

pH AND PHOTO-RESPONSIVE HYDROGEL ACTUATORS

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Hydrogels constitute a group of hydrophilic polymeric materials, capable of holding large amounts of water in their three-dimensional networks. By incorporating stimuli-responsive units in their structure, hydrogel actuators can be developed, that respond to a variety of stimuli such as light, pH, electric or magnetic fields [1].

In this study, pH responsive hydrogels were developed using copolymers of acrylic acid (AA) and acrylamide (AAM) 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 (Figure 1). In contrast, at $pH < 4.5$, the hydrogel contracts due to the formation of the hydrophilic AA form in the polymer backbone, which promotes release of water from the gel (Figure 2). In the case of the 50:50 AAM:AA p(AAM-*co*-AA), circular hydrogels were polymerised that show an area of 0.72 mm^2 at pH 3 compared with 3.56 mm^2 for the same hydrogel at pH 11. This dramatic increase of 396.14% is due to the greater amount of the more hydrophilic acrylate ion form being present in basic conditions (Figure 3).

In order to turn this pH response into a photo-response, a reversible photo-acid generator, namely spiropyran acrylate (SPA), was copolymerised in the p(AAM-*co*-AA) polymer backbone. In acidic environments, SPA will spontaneously convert to the protonated hydrophilic merocyanine ($MC-H^+$) form and switch back to the hydrophobic SPA when exposed to white light, expelling a proton in the process (Figure 4).

The monomer ratio used for the p(AAM-*co*-AA-*co*-SPA) hydrogels was 10:10:1 AAM: AA: SPA. When the hydrogel is immersed in water, in the dark, the AA dissociates and the proton is taken by the SPA to form $MC-H^+$, which gives the hydrogel a yellow colour. Under these conditions (A^- , $MC-H^+$) the polymer chains are more hydrophilic causing the hydrogel to expand (Figure 5, initial point $t=0s$). However, when exposed to white light, the $MC-H^+$ is converted back to the SPA form (colourless) expelling a proton, thus decreasing the local pH, and protonating the AA. This makes the polymer chains less hydrophilic, causing the hydrogel to contract (Figure 5, 0-10 min). Upon removal of the white light source, the reverse process occurs and the initial conditions are restored, resulting in hydrogel expansion (Figure 5, 10-20 min).

For the p(AAM-*co*-AA-*co*-SPA) hydrogel, the SPA unit serves as a reversible photo-acid generator. This ensures a localised pH change under different illumination conditions, determining the ratio of AA/A^- present, and therefore the hydrophilic character of the polymer backbone. In this case, photo-contraction of over 15% in diameter was achieved within 90 seconds of white light irradiation followed by reswelling to ~95% of its fully hydrated size after further ~30 seconds in the dark (Figure 6).

In both cases (pH and photo-responsive hydrogels) the stimuli-induced contraction/reswelling processes were reversible and repeatable over at least 3 cycles with no detectable hysteresis [2].

The fast actuation of the p(AAM-*co*-AA-*co*-SPA) hydrogels demonstrates great potential for their incorporation in microfluidic systems as reversible photo-controlled micro-valves [3].

Word Count: 500

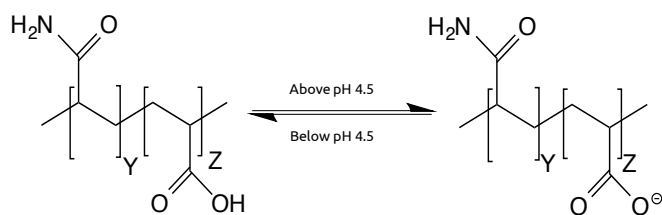


Figure 1. Chemical structure of *p*(AAm-co-AA) polymer chains under different pH conditions.

