Photoswitchable Ratchet Surface Topographies based on Self-Protonating Spiropyran-NIPAAM Hydrogels

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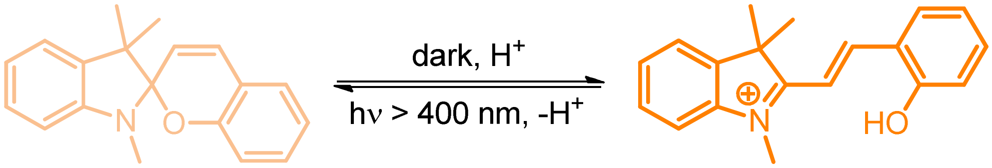
Abstract

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 neutral environment. Photoresponsive surface constrained films have been fabricated of 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 crosslink density thus forming a corrugated surface. Asymmetric ratchet-like photoresponsive surfaces have been prepared on pre-structured asymmetric substrates. Due to 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.

Introduction

Responsive surface topographies, manufactured from materials which can change their properties in a reversible fashion, are gaining a lot of attention in recent years.[1-2] By chemical design, the topographies can become responsive towards various stimuli, such as pH, temperature or light.[3-7] Photoresponsive materials are of particular interest, since they can be operated locally in a non-contact 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 type of coatings is 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 due to 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 increasing the surrounding temperature above the lower critical solution temperature (LCST), resulting in dehydration and collapse of the polymer chains. In case of addition of a crosslinking 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, whilst 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 environment is required to fabricate responsive surface topologies and up to now, most experiments are carried out in slightly acidic solution. Recently, we have reported the incorporation of a small amount of acrylic acid into the polymer backbone as internal proton source, to make freestanding photoresponsive polymer gels that operate in neutral environment.[28]



Scheme 1. Photoisomerization behavior of spiropyran into protonated merocyanine under acidic conditions.

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 crosslinker. 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 pre-structured surface, having a ratchet-like topography.[15] Due to the variable thickness of hydrogel present in different areas, the surface topography changes upon exposure with 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

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-propanone-1-one (Irgacure 2959) were purchased at Ciba Specialty Chemicals, acrylic acid, N-isopropylacrylamide (NIPAAM), *N*,*N*′-methylenebisacrylamide (MBIS), tripropylene glycol diacrylate (TPGDA), 1*H*,1*H*,2*H*,2*H*-perfluorodecyl triethoxysilane 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, respectively 92, 1, 5, 1, 1 mol%. For mixture 2 the ratio is 91, 1, 5, 2, 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 minutes) followed by treatment in a UV-ozone photoreactor (Ultra Violet Products, PR-100, 20 minutes). The surface of the glass substrates was modified by spincoating 3-(trimethoxysilyl)propyl methacrylate solution (1 v/v % solution in a 1:1 water-isopropanol mixture) or 1*H*,1*H*,2*H*,2*H*-perfluorodecyltriethoxysilane solution (1 v/v % solution in ethanol) on the activated glass substrate during 45 seconds at 3000 rpm. After curing for 10 minutes 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 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-triethoxysilane functionalized glass slide and an lower propyl methacrylate functionalized 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 sec, 48 mW/cm^2 intensity in the range 320-390 nm). This dose of UV-exposure leads to full polymerization (Fig. S1).

Preparation of symmetric patterned hydrogels coatings by polymerization-induced diffusion

Similar cells as for surface constrained coatings were capillary filled, before being placed on a black surface. This is required in order to minimize polymerization in non-exposed areas due to optical effects caused by 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 sec, 13.5 mW/cm^2 intensity in the range 320-390 nm). Afterwards, the mask was removed and the cell was fully exposed for another 300 seconds (48 mW/cm^2 intensity in the range 320-390 nm).

Preparation of asymmetric ratchet-like hydrogel coatings by pre-structured 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 sec, 13.5 mW/cm^2 intensity in the range 320-390 nm) in order to have unreacted acrylates left for covalent bonding between the template and the 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 1*H*,1*H*,2*H*,2*H*-perfluorodecyl-triethoxysilane functionalized glass slide was pressed firmly on top prior to photopolymerization for 300 seconds (48 mW/cm^2 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 the water uptake, the films become colored due to 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 hour, the film was stable (i.e. both the color of the film and its dimensions were in equilibrium).[29] Due to the pre-treatment 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 whilst 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, FWHM = 18 nm, 0-1000 mA) from Thorlabs, Inc. Photoresponsiveness of surface constrained films was performed at 700 mA for 5 minutes, masked exposures at 700 mA for 1 minute (mixture 1 and 2) or 10 seconds (mixture containing directly acrylated spiropyran, Fig. S5).[28] Surface topographies obtained by polymerization-induced diffusion or by pre-structured substrates were exposed at 700 mA for 15 minutes.

