Photoswitchable Ratchet Surface Topographies Based on Self-Protonating Spiropyran−NIPAAM Hydrogels

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Ⓢ Supporting Information

ABSTRACT: In this work, self-protonating spiropyran-based poly(N-isopropylacrylamide) polymer networks are prepared. These photoresponsive hydrogel coatings can change their surface topography upon exposure with visible light in a neutral environment. Photoresponsive surface-constrained films have been fabricated for which the swelling behavior can be controlled in a reversible manner. In a first step, symmetrical switchable surface topologies with varying cross-link density are obtained by polymerization-induced diffusion. Under light exposure, the areas with low cross-link density swell more than the areas with high cross-link density, thus forming a corrugated surface. Asymmetric ratchet-like photoresponsive surfaces have been prepared on prestructured asymmetric substrates. As a result of thickness variation of the surface-confined hydrogel layer, an asymmetric swelling behavior is obtained. Depending on the cross-link density of the hydrogel, it is possible to switch between a ratchet and flat surface topography or even an inverse ratchet surface by light.
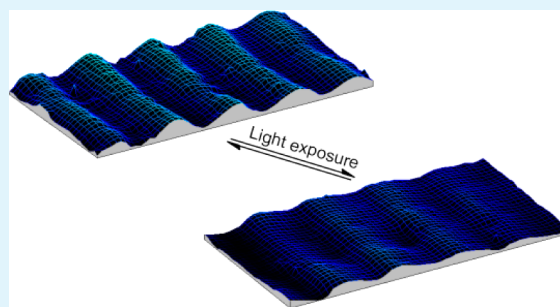
KEYWORDS: photoresponsive hydrogel, spiropyran, N-isopropylacrylamide, ratchet, surface topography

■ INTRODUCTION

Responsive surface topographies, manufactured from materials that can change their properties in a reversible fashion, have been gaining a lot of attention in recent years.[1,2] By chemical design, the topographies can become responsive toward various stimuli, such as pH, temperature, or light.[3−7] Photoresponsive materials are of particular interest because they can be operated locally in a noncontact way, without physically changing their chemical environment.[8] Such materials are attractive as coatings for incorporation in microfluidic devices, in order to provide new approaches for key functions like valving, pumping, and mixing.[9−11] These photoswitchable topographies might also be interesting for biological purposes, such as controlled cell growth.[12−14] So far, most of the research has been focused on symmetric responsive surface topographies, while asymmetric responsive topologies are rare.[15] Such types of coatings are interesting for transport or fluidic control. Especially, ratchet-like structures are appealing to induce unidirectional transport of liquids and particles.[16−19]

Suitable materials for photoresponsive coatings are hydrogels, which can undergo reversible volume changes in aqueous media because of differences in their hydrophilicity. A well-known responsive polymer is poly(N-isopropylacrylamide) (PNIPAAM).[20−22] Its thermoresponsive behavior makes the hydrogel more hydrophobic upon an increase in the surrounding temperature above the lower critical solution temperature, resulting in dehydration and collapse of the polymer chains. In the case of the addition of a cross-linking agent to the polymer backbone, a hydrogel is formed. Dehydration of the polymer chains will lead to shrinkage of the hydrogel. Modification of the polymer backbone by hydrophobic functionalities leads to a decrease or disappearance in the ability of the polymer film to absorb water and swell, while the incorporation of hydrophilic compounds leads to an increase in water uptake. Implementing spiropyran, a photochromic moiety of which the isomers have a high difference in polarity, in the polymer backbone causes the entire polymer gel to change its hydrophilicity upon light irradiation.[23] Hydrophobic spiropyran causes the hydrogel to shrink, while hydrophilic protonated merocyanine leads to swelling. In order to create hydrogel surface topographies based on spiropyran and NIPAAM, which shrink upon light exposure,
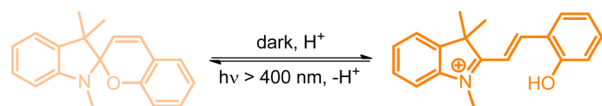
the spiropyran moiety needs to be in its hydrophilic protonated merocyanine form (Scheme 1).[24−27] Therefore, an acidic

