Reversible Chemical Patterning on Stimuli-Responsive Polymer Film: Environment-Responsive Lithography

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Abstract: We report on a novel type of chemical patterning based on thin stimuli−responsive polymer films. The basic concept is the permanent storage (writing) of a pattern, which is reversibly developed and erased upon exposure to appropriate environment, e.g., solvent, pH, and temperature. The smart surface is fabricated from the mixed brush of poly(2-vinylpyridine) and polyisoprene. The mixed brush demonstrates switching behavior upon exposure to different solvents. Cross-linking of polyisoprene via illumination through a photomask results in formation of patterns with suppressed switching. Due to the contrast in switching between illuminated and dark areas, exposure of the smart surface to different solvents causes either reversible formation or erasing of chemical contrast between the illuminated and dark areas. Thus, the pattern surface can very locally attract colloidal particles or can be wetted by water only upon exposure to the special solvent which introduces the contrast between the illuminated and dark areas. Appearance of the patterns indicates particular environment and can be used for local switching of adsorption.

Introduction

Chemical patterning of surfaces finds numerous applications in printing technologies, electronic chip production, fabrication of bioanalytical assays, sensors, etc. In traditional lithography, a photoresist film is deposited on a solid support and irradiated (UV, X-ray, plasma, etc.) through a photomask. Radiation initiates chemical reactions responsible for a contrast in the physical and/or chemical properties of the irradiated and dark areas. This contrast is very useful to very locally adsorb protein molecules, ink, colloidal particles, etc. Different chemical reactions have been proposed and tested in order to improve lithography based on polymerization/grafting,[1] polymer cross-linking,[2] and polymer degradation.[3] It may happen that the

reaction products are extracted by a gas rather than by a selective solvent or, better, that they eliminate themselves as result of high volatility. More elegant approaches rely on the photoinduced chemical reactions of functional groups of the photoresist. Indeed, the irradiated polymer must not be removed (at worst, a small fraction of it), which decreases the environmental impact[4] of the technique.

In most approaches for chemical patterning, irradiation is responsible for irreversible modifications of the photoresist and/ or irreversible patterning. Therefore, photosensitive layers prone to reversible modifications of properties are highly desired as an effective basis for either environmentally friendly technologies or smart surfaces. One possible approach could be found in stimuli-responsive materials with a reversible switch in the surface properties from hydrophilicity to hydrophobicity or vice versa. The reversible cis−trans photoisomerization of azobenzene chromophores[5] is an example of reversible change in molecular shape that has been used in storage devices,[6] in the control of surface orientation of liquid crystals,[7] and in photocontrolled wetting.[8] The cis and trans isomers have deeply different wetting properties, and the patterns written with light

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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		PI brush (reference)		P2VP brush (reference)	
	Θ_A on non-UV-irradiated area	Θ_A on UV-irradiated area	Θ_A on non-UV-irradiated area	Θ_A on UV-irradiated area	Θ_A on non-UV-irradiated area	Θ_A on UV-irradiated area
toluene	80	69	105	102	63	69
ethanol	69	69	107	98	66	70
acidic water (pH = 2)	42	69	97	90	18	35

can be visualized by surface decoration with water droplets.[8] The problem is that these responsive surfaces are not stable in a liquid environment and that the patterns disappear spontaneously.

This paper reports on a novel type of chemical patterning based on thin stimuli-responsive polymer films. The basic concept is the permanent storage (writing) of a pattern, which is reversibly developed and erased upon exposure to appropriate environments, e.g., solvent, pH, and temperature. This technique is promising for the design of smart sensors, nanodevices, and in microfluidic technologies.

The approach is based on stimuli-responsive mixed polymer brushes of two immiscible polymers randomly tethered (grafted by an end functional group) to a solid substrate.[9] The morphology and surface chemical composition of these films depend indeed on the environment, in direct relation to the interplay of lateral and perpendicular phase segregation in the mixed brush.[10] For instance, in contact with a selective solvent, the solvated polymer is preferentially at the top of the brush and dictates the surface properties of the film.

