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Hybrid brushes composed of two liquid polymers, poly(dimethylsiloxane) (PDMS) and a highly branched ethoxylated polyethylenimine (EPEI), were synthesized on Si wafers by the “grafting to” method and by applying a combinatorial approach (fabrication of gradient brushes). The combinatorial approach revealed a strong effect of “layer assisted tethering”, which allowed us to synthesize hybrid brushes twice as thick as the reference homopolymer brushes. The hybrid brushes are stable thin films that can rapidly and reversibly switch between hydrophilic and hydrophobic states in water and air, respectively. The switching in water affects a rapid release of amino functional groups which can be used to regulate adhesion and reactivity of the material. The switching in air rapidly returns the brush to a hydrophobic state. The hybrid brush is hydrophilic because of two mechanisms: (1) exposure of EPEI chains to the brush-water interface under water, and (2) retention of some fraction of water via swollen EPEI chains (the EPEI chains swell by 2-3 times), which are conserved by a PDMS cap in air. The hybrid brush is wettable under water, and at the same time, the brush is nonwettable in air because water droplets are trapped in a metastable state when the water contact angle is above 90°.

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Enclosure 1

Nonwettable Thin Films from Hybrid Polymer Brushes Can Be Hydrophilic†

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Hybrid brushes composed of two liquid polymers, poly(dimethylsiloxane) (PDMS) and a highly branched ethoxylated polyethylenimine (EPEI), were synthesized on Si wafers by the “grafting to” method and by applying a combinatorial approach (fabrication of gradient brushes). The combinatorial approach revealed a strong effect of “layer assisted tethering”, which allowed us to synthesize hybrid brushes twice as thick as the reference homopolymer brushes. The hybrid brushes are stable thin films that can rapidly and reversibly switch between hydrophilic and hydrophobic states in water and air, respectively. The switching in water affects a rapid release of amino functional groups which can be used to regulate adhesion and reactivity of the material. The switching in air rapidly returns the brush to a hydrophobic state. The hybrid brush is hydrophilic because of two mechanisms: (1) exposure of EPEI chains to the brush−water interface under water, and (2) retention of some fraction of water via swollen EPEI chains (the EPEI chains swell by 2−3 times), which are conserved by a PDMS cap in air. The hybrid brush is wettable under water, and at the same time, the brush is nonwettable in air because water droplets are trapped in a metastable state when the water contact angle is above 90°.

Introduction

A combination of various contradicting properties in the same material is a unique characteristic of responsive materials.[1] This combination becomes possible due to an incorporation of several ingredients in the material’s complex architecture. A hybrid thin polymer film is one of the successful examples of such a combination.[2] Several unlike polymers combined in the same thin film provide different properties of the hybrid film. The interaction of the thin film with its environment results in switching between different properties. The switching is self-regulated by a response of the thin-film structure to changes in the material’s environment. The stability of the thin film is secured via covalent bonds. Block-copolymer and mixed polymer brushes were designed using this concept.[3] In the mixed brushes, two different polymers are end-grafted to the same substrate. To avoid unfavorable interactions, the polymers segregate laterally into microscopic domains (size of the domains is in the range of the polymer chain size). Selective interactions of one of the polymers with the brush’s environment provoke a layered segregation (stratification) and preferential exposure of this polymer to the environment.[4] This mechanism results in switching of the surface properties of the brush between properties of the two unlike polymers. For many reported systems, the mixed brushes were explored at temperatures well below bulk glass transition temperatures of the polymers. A typical example of the responsive property was shown in the experiment when the mixed brush was exposed to a selective solvent, switched, and dried by a rapid evaporation of the solvent. In the dry state, the morphology of the brush is frozen by the glassy polymers. In this way, for example, the mixed brush was switched from hydrophilic to hydrophobic state and vice versa. Hydrophilic brushes were also switched to hydrophobic state by a temperature increase above the glass transition temperature when hydrophobic chains diffused to the outer layer.[5,6] This mechanism also works very well for block-copolymer brushes.[7] However, when properties of two polymers were very different, a selective solvent for one polymer was a very bad solvent for the second polymer. That created some kinetic limits for the switching. For example, at a high fraction of a hydrophobic polymer, the switching in water was very slow.[8] In many cases, a bad solvent switched mixed brushes, only partially demonstrating some “memory effect” when the brush morphology was sensitive to the sample history.[9]

The second interesting problem is a spontaneous switching in air. Water is used as an external stimulus to switch properties of responsive materials. For many applications, it will be important to have a spontaneous reverse transition of the material property as soon as water is removed from the material surface. Reverse spontaneous switching is a very interesting phenomenon. Its application depends on kinetics. It is well-known that functional polymers undergo interface reconstruction in water and in dry air.[10−12] Typically, the reconstruction kinetics are measured in hours. Polymer surfaces slowly switch to a more hydrophilic state when in water. Then the dried surface slowly switches to a hydrophobic state once in air. This kinetics of the reconstruction is very slow for many applications. A rapid reconstruction takes place for low molecular weight polymers at temperatures above

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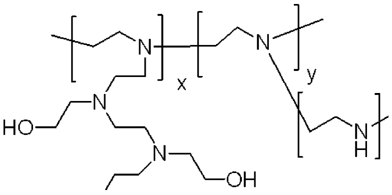

Figure 1. Highly branched ethoxylated polyethylenimine (EPEI)

the glass transition temperature. However, application of these conditions will cause substantial loss of many bulk properties of the polymer materials. Polymer additives with "buoy surface active groups" (hydrophobic groups) were suggested to accelerate the reconstruction process.[13,14] The additive is a block- or graft-copolymer that combines polar and nonpolar functional groups. The "buoy groups" (typically fluorinated functional groups) force the additive to segregate at the polymer−air interface in such a way that the polar groups are hidden by the "buoy blocks" and are located in close vicinity to the interface. As soon as the surface comes in contact with a polar liquid (or a polar substrate), the interface reconstructs and exposes the polar functionalities toward this stimulus. Most experimental examples use fluorinated "buoy groups".[13,15,16] This limits a broad application of the "buoy approach."