Scheme 1. Photoisomerization Behavior of Spiropyran into Protonated Merocyanine under Acidic Conditions

environment is required to fabricate responsive surface topologies, and up to now, most experiments are carried out in a slightly acidic solution. Recently, we have reported the incorporation of a small amount of acrylic acid into the polymer backbone as an internal proton source, to make free-standing photoresponsive polymer gels that operate in a neutral environment.[28]

In this work, we report on unprecedented asymmetric light-responsive topographies based on self-protonating spiropyran−PNIPAAM hydrogels. Initially, we have prepared surface-constrained films to study the photoresponsive behavior of our coating at neutral pH. It was found that the response time is similar to hydrogels operating at pH = 2.7 and that the degree of swelling can be controlled by the amount of cross-linker. Subsequently, symmetrical switchable surface topologies with varying cross-link density within the polymer network are obtained by polymerization-induced diffusion. Asymmetric surface topographies are prepared by a single photopolymerization step on a prestructured surface, having a ratchet-like topography.[15] Because of the variable thickness of hydrogel present in different areas, the surface topography changes upon exposure to visible light. A thicker layer will result in a greater degree of swelling of the confined pattern. Depending on the cross-link density in the polymer film, asymmetric responsive surfaces can be fabricated that switch between a ratchet and flat surface or mirror image ratchet topographies.

■ EXPERIMENTAL SECTION

Materials. Unless stated otherwise, all reagents and chemicals were obtained from commercial sources, UV photoinitiators 2-hydroxy-2-methyl-1-phenyl-1-propanone (Darocur 1173) and 2-hydroxy-1-[4-(2-hydroxyethoxy)phenyl]-2-methyl-1-propan-1-one (Irgacure 2959) were purchased from Ciba Specialty Chemicals, and acrylic acid, N-isopropylacrylamide (NIPAAM), N,N'-methylenebis(acrylamide) (MBIS), tripropylene glycol diacrylate (TPGDA), $1H,1H,2H,2H$-perfluorodecyltriethoxysilane, and 3-(trimethoxysilyl)propyl methacrylate were obtained from Sigma-Aldrich and used without further purification. 6-[(1′,3′,3′-Trimethylspiro[chromene-2,2′-indolin]-6-yl)-oxy]hexyl acrylate (SPA) was prepared as described before.[25] Two monomer mixtures are used. Mixture 1 consists of NIPAAM, SPA, acrylic acid, MBIS, and Darocur 1173 of respectively 92, 1, 5, 1, and 1 mol %. For mixture 2, the amounts are 91, 1, 5, 2, and 1 mol %. Both mixtures are dissolved in an equal (weight) amount of anhydrous dioxane.

Substrate Preparation. Glass substrates were cleaned by means of sonication (ethanol, 15 min) followed by treatment in a UV−ozone photoreactor (Ultra Violet Products, PR-100, 20 min). The surface of the glass substrates was modified by spin-coating a 3-(trimethoxysilyl)-propyl methacrylate solution (1% v/v solution in a 1:1 water−isopropanol mixture) or a $1H,1H,2H,2H$-perfluorodecyltriethoxysilane solution (1% v/v solution in ethanol) on the activated glass substrate for 45 s at 3000 rpm. After curing for 10 min at 100 °C, the substrates were ready for use.

Preparation of Surface-Constrained Coatings. Substrate-attached patterned films were prepared in a home-made cell, which consisted of one upper $1H,1H,2H,2H$-perfluorodecyltriethoxysilane-functionalized glass slide and a lower propyl methacrylate function-alized glass slide with a spacing of ∼55 μm. The cells were capillary-filled with the monomer solution and subsequently exposed to UV light (unfiltered spectrum of a collimated EXFO Omnicure S2000 lamp, 300 s, 48 mW/cm² intensity in the range 320−390 nm). This dose of UV exposure leads to full polymerization (Figure S1 in the Supporting Information, SI).

