Switching of Polymer Brushes

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Switching of Polymer Brushes

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Polymer coatings of brushlike monolayers composed of two different polymers, polystyrene and poly-
(2-vinylpyridine), are grafted by radical polymerization on the surface of silicon wafers. Thickness, grafting
density, molecular weight of grafted chains, and the composition of the coatings were regulated by grafting
time, monomer concentration, and additional initiator in solution. A typical dry film thickness is between
10 and 100 nm, and the molecular weights of the components range from 100 to 300 kg/mol. The fabricated
coatings turn out to be sensitive to the composition of the environment. For instance after exposition to
toluene the layer becomes hydrophobic and the top of the layer is covered by polystyrene. After exposition
to HCl the layer becomes hydrophilic with polyvinylpyridine in the upper layer. This reconstruction of the
polymer layer was observed with contact angle and X-ray photoelectron spectroscopy measurements. The
composition of the top layer in different media is controlled by the composition and molecular weight of
the two polymers in the coating. The "switching" properties of the coating are shown to be reversible.

1. Introduction

Tethered polymer layers are interesting from a theoretical and practical point of view[1] and were shown to be effective for the colloidal stabilization,[2] size exclusion chromatography,[3] control of adhesion,[4] lubrication,[5] and many other applications.

The aim of this work is the fabrication of heterogeneous (with respect to composition) polymer brushlike layers (HPB) chemically tethered to a solid substrate and composed of two incompatible polymers and the study of their properties in selective and nonselective solvents. Chemically grafted polymer chains of different chemical nature statistically distributed on the substrate are not able to form separated macrophases and are in that respect similar to block copolymers. However, we assume that the interaction of the polymers with a selective solvent might cause a change of surface properties of the HPB when one of the two polymers would preferentially occupy a top layer. The osmotic driving force would push the swollen chains out of the collapsed layer of the second polymer. With this mechanism one can approach unique opportunities to change the surface properties of polymer coatings as a response to the change of the surrounding media. We may speculate that this behavior can extend

diverse applications of polymer coatings for various industrial problems and used for the fabrication of new smart materials. Such a mechanism can be effective if the polymer chains are covalently bonded to the substrate. Most effective would be tethered layers in the regime of brushlike conformations, when the substrate is completely covered with a relatively dense monolayer of stretched grafted chains.[1] It was shown theoretically[6] and experimentally[7,8] that the brush collapse proceeds continuously as the solvent quality decreases, which is in contrast to the discontinuous phase separation of bulk (diblock co-)polymers or the collapse at the coil−globular transition of isolated polymer chains. Consequently, one may achieve to approach a great variety of surface properties of the HPB by changing solvent quality or temperature.

There are two methods for the fabrication of tethered polymer layers: (1) grafting of telechelic polymers to a solid substrate and (2) grafting from the substrate using a polymerization process initiated from the solid surface. The fabrication of tethered polymer layers in the brushlike regime by the "*grafting to*" process is limited due to the kinetic reasons. Usually one can reach the concentration regime where the chains start to overlap on the surface which corresponds to the beginning of a brush formation.[9] The amount of grafted polymer does not exceed approximately $2-10$ mg/m^2. It was reported that a big amount of polymer can be grafted on the surface using polymerization from the substrate.[8,10−16] The most common

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Scheme 1. Schematics of the Chemical Reactions for the Attachment of the Azo-Initiator to the Surface of the Si Wafer
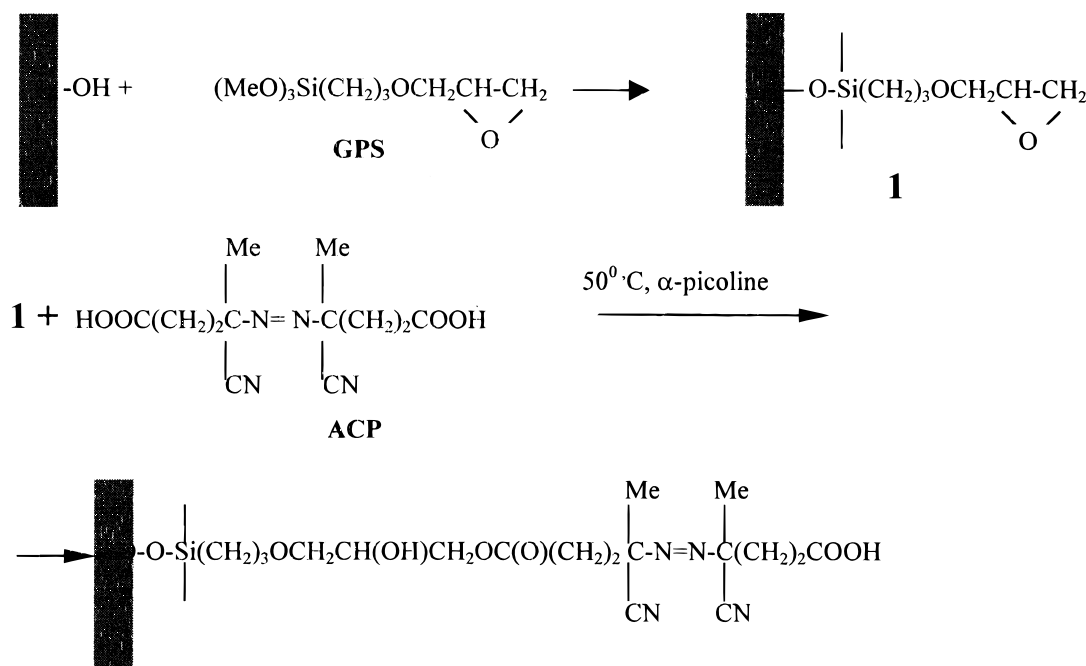
way of the "*grafting from*" process includes the introduction of an initiator for radical polymerization into a substrate surface usually using silane chemistry where a dense monolayer of initiator on metal or silicon oxide surfaces can be formed.[17] In the next step the grafting of vinyl monomer is performed from solution or gas phase. Several regimes of the process were identified. There are two limiting cases for the reaction: (1) the grafting levels off at relatively small grafting amount or (2) the grafting runs with self-acceleration, when the layer grows by the mechanism of frontal polymerization. Detailed analysis of the morphology of the grafted layers,[18] modeling the kinetics,[19] and study of the mechanism[20,21] allowed to explain the role of different side reactions on the grafted layer formation. By appropriate choice of monomer concentration, temperature, and additional initiator (non-attached to the solid substrate), it seems to be possible to find a regime where formation of thick grafted monolayers is possible.

