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Switching and Structuring of Binary Reactive Polymer Brush Layers

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Summary: Switchable binary polymer brushes grafted to Si-wafers were prepared from hydrophilic and hydrophobic polymer components. When exposed to solvents, either the hydrophobic or the hydrophilic component extends in to the liquid phase, depending on the polarity of the solvent. The hydrophilic component was poly-2-vinylpyridine; the hydrophobic component was made photocrosslinkable in that a polystyrene copolymer containing a photodimerizing chromophore was used. In this system surfaces differing in water contact angle between 60° and 100° can be produced by variation of the solvent. The chromophore was phenylindene, which forms crosslinks upon direct UV-irradiation. Therefore, the polystyrene component can be fixed in the extended or collapsed state. It will be shown that by irradiation through an appropriate mask, surfaces can be structured and the structures fixed.

In both the systems structural patterns differing in surface properties were produced and fixed photochemically.

Keywords: networks; photochemistry; stimuli-sensitive polymers surfaces; thin films;

Introduction

Tethered polymer layers[1] were shown to be effective for the colloidal stabilization[2], size exclusion chromatography[3], control of adhesion[4], lubrication[5], liquid-crystal displays[6], biomaterials[7], etc. Chemical grafting of polymers ensures the stable polymer-solid interaction via covalent bonds that is very important for the most applications. Via tuning the parameters, which control the brush, properties (grafting density, chain length, chemical composition of the chains) one can approach a variety of nano-scale structures and thin film properties.

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A highly interesting class of brushes is the mixed polymer brushes consisting of two incompatible polymers tethered to the substrate. Anchoring prevents the macroscopic segregation of polymers[8]. The theoretical analysis of nano-scale phase segregation in binary brushes results in a complicated phase diagram and plenty of thin film morphologies[9]. Depending on the solvent quality, layered and rippled phases (or their mixture) were observed experimentally. A transition between different morphologies upon external stimuli (solvent, temperature, etc.) results in switching of the surface properties of the film, e.g., switching from hydrophilic to hydrophobic[10] or from smooth to rough.

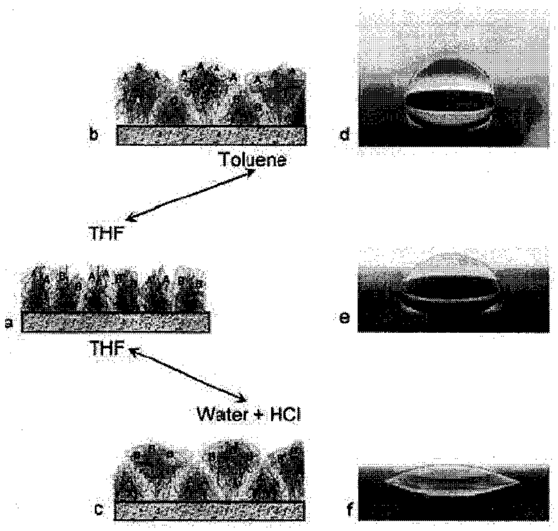

Figure 1. Wetting of the heterogeneous polymer brush composed of polystyrene and poly(2-vinylpyridine) chains on a Si-wafer

The concept of switching of surface properties is illustrated on Fig. 1. At least two different polymers A and B containing functional groups F1 and F2, respectively, may be grafted to a solid substrate to form a heterogeneous polymer brush (Figure 1a). The ratio between chain length of the polymers A and B, the composition of the brush and the nature of the functional groups F1 and F2 affect layer properties such as roughness, wettability, reactivity, adhesion to other materials, biocompatibility, etc. It is clear that interplay of the above-mentioned parameters of the heterogeneous brush allows approaching a wide variety of diverse surface properties. Besides, the heterogeneous brush has the unique capability to change the properties responding on a change of surroundings. Let us assume that the initial stage (Figure1a) was obtained in a nonselective solvent with respect to both polymers A and B. Then a change of the surroundings by addition of a selective solvent (e.g. for polymer A), or a change of pH (if one or both A and B are sensitive to pH) brings about selective swelling of the polymer A, and collapse of chains of the polymer B (Figure 1b). If we use a selective solvent for the polymer B the inverse behavior of the layer is expected (Figure 1c). A degree of coverage of the top of the brush by one of the polymers depends on the composition of surrounding and layer and can be adjusted very carefully to any desirable value. Consequently, one may obtain the desirable composition of the top layer with respect to F1 and F2 as a respond to the composition of the surrounding (liquid or a gas phase).