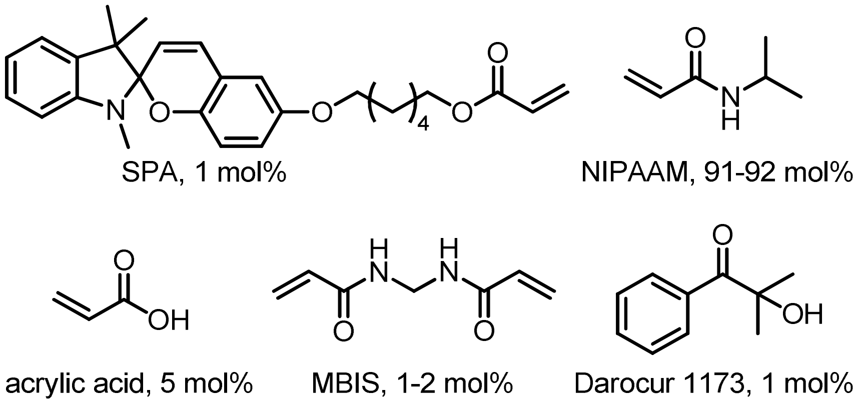
Characterization of the hydrogels

UV/Vis experiments were performed on an HR2000+ high resolution spectrometer from Ocean Optics, mounted on a DM6000 M microscope from Leica microsystems. 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 similar chemical composition was used as previously reported for the non-constrained polymer films (Scheme 2).[28] N-Isopropylacrylamide (NIPAAM) was used as main component (91 and 92% in mixture 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% of *N*,*N'*-methylenebisacrylamide (MBIS) was used (mixture 1 or 2).[30] Darocur 1173 was utilized as photoinitiator. The monomer mixture was dissolved in anhydrous dioxane prior to use. Unless stated otherwise, mixture 1 was used in all experiments.



Scheme 2. Materials used for the preparation of the polymer coatings.

The acrylamide based hydrogels were covalently attached to a glass surface by 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 the 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 hour, 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 non-rigid network. Due to the double amount of crosslinks present, polymer coatings prepared from mixture 2 swell slightly less. Here a thickness of 120 μm (4.8 times) was obtained. As 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 (Fig. S2), which indicates that the protonated merocyanine isomer forms spontaneously in water due to the carboxylic acid which is incorporated in the polymer backbone. Absorption measurements of the film showed an absorption maximum of $\lambda = 470$ nm which is consistent with the formation of the self-protonated merocyanine hydrogel.[25, 32] When the sample was exposed to visible light ($\lambda = 455$ nm) for 5 minutes, the protonated merocyanine absorbance at 470 nm almost completely disappears (Fig. 1b), demonstrating complete reversion of the protonated merocyanine to the spiropyran form (Scheme 1).

