pH and photo-responsive hydrogels based on acrylic acid and acrylamide

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Hydrogels are three-dimensional polymeric networks that can absorb and retain large quantities of water in relation to their physical size. By incorporating stimuli-responsive units into the gel structure, hydrogel materials can be actuated by external stimuli such as photo, thermal, electro and pH, respectively. In this study, pH responsive hydrogels were developed by using copolymers of acrylic acid (AA) and acrylamide (Am) in different molar ratios (30:70, 50:50 and 70:30, respectively). At pH above the pK_a of AA (pH>4.5) the AA dissociates to the more hydrophilic acrylate (A^-) form triggering swelling of the hydrogel. In contrast, at pH < 4.5, the hydrogel contracts due to the formation of the hydrophilic AA form in the polymer backbone, which triggers release of water from the gel.

In order to turn this pH response into a photo-response, a reversible photo-acid generator, spiropyran acrylate (SP-A), was copolymerised in the polymer backbone. In acidic environments, the SP-A will spontaneously convert to the protonated hydrophilic merocyanine ($MC\text{-}H^+$) form and switch back to the hydrophobic SP-A when exposed to white light, expelling a proton in the process. The switching between these two forms can be used to trigger LCST behaviour in the gel, leading to photo-controlled swelling/contraction due to water uptake and release.

The composition used for the photo responsive hydrogel was AA: Am: SP-A in a 10:10:1 molar ratio. When the hydrogel is immersed in water, in the dark, the AA dissociates and the proton is taken by the SP-A to form $MC\text{-}H^+$, which gives the hydrogel a yellow colour. Under these conditions (A^-, $MC\text{-}H^+$) the polymer chains are more hydrophilic causing the hydrogel to expand (Fig. 1, initial point). However, when exposed to white light, the $MC\text{-}H^+$ is converted back to the SP-A form (colourless) expelling a proton, decreasing the local pH, and protonating the AA. This makes the polymer chain less hydrophilic and the hydrogel contracts (Fig. 1, 0-10 min). As seen in Fig. 1, this process is reversible and with the initial photo-contraction complete in seconds. After ca. 10 min, the white light is switched off, and the hydrogel reswells to about 95% of its fully hydrated size after ca. 15 min in the dark.

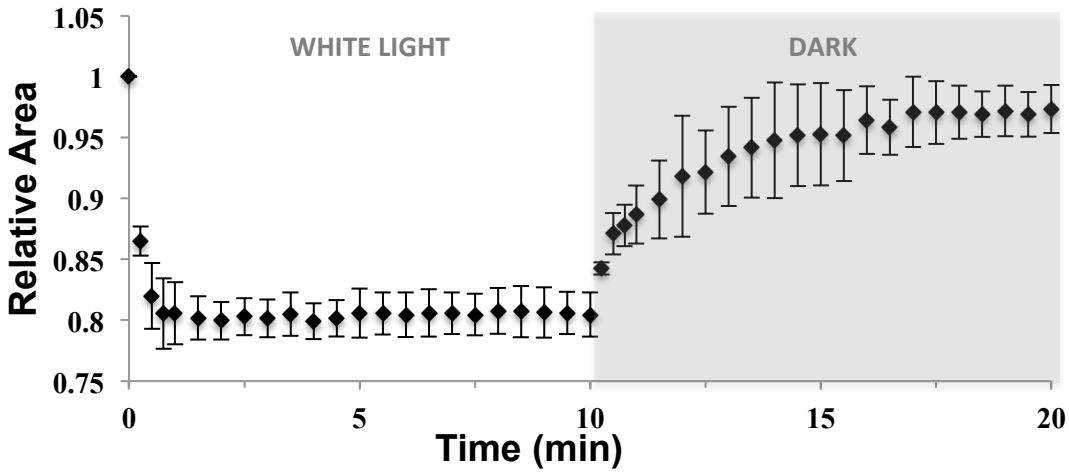

Fig 1. Shrinking and swelling of photo-responsive p(AA-*co*-acrylamide-*co*-SP-A) hydrogel (10:10:1) under different illumination conditions.