Crosslinking is a well-known method of modifying bulk properties of polymers. For the thin polymer layers the field of photocrosslinking of monomers, oligomers and polymers has grown into an important branch of polymer science. The photocrosslinkable and photofunctional polymers find wide applications in the field of optical photolithography, for printing plates, photocurable coatings, photorecorders, photoconductors and photosensitizers for organic synthesis. The widely used photoresists are based on various photoactive groups like cinnamate esters, acetylene, stilbene, azide, arylidene, etc. The most common method to produce crosslinks is the use of low molecular crosslinking agents. However, mixing and distribution of the crosslinking agent adds additional problems. This can be avoided if one of the comonomers is capable of crosslinking. Pendant photoreactive groups are introduced during homo- and copolymerization. Examples of utilizations of this approach are polyvinylcinnamates, acetylenes, and polymers with bound anthryl, stilbazolium, tetrazole, benzylidenephthalimidine, and stilbene substitutents. Photocrosslinking is widely used for the modification of thin polymer films. Nevertheless, this process was not applied to the polymer brush-like layers. Here we report on two distinct attempts in this field.

Polyisoprene system

We have chosen step - by - step “grafting to“[8] of the polyisoprene (PI) – poly-2-vinylpyridine (P2VP) pair of polymers onto a Si-wafer. The choice of PI as a hydrophobic component is based on the very high concentration of double bounds. Crosslinking of them can ensure a dense polymer network, enough to suppress switching.

Data of water contact angles are reported in Table 1 and show that the mixed brush can be switched from a hydrophobic surface (upon exposure to toluene) to a hydrophilic surface when water at pH = 2) is substituted for toluene. The hydrophobicity of the brush-like layer is easily accounted for by the selective interactions of toluene with PI. In contrast, PI is insoluble in low pH water, which is a protonating agent for P2VP. The top of the brush is then hydrophilic and ionized. In contact with ethanol, a selective solvent for P2VP, the top layer is non-ionized P2VP, and the surface is less hydrophilic (Table 1). After exposure to toluene, the brush has been irradiated by UV light through a mask to cross-link polyisoprene selectively in the illuminated areas. Table 1 shows that the contact angle of water for the film previously exposed to toluene changes from 80° before local cross-linking to 69° after crosslinking. This can be attributed to the modification of the polymers by the photoinitiator. To minimize this effect and to extend the range of switching, it would be effective to select appropriate photoinitiators (the selection should be based on polarity/ solubility of the photoinitiator molecules). The most important fact is that switching is suppressed in the irradiated area. The non-irradiated area, however, retains its capability of switching.

Table 1. Water Contact Angle Data on non-UV-irradiated and on UV-irradiated areas upon exposure to different solvents

solvent	mixed PI/P2VP brush	
	Θ_A on non – UV irradiated area	Θ_A on UV irradiated area
toluene	80°	69°
ethanol	69°	69°
acidic water (pH=2)	42°	69°

The different behavior of irradiated and non-irradiated areas in different media can be used for sensors. After photoprinting at the micrometer scale, the patterned brush is washed with ethanol for several minutes, dried, and then exposed to water vapor. No pattern is developed on the surface (Figure 2b). The same treatment is repeated with water (pH = 2) instead of ethanol. The local condensation of water droplets reveals quite clearly the image printed on the brush (Figure

2a). A nicely contrasted image is formed because the light reflection changes with the size and shape of the water droplets. The image can be erased (Figure 2b) merely by washing with ethanol or neutral water (pH = 6.5). This general observation can be repeated at will, which is the evidence that the film is sensitive to acidic water and that this specific interaction can be repeatedly visualized.