2. Experimental Section

2.1. Materials. *Monomers:* Styrene (Merck) and 2-vinylpyridine (2-VP, Aldrich) were purified with an ALOX B chromatographic column and distilled under reduced pressure under argon.

Solvents: Toluene, tetrahydrofuran (THF), and 1,4-dioxane were distilled after drying with sodium. Dimethyl sulfoxide (DMSO) was distilled under reduced pressure after drying with calcium hydride. Methanol was used as received.

Initiators: 4,4′-Azobis(4-cyanpentanoic acid) (ACP) from Aldrich and 4,4′-azobis(isobutyronitrile) (AIBN) from Fluka were purified by recrystallization from methanol. All reagents were used immediately after purification.

Silicon wafers obtained from Wacker-Chemitronics are composed of silicon (100) crystals, and the top natural SiO$_2$ layer is typically 1.6 nm thick. The thickness of the SiO$_2$ layer was determined with ellipsometry for every sample. The following cleaning procedure was used to ensure the reproducibility of the results:[22] 2 cm × 2 cm pieces cut from the wafer were rinsed with dichlormethane in an ultrasonic bath at 30 °C for 15 min, then they were rinsed with the 10% aqueous oxidizing solution (50:50 mixture of 25% NH$_3$ water solution and 35% H$_2$O$_2$ water solution) at 80 °C for 25 min, and then the wafers were rinsed in water (Millipore) and dried in a flow of dust-free nitrogen.

2.2. Attachment of the Initiator. The introduction of the azo initiator onto surface of the Si wafer was performed according to the method described by Tsubokawa et al.[23] In the first step the Si wafers were treated by 3-glycidoxypropyltrimethoxysilane (GPS) (Aldrich) from 5% solution in toluene for 8 h. Then the Si wafers were washed by methanol. On the next step ACP was introduced on the surface of the Si wafers from 2% solution in DMSO with a catalytic amount of α-picoline (Aldrich) at 50 °C for 5 h. The resulting samples of Si wafers with chemically attached initiating groups (Scheme 1) were rinsed six times with freshly distilled THF.

2.3. Grafting Procedures. Oxygen was removed from the solution of monomer (styrene or 2-VP, 5 to 6 mol/L) and AIBN[24] at a concentration of (5 to 9) × 10^{-4} mol/L in 1,4-dioxane using five freeze−pump−thaw cycles. The samples of the Si wafers with the chemically attached initiator were placed in monomer solution under argon atmosphere at a glass flask. The flasks were immersed in a water bath (60 ± 0.1 °C) for various periods (1−40 h). The ungrafted polymer was obtained by precipitation in methanol. The Si wafers were rinsed six times with THF.

In the next step the same procedure was used to graft the second polymer using the Si wafer with the first grafted polymer. The ungrafted polymers were removed by a Soxhlet extraction with THF. We found out that 4 h of Soxhlet extraction was enough to reach the constant mass of the polymer coating. However we selected the two times larger extraction time of 8 h.

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(24) AIBN was used as an additional initiator in the volume to control molecular weight of grafted chains (see refs 18−21).

We assumed that molecular weights of the grafted and ungrafted polymers (PS and PVP) are similar. It was reported in the literature that the polydispersity of grafted polymers is larger than that for ungrafted,[15,25] while there are contradictions concerning molecular weight. Molecular weight for the grafted chains was found to be smaller[26,27] or of the same value[12,25] as for the ungrafted polymer. Obviously, it depends on the particular mechanism of the polymerization. Anyway, there is a relationship between both molecular weights. For the case of similar conditions of the grafting process we may expect that molecular weight of ungrafted polymer can be used as a reference value to estimate molecular weight of the grafted chains. Molecular weights of ungrafted PS and PVP were determined by gel permeation chromatography (GPC) technique. In this paper we refer to number average values of molecular weight (M_n).