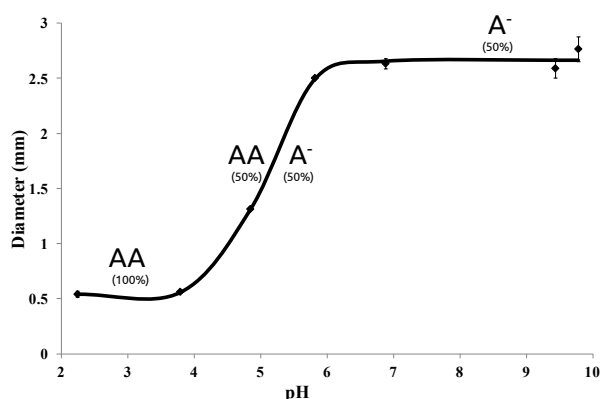


Figure 2. Size change of pH-responsive *p*(AAm-co-AA) hydrogel under different pH conditions due to the ratio of AA/A⁻ present in the polymer chain.

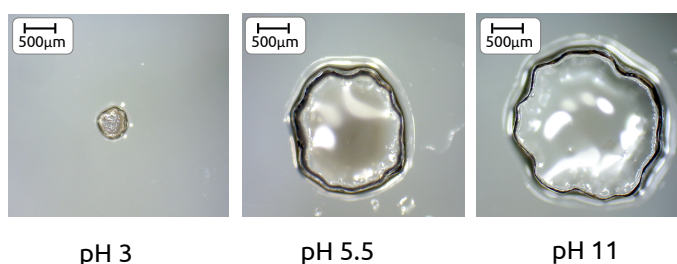


Figure 3. Photos showing the area change of the *p*(AAm-co-AA) hydrogels in different pH conditions.

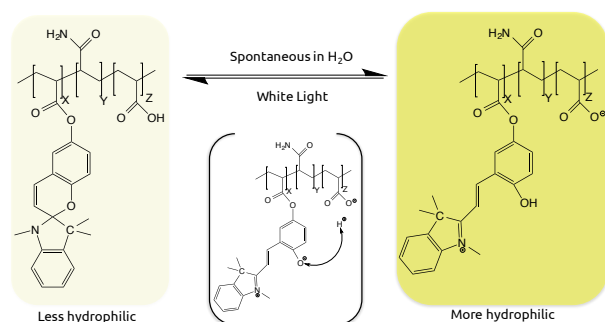


Figure 4. Chemical structure of *p*(AAm-co-AA-co-SPA) polymer chains under different illumination conditions.

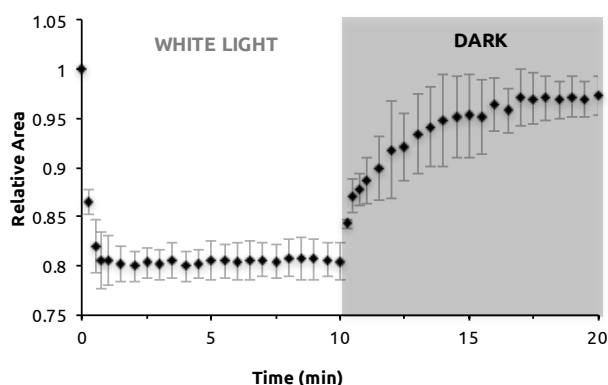


Figure 5. Relative area change of photo-responsive *p*(AAm-co-AA-co-SPA) hydrogels under different illumination conditions.

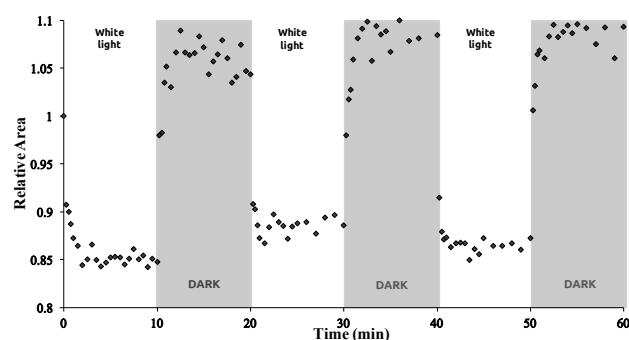


Figure 6. Repeatabile and reversible photo-induced actuation study of *p*(AAm-co-AA-co-SPA) hydrogels.

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