Preparation of Symmetric Patterned Hydrogel Coatings by Polymerization-Induced Diffusion. Cells similar to those for surface-constrained coatings were capillary-filled, before being placed on a black surface. This is required in order to minimize polymerization in nonexposed areas because of optical effects caused by the reflection of light that has already passed through the sample. A mask was placed on top of the sample and the sample exposed to UV light (unfiltered spectrum of a collimated EXFO Omnicure S2000 lamp, 45 s, 13.5 mW/cm² intensity in the range 320−390 nm). Afterward, the mask was removed and the cell was fully exposed for another 300 s (48 mW/cm² intensity in the range 320−390 nm).

Preparation of Asymmetric Ratchet-Like Hydrogel Coatings by Prestructured Substrates. An inverse copy of a Fresnel lens was prepared as follows. A droplet of TPGDA containing 2 wt % photoinitiator Irgacure 2959 was placed on a propyl methacrylate functionalized glass slide. The Fresnel lens was placed firmly on top, and the sample was mildly exposed to UV light (60 s, 13.5 mW/cm² intensity in the range 320−390 nm) in order to have unreacted acrylates left for covalent bonding between the template and hydrogel in the next processing step. The Fresnel lens was carefully removed using a razor blade. A droplet of the monomer mixture was placed on the copy and a $1H,1H,2H,2H$-perfluorodecyltriethoxysilane-function-alized glass slide was pressed firmly on top prior to photo-polymerization for 300 s (48 mW/cm² intensity in the range 320−390 nm).

Photoresponse of the Films. For all samples, the upper glass slide of the hydrogel films was removed and the dioxane was allowed to evaporate, before the hydrogel was swollen in deionized water. During water uptake, the films become colored because of the protonation of merocyanine. Furthermore, the dimensions increase more than 2 times compared to the film in dioxane. After being immersed in water for 1 h, the film was stable (i.e., both the color of the film and its dimensions were in equilibrium).[29] Because of the pretreatment of the substrate, the film is covalently attached to the surface. This is confirmed by the fact that no detachment of the coating occurs during the swelling procedure. The photoresponse of the material was determined while it was immersed in deionized water. Light irradiation of the films was performed with a DC4100 4-Channel LED driver, equipped with a M455L3-C2 collimated LED (455 nm, full width at half-maximum = 18 nm, 0−1000 mA) from Thorlabs, Inc. The photoresponsiveness of surface-constrained films was performed at 700 mA for 5 min, masked exposures at 700 mA for 1 min (mixture 1 and 2) or 10 s (mixture containing directly acrylated spiropyran; Figure S5 in the SI).[28] Surface topographies obtained by polymer-ization-induced diffusion or by prestructured substrates were exposed at 700 mA for 15 min.

Characterization of the Hydrogels. UV/vis experiments were performed on an HR2000+ high-resolution spectrometer from Ocean Optics, mounted on a DM6000 M microscope from Leica micro-systems. The corresponding light source emits between 400 and 800 nm. Height profiles and 3D images of patterned films were recorded using a 3D interferometer (Fogale Nanotech Zoomsurf with a vertical resolution of 0.1 nm).

■ RESULTS AND DISCUSSION

Preparation and Photoresponse of Surface-Constrained Hydrogel Films. Initially, the photoresponsive behavior of self-protonating spiropyran hydrogels, covalently attached to a surface, was investigated. For these hydrogels, a chemical composition similar to that previously reported was used for the nonconstrained polymer films (Scheme 2).[28]

Scheme 2. Materials Used for the Preparation of Polymer Coatings

SPA, 1 mol%   NIPAAM, 91-92 mol%

acrylic acid, 5 mol%   MBIS, 1-2 mol%   Darocur 1173, 1 mol%
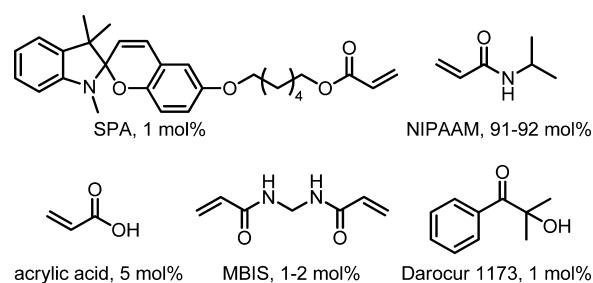
NIPAAM was used as main component (91 and 92% in mixtures 1 and 2, respectively). Spiropyran derivative SPA was incorporated as the photochromic unit (1%), and acrylic acid (5%) was added to obtain the self-protonated merocyanine form.[25,28] For chemical cross-linking of the network, 1 or 2 mol % MBIS was used (mixture 1 or 2).[30] Darocur 1173 was utilized as the photoinitiator. The monomer mixture was dissolved in anhydrous dioxane prior to use. Unless stated otherwise, mixture 1 was used in all experiments.