Results and Discussion

A mixed polymer brush has been prepared by step-by-step grafting of carboxylic acid terminated polyisoprene (PI) and poly(2-vinylpyridine) (P2VP) according to a procedure detailed elsewhere.[11] Si wafer is first functionalized with glycidoxypropyl trimethoxysilane (GPS) from toluene solution (layer thickness = 0.8 nm). PI-COOH is then spin coated onto the substrate and grafted by reaction of the carboxylic acid end groups with the epoxy (and hydroxyl) groups of the GPS layer. The experimental conditions have been optimized for the grafting yield to be limited to ca. 50% (thickness of the PI layer is 2.6 nm), therefore making possible the grafting of P2VP under the same conditions. The thickness of the final mixed brush is 5.1 ± 0.1 nm. The thickness of each layer has been measured by ellipsometry.

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 acidified water (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 nonionized P2VP, and the surface is less hydrophilic (Table 1).

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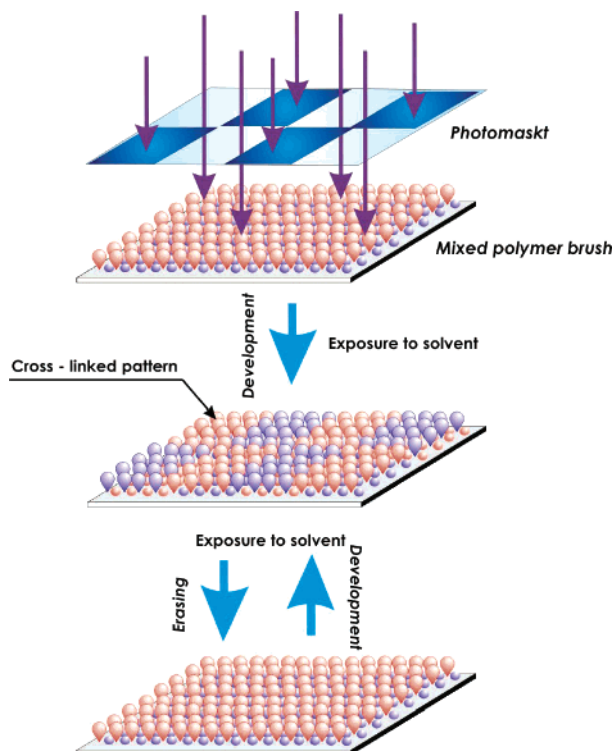
After exposure to toluene, the brush has been irradiated by UV light through a mask with to cross-link polyisoprene selectively in the illuminated areas. Table 1 shows that the contact angle of water for the film previously exposed to toluene changes from 80° before local cross-linking to 69° after cross-linking. The NEXAFS spectra recorded by X-ray photoemission electron microscopy for the illuminated and dark areas after exposure to ethanol are the same, confirming that the UV irradiation is not destructive. The same conclusion was drawn from the XPS spectra (take off angle 0°) showing that the N/C atomic ratio (1:11) is independent of the exposure to UV light. Therefore, the chemical composition throughout the film thickness is the same in both dark and illuminated areas and the contrast in the film behavior (introduced upon exposure to different environments, see below) in illuminated and dark areas cannot be introduced by a modifying/destructive effect of UV light.

Photoirradiation through the mask thus changes the phase morphology. Moreover, the contact angle on the cross-linked areas (69°) is independent of the solvent used in a post-treatment, which indicates the loss of the switching properties upon irradiation. We mention here that the change of wetting behavior, represented as a shift of water contact angle from 80° (before cross-linking) to 69° (after cross-linking) observed after treatment with toluene, is not obvious. We expected that the morphology and hydrophobic behavior after toluene would be frozen by cross-linking. We may speculate that the cross-linking changes compatibility of the polymers, kinetically freezes morphology of the film, and PI is modified by fragments of the photoinitiator. The results of contact angle experiments on the reference homopolymer brushes (Table 1) give evidence for that. Cross-linking of the PI brush results in the decrease of water contact angle, while irradiation of the P2VP brush in the presence of benzophenone results in the increase of water contact angle. Consequently, the experiments clearly show that fragments of the photoinitiator modify wetting behavior of the brushes in some extend. 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), which is beyond the scope of this paper.