Thus, we formulated as the goal of this work to develop a stable thin film that can rapidly and reversibly switch between hydrophilic and hydrophobic states in water and air, respectively. The switching in water should rapidly release polar functional groups that can be used to regulate adhesion and reactivity of the material. The switching in air should rapidly protect the material with a hydrophobic and nonadhesive layer (for example, self-cleaning properties[17]) with no fluorine group contents.

Our desire to achieve these applications was, in fact, the goal that stimulated our study of the hybrid brushes composed of two liquid polymers, poly(dimethylsiloxane) (PDMS) and a highly branched ethoxylated polyethylenimine (EPEI; Figure 1). We demonstrate here that hybrid brushes prepared from these two polymers can perform the functions formulated in our stated goal. We show that the hybrid brush is hydrophilic because it absorbs water into EPEI clusters. At the same time, the brush is nonwettable with the advancing contact angle of above 90°, even in a humid atmosphere.

Experimental Section

Materials. Aminopropyl-terminated PDMS (PDMS−NH_2, M_w = 30 000 g/mol) was purchased from Gelest Inc., and polyethylenimine, 80% ethoxylated (highly branched, symmetrical polymer; about 80% of the primary and secondary amines are ethoxylated), 37% solution in water (EPEI M_w = 50 000 g/mol), was purchased from Sigma-Aldrich. Toluene (Sigma-Aldrich) was distilled after drying over sodium. MEK and methanol were used as received from Sigma-Aldrich. Highly polished silicon wafers (purchased from Semiconductor Processing, Union Miniere USA Inc.) were first cleaned in an ultrasonic bath for 30 min with dichloromethane, then placed in cleaning solution (prepared from NH_4OH and H_2O_2) at 60°C for 1 h, and finally rinsed several times with Millipore water (18 MΩ cm^{-1}). 3-Glycidoxypropyl trimethoxysilane (GPS) was purchased from Gelest Inc. and used as received.

Preparation of the Hybrid Brushes. In our route of synthesis, we explore the "grafting to" method of grafting of an end-terminated polymer from the melt[18] or solution. GPS was chemisorbed on the surface of the cleaned Si-wafers from 1% solution in the dried toluene for 16 h at room temperature (Figure 2a). Afterward, the reaction samples were carefully rinsed with toluene and ethanol to remove ungrafted GPS.

In the next step, we used a combinatorial approach to study the grafting kinetics of the PDMS brush. The GPS-modified Si-wafer was slowly immersed in the bath with liquid PDMS−NH_2. The bath was thermostated at 70°C. The sample (3 cm × 1 cm) was immersed vertically using a step-motor with a constant velocity of 21.6 mm/h (Figure 2b). The nongrafted polymer was removed by rinsing the samples in toluene multiple times.

Then, the second polymer, EPEI, was grafted by immersion of the Si-wafer in the bath with 10% solution of EPEI in water (pH 6.8 adjusted with HCl) for 3 h at 70°C (Figure 2c). The ungrafted polymers were removed by multiple rinsing with water, acidic water of pH 3, MEK, and methanol

The homopolymer EPEI brush was grafted by casting 20% EPEI solution in methanol on the surface of the GPS-modified Si-wafer. The Si-wafer was left for several hours in air to evaporate methanol from the 1 mm thick deposited film. Afterward, the sample was heated at 70 °C for 1 h. The ungrafted polymer was removed by multiple rinsing with water, acidic water of pH 3, MEK, and methanol.

Each step was monitored with ellipsometry, atomic force microscopy (AFM), and contact angle measurements. Control experiments showed that PDMS−NH_2 deposited (nongrafted) on the bare Si-wafer was completely removed by rinsing with toluene, while EPEI left a small amount (0.5 mg/m^2) of the adsorbed polymer after rinsing with water, acidic water pH 3, MEK, and methanol.

