Solvato-Morphologically Controlled Photo-Responsive Hydrogels For Micro-Valve Applications

In recent literature, photo-responsive hydrogels have been synthesised by co-polymerisation of *N*-isopropylacrylamide (NIPAAM) with spiropyran (SP) derivatives. This process demands external protonation of the hydrogels to induce re-swelling, typically by immersing the hydrogel in strong acidic environments. Also the re-swelling times are long, typically up to several hours. These disadvantages have restricted the use of photo-actuated hydrogels to single-use applications.

Recently, we reported that the addition of acrylic acid (AA), copolymerised within the hydrogel, provides an internal source of protons that allows photo-actuation in neutral pH environments. [Bartosz, et al. [1]]

The polymerisation solvent influences the morphology of the hydrogel, by producing porous hydrogels of different pore sizes. This impacts the diffusion path length for water molecules moving in/out of the hydrogel matrix, thus altering the swelling and shrinking kinetics of the hydrogel.[[2]]

In this study photo-actuated hydrogels were generated using p(NIPAAM-*co*-SP-*co*-AA) copolymer, in a 100-1-5 mole ratio. Different ratios of water: organic solvent (tetrahydrofran (THF), dioxane and acetone) were used as the polymerisation solvent. This resulted in hydrogels with different pore sizes and different swelling/shrinking and actuation kinetics. By using THF:water (4:1 v:v) as the 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 reproducible shrinking and reswelling cycles.

Using the different polymerisation solvents, hydrogel microstructures were photo-polymerised around pillars *in-situ* inside PDMS/glass microfluidic channels for valve applications. When actuated, the valve contracted thus opening the channel and allowing fluid to flow. The opposite was seen when the valve was kept in the dark. Thus demonstrating successful photo-controlled valves in microfluidic systems.

1. Bartosz, Z.*, et al.*, *Soft Matter* (2013) **9**
2. Xian-Zheng, Z.*, et al.*, *Langmuir* (2002) **18**