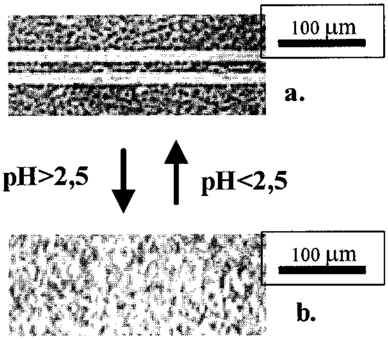

Figure 2. Adsorption of water drops (optical microscopy, bar – 100 µm) on the polymer brush with developed patterns by exposure to water with pH<2,5 (a.) and hidden by water with pH>2,5 (b.)

Phenylindene system

Another switchable system different from the one above was also investigated. Instead of polyisoprene a photosensitive styrene/2-(4-styryl)-indene copolymer was used as a photocrosslinkable hydrophobic component, cf. [11]. The hydrophilic part of the binary brush was again taken by poly-2-vinylpyridine. Photochemical cross-linking occurs when a ground state phenylindene moiety encounters an excited phenylindene moiety during the lifetime of the latter. Thereby defined crosslinks are brought about via photodimerization, i.e. the formation of cyclobutane derivatives (Figure 3). Compared to systems that need a photoinitiator such a system is advantageous in that the degree of cross-linking can be adjusted by switching on and off the light and in that no photoinitiator affects the surface properties.

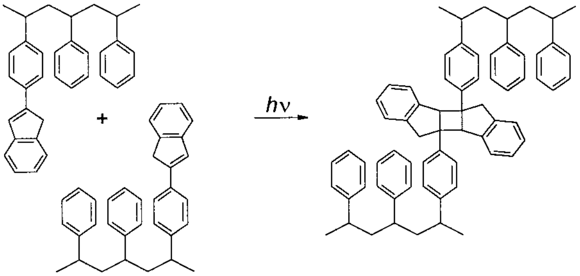

Figure 3. Mechanism of copolymer cross-linking via phenylindene photodimerization

In order to synthesize the polymer containing the phenylindene chromophore it was necessary to use a monomer with a protected double bond at the five membered indene ring to avoid network formation during polymerization. This special monomer, i.e. 2-trimethylsiloxy-2-(4-styryl)-indane, is formed in a two-step-synthesis: 1. coupling of 2-indanone to 4-bromostyrene, 2. addition of trimethylsilylchloride.

The copolymer used here contained 9 % styrylindene.

P2VP and the styrene/2-trimethylsiloxy-2-(4-styryl)-indane-copolymer were attached simultaneously to the Si-wafer by a photochemical grafting method[12], which makes use of the photoreductive addition of hydrocarbons to benzophenone. This photochemical grafting method has several advantages: special anchor groups at the polymer chain ends are not required, solid supports with benzophenone-layers can be stored easily, and the grafting conditions are mild.

Table 2. Water contact angle data of photochemically attached layers upon exposure to different solvents

system	solvent	
	toluene	hydrochloric acid pH=2
P2VP/PS (1:1) brush with 9 % cross-linker (protected)	92°	57°
PS brush with 9 % cross-linker (protected)	90°	90°
P2VP brush	70°	50°

After the removal of the trimethylsilyl- protection groups by acidic hydrolysis and the according formation of the phenylindene double bond, the grafted polymer brush is sensitive to light with wavelengths below 400 nm. After exposure to hydrochloric acid at pH = 2, the brush has been irradiated by UV light through a mask to cross-link phenylindene groups selectively in the illuminated areas. Then the brush was switched to the other state by treatment with toluene and the whole surface was irradiated to fix the pattern. Figure 4 shows the pattern produced as the result of this procedure. The visibility of the pattern here does not rest on water vapor condensation as in the polyisoprene system.

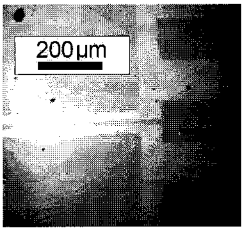

Figure 4: Photographical image of photochemically patterned Si-wafer. Light areas have been initially illuminated with UV light and show different reflectivity as compared to the dark areas irradiated after switching the state of the brush

Conclusions

Structural patterns (differing in surface properties) in switchable binary polymer brushes can be generated and fixed via selective photochemical cross-linking.

Acknowledgement

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