2.4. Ellipsometric Measurements. Null ellipsometry was used to measure the adsorbed amount of the initiator as well as the grafted amount of PS and PVP on the Si wafers.

The measurements were carried out with a computer-controlled null ellipsometer in a vertical polarizer–compensator–sample analyzer (PCSA) arranged as described elsewhere.[28] A He–Ne laser ($\lambda = 632.8$ nm) was used as a light source. The angle of incidence was fixed at 70.0°.

For the data interpretation, a multilayer model of the coating was assumed. This model considers the coating as a sandwich-like structure with the following layers: Si wafer with a top silica layer, adsorbed initiator, and a grafted polymer layers. In this layer model, the substrate is characterized by means of ellipsometry (thickness of SiO_2 layer was measured for every specimen as well as the initiator layer).

Two parameters of the grafted polymer layer, refractive index n_1 and thickness d_1, can be obtained from the following relationship:

$$e^{i\Delta} \tan \psi = R_p/R_s = F(n_k, d_k, \lambda, \phi) \qquad (1)$$

where R_p and R_s represent the overall reflection coefficients for the basis p- and s-waves. They are a function of n_k and d_k, which are the refractive indices and thickness of each layer, respectively. λ is the wavelength and ϕ the incident angle. Measurements of a pair of the ellipsometric angles Δ and ψ allow the evaluation of the above-mentioned two unknown parameters.[29] Thickness of the grafted brushes was measured for the dry layers with accuracy 5%. In this case we may assume that layer density is the same as that for bulk polymer and calculate the grafted amount of the polymers. The details of ellipsometric data computation are given elsewhere.[25,26]

2.5. Infrared spectroscopy characterization of polymer coverings was performed with a Nicolet-730 FTIR spectrometer in transmission mode (4000 scans, resolution 2 cm^{-1}). The Si wafers with the chemically attached initiator were used as a reference.

2.6. Contact Angle Measurements. Static contact angles Θ of water (Millipore) were determined with the sessile drop method. The measurements were carried out after 1 min of equilibration of the drop shape. The contact angles in such a short period of time were selected as reference values because of the reconformation of the HPB layer and slight swelling of PVP chains induced by water. In this case the contact angle is not an equilibrium value and reflects the composition of a top layer of the HPB in the initial moment.

For each sample three to five successive measurements were made. In most cases, the root-mean-square (rms) deviation did not exceed 2°. The relationship between contact angle and fractions of Si wafer surface covered by polymers can be evaluated
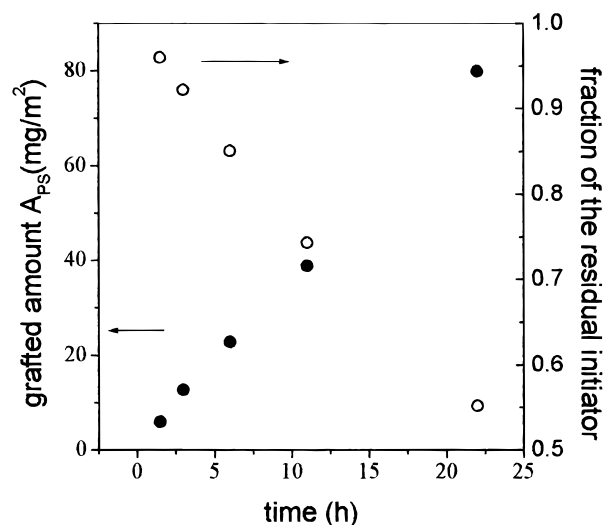

Figure 1. Grafted amount of PS (open circles) and fraction of the residual initiator (solid circles) on the Si wafer as a function of polymerization time.

by the Cassie–Baxter equation:[30]

$$\cos(\Theta) = \varphi_1 \cos(\Theta_1) + \varphi_2 \cos(\Theta_2) \qquad (2)$$

where Θ is the contact angle on the surface of grafted layer, Θ_1 and Θ_1 are the contact angles of wetting of polymer 1 and 2, respectively, and φ_1 and φ_2 is the fraction of the polymer 1 and 2 on top of the grafted layer, respectively. We assume here that the Si wafers are completely covered with grafted layers and that there is no uncovered area of the bare surface of the wafer for the wetting liquid. This situation was found for PS and PVP coatings above the grafted amount of 4 and 7 mg/m^2, respectively, by comparing contact angles on grafted layers and on the surface of corresponding polymers (91° for PS and 66.7° for PVP) and Si wafers coated with the initiator (to be 37.5°, 38.1°, and 36.9° ± 0.5° after rinsing with THF, toluene and water, respectively).

2.7. X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed using a setup "Multitechnique 5600CI" from Physical Electronics, Minnesota, with spherical multichannel analyzer and Mg Kα radiation (maximum at $E = 1253.6$ eV).

3. Results

Grafting. The synthesis of HPB was performed in three stages: (1) *Immobilization of the initiator* on the substrate surface was carried by subsequent treatment of the Si wafers with GPS and with ACP (Scheme 1). Ellipsometric measurements allowed us to estimate the amount of chemisorbed GPS. Using the refractive index of GPS ($n = 1.429$ from ref 31), the typical amount of chemisorbed GPS was evaluated to be $(1.5 \pm 0.5) \times 10^{-5}$ mol/m^2.