The acrylamide-based hydrogels were covalently attached to a glass surface using a propyl methacrylate functionalized glass slide. This results in a surface-constrained polymer coating. Therefore, a glass cell (spacing = 55 μm) with a methacrylate-functionalized surface on one side was used. This was filled with the dioxane mixture, which was subsequently photopolymerized to full conversion. The upper glass plate was then removed, and dioxane was evaporated, resulting in a ca. 25-μm-thick film. Subsequently, the polymer coating was placed in demineralized water, leading to swelling of the film. After swelling for at least 1 h, the thickness of the film was increased to roughly 140 μm. This high degree of swelling (5.6 times) is probably caused by the fact that the polymer network is prepared in solution, leading to a nonrigid network. Because of the double amount of cross-links present, polymer coatings prepared from mixture 2 swell slightly less. Here a thickness of 120 μm (4.8 times) was obtained. Because the swelling occurs mostly in the z direction, the hydrogel is not able to swell in a unidirectional fashion, therefore the swelling behavior is different than for freestanding films.[31]

During swelling of the hydrogels, the slightly off-color hydrogel film changed to a more intense orange color (Figure S2 in the SI), which indicates that the protonated merocyanine isomer forms spontaneously in water because of the carboxylic acid that is incorporated in the polymer backbone. Absorption measurements of the film showed an absorption maximum of λ = 470 nm, which is consistent with the formation of the self-protonated merocyanine hydrogel.[25,32] When the sample was exposed to visible light (λ = 455 nm) for 5 min, the protonated merocyanine absorbance at 470 nm almost completely disappeared (Figure 1b), demonstrating complete reversion of protonated merocyanine to the spiropyran form (Scheme 1).

The back-isomerization of spiropyran to protonated merocyanine was monitored with UV/vis spectroscopy. After 50 min at room temperature, the absorption band at λ = 470 nm returned to its initial intensity (Figure 1b,c), demonstrating complete recovery. Four successive exposure cycles show that this recovery is fully reversible and can be repeated multiple times.[33] The $t_{1/2}$ value of the recovery is ~10 min, which is slightly faster than the hydrogels without acrylic acid in an acidic environment, which we reported before.[25] When the
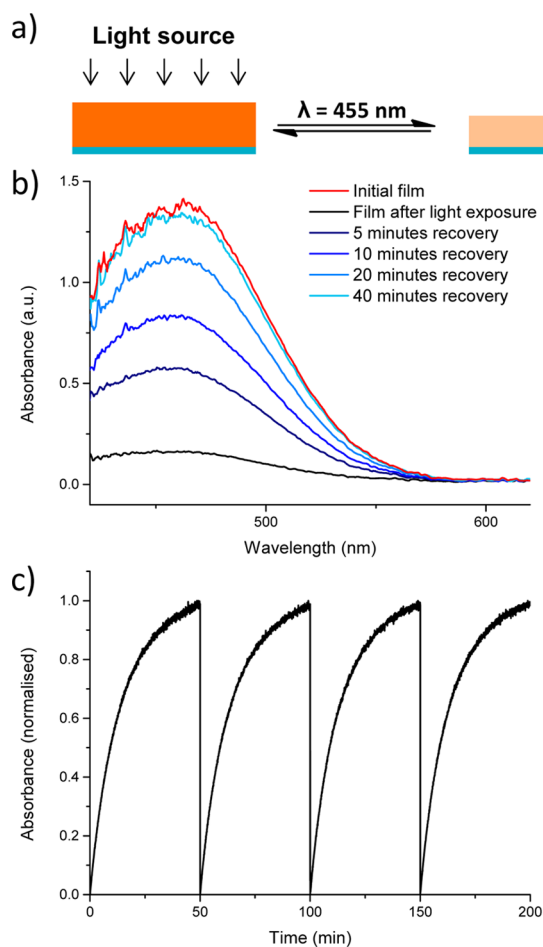

