

Environmentally Responsive Polymer Brush Layers for Switchable Surface Properties

Sergiy Minko¹, Manfred Stamm¹, Evgeniy Goreshnik¹, Denys Usov¹, and Alexander Sidorenko²

(1) Institut für Polymerforschung Dresden e.V., Hohe Straße 6, 01069 Dresden, Germany, fax: x49 3514658281, minko@ipfdd.de, (2) Max-Planck-Institut für Polymerforschung, Ackermannweg 10, 55021 Mainz, Germany

Introduction

Polymer chain conformations are sensitive to a change of surrounding medium. The radius of gyration of a polymer coil increases several times when the chain switches from a collapsed to a swollen conformation upon exposure to poor and good solvent, respectively. If the chain is tethered to a solid substrate one can employ this switching behavior to construct a device or a sensor, sensitive to the surrounding and with the characteristic dimension of the chain size. Densely tethered chains form a polymer brush layer, where chains are stretched away from the substrate due to the excluded volume effect. Such a kind of self-organization results in a co-operative change of the conformation of tethered chains of the brush as a response to a change of the surrounding. Therefore a change of macroscopic properties (e.g. optical) may occur, which can be used for sensing of the composition of the surrounding medium.¹ For the case of a two component polymer brush we may assume a different behavior of each chain of the two interacting with the surrounding medium. If the polymers are immiscible we can expect a variety of surface morphologies of the binary brush in different solvents², where chains of one of the polymer preferentially occupy top or bottom of the layer.³ Such layers form a new family of transducer-active materials for chemical sensors, optical devices or controlled release agents.

In this paper we report experimental results which indicate the reversible switching of macroscopic properties and morphologies of binary brushes responding to a change of the surrounding medium.

Experimental

Materials. *Monomers* - styrene (Merck), 2-vinylpyridine (VP, Aldrich), and 2,2,3,4,4,4-hexafluorobutylmethacrylate (FA) were purified with ALOX B chromatographic column and distilled under reduced pressure under argon. *Solvents*. Toluene, tetrahydrofuran (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* were cleaned with dichloromethane in an ultrasonic bath, hot piranha solution and rinsed several times in Millipore water. 3-glycidioxypropyltrimethoxysilane (GPS) (Aldrich), p-amino phenyltrimethoxysilane (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 for the introduction of the azo-initiator onto the surface of the Si-wafer described as by Tsubokawa et al.⁴ and Schouten et al.⁵ 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°C 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 phosphorus pentachloride to a suspension of ACP in dichloromethane at 0°C. The product (ACPC) after crystallization from hexane - dichloromethane mixture at 0°C was washed and dried in vacuum. 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.

Graft polymerization. Oxygen was removed from the solution of monomer (styrene, FA or 2-VP, 5÷6 mol/l) and AIBN⁶ ($5\div 9 \times 10^{-4}$ 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 a monomer solution under argon atmosphere in a glass flask. The flasks were immersed in a water bath ($60 \pm 0.1^\circ\text{C}$) 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 polymer was removed by 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 the grafted amount of PS and PVP. For data interpretation, a multilayer model of the grafted film was assumed. In addition the layer composition was determined with FTIR in transmission mode (using Si-wafers polished from both sides). Contact angles of water were determined with the sessile drop method. Morphology of the grafted films was studied with AFM after the rapid evaporation of solvent. The detailed description of the grafting and characterization procedure is published elsewhere.³

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 APTS 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. (2) Grafting of PS or PS-FA 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.

Finally, we synthesized binary brushes of 0.05 - 0.3 nm² 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 calculated from the ellipsometric measurements performed after every step of grafting.

The characteristics of two representative samples are presented in Table 1. In this table we demonstrate that many parameters of the binary brush are important: composition, grafting density, molecular weight of both polymers and their ratio, which can be concluded from the graft polymerization mechanism.⁷

Table 1. Composition of the Binary Brushes

Sample	Amount of grafted PS (or PS-FA), mg/m ²	Amount of grafted PVP, mg/m ²	M _w PS, g/mol	M _w PVP, g/mol	Total grafting density, nm ⁻²
B1*	14.9	0.45	265 00	63 000	0,06
B2	6.27	3.07	94 000	280 000	0,08
B3	8.14	3.29	144000	346000	0.067

* PS:FA=0.8:0.2

Switching behavior of the binary brushes is demonstrated via the following experiment. The same wafer with a grafted polymer layer was subsequently dipped in different solvents for several minutes (it was confirmed that the layer reorganization occurs within few minutes). After the exposure to each solvent the wafer was taken out of the solvent and dried in a nitrogen flux. Then the advancing water contact angle on the surface of the wafer was measured within 30 seconds. The values of contact angles were found to be stable within this period of time. Then the wafer was exposed to the next solvent and the same measurements were carried out (Table 2).

