Photo-Responsive Hydrogels with Enhanced Volume Changes due to Local pH alterations

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Photo-responsive hydrogels of varying compositions containing spiropyran photochromic units have been widely studied in recent years due to their many potential applications, including photo-actuated micro-valves for microfluidic devices [1,2].

In this study two hydrogel formulations were employed to produce reversible photo-responsive hydrogel actuators operative in neutral pH. Both compositions contain the photochromic unit spiropyran acrylate (SP) and acrylic acid (AA) copolymerised in the main polymer backbone, together with *N*-isopropylacrylamide (NIPAAm) or acrylamide (AAm), respectively. At neutral pH, the AA comonomer dissociates to the acrylate anion (A^-) and the proton transfers to the SP unit to give the more hydrophilic protonated merocyanine ($MC\text{-}H^+$) form, which triggers water uptake and hydrogel expansion. Under white light irradiation, the $MC\text{-}H^+$ reverts to the more hydrophobic SP isomer, with simultaneous reformation of acrylic acid, and hydrogel contraction.

In the case of p(NIPAAm-*co*-AA-*co*-SP) hydrogel, an area contraction of up to 45% of its fully hydrated size was achieved after 4 min of white light exposure followed by reswelling to up to 85% of the initial size after 11 min in the dark.

In the case of p(AAm-*co*-AA-*co*-SP) hydrogel, the SP unit serves also as a reversible photo-acid generator changing the local pH which in turn determines the ratio of AA/A^-, and therefore the hydrophilic character of the polymer backbone. In this case, photo-contraction of ~15% in diameter is 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.

In both cases the photo-induced contraction/reswelling processes were reversible and repeatable over at least 3 cycles with no detectable hysteresis.

1. ter Schiphorst, J., et al., Chemistry of Materials, 2015. **27**: 5925-5931.
2. Ziółkowski, B., Florea, L. et al., Soft Matter, 2013. **9**: 8754-8760.

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