Figure 1. (a) Schematic representation of the photoinduced changes in the hydrogel coating. (b) UV/vis spectrum showing spontaneous isomerization of spiropyran to protonated merocyanine after exposure to light (455 nm). (c) Reversible photoresponsive behavior of the hydrogel film. The change in absorption at 470 nm is depicted during four successive 5 min exposure steps.

amount of cross-linker was increased from 1 to 2 mol %, the same recovery time scale was observed, despite the difference in the cross-link density (Figure S3 in the SI). The faster recovery is most likely related to the use of a different cross-linker rather than the difference between internal or external protonation (Figure S4 in the SI compares two different cross-linkers). Furthermore, the spiropyran moiety modified with hexyl acrylate leads to a faster recovery than its directly acrylated spiropyran analogue (Figure S5 in the SI). This behavior can be explained by the stronger electron-donating character of the ether group versus the ester group on the benzene ring.[32]

To measure the swelling behavior of the initially flat hydrogel coating, masked exposure (λ = 455 nm) was performed through a line mask with dark lines of 1 mm and a pitch of 2 mm (schematic representation in Figure 2a). After this masked exposure step, the exposed areas lost their color, while the nonexposed areas remain unchanged (Figure 2b). Therefore, it can be concluded that isomerization only took place in the exposed parts of the film. As with the experiments performed without photomask, spiropyran isomerized back into the protonated merocyanine isomer in ca. 50 min.

After masked exposure, the surface topography was investigated. Interferometry measurements revealed (Figures 2c and S6 in the SI) that the exposed areas were shrunken after
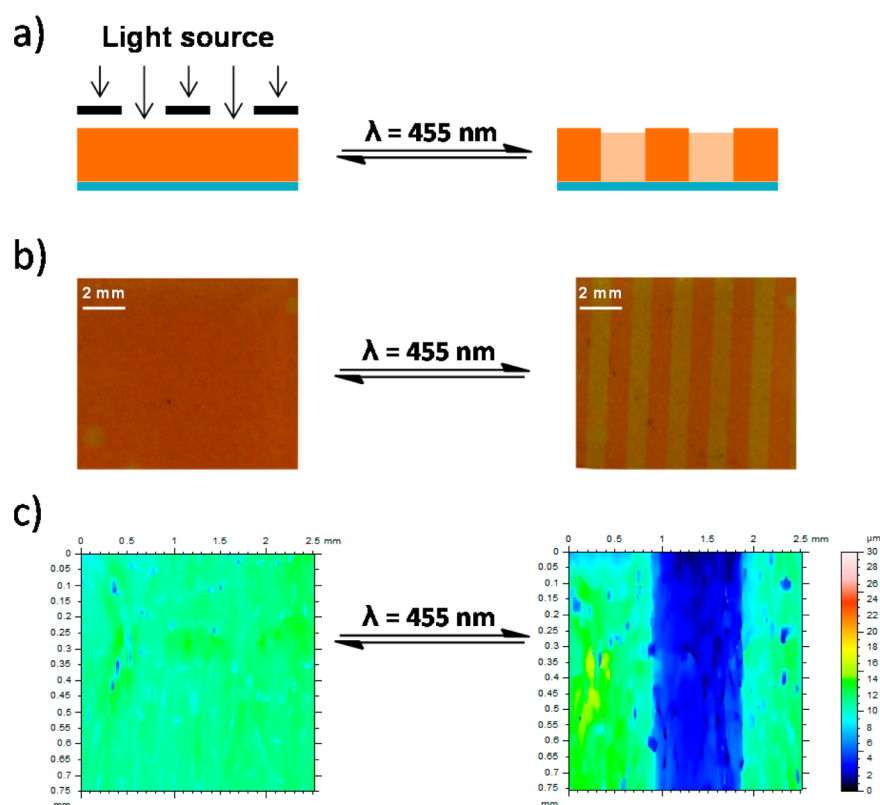
Figure 2. (a) Schematic presentation of masked illumination of the initially flat hydrogel coating. (b) Photographs of a hydrogel (mixture 1) before (left) and after (right) masked illumination (455 nm). (c) Corresponding height profile, as observed by interferometry. The lowest area is set as zero.
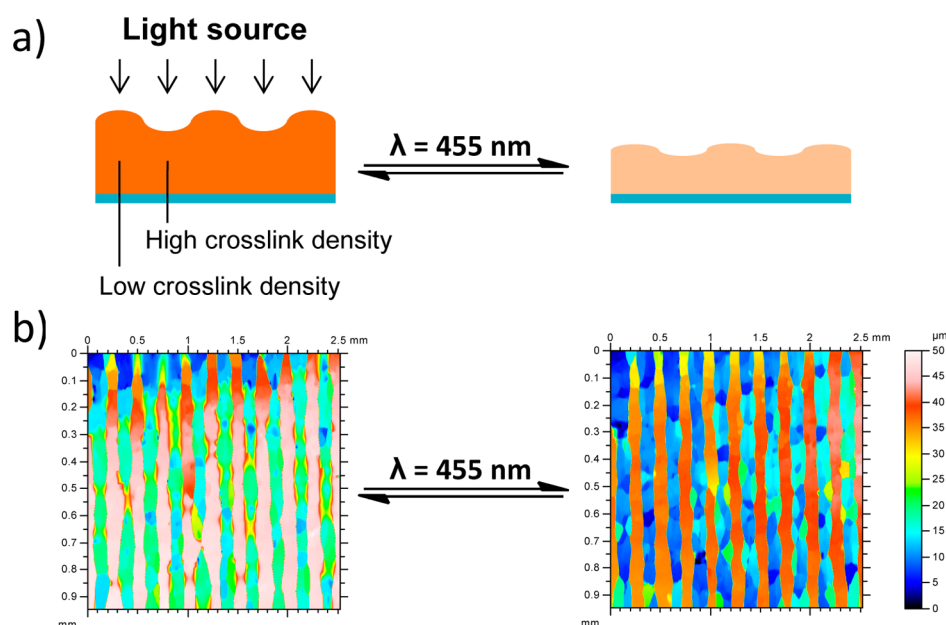