The most important observation is however that the nonirradiated areas retain their capability to respond to external stimuli, particularly to the thermodynamic quality of the solvent. Thus, after treatment with toluene the dark (nonirradiated) areas are more hydrophobic than the illuminated ones. After exposure to ethanol, both the dark and illuminated areas have the same wetting properties. However, after treatment with acidic water, the dark areas are more hydrophilic than the illuminated areas. The XPS measurement after exposure to acidic water demonstrates an increased N/C ratio (1:10) for the dark areas (as compared with the ratio 1:11 for the illuminated areas), which is consistent with the fact that the very top of the layer is enriched with P2VP segments. We should mention that the XPS

Figure 1. Scheme of photolithography on mixed polymer brushes.

method (take off angle 75°) gives integral information about the chemical composition of the polymer film from several nanometers in depth. It is comparable with the brush thickness. Switching of the mixed brush results in a change of composition of the very top layer of the brush.[10] Thus, the small integral difference in N/C ratios recorded with XPS corresponds to a large change in the composition of the top layer, which is in good agreement with the wetting experiment. Consequently, the mere tuning of the solvent quality allows the local contrast in surface composition, wetting, adsorption, and adhesion characteristics of the brush to be tuned. This remarkable control can be used to design smart surfaces capable of detecting specific interactions with a well-defined environment.

The general concept of this novel type of environment-responsive lithography is illustrated in Figure 1. The thin film of the mixed polymer brush is exposed to a selective solvent and illuminated through a photomask with the purpose of cross-linking the chains selectively in the illuminated areas. In the dark areas, the chains retain their capability of switching conformation and properties. The accordingly designed pattern can be developed by exposure to a selective solvent for one constitutive polymer (PI or P2VP), which changes the chemical composition of the top layer in the dark areas as a result of phase segregation but not that of the illuminated areas. Whenever the patterned mixed brush is exposed to a nonselective solvent, any contrast in the chemical composition of the top layer disappears and the image is erased. This process is reversible, and the pattern development and erasing can be repeated many times. Several examples are reported hereafter, which illustrate this environment-responsive lithography.

Figure 2 shows the characteristic features of the patterned brush as result of interaction with different solvents. 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). The inset emphasizes the difference in the wetting properties of the dark and illuminated areas. Water barely wets the surface of the illuminated areas (semispherical droplets), whereas water is more extensively spread over the surface of the dark areas. 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.

The printed features are visualized with colloidal particles. The same sample as above is dipped in a toluene dispersion of Si particles stabilized by grafted polystyrene chains, for 5 min. In toluene, the colloidal particles are preferentially adsorbed onto the dark areas (Figure 3) because of a stronger affinity with the less polar surface of the dark areas compared to the illuminated ones (Table 1). The image is thus revealed by the selective adsorption of the colloidal particles. When the same experiment is conducted in water with nonmodified silica particles, no image is observed. Thus, this experiment demonstrates the possibility of local switching of adsorption.

Formation of regular arrays of microreactors and microchannels may be very important for analytical purposes.[12] A properly patterned surface with a sharp contrast in the wetting properties of illuminated and dark areas is a possible way to draw channels of water droplets. The lithography on mixed polymer brushes which is proposed in this paper can be used to trace quite complex arrays of microchannels. A grid of 12.5 μm gold wires has been used as photomask. Two samples of the same mixed PIP/P2VP brush have been irradiated through the mask either in direct contact with the sample or 100 μm away from the sample surface. The surface of the illuminated and dark areas can be tuned precisely by changing the distance between the mask and the substrate. These samples have been exposed to acidic water and, afterward, to water vapor. The image of the deposited water droplets is shown in Figure 4. A lattice of water droplets is formed in the case of irradiation through the mask 100 μm away from the sample. Whenever the mask is in direct contact with the sample, a network of water channels is drawn.

It is noteworthy that illuminated mixed PI/P2VP brushes stored for more than 1 month after exposure to one selective solvent (e.g., acidic water) preserves the morphology and the information accordingly developed. These samples exposed to water vapor reveal the photoprinted images, which is however erased upon heating above 80 °C (glass transition temperature of PI is below room temperature and PI occupies the top of the brush upon heating to the temperature even slightly below T_g = 85 °C for P2VP). Further exposure to acidic water followed by drying and contact with water vapor restores the image. Therefore, the sample heating erases the image without destroying the brush.

We report two different examples for practical application of the environment-responsive lithography. The first example demonstrates that this approach can be used for the fabrication of switchable microchannels to cause a valve to reversibly open

