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14. ABSTRACT

We have developed temperature-responsive 3-D actuating hydrogel microstructures based on lithographically-patterned photo-crosslinkable poly(N-isopropyl acrylamide) copolymers. In one approach, a bilayer gel microstructure is constructed by joining together patterned layers of chemically distinct polymers with differing propensities to swell when placed in water. In a second approach, a single copolymer is used, but the duration of exposure to UV light (365 nm) is spatially varied, leading to lateral patterning of the crosslink density

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Abstract

We have developed temperature-responsive 3-D actuating hydrogel microstructures based on lithographically-patterned photo-crosslinkable poly(*N*-isopropyl acrylamide) copolymers. In one approach, a bilayer gel microstructure is constructed by joining together patterned layers of chemically distinct polymers with differing propensities to swell when placed in water. In a second approach, a single copolymer is used, but the duration of exposure to UV light (365 nm) is spatially varied, leading to lateral patterning of the crosslink density of the polymer network, and therefore its degree of swelling. In either case, the swelling of the more expansive elements is constrained by the presence of the less expansive elements, generating swelling stresses within the 2-D patterned hydrogel film, driving deformation into a 3-D microstructure that actuates in response to changes in temperature.

1. List of Illustrations and Tables

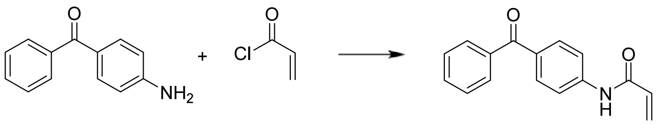
2. Statement of problem studied

The focus of this STIR project has been to develop a simple approach to create micro-patterned constructs of responsive hydrogels based on photo-crosslinkable polymers. To demonstrate this concept, we have focused on two cases: (i) bilayer structures that undergo reversible bending with changes in temperature, and (ii) gel sheets with laterally patterned swelling profiles that deform into simple, well-defined 3D shapes upon swelling. The processing strategies developed during this project will enable our ongoing work on fabrication of a diversity of active polymer micro-constructs with complex geometries, and containing a wide variety of polymers with different materials properties, responses to stimuli, and chemical or physical functionalities.

3. Summary of key results

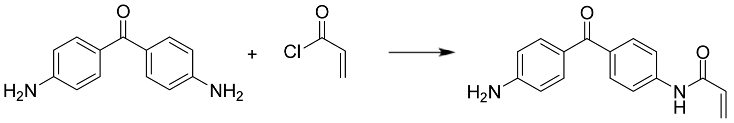
3.1 Synthesis of photo-crosslinkable polymers

Our approach to photo-crosslinkable copolymers relies on the well-know non-specific grafting of benzophenone to aliphatic hydrocarbons upon irradiation with UV light (at 365 nm). In the simplest case, 4-aminobenzophenone is reacted with acryloyl chloride, as shown in Scheme 1, yielding a crosslinkable monomer abbreviated as BP-acrylamide.



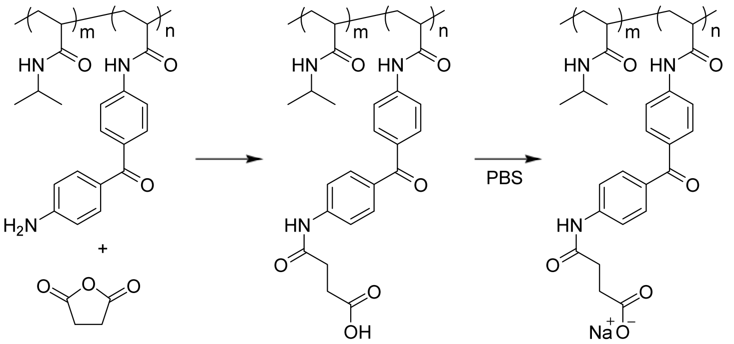
Scheme 1. Synthesis of BP-acrylamide

Unfortunately, this monomer is relatively hydrophobic, complicating its use in hydrogels. To address this problem, a second monomer, NH_2-BP-acrylamide was prepared from 4,4’-diaminobenzophenone and acryloyl chloride as shown in Scheme 2 (the desired product was purified using column chromatography).