Figure 3. (a) Schematic representation of the hydrogel prepared by polymerization-induced diffusion. (b) Height profiles of a hydrogel prepared by polymerization-induced diffusion before and after exposure, as observed by interferometry. The lowest area is set as zero (note: due to smoothing software, the topographies are presented as more blocklike than their actual shape; however, the minima and maxima were measured accurately).

masked exposure, leading to a symmetric structured surface topography.[34] At the exposed areas, the film thickness decreased by approximately 5 μm, revealing shrinkage of the swollen film by 3.6%. To investigate the influence of the amount of cross-linker, similar experiments were performed in which the amount of MBIS was doubled (mixture 2; gel thickness is 120 μm; Figure S7 in the SI). The structures

obtained using these hydrogels decreased by only 3.2 μm after the masked exposure step, which is considerably lower. This lower 2.7% shrinkage is caused by the higher cross-link density, which leads to a lower degree of swelling and shrinkage. The results show that photoresponsive surface topography changes can be fine-tuned by varying the cross-link density of the hydrogel.

Symmetric Photoresponsive Surface Topographies by Polymerization-Induced Diffusion. We have first created symmetric photoresponsive surface topography hydrogels that operate at neutral pH. Such films were created via a controlled spatial distribution of the cross-link density, leading to patterned swelling.[35,36] Therefore, hydrogels were prepared by polymerization-induced diffusion in the presence of a solvent (see Figure S8 in the SI for the preparation method).[3,25] Polymerization-induced diffusion occurs during patterned UV-light exposure of a monomer mixture because of the different diffusion and polymerization rates of the monomers. This leads to a patterned cross-link density following the pattern of the mask that is used during the photopolymerization step. In previous solvent-free experiments at elevated temperature, the polymerization was faster than the diffusion, resulting in accumulation of the diacrylate monomers near the edges of the photomask.[25,37,38]

The same types of cells as those for the preparation of surface-constrained hydrogel films were used, but in these experiments, the photopolymerization process consisted of two sequential photoexposure steps at room temperature. The first step was a masked photoexposure, after which the mask was removed and flood UV exposure applied to ensure the formation of a polymer film over the entire surface area. Because these polymerizations were performed in solution, there is a high degree of monomer mobility, and diffusion of the monomers during the first exposure step is therefore faster than that in the solvent-free experiments, resulting in smooth structures instead of accumulation of monomers at the edges of the exposed areas (Figures S9 and S10 in the SI).

