

## Solvato-morphologically controlled photo-actuated hydrogels

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In recent years, photo-responsive hydrogels reported in the literature have been synthesised by co-polymerisation of *N*-isopropylacrylamide (NIPAAm) with spirocyan (SP) derivatives. This approach requires external protonation of the hydrogels in order to induce re-swelling, typically by immersing the hydrogel in strongly acidic environments[1-3]. Moreover, re-swelling times are long, typically up to several hours. These disadvantages have restricted the use of photo-actuated hydrogels to applications that employ single-use methods.

Recently, we reported that the addition of acrylic acid copolymerised within the hydrogel provides an internal source of protons that allows photo-actuation in neutral pH environments[4].

The polymerisation solvent has been shown to directly influence the morphology of the hydrogel, by producing porous hydrogels of different pore sizes[5]. This has an impact on the diffusion path length for water molecules moving in/out of the hydrogel matrix, thus improving the swelling and shrinking kinetics of the hydrogel[6].

In this study photo-actuator hydrogels were generated using a *N*-isopropylacrylamide-co-acrylated spirocyan-co-acrylic acid (p(NIPAAm-co-SP-co-AA) copolymer, in a 100-1-5 mole ratio. Different ratios of organic solvent:water (tetrahydrofuran(THF), dioxane and acetone) were used as the polymerisation solvent. Varying the volume ratio of the solvent mixtures, resulted in hydrogels with different pore sizes and therefore different extent of swelling/shrinking and actuation kinetics. For example, when THF:water (4:1 v:v) was used as polymerization solvent, a remarkable contraction in hydrogel size of up to 50% was obtained after four minutes of white light irradiation.

Optimising these hydrogels by varying the polymerization solvent has resulted in faster and more reproducible shrinking and reswelling cycles.

1. Taku, S., et al., *Fast-reversible light-driven hydrogels consisting of spirobenzopyran-functionalized poly(N-isopropylacrylamide)*. *Soft Matter*, 2011. **7**.
2. Sumaru, K., et al., *Photoresponsive properties of poly(N-isopropylacrylamide) hydrogel partly modified with spirobenzopyran*. *Langmuir : the ACS journal of surfaces and colloids*, 2006. **22**(9): p. 4353-4356.
3. Satoh, T., et al., *Isomerization of spirobenzopyrans bearing electron-donating and electron-withdrawing groups in acidic aqueous solutions*. *Physical chemistry chemical physics : PCCP*, 2011. **13**(16): p. 7322-7329.
4. Ziolkowski, B., et al., *Self-protonating spirocyan-co-NIPAAm-co-acrylic acid hydrogel photoactuators*. *Soft Matter*, 2013. **9**(36): p. 8754-8760.
5. Zhang, X., R. Zhuo, and Y. Yang, *Using mixed solvent to synthesize temperature sensitive poly (< i> N</i>-isopropylacrylamide) gel with rapid dynamics properties*. *Biomaterials*, 2002.

6. Xian-Zheng, Z., Y. Yi-Yan, and C. Tai-Shung, *Effect of Mixed Solvents on Characteristics of Poly( N - isopropylacrylamide) Gels*. *Langmuir*, 2002. **18**.