(2) *Grafting of monomer 1* is performed by in situ radical polymerization initiated from the substrate surface. The amount of the grafted polymer and residual initiator on the surface depends on time of polymerization. An example of the kinetics of the grafting of styrene in terms of grafted amount of PS (A_{PS}) vs time of polymerization is presented in Figure 1 (solid circles). The concentration of the residual ACP on the surface of the Si wafer during the polymerization may be evaluated (Figure 1, open circles) using the kinetics of the first-order decomposition reaction with the rate constant $k_d = 7.5 \times 10^{-6}$ s^{-1} at 60 °C, since it was

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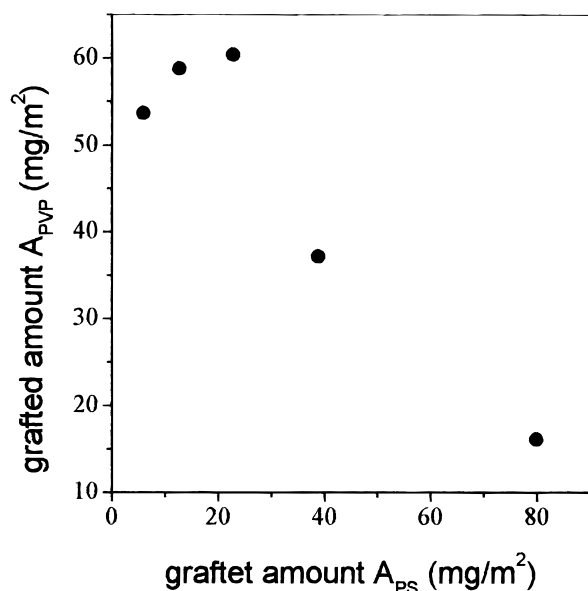(31) Elender, G.; Kühner, M.; Sackmann, E. *Biosensors Boielectron.* **1996**, *67*, 565.

Figure 2. Grafted amount of PVP obtained after the second step of grafting as a function of the grafted amount of PS obtained on the first step of grafting.

Figure 3. FTIR spectra of grafted layers of (a) PVP and PS and (b) HPB composed of these two polymers (at ratio1:1). The spectra were normalized numerically for the thickness of 1 nm.

shown previously that for this case the decomposition of ACP is the same as that in solution.[8,14]

Finally, (3) the *grafting of the second monomer* was carried out after the first grafting procedure was finished and ungrafted polymer was washed out. In this case we use the residual ACP on the surface to initiate the polymerization of the second monomer. We present in Figure 2 the grafted amount of the second monomer 2-VP (A_{PVP}) as a function of the PS grafted on the first step of the procedure. Comparing the data of Figure 1 and Figure 2 we may conclude, that the amount of the second grafted polymer decreases as the amount of the first grafted polymer increases and as the amount of the residual ACP decreases. Combining the first and second step one may change the ratio between the two grafted polymers.

In addition to the ellipsometric measurements the composition of the grafted layers was analyzed by FTIR investigations. Spectra of the individual grafted PS and PVP layers are presented in Figure 3a. The spectra are normalized for 1 nm layer thickness. The spectrum of the combined grafted layer which consists of two grafted polymers is shown in Figure 3b. The very well pronounced differences in the spectra of the individual polymers at 1400–1750 cm^{-1} (aliphatic $-C-C-$ bonds) and 2750–3200 cm^{-1} (aromatic rings) allowed us to analyze the composition of the layer. The characteristic bands of individual polymers are present in the spectra of the HPB layer. We use the intensities of these bands for the calculation of the fractions of both polymers in the layer. The layer composition and total amount of the grafted polymers in HPB (A_{HPB}) evaluated from the ellipsometric and FTIR measurements for different experiments are presented in Table 1. Here we list the grafted amount of the layer with the grafted PS from the first step, A_{PS}, and the grafted amount of PVP, A_{PVP}, from the second step, where the sample is denoted by PS−PVP. We also prepared layers in the opposite order, first PVP and then PS, which we denote by PVP−PS. From the data of Table 1 one can conclude that the results of two preparation methods are in good agreement for most cases. Some differences between the ellipsometric and FTIR data are obtained for the sample PVP−PS. We may speculate that in this case ungrafted PVP from the first step was not washed out
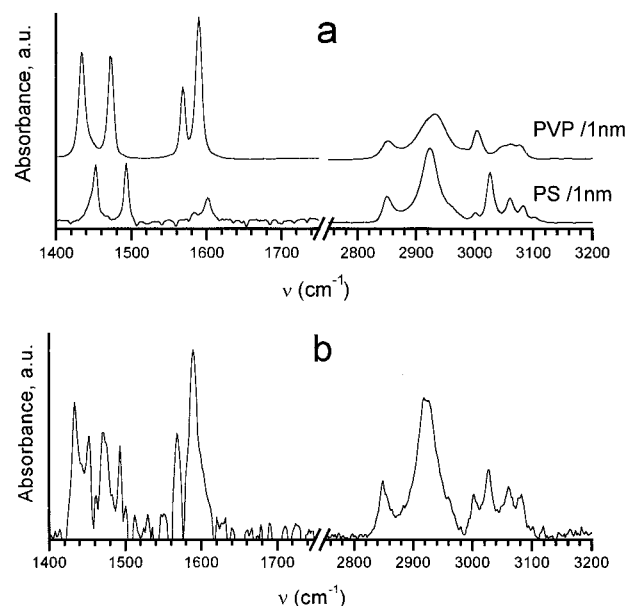
completely because of the strong affinity of PVP to the silica surface. Consequently, ellipsometric data overestimate the amount of the grafted PVP. In the second step the ungrafted PVP may be removed from the layer during grafting of the PS.