Sample Characterization. *Ellipsometry*. Layer thickness and grafted amounts were evaluated at $\lambda = 633$ nm and an angle of incidence of 70° with an Optrel Multiscop (Berlin, Germany) null-ellipsometer equipped with an *XY*-positioning table for mapping of the sample surface (lateral resolution is defined by the beam spot of about 2 mm). The measurements were performed for each sample after each step of the modification in order to use the measurements of the previous step as a reference for the simulation of ellipsometric data. Initially, the thickness of the native SiO_2 layer (usually 1.4 ± 0.2 nm) was calculated at refractive indexes $N = 3.858 - i0.018$ for the Si-substrate and $n = 1.4598$ for the SiO_2 layer. The thickness of the GPS layer (typically 1.0 ± 0.1 nm) was evaluated using the two-layer model: SiO_2/GPS for a refractive index of GPS equal to 1.429. The thickness of PDMS−NH_2 as the first grafted layer (typically 1−4 nm) was evaluated with the three-layer model of SiO_2/GPS/PDMS−NH_2, with $n = 1.405$ or in the case of SiO_2/GPS/EPEI, $n = 1.42$. Finally, the thickness of the whole polymer film (typically 4−7 nm) after grafting of the second polymer was calculated using the two-layer model of SiO_2/polymer considering the thin polymer film as an effective optical medium, with $n = 1.41$. We estimated that this calculation results in an error no larger than ±5% for the 5 nm thick films since the difference between refractive indexes of all organic ingredients is small. From the obtained values, we calculated the grafting amount of each polymer $A = H\rho$, and the grafting density $\Sigma = AN_A/M_w$, where H is the ellipsometric thickness, ρ is the density, N_A is Avogadro's number, and M_w is the molecular weight. Thickness of films swollen in water was measured in a sample liquid cell with a tube design (the extension tubes are fixed tubes on the laser and detector-arm of the Multiskop and dipped into the sample liquid cell).[19] The swollen layer thickness was calculated using the two-layer model of SiO_2/ swollen polymer considering the swollen polymer film as an effective optical medium, with $n = 1.41$. We estimated that this calculation results in an error no larger than ±10% for the 3 times swollen films in water.

AFM. AFM studies were performed on a Dimension 3100 for dry samples and MultiMode microscopes (VEECO, NY) in the liquid

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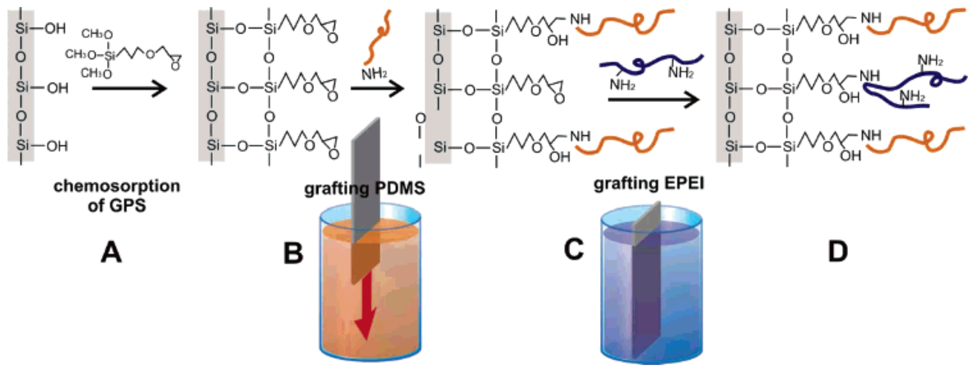

Figure 2. Grafting of the hybrid brushes: chemisorption of GPS (a), grafting of the PDMS gradient brush (b), and grafting of EPEI (c).

cell. The tapping mode was used to map the film morphology at ambient conditions and under water. AFM tips of “Veeco NP” and “Veeco DNP” with a resonance frequency of 75 kHz and a spring constant of 0.58−0.32 N/m were used at ambient conditions. AFM tips of “BS-Tap 300” with a resonance frequency of 300 kHz and a spring constant of 40N/m were used under water. Root-mean-square (rms) roughness was calculated using a commercial software.

Contact Angle. The wettability of the surfaces was characterized by contact angle measurements of sessile water droplets using a homemade system, which included a sample stage, a long focus microscope, a source of light, a CCD camera, a PC, and self-coded software for processing drop images. Advancing (adv) and receding (rec) contact angles from six individual drops placed on six new surface areas were measured by adding or withdrawing a small volume of water through a syringe. The needle was maintained in contact with the drop during the experiments. All readings were then averaged to give a mean advancing and receding contact angle for each sample. The accuracy of this technique is on the order of ±2°.

Results

Grafting of GPS. Our synthetic procedure (Figure 2a) starts with the covalent grafting of GPS to the surface of a Si-wafer as mentioned in the Experimental Section and according to the protocol explained in detail elsewhere.[20] The ellipsometric thickness of the GPS films of about 1.0 ± 0.1 nm corresponds to the 1 ± 0.1 theoretical monolayers of the GPS. The average surface concentration of GPS calculated from ellipsometry data is in the range of 3 molecule/nm^2.

Grafting of PDMS−NH$_2$. The next step of the synthetic procedure comprises the grafting of the PDMS−NH$_2$ from a bath with liquid polymer. A vertically held sample of GPS-modified Si-wafer was slowly dipped into the bath with a constant velocity (Figure 2b). Thus, the bottom of the wafer was in contact with polymer for the longest period of time, whereas the top of the wafer stayed in contact with polymer for the shortest period of time. With this method, we prepared a sample of the brush with a gradient of grafting density. The kinetics of the grafting of PDMS−NH$_2$ in terms of the grafting amount vs time of grafting is presented in Figure 3a. The grafting kinetics demonstrates three very pronounced stages: (1) fast grafting, controlled by the rate of chemical reaction and segmental diffusion of chains located in a close vicinity to the substrate, (2) slow grafting controlled by diffusion of free chains through the already grafted PDMS, and (3) accelerating grafting or “layer assisted tethering”. This kinetics is in very good agreement with the grafting kinetics reported by Penn et al.[21,22] for grafting amino-terminated polystyrene on GPS-modified substrates.

