Reversible photo-actuated hydrogels for micro-valve applications

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Abstract

In recent years, a popular way of photo-modulating flow control in microfluidic channels has been through the use of acidified spiropyran (SP) hydrogels that needed to be externally protonated with HCl solutions.[1,2] In the swollen protonated merocyanine (MCH^+) form, the hydrogel blocks the channels and prevents flow. When exposed to white light, the positively charged MCH^+ is converted to the uncharged SP form, triggering shrinking of the hydrogel, and the channel opens. The addition of acrylic acid copolymerised within the hydrogel provides an internal source of protons that allows repeatable photo-actuation in neutral pH environments. Here we report the effect of the polymerization solvent on the shrinking and swelling kinetics of the photo-responsive hydrogel. Using this approach, reversible fast photo-actuated hydrogels have been obtained and have been successfully used for micro-valves applications in micro-fluidic channels.

1. Introduction

Previously photo-control of flow in microfluidics has been performed using acidified hydrogel networks. Despite the attractiveness of photo-actuated polymer valves for microfluidics, this approach had great disadvantages, as such the requirement of strong external acidic solutions to induce hydrogel re-swelling and slow re-swelling times of up to several hours. These disadvantages have restricted the use of photo-actuated hydrogels to single-use applications.

More recently, acrylic acid (AA) has been incorporated as an internal source of protons, removing the requirement of external acidic environments.[3] In water, the acrylic acid comonomer dissociates, resulting in the protonation of the photochromic spiropyran (SP) to protonated merocyanine ($MC\text{-}H^+$). This form is hydrophilic, allowing the hydrogel to swell. Exposure to white light promotes isomerisation of the $MC\text{-}H^+$ form to the hydrophobic SP form, which triggers contraction of the hydrogel. (Figure 1)

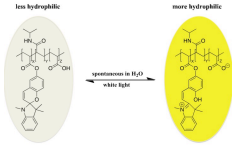

Figure 1. Isomerisation of SP to $MC\text{-}H^+$.

The polymerisation solvent has been shown to directly influence the morphology of hydrogels, by producing porous hydrogels of different pore sizes. 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.

2. Results

In this study photo-actuator hydrogels were generated using a *N*-isopropylacrylamide-co-acrylated spiropyran-co-acrylic acid (p(NIPAAM-*co*-SP-*co*-AA) copolymer, in a 100-1-5 mole ratio. Different ratios of organic solvent: water were used as the polymerisation solvent. The organic solvents employed in this study were tetrahydrofran (THF) and dioxane. The gel with the best response was then photo-polymerised in-situ inside a microfluidic channel functioning as a micro-valve.

By varying the solvent ratio in the solvent mixtures, hydrogels with different pore sizes and therefore different extent of swelling/shrinking and actuation kinetics were obtained. 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 (Figure 2).

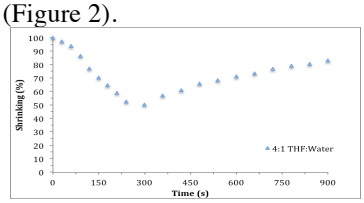

Figure 2. Shrinking and Swelling kinetics of 4:1THF:Water.

Hydrogel microstructures were photo-polymerised *in-situ* in PDMS/glass microfluidic channels for valve applications. The hydrogels were photo-polymerised around 550µm diameter pillars using photo-masks. When exposed to white light, the valves contracted, opening the channel and allowing fluid flow. The opposite was seen when the valve was kept in the dark (Figure 3).

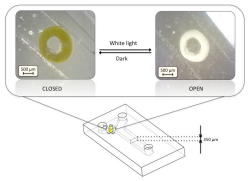

Figure 3. Micro-valves ON/OFF demonstration

3. Conclusion

Optimization of the polymerization solvent mixture has resulted in the fabrication of hydrogels with faster and reproducible shrinking and reswelling cycles. This study demonstrates these hydrogels can be successfully used as photo-controlled valves in microfluidic systems for repeatable ON/OFF flow control in neutral environments.

4. References

1. *Sumaru, K., et al., Langmuir (2006)* ***22*** *(9), 4353.*
2. *Taku, S., et al., Soft Matter (2011)* ***7.***
3. *Bartosz, Z., et al., Soft Matter (2013)* ***9.***