Photochemical Structuring of Binary Polymer Brush Layers via Photodimerization

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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 nanoscale structures and thin film properties.

A highly interesting class of brushes are 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 nanoscale 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.

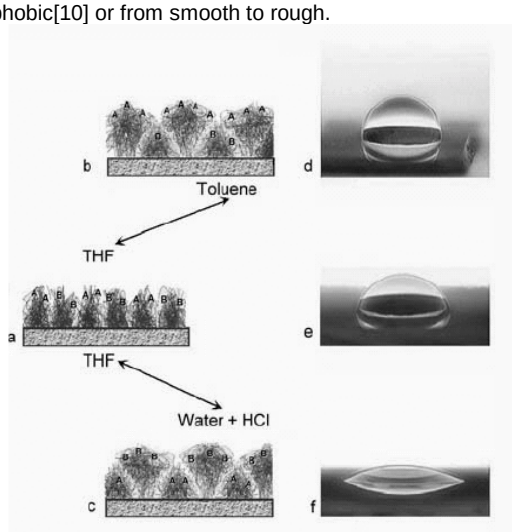

Figure 1. Wetting of the heterogeneous polymer brush composed of polystyrene and poly(2-vinylpyridine) chains on a Si-wafer

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 an interplay of the above mentioned parameters of the heterogeneous brush allows to approach 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 utilisation of this approach are polyvinylcinnamates,- acetylenes, polymers with bound anthryl, stilbazolium, tetrazole, benzylidenephthalimidine, 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.

PHENYLINDENE SYSTEM

A photosensitive styrene/2-(4-styryl)-indene copolymer was used as a photocross-linkable hydrophobic component, cf. [11]. The hydrophilic part of the binary brush was 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 2). 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.

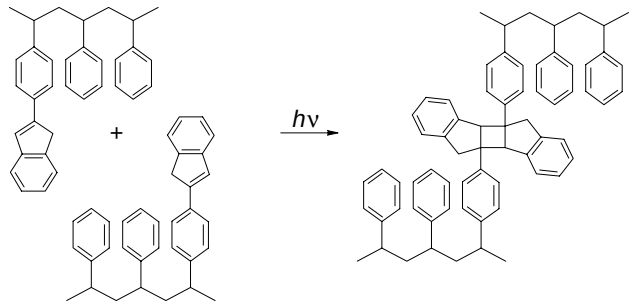

Figure 2. Mechanism of copolymer cross-linking via phenylindene photodimerization.

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 1. Water Contact Angle Data of Photochemically Attached Layers Upon Exposure to Different Solvents and Photochemical Crosslinking After Exposure to Different Media:

	Contact angle after pH=2	Contact angle after toluene
Before crosslinking	57°	92°
Crosslinked - after toluene	98°	105°
Crosslinked - after hydrochloric acid pH<2	69°	72°
PS brush with 9 % cross-linker (protected)	90°	90°
P2VP brush	50°	70°

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 3 shows the pattern produced as the result of this procedure.

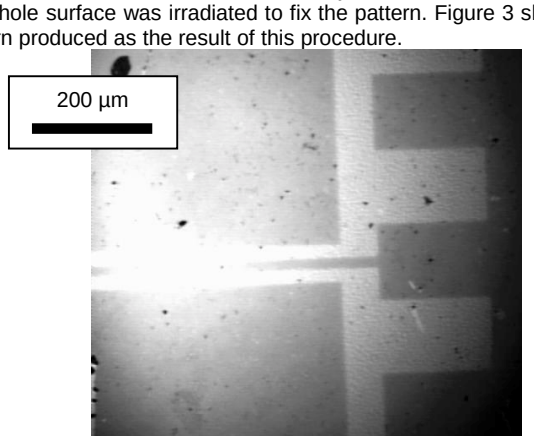

Figure 3. Photographical image of photochemically patterned Si-wafer. White areas have been illuminated with UV light and have different reflectivity as compared to non-irradiated areas.

CONCLUSIONS

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

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