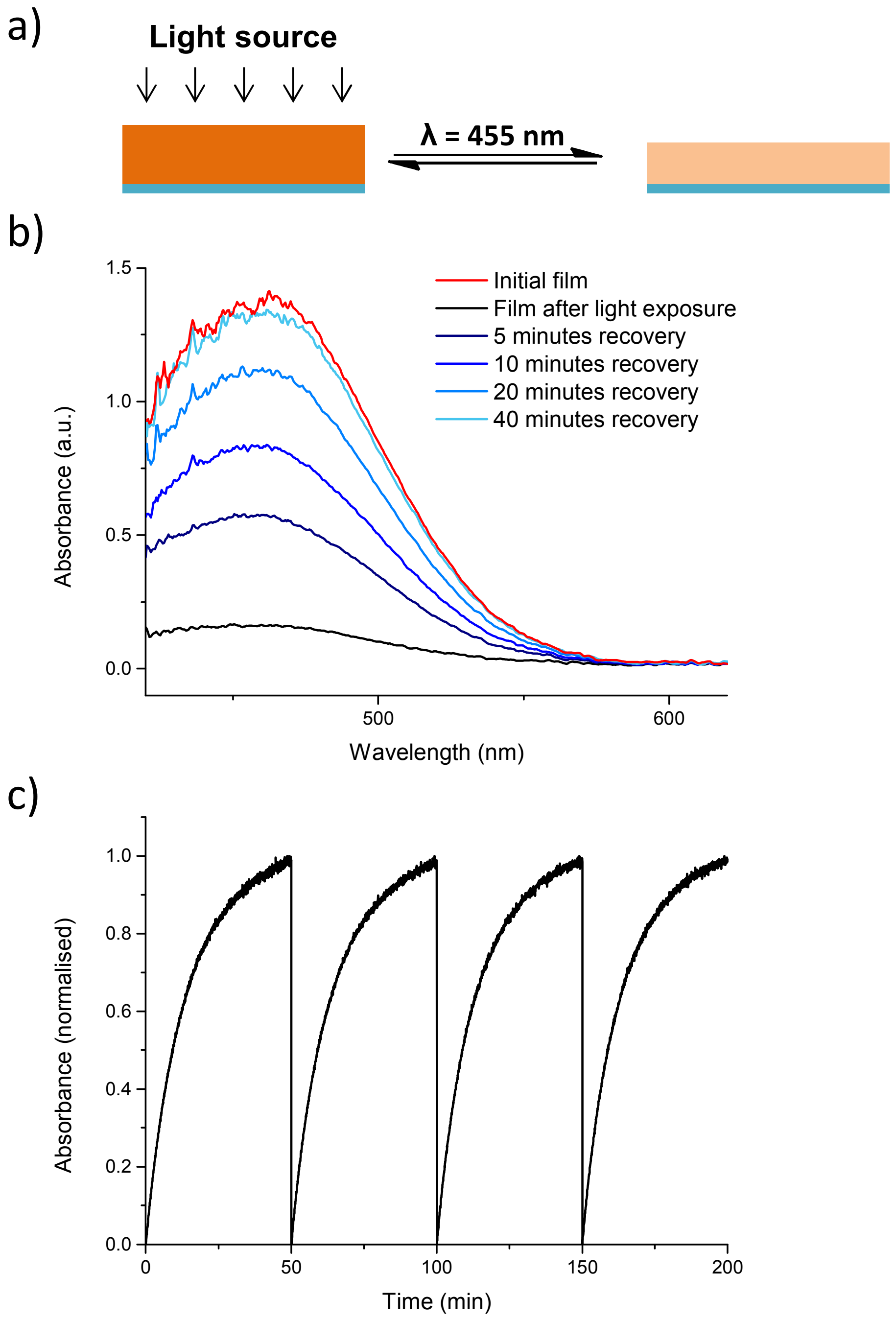


Figure 1. (a) Schematic representation of the photo-induced changes in the hydrogel coating, (b) UV-Vis spectrum showing spontaneous isomerization of spiropyran to protonated merocyanine after exposure to light (455 nm) and (c) Reversible photoresponsive behavior of the hydrogel film, change in absorption at 470 nm is depicted during four successive 5 minute exposure steps.

The back-isomerization of spiropyran into protonated merocyanine was monitored with UV/Vis spectroscopy. After 50 minutes at room temperature, the absorption band at λ = 470 nm returns to its initial intensity (Fig. 1b, c), demonstrating complete recovery. Four successive exposure cycles show that this recovery is fully reversible and can be repeated multiple times.[33] The $t_{½}$ value of the recovery is ~10 minutes, which is slightly faster than the hydrogels without acrylic acid in acidic environment which we reported before.[25] When increasing the amount of cross linker from 1 to 2 mol%, the same recovery timescale was observed, despite the difference in cross-link density (Fig. S3). The faster recovery is most likely related to the use of a different cross-linker, rather than the difference between internal or external protonation (Fig. S4 compares two different cross-linkers). Furthermore, the spiropyran moiety modified with hexyl acrylate leads to a faster recovery than its directly acrylated spiropyran analogue (Fig. S5). This behavior can be explained due to 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 Fig. 2a). After this masked exposure step, the exposed areas lost their color, whilst the non-exposed areas remain unchanged (Fig. 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 minutes.