Switching Properties of the Layers. Switching properties of the layers synthesized are observed using contact angle measurements and XPS. The switching properties are caused by the different behavior of PS and PVP chains in the solvents which are selective for one or the other polymer. The selective solvent swells the chains of one polymer while chains of the other polymer adopt a collapsed conformation. Consequently we may assume that the composition of the top layer of the HPB depends on solvent. Such behavior might be detected with contact angle measurements using water as a probe liquid. Water is a poor solvent for PS. For the case of contact angle measurements on the surface of the protonated PVP layer we may assume that protons are released in the water drop. Since there are only few protons compared to water molecules, the equilibrium might be shifted to the side of the nonprotonated PVP. We used a very rough model calculation to evaluate degree of protonation of the PVP brush under the drop of water. From the magnitudes of a drop volume (0.01 cm^3) and contact angle (in the case of PVP brush 12°) using the expression for the spherical segment volume and the relationship between the drop size and contact angle ($tg(\theta/2) = h/R$, where h and R is the height and radius of the drop) we calculate the surface of the PVP brush capped by the drop (0.3 cm^2). Assuming that all the layers under the drop can release protons, we calculate the apparent concentration of the 2-vinylpyridine units in the drop for the 50 nm thick brush ($C_{VP} = 0.0015$ mol/L). On the next step we calculate the degree of protonation and pH in the drop using the Henderson−Hesselbach equation: $pK_\alpha = pH + n\log((1 - \alpha)/\alpha)$, where $\alpha = \alpha'-[H^+]/C_{VP}$, pK_α is the apparent constant of protonation for PVP, and α and α' are degrees of the dissociation and neutralization, respectively. We use the following magnitudes: $pK_\alpha = 2.3$ and $n = 2$. We take $\alpha' = 1$. The brushes are treated by 0.1 N HCl, but even in this conditions it is hardly probable to reach such a large degree of protonation. Usually it is lower. We obtained pH = 3.9,

Table 1. Composition of the HPB Obtained from Ellipsometry and FTIR Data

	ellipsometry data				FTIR data			
sample	A_{PS}, mg/m²	A_{PVP}, mg/m²	A_{HPB}, mg/m²	fraction of PS	A_{PS}, mg/m²	A_{PVP}, mg/m²	A_{HPB}, mg/m²	fraction of PS
PVP	0.0	17.4		0.00	0.0			0.00
PVP−PS	4.0	7.5	11.5	0.35	4.7	5.0	9.7	0.48
PS−PVP	4.2	4.3	8.5	0.49	4.1	4.1	8.2	0.50
PS−PVP	2.0	25.0	27.0	0.07	0.9	25.2	26.1	0.03
PS	52.2	0.0		1.00		0.0		1.00

Table 2. Contact Angles of Water on Top of HPB Exposed to Various Solvents

		contact angles $\Theta \pm 0.5°$			
sample	fraction of PS in the layer	after THF	after acidic bath	after toluene	after THF
1	PS	1	91.0	91.1	91.8	91.0
2	PVP	0	66.4	12.5	67.1	66.6
3	PS−PVP	0.10	67.2	15.0	67.7	67.5
4	PS−PVP	0.18	68.7	14.3	76.0	69.3
5	PS−PVP	0.27	72.5	13.8	81.3	71.5
6	PS−PVP	0.50	82.5	16.5	87.5	81.5
7	PS−PVP	0.83	90.1	40.8	90.5	89.1

$\alpha = 0.9$. It is known[33] that PVP is soluble at pH<4 and α<0.95. Consequently, in this experiment PVP is in the transition area between soluble and insoluble states. We choose the "hard" conditions in this quantitative evaluation. In most experiments we studied the HPB, where concentration of PVP is smaller and contact angle is larger and, consequently, C_{VP} is several times smaller. Besides, the brushes are usually rinsed for a few seconds with water and dried after treatment with HCl. Consequently, we may accept that α' is smaller than 1 in the real experiments. It is noteworthy that pK_α values of organic functional groups with basic properties are usually smaller on the surface as compared to solution.[34] Hence, we may assume that in most experiments pH > 4 and the PVP brush might be only slightly swollen by water.

Thus we suppose that surface properties of thee HPB are not changed by a water drop which sits on top of the layer during the very short time of the measurement (1 min). The data obtained from the contact angle experiments for HPB of different compositions are presented in Table 2.