The coatings prepared by polymerization-induced diffusion had an initial thickness of approximately 30 μm (Figures S9a and S10a in the SI). After swelling, the thickness of areas with a low cross-link density increased to 200 μm (6.6 times swollen). The height of the relief structure is 28 μm in which the twice-exposed areas swell less (5.6 times; Figure 3b). This behavior indicates that these areas contain more cross-linker because in the first exposure step the more reactive diacrylate cross-linker diffuses to the exposed areas.

After exposure with visible light (λ = 455 nm), the total thickness of areas with a low cross-link density decreased to 180 μm (−10%) and the relief structure decreased to 23 μm (−18%; Figures 3b and S10 in the SI). Therefore, it can be concluded that a cross-link density difference throughout the film can be obtained with the use of polymerization-induced diffusion for solubilized systems as well because the polymer film is surface-constrained and therefore can only swell in the direction perpendicular to the surface. It should be noted that the swelling and light-response behavior of the coating are larger in comparison with those of the constrained homogeneous polymer coatings (vide supra). This behavior indicates that the areas with low or high cross-link density do not behave independently.

Asymmetric Photoresponsive Surface Topographies by Prestructured Substrates. In order to fabricate asymmetric photoresponsive surface topographies, an asymmetric ratchet substrate was used. This approach is based on the fact that a thicker surface-constrained hydrogel film shows a larger degree of swelling, and because of the asymmetry in the substrate, asymmetric swelling occurs.[15] A copy of a ratchet template was made using TPGDA, which was partly photopolymerized.[39] Because of incomplete polymerization, pendant acrylate groups are still present at the copy. Subsequently, the

structure was filled with the hydrogel mixture and photopolymerized, leading to a hydrogel that is covalently linked to the asymmetric substrate. Following evaporation of dioxane after polymerization, the dried film has a similar, but less steep, topography compared to that of the TPGDA substrate (Scheme 3a,b and Figure S11 in the SI).

Scheme 3. Working Mechanism of the Ratchet Topography
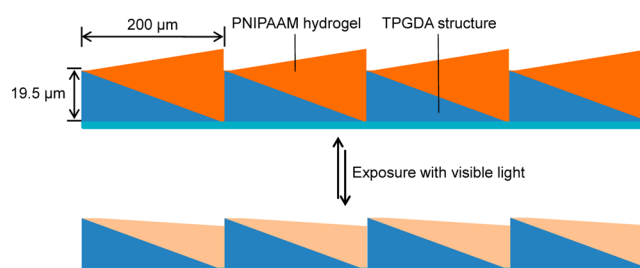
In its dry state, the maximum height of the polymer network is 10.7 μm. The surface, after the film is swelled in demineralized water, shows an inverse ratchet topography (Figures 4 and S12 and S13 in the SI) compared to that of the
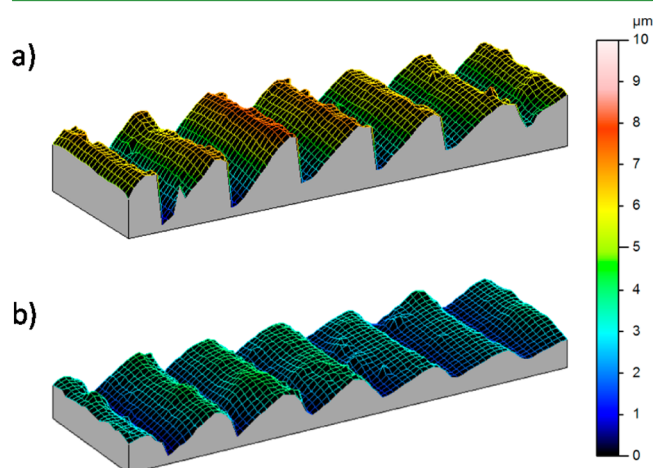