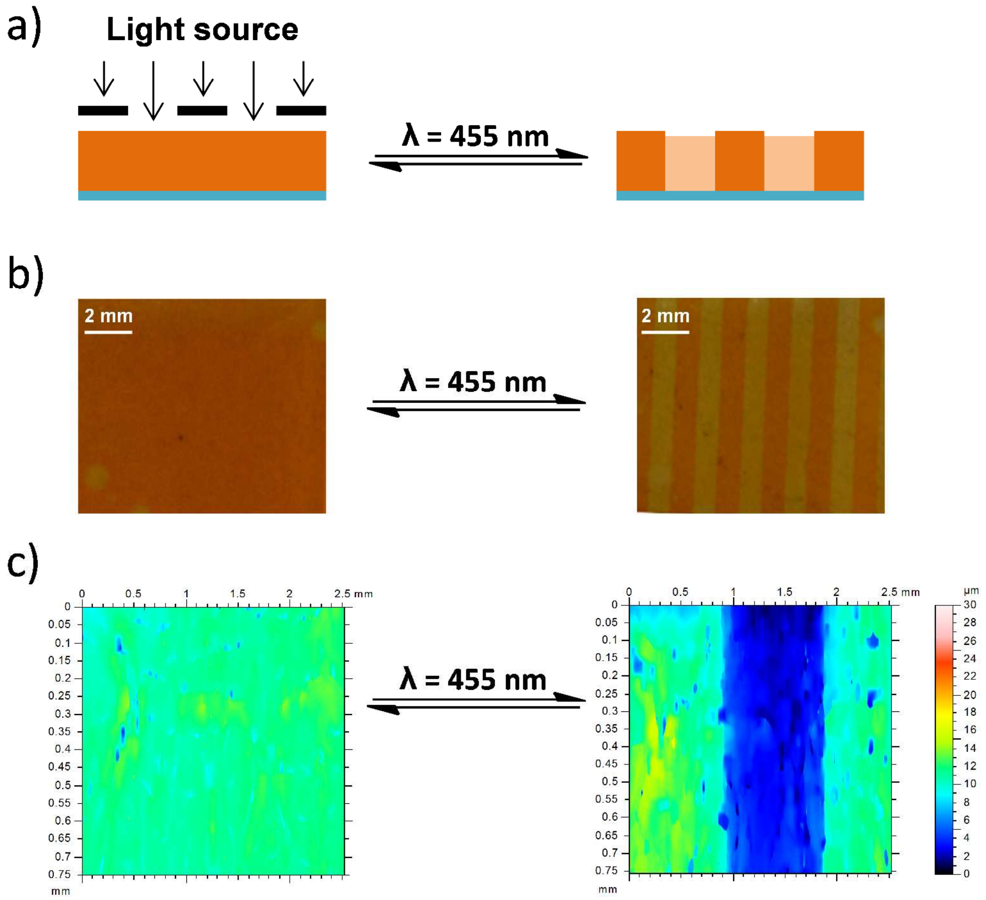


Figure 2. (a) Schematic presentation of masked illumination of the initially flat hydrogel coating, (b) photographs of a hydrogel (mixture 1) before (left) and after (right) masked illumination (455 nm), (c) corresponding height profile, as observed by interferometry. The lowest area is set as zero.

After masked exposure, the surface topography was investigated. Interferometry measurements revealed (Fig. 2c, S6) that the exposed areas were shrunken after 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, Fig. S7). 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 topographies hydrogels that operate at neutral pH. Such films were created via a controlled spatial distribution of the crosslink density leading to patterned swelling.[35-36] Therefore hydrogels were prepared by polymerization-induced diffusion in the presence of a solvent (see Fig. S8 for the preparation method).[3, 25] Polymerization-induced diffusion occurs during patterned light UV-exposure of a monomer mixture, due to 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 type of cells as for the preparation of surface constrained hydrogel films was used, but in these experiments, the photopolymerization process consisted of two sequential photo-exposure steps at room temperature. The first step was a masked photo-exposure, after which the mask was removed and a flood UV-exposure applied to ensure the formation of a polymer film over the entire surface area. As 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 in the solvent-free experiments, resulting in smooth structures instead of accumulation of monomers at the edges of the exposed areas (Fig. S9 and S10).

