Environment Friendly and Switchable Polymer Brushes

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Introduction

The behavior of a solid surface with respect to surrounding medium is essential for many applications in industry, biology, medicine and environmental science, where wetting or in other cases non-wetting situations are envisaged. In this respect the concept of the hydrophobic or hydrophilic nature of a surface is widely used describing the interaction of water with materials. It was shown that wetting behavior of solid surfaces can be tuned by composition of random copolymers grafted to the solid substrates[1]. We have addressed the question whether one can prepare a surface, which can change its behavior depending on the environment, and whether this change is even reversible. Thus for instance an initially hydrophobic surface will gradually change to hydrophilic in water, in that way responding to the changing environment and optimizing its wetting properties, while it will become hydrophobic again in contact with a nonpolar organic solvent. It thus can be reversibly switched between those two states and can also adopt any intermediate state in between. This behavior has some resemblance to an artificial chameleon, which can adopt its appearance to changing surroundings.

Our approach for the fabrication of a surface with the chameleon behavior is synthesis of a binary polymer brush composed of two incompatible polymers of a very different solubility in water. We assume that the interaction of the binary polymer brush with a selective solvent causes a change of surface properties of the brush when one of the two polymers preferentially occupies a top layer. With this mechanism one can approach unique opportunities to change the surface properties of a polymer film as a response to the change of the surrounding media.

Experimental

Materials. *Monomers* - styrene (Merck) and 2-vinylpyridine (VP, Aldrich) were purified with ALOX B chromatographic column and distilled under reduced pressure under argon. *Solvents.* Toluene, tetrahydrofurane (THF), 1,4-dioxane and hexane were distilled after drying with sodium, dimethylsulfoxide (DMSO) was distilled under reduced pressure after drying with calcium hydride, methanol and ethanol were used as received. Dichloromethane was dried on molecular sieves. *Initiators* - 4,4'-azobis(4-cyanopentanoic 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 GmbH (Burghausen, Germany) were cleaned with dichloromethane in an ultrasonic bath, hot piranha solution and rinsed several times in Millipore water. 3-glycidoxypropyltrimethoxysilane (GPS) (Aldrich), p-Aminophenyltrimethoxysilane (APTS) from ABCR GmbH & Co. (Karlsruhe, Germany) and phosphorus pentachloride (Merck) were used as received. Triethylamine was dried on calcium hydride.

Attachment of the Initiator. We used two different methods of the introduction of the azo-initiator onto surface of the Si-wafer described by Tsubokawa et al.[2] and Schouten et al.[3] Due to the first method the Si-wafers were treated by GPS from 5% solution in toluene for 8h. 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 catalytic amount of α-picoline (Aldrich) at 50^0C for 5h. The resulting samples of Si-wafers with chemically attached initiating groups were rinsed 6 times with freshly distilled THF. Due to the second method the Si-wafers were treated by APTS from 2% solution in toluene for 12 h. Then the Si-wafers were washed by toluene and ethanol in ultrasonic bath. Separately the acid chloride derivative of ACP was prepared by adding of the slurry of phosphorus pentachloride to a suspension of ACP in dichloromethane at 0° C. The product (ACPC) after crystallization from hexane - dichloromethane mixture at 0^oC was washed and dried *in vacuo*. On the next step ACPC was introduced on the surface of the Si-wafers from 5% solution in dichloromethane with catalytic amount of triethylamine at room temperature for 10h. The resulting samples of Si-wafers with chemically attached initiating groups were rinsed in ethanol in an ultrasonic bath.

Every step of the modification of Si-wafers was controlled by ellipsometric measurement of the layer thickness.

Graft polymerization. Oxygen was removed from the solution of a monomer (styrene or 2-VP, 5÷6 mol/l) and AIBN[4] $(5\div9)\times10^{-4}$ 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 a monomer solution under argon atmosphere in a glass flask. The flasks were immersed in a water bath (60 ± 0.1^0C) for various periods (1 ÷ 40 h). The Si-wafers were rinsed 6 times with THF. In the next step the same procedure was used to graft the second polymer using the Si-wafers with the first grafted polymer. The ungrafted polymers were removed by a Soxhlet extraction for 8 hours using THF.