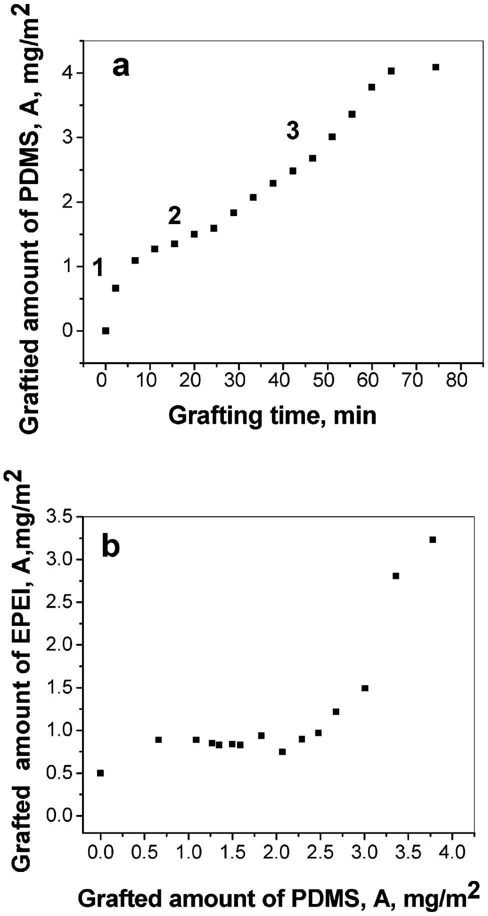

Figure 3. Grafting kinetics of PDMS (a) with three stages: grafting in diluted surface concentration regime (1), regime limited by diffusion of chains through the brush (2), and regime of “layer assisted tethering” (3); and the plateau grafted amount of EPEI (the second grafted polymer) vs grafted amount of PDMS (the first grafted polymer) (b).

The sample of the homopolymer brush at the highest grafting density, which corresponds to the plateau amount, was synthesized simply by immersing the wafer in the bath with PDMS−NH$_2$. This sample was used for the reference experiments. The reference brush was visualized with AFM as a macroscopically homogeneous flat thin film with segregated domains (clusters with a 53±6 nm diameter, rms roughness of 1.4 nm; Figure 4a), which indicate the dimple (pinned micelles) regime of the brush.[23] The clusters are larger than the dimensions of the PDMS chains (gyration radius R_g for PDMS of M_W = 30 000 g/mol in melt

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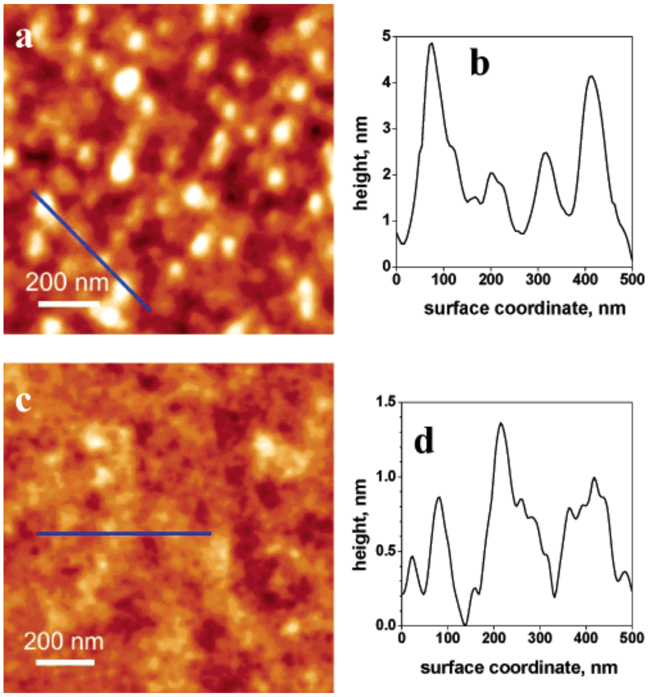

Figure 4. AFM topographical images (a and c) and cross-sections (b and d) of the homopolymer grafted layers PDMS, rms roughness 1.4 nm (a), and EPEI, rms roughness 0.5 nm (b).

is $R_g = 3.8$ nm [24]). The same experimental facts were frequently reported for various brushes and could be explained by random character of grafting.[25] Since accurately determining the thickness is a critical step for the calculation of brush layer parameters, values found with ellipsometry were verified by an AFM scratch test. In this experiment, the polymer layer is scratched with an ultrasharp needle to delaminate the layer down to the Si wafer. The sample is then scanned over an area with the scratched line to verify quality of the scratch and the actual thickness. The thickness obtained from the scratch test (4 nm) is in good agreement with the ellipsometric thickness. The PDMS brush is a hydrophobic and nonwettable thin film (water advancing contact angle of 103°).