Figure 4. 3D height profiles of a ratchet prepared from mixture 1 before (a) and after (b) light exposure, as observed by interferometry (dimensions of the surface are 379 × 1262 μm^2).

dry film. This behavior shows that the thicker surface parts swell more, as expected (Scheme 3). The maximum height difference is around 6 μm (the total height of the swollen hydrogel is 26 μm). Upon light exposure, the ratchet slope decreased. The maximum change that could be obtained was a reduction of 3 μm in height. Subsequent illumination and reswelling cycles resulted in similar shrinkage and swelling behavior, showing that the hydrogel coating can be reversibly switched between a ratchet and a more flat surface topography.

In order to show that the surface topography can be controlled by varying the amount of cross-linker, similar ratchet films were prepared from mixture 2 containing 2 wt % cross-linker (Figures 5 and S12 and S14 in the SI). Because of the higher cross-link density, the obtained hydrogel swells less than the previously discussed hydrogel (the initial height is 10.8 μm, and the height of the swollen hydrogel is 21.3 μm). This results in an asymmetric structure with a difference in height of only 1.8 μm after being swollen in demineralized water, which is comparable with the difference in the case of surface-

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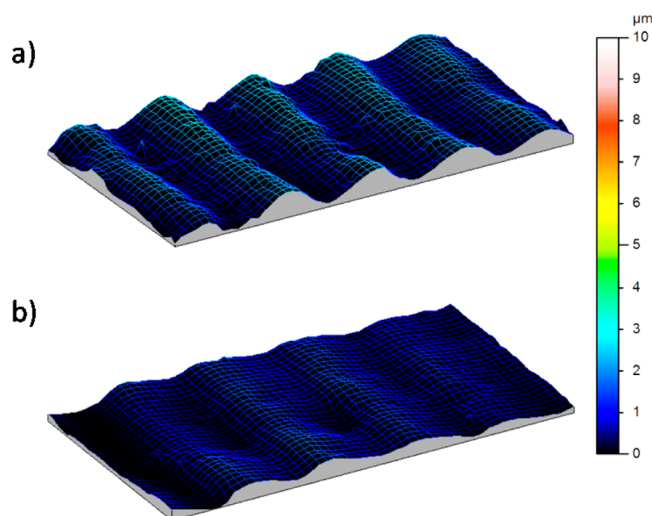dx.doi.org/10.1021/am500542f | *ACS Appl. Mater. Interfaces* 2014, 6, 7268−7274

Figure 5. 3D height profiles of a ratchet prepared from mixture 2 before (a) and after (b) light exposure, as observed by interferometry (dimensions of the surface are $505 \times 946 \ \mu m^2$).

constrained films (vide supra). Upon exposure to visible light, the surface went from ratchet-structured to flat and even formed an inverse ratchet structure that had a 1 μm height difference. Furthermore, alteration of the protrusions could be easily controlled, depending on the intensity of the illumination and the exposure time (Figure S15 in the SI). Both ratchet structures could be photoswitched many times. After several months of storage in demineralized water, the response of the coating toward light is still present (i.e., there is no decrease in the response compared to fresh samples), showing that it is possible to fabricate durable photoresponsive topographies.

CONCLUSIONS

Hydrogels based on polymers of NIPAAM, spiropyran, and acrylic acid have been used to produce photoresponsive symmetric and asymmetric surface topographies that can operate in a neutral aqueous environment. By using prestructured ratchet substrates, the light-responsive asymmetric surface topography can, in principle, be fully controlled by the chemical composition of the mixture. Furthermore, one can expect that even more complex surface topographies are possible by combining the approaches reported here, i.e., local light exposure, polymerization-induced diffusion, and prestructured substrate approaches. Our results show that dynamic robust asymmetric hydrogel surfaces can be fabricated that can be useful in microfluidic, biological, and tribological applications. Currently, we have initiated investigations into the behavior of cell growth on these coatings and started to implement the practical incorporation of these photoresponsive materials within microfluidic devices.[8,40]

ASSOCIATED CONTENT

Ⓢ Supporting Information

Photoresponsive behavior of different hydrogel films and surface topographies as observed by interferometry. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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