Scheme 2. Synthesis of NH_2-BP-acrylamide

Upon copolymerization with *N*-isopropylacrylamide (NIPAM), NH_2-BP-acrylamide was derivatized with succinic anhydride as shown in Scheme 3 to introduce a carboxylate group and increase the water solubility of the crosslinking group.



Scheme 3. Incorporation of carboxylate functionalities to increase water solubility of photo-crosslinkable polymers based on NH_2-BP-acrylamide.

In similar fashion, a non-swelling photo-crosslinkable polymer was made from hydroxy ethyl methacrylate (HEMA) and BP.

3.2 Fabrication of actuating hydrogel microstructures

In both approaches to fabricate gel microstructures, the first step was to prepare a sacrificial layer of rhodamine-labeled poly(sodium acrylate) by spin-coating on a glass substrate, then immersing in 1 M $CaCl_2$ solution, leading to an ionically crosslinked film that is only soluble in high ionic strength aqueous solutions. As the final processing step, this sacrificial layer is dissolved in NaCl solution, liberating the patterned hydrogel from the substrate.[1]

To fabricate bilayer strips, poly(HEMA-*co*-BP-acrylamide) and poly(NIPAM-*co*-BP-acrylamide) were coated sequentially from solution on top of the sacrificial layer. This trilayer polymer film was then exposed to UV light (365 nm) through a photomask, leading to crosslinking of both HEMA and NIPAM layers as well as covalent grafting to the two layers to each other in irradiated regions. A developing step was then used to dissolve the uncrosslinked regions, followed by detachment of the resulting patterned bilayer hydrogel film from the substrate into water by adding a drop of NaCl solution to dissolve the sacrificial layer.

In the second approach, lateral patterning of the swelling propensity of a gel film was achieved by first coating poly(NIPAM-*co*-BP) on the sacrificial layer. This film was then illuminated with UV (365 nm) through a photomask for a given period of time, t_1. Subsequently, irradiation with visible light (560 nm) through the same photomask was conducted for 20 minutes to bleach the rhodamine signal in the exposed regions of the sacrificial layer, providing an alignment mark for exposure through the second photomask. Using a “mask-aligner” consisting of micromanipulators for positioning and a microscope objective for illumination, the second photomask was aligned against the hydrogel film, and UV (365 nm) was applied for a period of time, t_2. A given exposed region of the gel could thus receive a dose of UV light proportional to t_1, t_2, or $t_1 + t_2$, depending on whether it was exposed through the first, second, or both masks, respectively. After adding a drop of NaCl solution to dissolve sacrificial layer, the detached hydrogel microstructures were immersed in ethanol, or in water or phosphate buffered saline for poly(NIPAM-*co*-BP-COOH).

3.3 Thermally actuating hydrogel bilayer strips

To demonstrate the fabrication of actuating gel microstructures, we prepared hydrogel bilayer strips consisting of a layer of temperature responsive poly(NIPAM-*co*-BP) and a layer of non-swelling poly(HEMA-*co*-BP). While the linear expansion ratio α (swollen length / initial length of hydrogel) of poly(HEMA-*co*-BP) was 1.0 and did not change with temperature, α of poly(NIPAM-*co*-BP) varied from 1.5 at room temperature to 0.8 at 35 ^{o}C. This temperature responsive swelling along with the covalent attachment between the two layers allows actuation of the strip in response to temperature. Figure 1 shows coiling of the strip with poly(HEMA-*co*-BP) as an outer layer at 35 ^{o}C (left) and, as temperature goes down, the strip first uncoils to become flat, then coils in the opposite direction with poly(NIPAM-*co*-BP) as the outer layer (right).