Grafting of EPEI. EPEI is a highly branched polymer with a large number of primary and secondary amino groups (Figure 1) that can react with epoxy groups of GPS on the modified Si-wafers. The grafting of EPEI is a complex process. We studied grafting of EPEI from melt and from 10% aqueous solution. The grafting in both cases is a fast process. The grafting from melt was performed from a 0.1 mm film of EPEI as described in the Experimental Section. The result was that the brush approached the plateau value at 3.5 ± 0.5 nm. Grafting the brush from 10% solution in water for 2 h resulted in a 0.5 nm thick layer. We speculated that EPEI strongly interacted with the substrate via many amino groups per molecule and blocked the reactive epoxy sites on the surface immediately (Figure 5a). This mechanism resulted in a higher grafting density from melt, when many chains were present in a close vicinity to the substrate. The grafting density was much smaller for the grafting from the solution. In the latter case, chains, which arrived first, spread on the substrate and blocked all reactive sites on the surface. A study of this process in detail was out of the scope of this work. The grafting from the melt was used to prepare the reference sample. The grafting was followed by multiple washings with water, acidic water of pH 3, MEK, and methanol. An AFM study of the grafted layer revealed a macroscopically smooth layer with rms roughness of 0.5 nm (Figure 4b). The grafted layer is a thin hydrophilic film that is completely wettable by water.

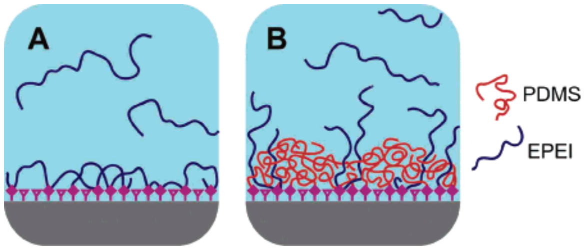

Figure 5. Schematics for grafting EPEI to the solid substrate (a) and “layer assisted tethering” on the substrate with pre-grafted PDMS (b).

Table 1. Samples of Hybrid Brushes

	grafted amount, A, mg/m^2/$\Sigma\times10^2$, nm^{-2}		
sample #	PDMS	PEI	PEI/PDMS ratio
A	3.0/5.90	3.9/5.07	1.3
B	3.4/6.67	2.8/3.64	0.8
C	3.7/7.26	2.5/3.25	0.7
D	3.5/6.88	1.1/1.43	0.3

Grafting of Hybrid Brush. The sample with the gradient PDMS brush was immersed in 10% EPEI solution in water (pH 6.8) at 70 °C for 3 h (Figure 2c). Afterward, the sample was rinsed using the same procedures as described above for grafting EPEI. Grafting of the second polymer was measured with ellipsometry by mapping the sample and was presented in terms of EPEI grafting amount vs PDMS grafting amount on the gradient sample (Figure 3b). It is noteworthy that experiments with EPEI melt were unsuccessful. We were not able to graft EPEI as a second polymer from melt. It is also important that we observed the grafting of the second polymer only when PDMS was initially grafted and then EPEI was grafted on the second step. For the inverse case when PDMS was attempted to graft after EPEI, we observed only a few grafted PDMS. Consequently, this procedure is effective if the polar component is grafted after the nonpolar component. In the latter case, there is a driving force to penetrate the polymer brush of the first polymer and to approach the substrate surface with residual reactive groups. The plot in Figure 3b reveals the surprisingly strong effect of “layer assisted tethering”. The grafting amount of EPEI was tripled due to the effect. We speculate that at low grafting densities of PDMS, the second polymer, EPEI, adsorbs on unoccupied surface centers and blocks the surface in the same way as that for grafting of homopolymer EPEI brushes. As soon as the grafting density (Σ) of PDMS increases and approaches the critical value of $\Sigma = 0.022$ nm^{-2} or $A = 1.1$ mg/m^2 (calculated as $\Sigma_c = 1/\pi R_g^2$) for the transition from mushroom regime to the brush regime, the surface is protected by the PDMS brush.[23] This value is in very good agreement with the experimental data in Figure 3. The second polymer, EPEI, diffuses through the PDMS brush and reacts via limited number of amino functional groups because its chain experiences a strong lateral compression in the PDMS brush (Figure 5b).

Based on the grafting kinetics, we prepared four samples (A−D) with different grafting densities of PDMS brushes (Table 1) on the first step and grafted EPEI on the second step. The total grafting density of both polymers is larger than 0.1 nm^{-2}, which corresponds to the 1.8 nm average distance between grafting points (calculated as $R_e = (\pi\Sigma)^{-1/2}$). This value is two times smaller than the gyration radius of grafted polymer coils. Consequently, the swollen polymer film can be considered as a