The contact angles on the pure PS grafted layer are the same after treatment of the layer with different solvents. The PVP grafted layer already shows some switching properties. The contact angle decreases dramatically after treatment of the layer by 0.1 N hydrochloric bath due to the reaction of pyridine nitrogen with HCl which yields the protonated PVP chains largely swollen in water. However, subsequent treatment with different organic solvents does not change the wettability of the PVP layer which can be switched to the initial state again after an alkaline bath. Completely different behavior was observed in the case of HPB. The layers are very sensitive to the solvents and wettability differs after every treatment by a new solvent. The most pronounced effect is observed for the layers composed of 20−50% of PS. We take as an example the HPB composed of 27% of PS. After the synthesis and rinsing in THF the contact angle of water on top of the layer is 72.5°; the contact angle after treatment in toluene is switched to 81.3°. Protonation in an acidic bath results in a 13.8° contact angle. The behavior thus switches from hydrophobic to hydrophilic by the

exposition of the layer to different solvents. Finally, it is very important to note that after rinsing in an alkaline bath (0.1 N NH₄OH) and in THF the layer properties return back to the origin state with the contact angle of 71.5°. We repeated this exposition cycle three times and obtained the same results.

The switching properties of the HPB can be discussed very nicely if we recalculate the values of contact angles in the fraction of PS on a top layer of the HPB using the Cassie equation. In Figure 4 we present the data of two series of the experiments in different conditions of the grafting polymerization. For the data of Figure 4a the molecular weights of PS and PVP grafted chains were approximately of the same magnitude (210K and 230K g/mol, respectively). For the data presented in Figure 4b the molecular weight of PS chains is three times larger than that of PVP chains (300K and 100K g/mol, respectively).

The data of Figure 4a show that after THF treatment the HPB composed of 50% of PS has 60% of PS monomers on top. Exposition to toluene switches the composition of the top layer to approximately 95% of PS, while exposition to 0.1 N HCl solution changes the composition to less than 5% of PS on top. Neutralization with ammonium hydroxide, rinsing with water, and exposition to THF return the layer properties back to the initial stage. Other HPB layers of different compositions in that range show quite similar behavior.

If the molecular weight of PS chains is larger than the PVP chains in HPB the whole picture is shifted to the area of smaller fraction of PS (Figure 4b). In this figure we demonstrate also the effect of the rinsing of the protonated HPB with ammonium hydroxide solution. After this procedure the fraction of PS at the surface decreases even more. We may speculate that this difference is caused by different behavior of protonated (H−PVP) and neutralized PVP in water. In the first case positively charged H−PVP segments repel one another and their concentration in a top layer is limited by this repulsion effect. In the second case PVP is not soluble in water and can approach a collapsed conformation. Water is even a worse solvent for PS. Consequently the top layer of HPB consists of collapsed PS chains covered by collapsed PVP chains. During neutralization some additional amount of PVP can occupy a top layer because the repulsion effect disappears and PVP has a larger affinity to water than PS.

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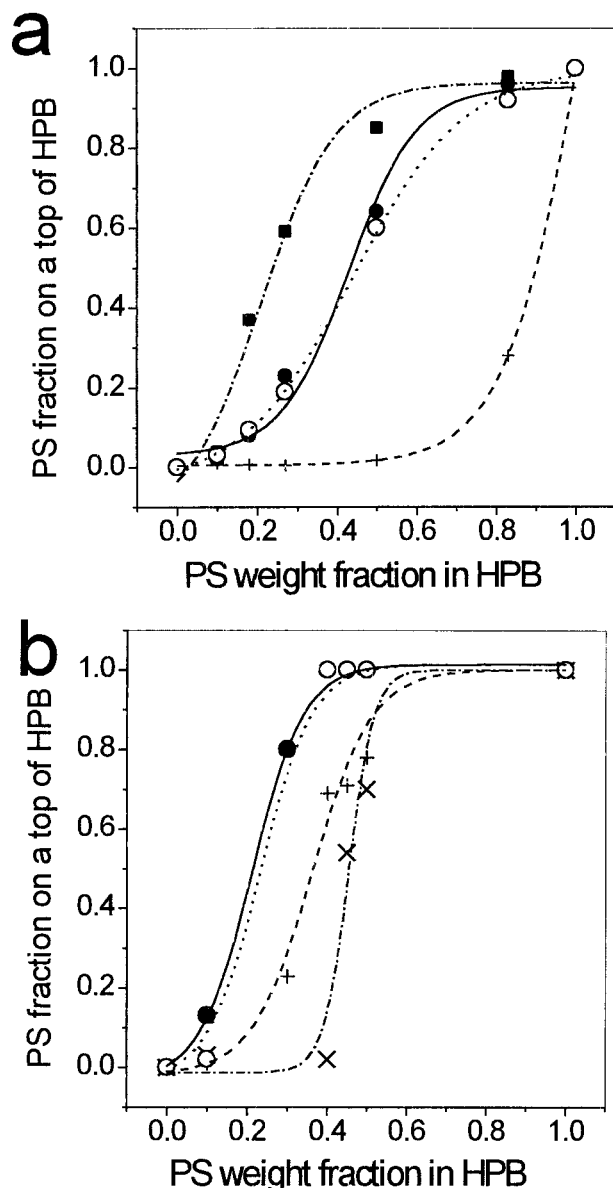
Figure 4. 4 Composition of a top HPB layer as a function of the HPB composition after exposition of the layers to different solvents as calculated from the contact angle measurements: after 1,4-dioxane (full circles); after 0.1 N HCl water solution (crosses +); after NH4OH washing out (crosses ×); after 1,4-dioxane again (open circles). (a) The HPB samples obtained in the following grafting procedure: PVP grafting (0.7×10^{-3} mol/L of AIBN, 4.5 mol/L of 2-VP), then PS grafting (0.7×10^{-3} mol/L of AIBN, 5.3 mol/L of styrene). The grafting temperature in both cases is 60 °C; solvent is 1,4-dioxane. The HPB layer thickness is in the range of 10−30 nm. M_n of PS samples is 300K, M_n of PVP samples is 100K. (b) The HPB samples obtained in the following grafting procedure: PS grafting (0.8×10^{-3} mol/L of AIBN, 5.0 mol/L of PS), then PVP grafting (0.8×10^{-3} mol/L of AIBN, 6.0 mol/L of 2-VP). The grafting temperature in the both cases is 60 °C; solvent was 1,4-dioxane. The HPB layer thickness is in the range of 60−100 nm. M_n of PS samples is 210K; M_n of PVP samples is 230K.