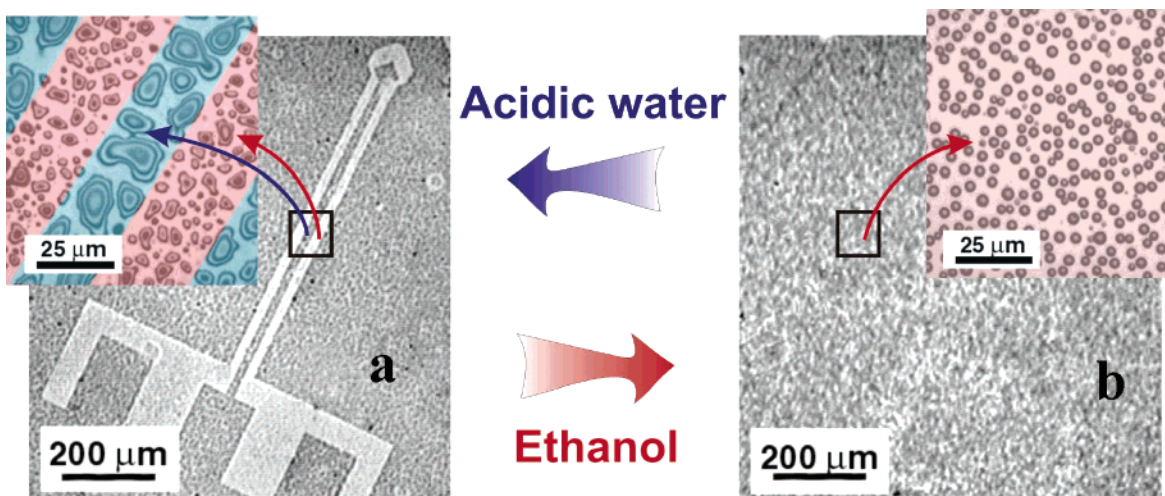(12) Gau, H.; Herminghaus, S.; Leny, P.; Lipowsky, R. *Science* **1999**, *283*, 46–49.

Figure 2. Adsorption of water drops (optical microscopy) on the polymer brush with developed (a) and erased (b) patterns. Insets demonstrate zoomed in details: hydrophilic and hydrophobic regions are artificially colored in blue and red, respectively.
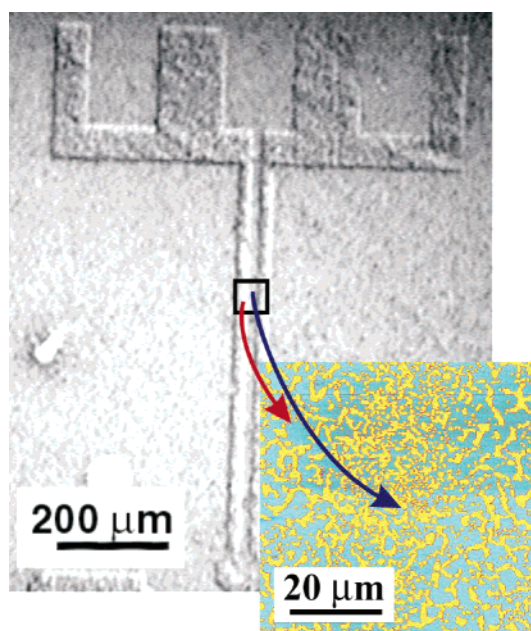

Figure 3. Adsorption of silica particles stabilized by grafted polystyrene chains on patterned surface (optical microscope image). Inset shows an AFM image at the location marked with arrows.

or close the channel upon external stimuli. The switchable channel was prepared as shown in Figure 5. The mixed brush (1) was grafted between two hydrophilic channels (2) (Figure 5a) on a solid substrate. The switchable channel was fabricated (Figure 5b) by photo-cross-linking of the brush through the photomask (3) so that the irradiated areas (4) lose the switching properties and serve as walls of the channel. The bottom of the channel (6) is hydrophilic upon exposure to acidic solution and water can flow through the channel (Figures 5c and e). Upon heating above 80 °C or by changing of pH (Figures 5d and f) the bottom surface of the channel switches into hydrophobic state, closing the channel (5). This sample represents the general principle. Much more complicated systems can be fabricated using photolithography on mixed brushes.

The second experiment presents fabrication of smart sensors directly visualizing the result of the test. For example, if the pattern is visualized at a particular pH the smart surface can directly display the value of pH as an image (Figure 6).

Conclusion

A novel strategy for reversible environment-responsive lithography has been implemented, which relies upon the chemical patterning of surfaces consisting of stimuli-responsive mixed polymer brushes. The information is written on the brush surface by local cross-linking of the polymer under UV irradiation. The nonirradiated areas are unaffected and retain their capability of switching their wetting properties under appropriate stimulation. The difference in the surface composition of the illuminated and dark areas of the top brush layer can be tuned by exposure to a solvent selective for one constitutive polymer or not, which results in the visualization and erasing of the written information, respectively. This behavior can find diverse applications for reversible chemical patterning, smart sensors, and microfluidic technologies.