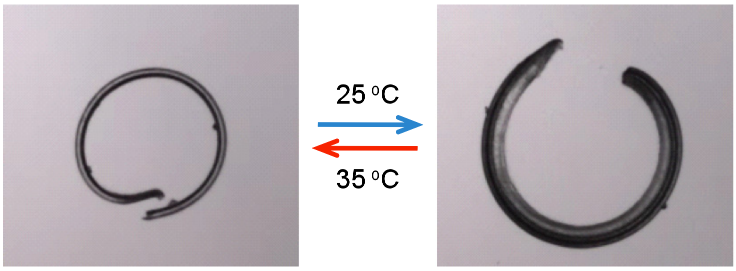


Figure 1. Actuation of a HEMA/NIPAM hydrogel bilayer strip (length ~ 100 μm)

3.4 Variations in degree of swelling as a function of UV irradiation time

By varying the UV irradiation time from, the density of crosslinks within the polymer network, and hence the swelling ratio, could be tuned. For example, Figure 2 shows the areal expansion ratio measured for uniformly crosslinked poly(NIPAM-*co*-BP-acrylamide) (10 mol %

BP-acrylamide) networks in ethanol. By varying the time of irradiation from 15 sec to 10 min, the swelling ratio was varied continuously from 4.1 to 2.0.

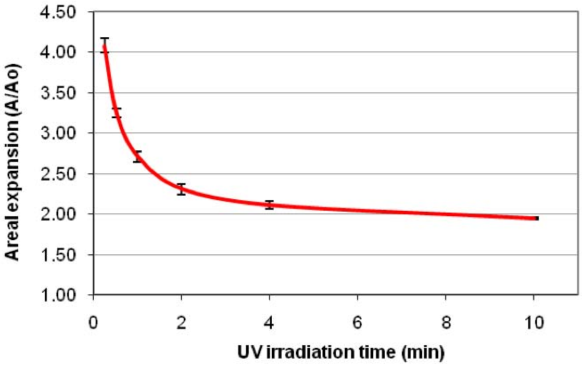


Figure 2. Areal expansion of NIPAM copolymer networks as a function of UV irradiation time

3.5 Formation of 3-D structures: cones and ruffled discs

As described above, two different photomasks were used to locally vary the UV irradiation time, and thus the swelling ratio, within a single hydrogel microstructure. Figure 3 shows the applied 2-D patterns, and the resulting 3-D microstructures obtained upon swelling in ethanol. For the case of annuli wherein the outer portion of the disc swells more extensively, the result was a ruffled structure. Discs with more extensively swelling inner portions were found to fold into cones when appropriately-sized wedges of material were "cut out" of the disc. We are currently working to quantify the deformation of these microstructures as a function of the pattern geometry and swelling contrast.

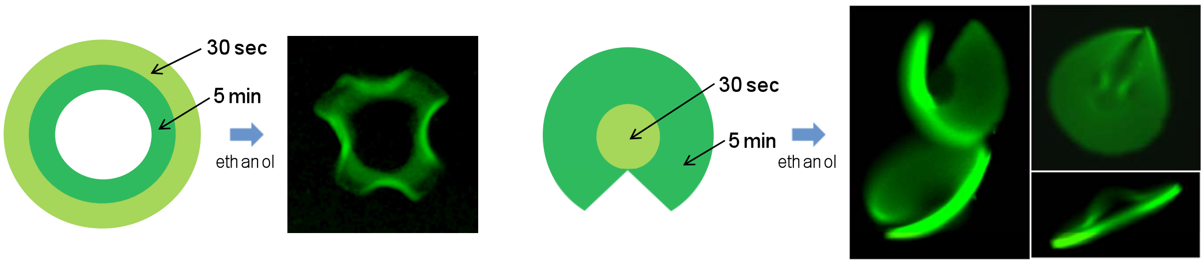


Figure 3. Deformation of 2D patterned hydrogel sheets into 3D microstructures upon swelling

4. *References*

1. V. Linder, B.D. Gates, D. Ryan, B.A. Parviz, G.M. Whitesides, Water-Soluble Sacrificial Layers for Surface Micromachining, *Small*, **1**, 730-736 (2005).