To prove the switching in the HPB we performed XPS analysis of the samples after exposition to different solvents. The spectra presented in Figure 5 were recorded for emission angle of 45°. The XPS spectra originate from a region close to the surface, where the signal is averaged over the emission depth of the electrons with an exponentially decaying contribution with increasing depth. For the given materials and energies this corresponds to a depth of examination of about 7 nm. Spectra of the grafted
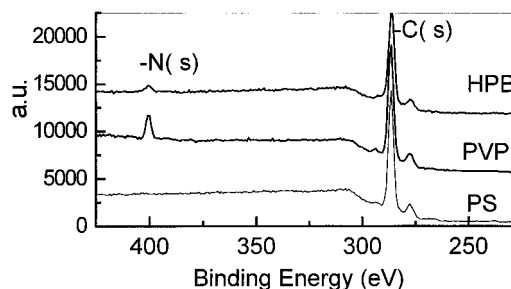

Figure 5. XPS spectra (at the emission angle 45°) of samples of the PS, PVP, and HPB grafted layers.
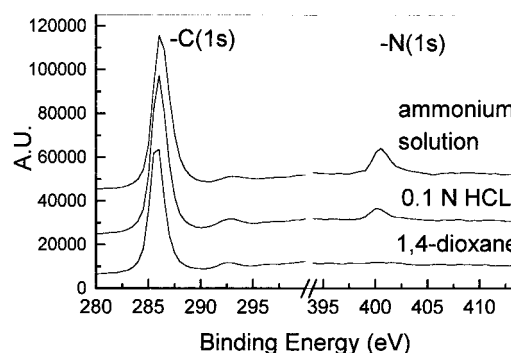

Figure 6. XPS spectra (at the emission angle 5°) of the HPB after exposition to different solvents: 0.1 N ammonium solution, 0.1 N HCl, and 1,4-dioxane.

Table 3. XPS Data: Ratio N1s (401 eV):C1s (286 eV) for Different Emission Angles

solvent	5^0	10^0	15^0
1,4-dioxane	0.021	0.012	0.009
0.1 N HCl	0.092	0.068	0.072
0.1 N NH4OH	0.192	0.204	0.247

PVP and HPB contain a N1s peak at 401 eV, while there is no such peak in the spectra of the grafted PS. Differences of intensity of the N1s peaks (at an emission angle of 5°) for the HPB exposed to different solvents are shown in Figure 6.

The data of the angle-resolved scans at different emission angles are shown in Table 3. Changing the emission angle changes the depth sensitivity of XPS according to a sin β law, where β is the emission angle of the electrons (corresponding to the angle between substrate and detector). Consequently the XPS spectra at an emission angle of 5° are very surface sensitive and originate from a surface layer of less than 1 nm. We present the ratio between two peaks N1s and C1s, which reflect the relative concentration of PVP chains in different depth from the surface of the HPB. The largest variation of the values was obtained for the emission angle of 15°. The data demonstrate the tendency of an increasing PVP concentration in a top layer of the HPB after 0.1 N HCl solution and ammonium hydroxide solution treatment. Consequently, XPS data are in good agreement with contact angle measurements.

4. Discussion

The results of contact angle and XPS experiments clearly demonstrate that the surface properties of the mixed layers can be tuned in a wide range. For a given dry layer contact angles with water may be obtained, which range between 14° and 81° depending on the previous treatment. All intermediate values may be obtained as well, and the values can be reversibly changed back to previous ones.