Experimental Section

The polyisoprene/poly(2-vinylpyridine) (PI/PVP = 1:1) mixed brush was prepared by the "grafting to" method reported elsewhere.[11] Carboxylic acid terminated PI (M_w = 30 000 g/mol) was synthesized by living anionic polymerization, as described elsewhere.[13] PI was dissolved in toluene (0.125 wt %) together with 0.01 wt % of 2,6-di-*tert*-butyl-4-methylphenol (inhibitor). A 5 nm thick PI film was spin-coated on a Si wafer precoated by 3-glycidoxypropyl trimethoxysilane (GPS) and heated at 110 °C for 4 h in an argon atmosphere. After extraction by toluene for 2 h (Soxhlet), the film thickness (2.6 nm) was measured by ellipsometry. The carboxylic acid terminated P2VP (M_n = 39 200 g/mol, M_w = 41 500 g/mol from Polymer Source, Inc.) was spin-coated from a 1 wt % solution in THF (with 0.01% of the same inhibitor), on the top of the PI brush. The 50 nm thick film was annealed at 130 °C for 8 h under argon. The nongrafted P2VP was extracted by THF (cold Soxhlet) for 5 h. The thickness of the mixed brush was 5.1 ± 0.1 nm, and the molar PVP:PI ratio was ca. 1:1. The layer thickness and the grafted polymers were analyzed at λ = 633 nm and an angle of incidence of 70° with a SENTECH SE-402 ellipsometer.

The mixed brushes were exposed to 0.5 wt % of benzophenone in toluene for 5 min and dried under Ar. They were illuminated through photomask with a UV mercury lamp (100 W) for 5 min.

Advancing *contact angle* of water was measured using DSA Krüss (Hamburg, Germany) equipment. The same samples of Si wafers with the grafted mixed brushes were exposed for 10 min to solvents of different thermodynamic quality for the polymers. After each treatment

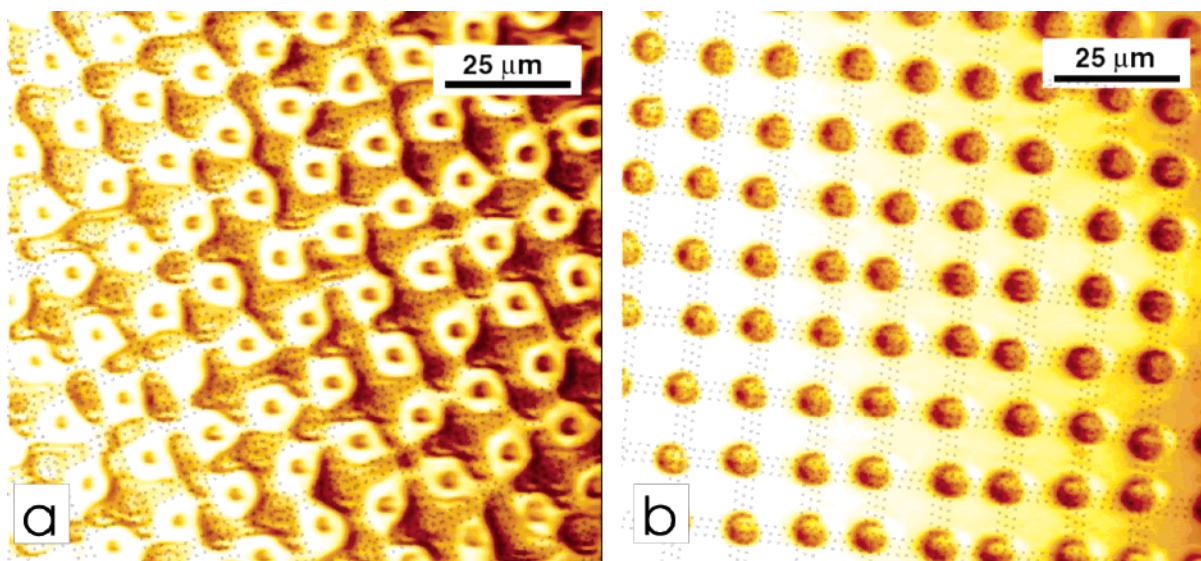(13) Broze, G.; Jérôme, R.; Teyssié, P. *Macromolecules* **1982**, *15*, 920−927.