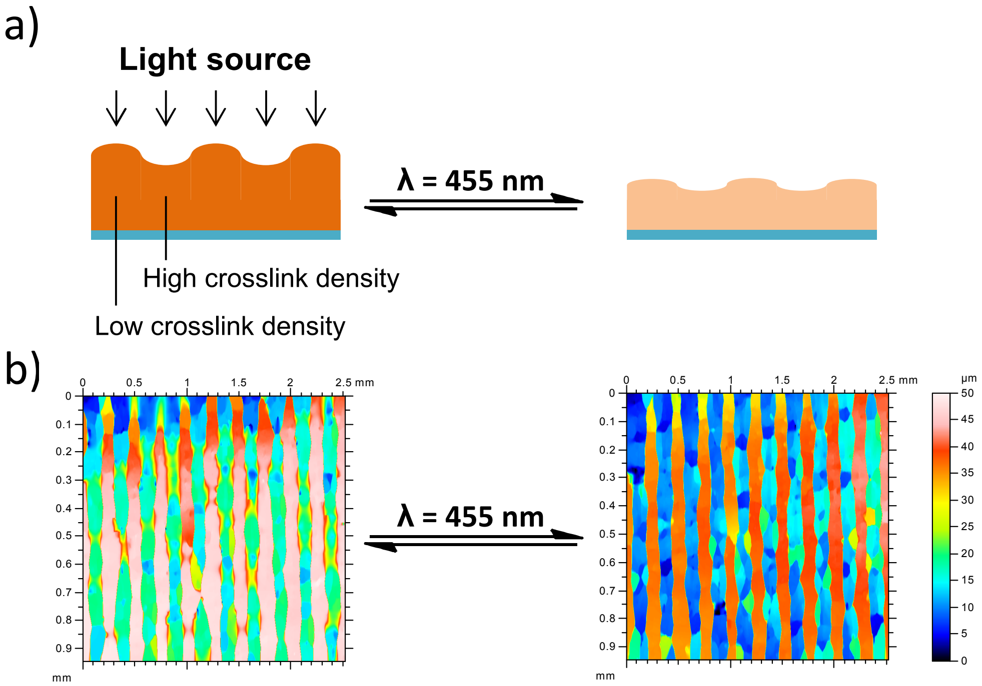


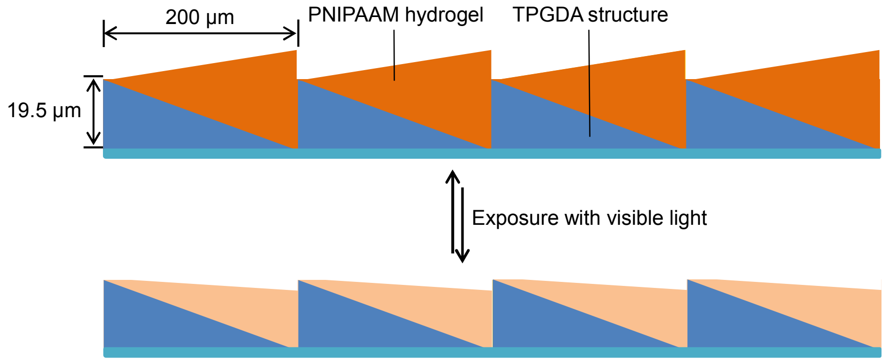
Figure 3. (a) Schematic representation of the hydrogel prepared by polymerization-induced diffusion and (b) height profiles of a hydrogel prepared by polymerization-induced diffusion before and after exposure, as observed by interferometry. The lowest area is set as zero (note: due to smoothing software,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

The coatings prepared by polymerization-induced diffusion had an initial thickness of approximately 30 μm (Fig. S9a and S10a). 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, Fig. 3b). This behavior indicates that these areas contain more cross linker as 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 %, Fig. 3b, S10). 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. As 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 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 pre-structured 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 due to asymmetry in the substrate, asymmetric swelling occurs.[15] A copy of a ratchet template was made using tripropylene glycol diacrylate (TPGDA), which was partly photopolymerized.[39] Due to the incomplete polymerization, pendant acrylate groups are still present at the copy. Subsequently, the structure was filled with the hydrogel mixture and photopolymerized, leading to hydrogel which is covalently linked to the asymmetric substrate. Following evaporation of dioxane after polymerization, the dried film has a similar, but less steep, topography as the TPGDA substrate (Scheme 3a-b, Fig. S11).



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 swelling the film in demineralized water, shows an inverse ratchet topography (Fig. 4, S12 and S13) compared to the dry film. This behavior shows that the thicker surface parts swell more, as expected (Scheme 3). The maximal height difference is around 6 µm (total height swollen hydrogel 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.