Table 2 Contact Angles of Water on the Surface of the Binary Brush (B3) after Exposure to Different Solvents

Solvent	Contact angle, deg	Fraction of PS on top of the layer
Toluene	90	1.0
Chloroform	77	0.45
Ethanol	68	0.08
Water, pH=7	74	
Water, pH=2.5	36	

The data of the contact angle measurements show that the layers switch their surface properties from a hydrophobic state to a hydrophilic one upon exposure to the selective solvents for PS (toluene) or PVP (ethanol or water, pH=2.5). Using the Cassie equation⁸ we estimate the fraction of each of the polymers in the top of the layer. We thus conclude that in toluene the top of the layer is preferentially occupied by PS, while in water (pH=2.5) the surface behavior is determined by PVP. In intermediate cases after exposure to water (pH=7) or chloroform the contact angles approach intermediate values and both of the polymers were found in the top of the layer. Repeating this procedure many times, the layer after a sequence of the treatments returns to the same state which is evidence of reversible switching. The surface properties of the films are sensitive to the composition of the mixture to different solvents. A series of toluene/THF and toluene/ethanol exposure is prepared with a step by step increase of the fraction of toluene. The particular Si-wafer with a binary brush is exposed to the mixed solvent and the contact angle is measured in dry state. Results are presented in Table 3.

Table 3. Sensitivity of the Top of the Layer of the Binary Brush (B2) to the Composition of Solvents

Solvent composition, % (by volume)	Contact angle, deg	Fraction of PS on a top of the layer
Ethanol:toluene 67:33	63.3	0.00
Ethanol:toluene 50:50	66.2	0.07
Ethanol:toluene 47:53	72.0	0.24
THF:toluene 83:17	78.6	0.51
Ethanol:toluene 43:57	80.0	0.57
Ethanol:toluene 37:63	88.1	0.92
THF:toluene 67:33	89.1	0.96

Images of the films obtained with AFM confirm the above mentioned switching mechanism (Fig.1).

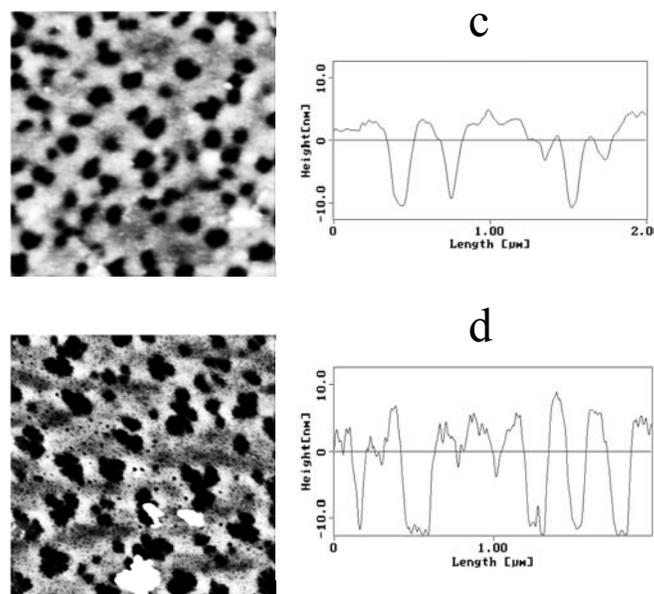
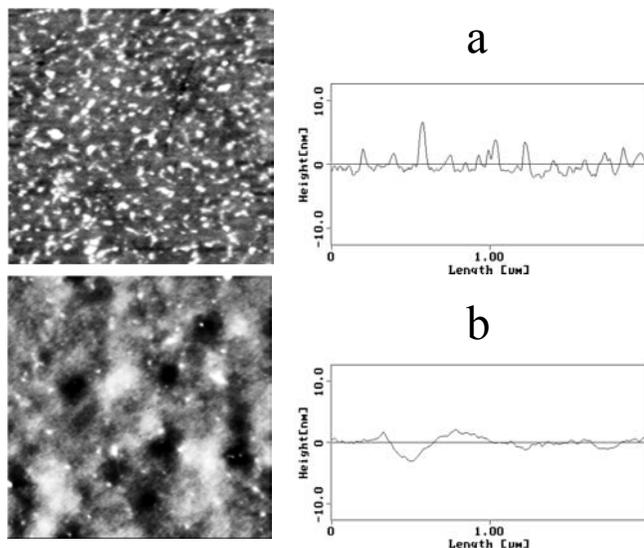


Fig.1. AFM images ($2 \times 2 \mu\text{m}$) and cross-sections of the B1 binary brush after exposure to chloroform (a), toluene (b), and water, pH=7 (c), and water pH=2.5 (d).

The morphologies of the layer differs dramatically upon exposure to different solvents. Nevertheless all changes are reversible. From the example, presented in Fig. 1, it is seen that the same brush can be switched from a state of a very smooth to a porous, rough film.

Conclusions

Experiments show that binary polymer brushes are sensitive to the exposure to different solvents and pH. The surface of the brush adopts the particular solvent to decrease the interfacial energy. It is possible to reversibly tune the composition of the top of the brush with the appropriate mixture of solvents very precisely. Such a sensitivity results in formation of different distribution of both polymers within the film. The rapid evaporation of the solvents allows to frees various surface morphologies of the films. This behavior we consider to be promising for the design of controlled release and sensors.

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