Characterization of the layers. Null ellipsometry was used to measure the amount of the chemisorbed initiator as well as grafted amount of PS and PVP. For the data interpretation, a multilayer model of the grafted film was assumed. In addition the layer composition was determined with FTIR in a transition mode (using Si-wafers polished from both sides). XPS measurements were used to study PVP and PS chain distribution in the grafted layer. Contact angles of water were determined with the sessile drop method. Morphology of the grafted films was studied with AFM. The detail description of the grafting and characterization is published elsewhere.[5]

Results and Discussion

The synthesis of binary polymer brushes was performed in three stages: (1) introduction of the initiator on the surface of Si-wafers. This stage consists of two procedures. In the beginning reactive (epoxy or amino) groups were introduced on the substrate surface with GPS or ATPS respectively. The layer thickness was of 8.5 Å and 7 Å respectively. Then the azo-initiator was introduced on the surface via the reaction of the epoxy derivative with ACP or the amino derivative with ACPC. The last reaction is well reproducible and the resulting layer thickness is about 21 Å, while the reaction of the epoxy groups with ACP shows poor reproducibility with the layer thickness for different experiments in the range of values between 12 Å and 22 Å.

(2) Grafting of PS chains was performed by in situ radical chain polymerization initiated by thermal decomposition of the azo-initiator covalently attached to the surface of Si-wafers.

(3) The grafting of PVP was carried out after the first grafting polymerization was finished and ungrafted polymer was washed out. In this stage a residual amount of the azo-initiator is used to carry out the graft polymerization. The grafting density after every stage depends on time of the grafting procedure. We obtained an increase of the layer thickness after every grafting stage typically in the order of 100-300 Å. Finally, we synthesized binary brushes of 0.05 - 0.3 nm^{-2} grafting density. Molecular weight of PS and PVP chains was varied from 5×10^4 to 3×10^5 g/mol. The composition of grafted layers was also determined using FTIR. The characteristics of several representative samples are presented in Table 1. In this table we demonstrate that many parameters of the binary brush can be varied: grafting density, molecular weight of both polymers and their ratio, that can be concluded from the graft polymerization mechanism.[6]

Table 1. Composition of the Binary Brushes

Amount of grafted PS, mg/m^2	Amount of grafted PVP, mg/m^2	M_n of PS, g/mol	M_n of PVP, g/mol	Total grafted density, nm^{-2}
6.3	3.1	54 200	173 000	0,08
2.0	25.0	215 000	220 000	0,08
21.9	11.0	164 000	120 000	0,14
45.4	44.2	210 000	230 000	0,25

With respect to composition the binary brushes can be subdivided into symmetric (the ratio PS:PVP≈1:1) and asymmetric brushes. AFM

investigations reveal different morphology of the films obtained from symmetric and asymmetric brushes after annealing (160 ^{o}C, 24h). Phase segregation in the symmetric brushes results in a rippled film while asymmetric brushes form layered phases (in good agreement with theoretical works[7-9]). Nevertheless, for all cases the film roughness is less than 1 nm. These results indicate the possibility to tune morphology of the films by a change of the composition. All brushes are hydrophobic after annealing (advancing contact angle of water is larger than 90°).