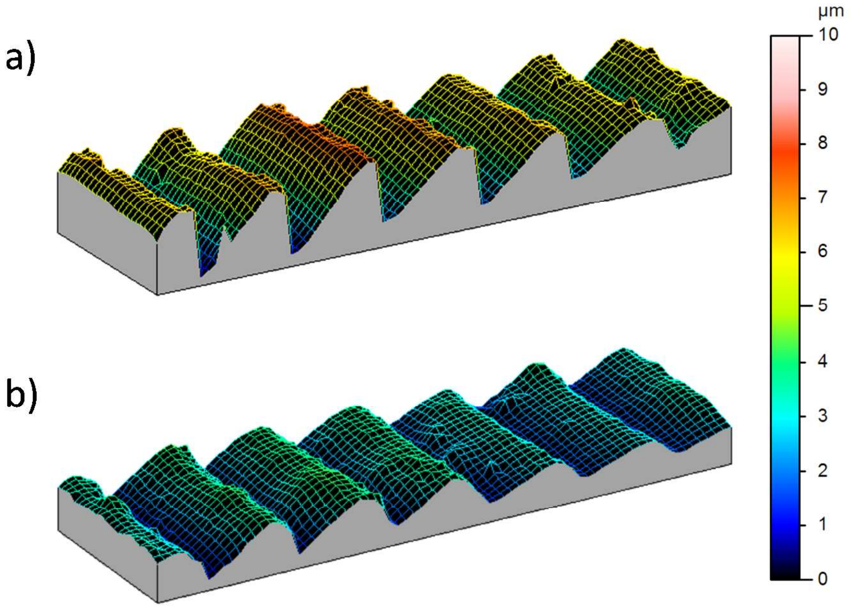


Figure 4. 3D height profiles of a ratchet prepared from mixture 1 before (a) and after (b) light exposure, as observed by interferometry (dimensions of the surface are 379 μm by 1262 μm).

In order to show that 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 (Fig. 5, S12 and S14). Due to the higher cross-link density, the obtained hydrogel swells less than the previously discussed hydrogel (initial height is 10.8 μm, 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 case of surface-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 1 μm height difference. Furthermore, the alteration of the protrusions could be easily controlled, depending on the intensity of the illumination and the exposure time (Fig. S15). Both ratchet structures could be photo-switched many times. After several months of storage in demineralized water, the response of the coating towards light is still present (i.e. there is no decrease in response compared to fresh samples), showing that it is possible to fabricate durable photoresponsive topographies.

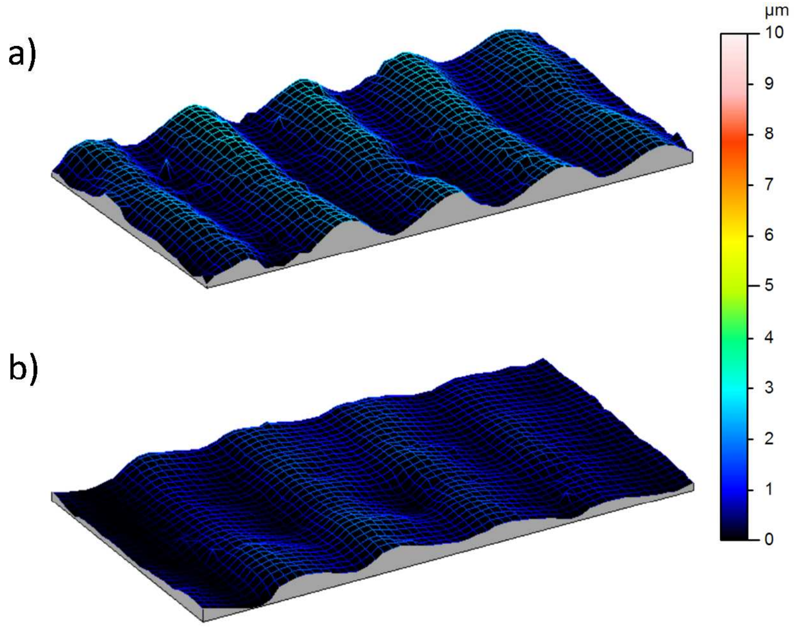


Figure 5. 3D height profiles of a ratchet prepared from mixture 2 before (a) and after (b) light exposure, as observed by interferometry (dimensions of the surface are 505 µm by 946 µm).

Conclusions

Hydrogels based on polymers of NIPAAM, spiropyran and acrylic acid have been used to produce photoresponsive symmetric and asymmetric surface topographies which can operate in neutral aqueous environment. By using pre-structured 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 pre-structured 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]

Supporting Information. Photoresponsive behavior of different hydrogel films; 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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