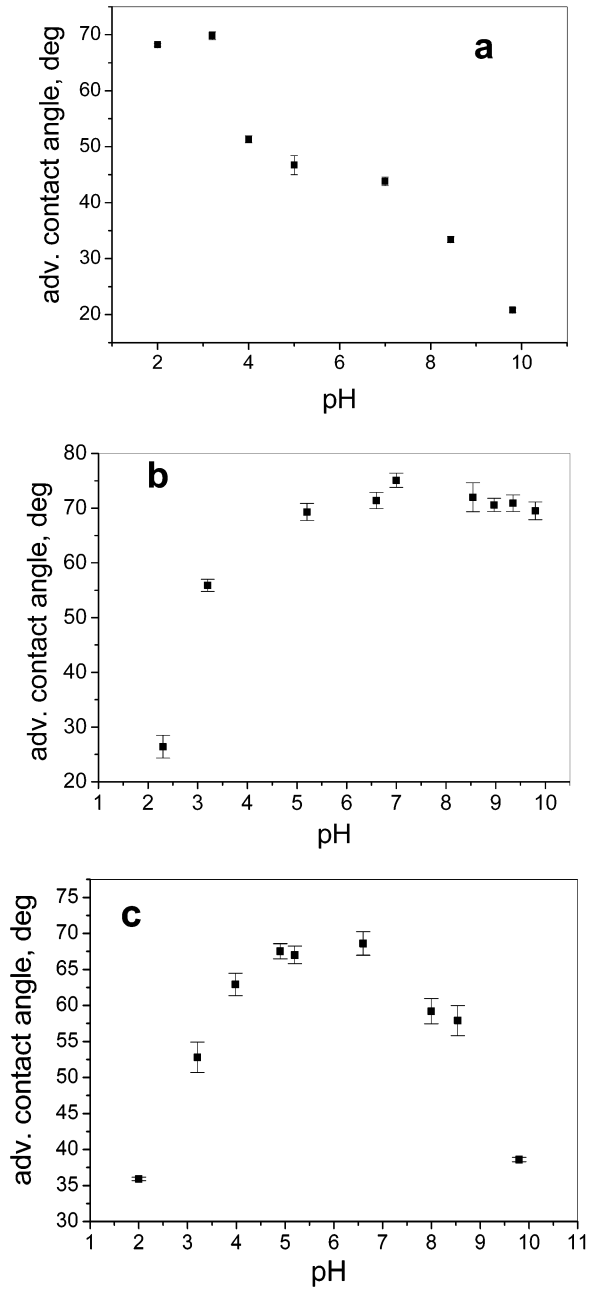

Figure 6. Advancing contact angle as a function of pH of aqueous bath for treatment of the samples measured on dry brush (rapidly dried after exposure to the bath for 10 min): PAA brush (a), P2VP brush (b), and PAA-P2VP mixed brush (c).

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