The brush-like layers were investigated to prove the above mentioned concept of switchable surfaces. We consider, as an example, a sample of a symmetric brush composed of PS and PVP of the same molecular weight. First the layer was rinsed with THF. The contact angle is 81.5^{o}, the wafer surface thus is intermediate between hydrophobic and hydrophilic. In the next step the Si-wafer is exposed to toluene solution. After some minutes the wafer is taken out, dried with nitrogen and the water contact angle is measured. It is 88°, the wafer covered with the binary brush has turned to hydrophobic. Then the wafer is exposed to ethanol. After this treatment the contact angle is 71, the wafer is now switched again towards hydrophilic properties. In the next step the same wafer is exposed to water solution of HCl (pH=3.0), which provides a much lower contact angle (16°, but in some cases a drop of water completely wet the surface). For the same samples we measured XPS spectra at an emission angle of 5° originated from a region close to the surface (less than 1 nm). Spectra of the films contain a N1s peak at 401 eV. We calculated the ratio between two peaks N1s and C1s, which reflect the relative concentration of PVP chains. We obtained the 4.5 times decrease of the ratio for the sample exposed to water (pH=3) compared to the sample rinsed in THF (0.09 in water and 0.02 in THF). Consequently PVP preferentially occupies a top of the layer in the acidic water solution.

The same procedure for contact angle measurements has been performed for silica wafers with binary brushes of different compositions. Using the Cassie-Baxter equation we calculated the fraction of each polymer on top of the layers after every treatment. The results are summarized in Fig. 1. We plot the fraction of PS in the top layer vs. the total weight fraction of PS in the binary brush. The best switching properties of the layers are observed for the case of equal fractions of both polymers in the brush. After exposition to water the top layer are completely covered by PVP, while after toluene most of the surface is covered by PS. In 1,4-dioxane the fraction of the polymers in the top layer is nearly the same as the layer composition.

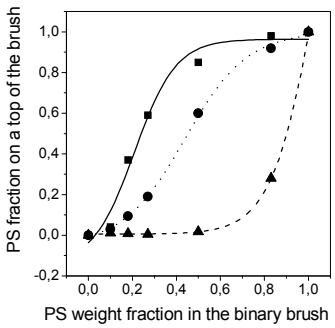

Figure 1. Fraction of PS on a top of the layer vs. the composition of the brush after exposition to different solvents: toluene (squares), 1,4-dioxane (circles), and water +HCl (triangles).

Kinetics of the change of the surface composition of the brushes was studied with contact angle method (Fig. 2). It take several minutes to approach a constant value of the contact angle. All changes in the brushes are reversible. We repeated a sequence of different treatments several times and all samples return to the same properties.

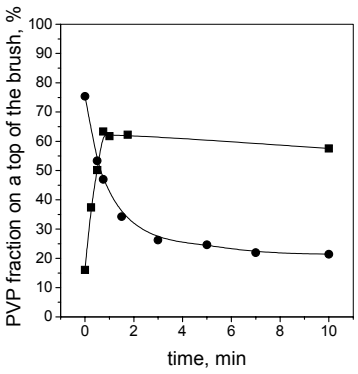

Figure 2. Change of contact angle on the surface of the brush (layer thickness 130 Å, PS:PVP=1:1) after exposition to water (squares) and toluene (circles) for different periods of time.

Morphology of the films, exposed to different solvents and dried, differs very much. The texture of the film surface depends also on the brush composition. For example, an asymmetric brush (95% PS and 5% PVP) after toluene forms a smooth film (roughness 1 nm). Surface of a symmetric brush in this conditions has a grained texture with the roughness of 2 nm. After a solvent selective for PVP the film has holes. Size of the holes depends on the brush composition and solvent. The largest roughness was obtained for the films after nonselective solvent. We observed with AFM a very pronounced memory effect when the film morphology of the same binary brush depends on history of the sample. The changes of morphology are also reversible as well as the changes of contact angles.

Conclusions

The above mentioned experiments reflect "smart" properties of the binary brushes which follow a changing environment by the adoption of the appropriate composition of a top of the layer. We assume a diverse exploitation of this effect, because such switching layers can be fabricated in various supports from nanoparticles[10] to flat surfaces. The binary brushes containing reactive functional groups may be used as a drug delivery systems exposing functional groups or releasing particular chemicals as a reponse to definite circumstances. Other possible areas of application include sensors sensitive to changes of humidity or to a composition of gas or liquid phases as well as temperature sensors. Universal fillers or colloidal particles capable to adjust their interaction with different matrices and stable in different dispersion media may be fabricated. The memory effect may be used for nano patterning of surfaces.

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