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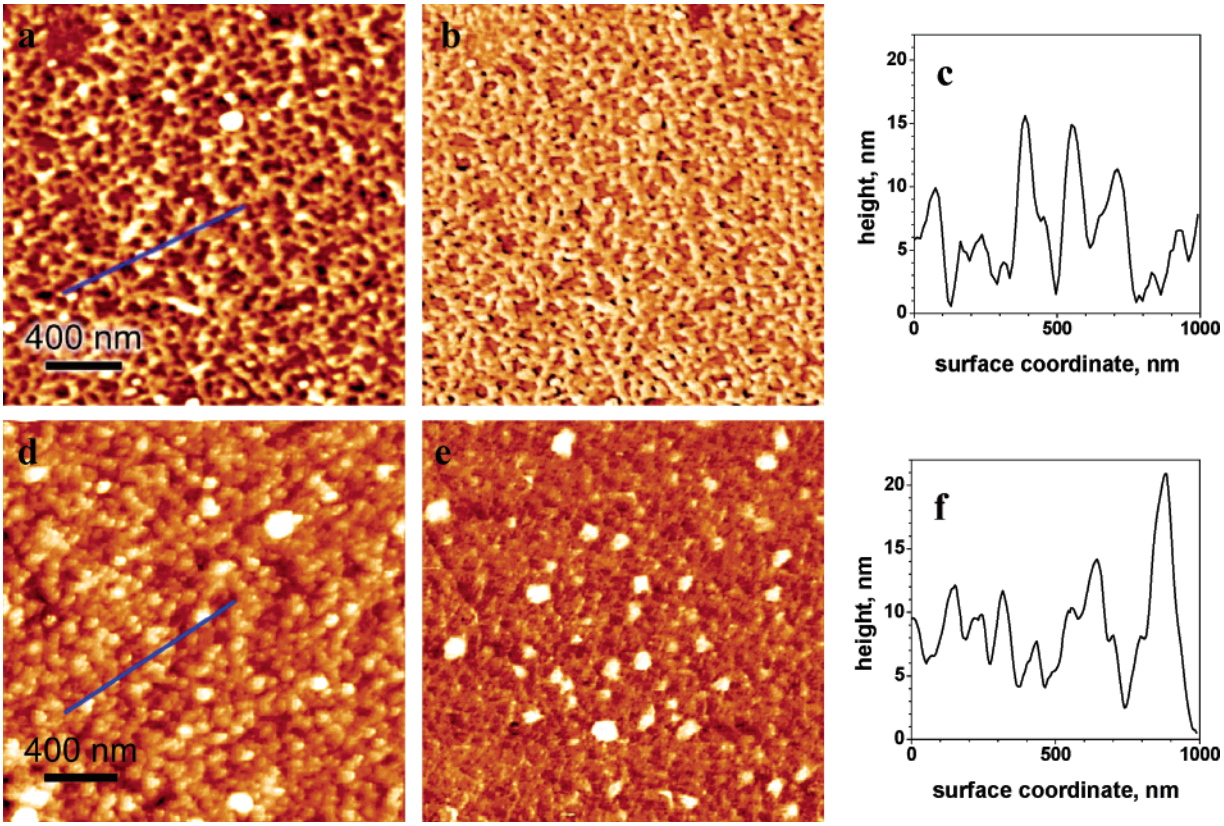

Figure 6. AFM topographical images (a and d), phase images (b and e) (Z range 7° and 30° for b and e, respectively), and cross-sections (c and f) of the hybrid brush (Sample A) in air, rms roughness 3.9 nm (a−c) and under water, rms roughness 4.8 nm (d−f).

hybrid brush-like layer. In this layer, we combine the PDMS brush and the randomly (via side functional groups) grafted EPEI. Our previous reports demonstrated that the grafted-by-side-groups highly branched polymers with different polymer arms (starlike heteroarm block-copolymers) behave similarly to mixed polymer brushes.[26] We speculated that the hybrid layer prepared in this work should behave similarly to mixed brushes. Here we apply the term "hybrid brush" for our mixed system because PDMS is in the brush regime and because the property of the film, as it is shown below, resembles the behavior of mixed brushes.

Morphology of the Hybrid Brush. Ellipsometric mapping shows the macroscopic homogeneity of the hybrid brush. The synthesized film morphology at smaller scales was investigated with AFM (Figure 6a). In AFM images, we observe phase segregation in the mixed brushes, which occurs at a nanoscopic dimension with the apparent average lateral size of domains of about 50−100 nm (rms roughness of 3.9 nm). The size of the domains is overestimated because it is almost impossible for this morphology to perform the deconvolution procedure correctly for the tip curvature radius. However, the observed morphology is in good agreement with the theoretical model of the randomly grafted chains in the brush when fluctuations of a distance between grafting points results in broad distribution of segregated phases by size.[25]

Switching/Adaptive Properties. The hybrid brushes reversibly switch their structure upon exposure to external stimuli, particularly upon change from an aqueous environment to air and vice versa. The mechanism is very similar to mixed brushes. The morphology of the brush obtained under water reveals well swollen bumps (Figure 6d). The phase contrast in the AFM images obtained under water is higher than for that obtained in air (that suggests that two different polymers are probed under water). The water advancing contact angle is 96° (Table 2). The water droplet immediately approaches a ground state and remains unchanged. The receding contact angle is 33°. This is evidence for very high wetting hysteresis (Figure 7). In contrast, the reference PDMS brush demonstrates very small differences between advancing and receding angles. The hybrid brush sample initially immersed in a water bath and afterward extracted from water is wet; water spreads on the surface. All hybrid brushes immersed in a water bath and removed from a water bath indeed show hydrophobic contact angles as soon as water flows out from the surface and the brush begins to dry. Thus, we may suggest that the brush spontaneously switches to a hydrophobic state in the air. This transition is fast (a few seconds). It is noteworthy that our experiments in humid atmosphere (95% relative humidity) showed no change in the wetting behavior of the brush. The samples remained nonwettable in high humidity. Consequently, only contact with water can switch the brush.

