

## Photo-acid generator comonomer turns pH-responsive into photo-responsive hydrogels

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### Abstract

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[1], thermal, electro and pH, respectively. In this study, pH responsive hydrogels were studied by using copolymers of acrylic acid (AA) and acrylamide (Am) in a 50:50 molar ratio. At pH values above the pK<sub>a</sub> of AA (pH>4.5) the AA dissociates to the more hydrophilic acrylate anion form (A<sup>-</sup>) triggering swelling of the hydrogel. In contrast, at pH < 4.5, the hydrogel contracts due to the formation of the less 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, namely spiropyran acrylate (SP-A), was copolymerised in the polymer backbone using a 10:10:1 molar ratio of AA: Am: SP-A. In acidic environments, the SP-A will spontaneously convert to the protonated hydrophilic merocyanine (MC-H<sup>+</sup>) 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 a localised pH change around the polymer backbone, leading to photo-controlled swelling/contraction due to photo-induced protonation/deprotonation of the AA comonomer.

In DI water under dark conditions (A<sup>-</sup>, MC-H<sup>+</sup>) the polymer chains are more hydrophilic allowing the hydrogel to expand. However, when exposed to white light, the MC-H<sup>+</sup> is converted back to the SP-A form (colourless) expelling a proton, and therefore decreasing the local pH, which in turn causes protonation of the AA making the polymer chains less hydrophilic. The SP-A comonomer acts as a reversible photo-acid generator resulting in a photo-induced change of the local pH, which in turn determines the ratio of AA/A<sup>-</sup> and therefore the hydrophilic character of the polymer backbone. In this case, photo-contraction of over 15% in diameter is achieved within 90 seconds of white light irradiation followed by reswelling to ~98% of its fully hydrated size after further ~30 seconds in the dark.

### References

- [1] ter Schiphorst, J.; Coleman, S., Stumpel, J.E., Ben Azouz, A., Diamond, D. and Schenning, A.P., *Chemistry of Materials*, **2004**, 27(17), 5925-5931.

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