Figure 4. Water drop adsorption on the mixed brush patterned by UV irradiation through the grid: (a) the grid was in direct contact with the brush; (b) the grid was 100 μm far away from the brush. Water drops are dark yellow. For convenience the grid is drawn with three parallel dashed lines indicating non UV-irradiated areas.
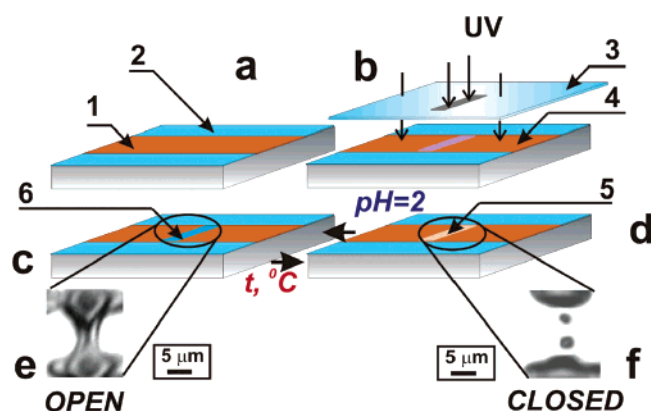

Figure 5. Fabrication of a switchable channel employing environment responsive lithography (for explanation see the text of the paper). The images e and f show open and closed states of the switchable channel, respectively, as they appear in optical microscopy.

Figure 6. Example of a smart sensor from the mixed brush grafted to Si wafer which displays the result of the analysis of acidic aqueous solution: the wafer was exposed to neutral water (top) and to water with pH 2.3 (bottom). The image appeared upon exposure to water vapor *only* if the sample had been treated with acidic water solution of pH <2.5.

with a particular solvent, the samples were dried in a flow of nitrogen and used for AFM and a rapid contact angle investigations. The experiments were repeated several times with each sample to prove the reversibility of the switching of surface properties. In these experiments we assume that the morphology of the dry film is directly correlated with the structure of the swollen film.[9-11] Time of the switching in a particular solvent is in the order of minutes (contact angle changes in 1-2 min and approaches to equilibrium in 5-10 min) which is much larger than the time to dry the film under nitrogen flux (several seconds). We may assume that we freeze the film morphology during solvent evaporation. At ambient conditions, P2VP in the dry film is in a glassy state and the film morphology is stable for a long period of time.

The film surface was observed with a Dimension 3100 AFM instrument (Digital Instruments, Inc., Santa Barbara, CA) and an optical microscope. The local chemical composition of the mixed brush was analyzed by X-ray photoemission electron microscopy (XPEEM)[14] at the Lawrence Ernest Orlando Berkeley National Laboratory with a Lateral resolution of about 60 nm. XPEEM took advantage of the near edge X-ray absorption fine structure contrast (probing of up to 12-15 nm thick films). The nitrogen k-line (electron binding
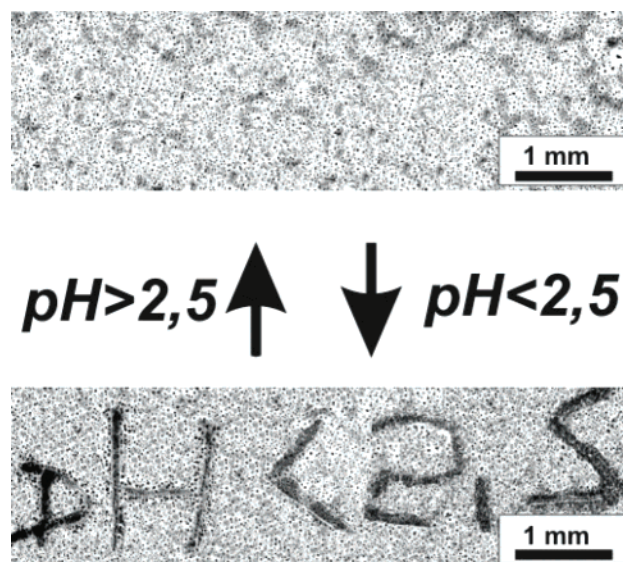
energy: 404 eV) was used to determine the P2VP fraction (N/C ratio) in the film.

XPS experiments were performed with an AXIS ULTRA spectrometer (Kratos Analytical, England) equipped with a monochromized Al Kα X-ray source of 300 W at 20 mA. The analyzer's pass energy was set to 160 eV to record survey spectra and 20 eV to take high-resolution spectra.

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