Table 2. Characteristics of the Brush Samples

	thickness, nm		volume of clusters, ±0.001 μ^3		water contact angle Θ,[b] ±1 deg				
					dry			swollen	
sample	dry ±1 nm[a]	wet ±2 nm	dry	wet	adv	rec	δ[c]	adv	rec
A	6.9/6.2	14	0.03	0.07	94	38	56	80	29
B	6.2/5.5	10	0.03	0.06	100	52	48	93	51
C	6.2/4.9		0.02	0.03	102	84	18	101	88
D	4.6/4.4	5.8			96	58	38	94	51
PDMS	4.0/4.0	4.0	0.004	0.004	106	103	3	106	103

[a] Ellipsometry/AFM scratch test. [b] adv, advancing; rec, receding. [c] δ = adv − rec.

Evidence for the brush switching mechanism was also collected in AFM measurements of force−distance curves for the

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(26) Lupitskyy, R.; Roiter, Y.; Tsitsilianis, C.; Minko, S. *Langmuir* **2005**, *21*, 8591−8593.

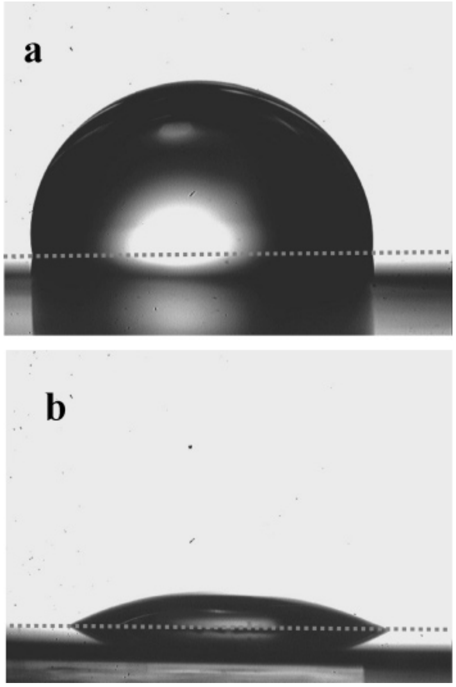

Figure 7. Photographs of advancing (a) and receding (b) drops of water on the hybrid brush (sample A). Dot lines show the border between the drop images and their reflections from the Si-wafer.

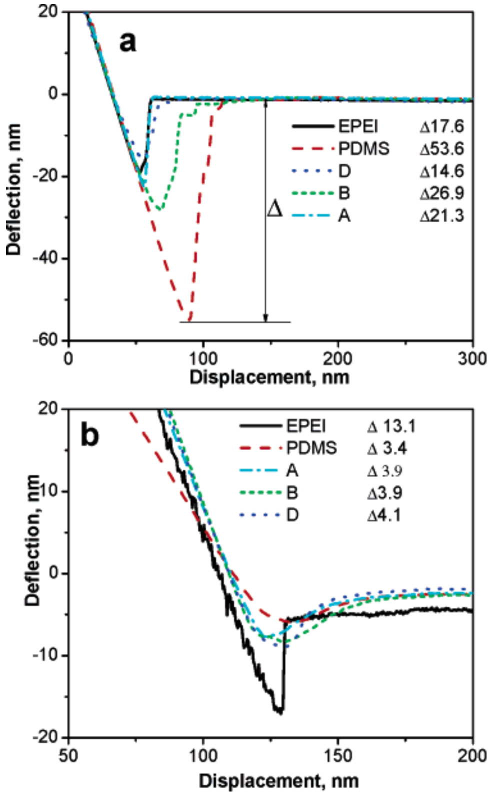

Figure 8. Cantilever deflection vs separation curves (retraction) for the hybrid brushes and the reference brushes (a) under water (all curves were obtained with the same tip), and (b) in air (all curves were obtained with the same tip). Value of Δ is proportional to adhesive force.

interaction of the hybrid brush with AFM tips for dry samples at ambient conditions and under water. In Figure 8, we demonstrate the force−distance plots for the reference PDMS and EPEI homopolymer brushes and the hybrid brush (samples A, B, and D). The measurements demonstrate identical adhesion forces for the reference PDMS and the hybrid brush. The EPEI brush demonstrates an interaction that is twice as strong with the same AFM tip (Figure 8b). Thus, the hybrid brush in air is protected by the PDMS chains.

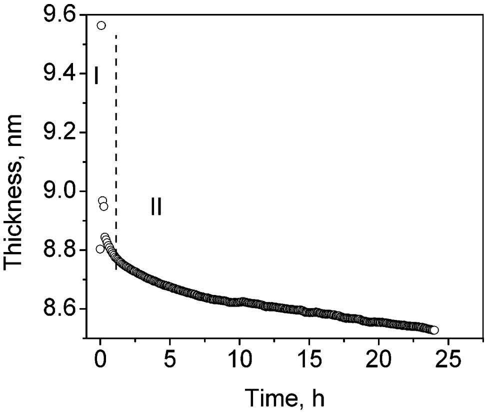

Figure 9. Kinetics of water evaporation from the swollen sample B in air (relative humidity 67%). Fast (I) and slow (II) water evaporation stages.

In water, the inverse situation occurred. The lowest adhesion was obtained for the EPEI reference brush, whereas the highest interaction between the tip and the brush was obtained for the PDMS reference brush. We attribute the obtained result to the effect of the capillary force. After the tip has contacted the sample, PDMS chains form a meniscus that exerts a strong adhesion force.[27] However, the hybrid brush has a poor interaction with the tip close to that for the EPEI reference brush (Figure 8a). Consequently, the hybrid brush under water exposes EPEI chains to the brush−water interface.