The changes are achieved by the exposition of the layers to different solvents, where those solvents are selective for the different components of the layer. Thus toluene is a good solvent for PS, but a worse solvent for PVP, while HCl can react with PVP, which makes it a good solvent for H−PVP, while it is a nonsolvent for PS. THF is in between. It is therefore reasonable to assume that the observed changes in the surface properties of the layers after drying are connected with a reorganization of the structure of the HPB due to the interaction with the solvent. This is confirmed by the XPS experiments, where different surface compositions of the layers after different treatments have been detected.

The first question concerns the structure of the HPB on a molecular level after preparation. One may assume in principle different possible models for the location of PS and PVP chains in the HPB synthesized. We should keep in mind that the polymerization is performed by a radical initiation process, where after the thermal initiation in the attached initiator monolayer always one chain is growing relatively fast at a particular polymerization site. To a good approximation those sites can be assumed to be statistically distributed on the surface, and each individual initiation and growth process will be essentially independent from previous ones. Due to the stepwise polymerization procedure and the strong incompatibility of the two components, the two-step grafting procedure may still cause a layer-by-layer structure, where the second polymer would be situated mostly on top of the first polymer layer or, alternatively, to a laterally statistical distribution of mixed PS and PVP chains within the layer, where each chain may be phase separated from the opposite ones on a molecular scale. The results of contact angle measurements and XPS contradict the first model. They show that chains of both polymers can be on top of the HPB depending on the solvent. Consequently, we accept the model of a brushlike polymer layer with laterally statistically distributed chains of the two kinds. The proposed structure is very schematically depicted in Scheme 2a. The structure should be of course more complex, and the grafting sequence of different chains in a particular direction will be statistical.

The phenomenon of "switching" of HPB surface behavior gives additional evidence of the structure. An exposition of HPB in a selective solvent for PVP polymer results in swelling of PVP chains while PS chains approach a collapsed conformation. Due to the osmotic pressure PVP chains are forced out to the top of the HPB (Scheme 2). The subsequent very fast drying procedure freezes the distribution of polymer chains in the HPB, which is detected with contact angle or XPS measurements. If we use a selective solvent for PS, the inverse behavior for the HPB is observed. A degree of coverage at the surface of the HPB by one or the other of the polymers depends on composition of the HPB and on the solvent used. One can conclude from the pictures in Figure 3a and Figure 3b that this coverage can be adjusted to any desirable value. The reversibility of the switching is also an additional feature of the model of the HPB.

As a consequence we can explain the switching behavior of the HPB by a purely physical reorganization of the layer structure, which offers a large variety of possibilities for surface manipulation of thin polymer layers. In the presented case a switching between hydrophobic and hydrophilic behavior has been demonstrated, but in principle also different chemical species, biologically,

Scheme 2. Schematics of the Molecular Structure of the Grafted Layer in Different Environments and Principle of Switching Properties: (a) Structure in a Nonselective Solvent, (b) in a Selective Solvent for Polymer P1, and (c) in a Selective Solvent for Polymer P2
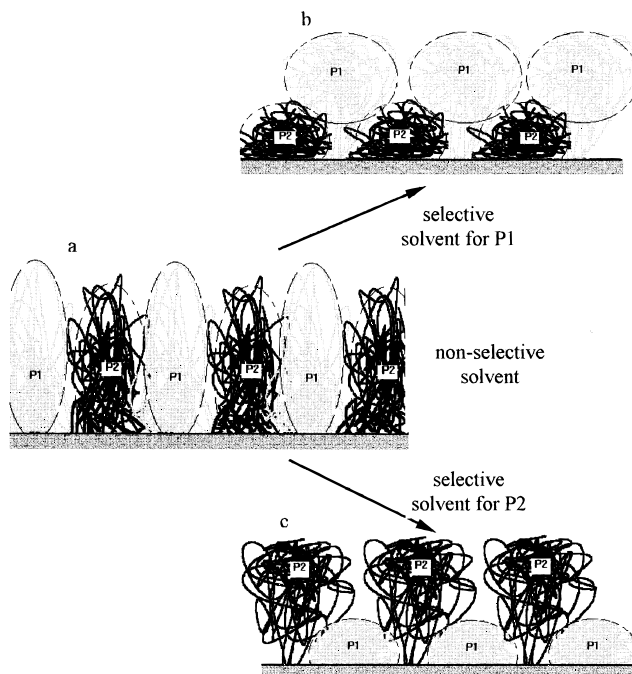
medically, or environmentally active compounds may be switched this way.

5. Conclusions

By use of a two-step grafting procedure, two different monomers, styrene and 2-vinylpyridine, were polymerized from the Si wafer surface and a heterogeneous (with respect to composition) polymer brushlike layer of different thickness within the range of 10 to 100 nm (for the dry layer) has been synthesized.

Such layers show reversible switching properties if they are exposed to different selective solvents. In a solvent selective for PS the polymer chains are swollen while PVP chains approach a collapsed conformation. The top brushlike layers consist in this case mainly of PS chains, and the surface of the layer becomes hydrophobic. In a solvent selective for PVP we obtain the inverse situation when the top layer is covered with PVP chains with hydrophilic properties. Such a behavior was observed with contact angle and XPS measurements which are in good agreement with the proposed scheme of the process.

The present quite novel switching properties may be used in different applications, where changing environments for the layers are present or where a fine-tuning of interfaces is necessary.

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