Ellipsometry in a liquid cell shows that the brush swells immediately as soon as water is injected into the cell. The swelling kinetics cannot be measured because of a time delay needed for the alignment of the instrument. Deswelling kinetics of the brush in air could be described by two very pronounced regimes of fast and slow water evaporation stages (Figure 9). The brush rapidly loses some fraction of the water Figure 9-I, and then on the second stage, the evaporation of water is slow Figure 9-II. The swelling/deswelling of the brush was also confirmed by AFM data. Using the "flooding mode" of the commercial software, we have estimated the volume of the segregated phases in dry and swollen states (Table 2). The volume of the clusters under water is two to three times higher than that for the dry brush. As soon as the brush is removed from the water bath, the volume of the clusters rapidly decreases to a certain value and remains unchanged for hours.

It is noteworthy that all switching experiments were performed about 30 times with the same samples. All described effects remained unchanged.

Discussion

Based on the experimental data, we suggest the following mechanism of the hybrid brush response. All changes in the brush environment are followed by transitions between segregated phases of PDMS and EPEI. In air, the EPEI clusters are protected by a shell from PDMS chains (Figure 10a; evidence: contact angle > 90°, low adhesion force between AFM tip and the brush). The brush is hydrophobic in air (even at 95% relative humidity). Water droplets on the surface of the hybrid brush remain trapped in a metastable state. The contact line is pinned by the protruded EPEI chains of the brush−water interface underneath the droplets

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[27] Cappella, B.; Dietler, G. *Surf. Sci. Rep.* **1999**, *34*, 1−104.

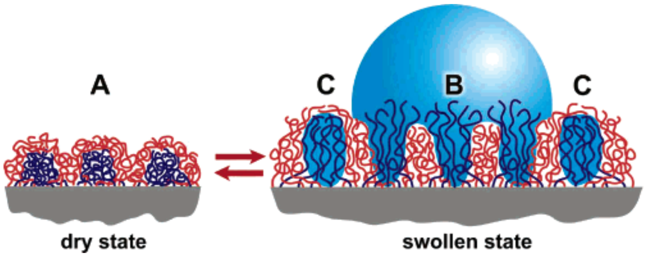

Figure 10. Schematic of the responsive behavior of the hybrid brushes: in air the brush is segregated and consists of EPEI clusters surrounded by PDMS chains (a), under water EPEI chains perturb through the film (b), and swollen film in air forms a swollen EPEI layer covered by a PDMS layer segregated to the top (c).

and cannot overcome the activation barrier created by the PDMS chains exposed to the brush-air interface near the contact line. Under water, the EPEI clusters swell and the polymer protrudes to the brush water interface (evidence: very high wetting hysteresis, adhesion force between the AFM tip and the brush is consistent with EPEI on the surface, AFM morphology shows swollen clusters, phase contrast in AFM images increases as compared to that obtained in air). Thus, the brush surface under water is hydrophilic (Figure 10b). As soon as water is removed from the brush surface, the brush rapidly loses some fraction of the water and indeed remains swollen (evidence: ellipsometry and AFM data prove that the brush is swollen but less than under water). The brush surface is immediately healed by the PDMS chains and switches from hydrophilic to hydrophobic (evidence: the sample extracted from water is wet, water spreads on the surface, but upon drying, the surface rapidly switched to nonwetting, contact angle >90°). The swollen EPEI is hidden by the PDMA protective shell (Figure 10c). In air, the brush loses water slowly until an equilibrium state is balanced by humidity in the air (evidence: slow water-release kinetics).

Consequently, the hybrid brush is hydrophilic because of two mechanisms: (1) exposure of EPEI chains to the brush−water interface under water and (2) retention of some fraction of water by swollen EPEI chains (the EPEI chains swell by 2−3 times), which are covered by PDMS chains in air. At the same time, the hybrid brush is nonwettable because water droplets are trapped in a methastable state when the water contact angle is above 90°.

The response of the brush depends on the composition and total grafting density. The increase of the PDMS fraction in the brush (compare samples B and C with the sample A) results in a less pronounced wetting hysteresis for dry films (see δ values in Table 2). However, the decrease of the grafting density of the polymers (sample D) results in the increased difference between advancing and receding contact angles. The less dense brush (sample D) is easier permeable for solvents. Thus, we may speculate that water can switch the brush if diffusion of water molecules can be realized through the thin PDMS coating in the less dense brush. An increase of the PDMS thickness will block the switching effect.

Conclusion

In summary, adaptive hybrid polymer brushes were synthesized on a Si substrate with the chemisorbed GPS via the sequential grafting of an amino-terminated PDMS on the first step and then a ethoxylated polyethylenimine on the second step. The combinatorial approach for synthesis of gradient brushes revealed a strong effect of “layer assisted tethering,” which allowed us to synthesize hybrid brushes twice as thick as the reference homopolymer brushes. The synthesized films that are macroscopically homogeneous possess phase segregation at the nanoscopic level and show switching behavior. The film response to the change of surroundings was detected with AFM, ellipsometry, and contact angle measurements. The hybrid brush can be rapidly switched from hydrophobic to hydrophilic surface energetic states and vice versa by dipping the brush in water and drying it in air at room temperature, respectively. The brush combines two opposite properties: the brush is nonwettable by water in air and the brush is hydrophilic and absorbs water when in contact with water.

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