Stimuli-responsive hydrogels based on acrylic acid and acrylamide

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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, hydrogels can be actuated by external stimuli such as light[1], temperature[2] and pH[3], among others. In this study pH responsive hydrogels were developed using copolymers of acrylic acid (AA) and acrylamide (Am) in different molar ratios (30:70, 50:50 and 70:30, respectively). 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.

1. Introduction

pH responsive hydrogels

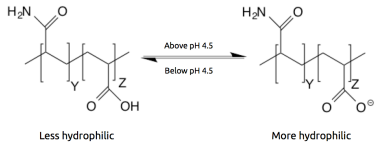

Figure 1: pH response of p($(Am)_y$-$(AA)_z$) polymers.

At pH above the pK_a of AA (pK_a~ 4.5) the AA dissociates to the more hydrophilic acrylate (A^-) form 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.

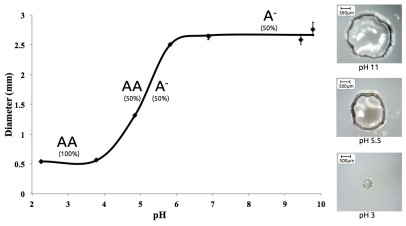

Figure 2: Diameter change of p($(Am)_y$-$(AA)_z$) hydrogels when immersed in different pH solutions.

2. From pH to photo-response

Spiropyran acrylate (SP-A) was copolymerised in the polymer backbone as a photo-acid generator.

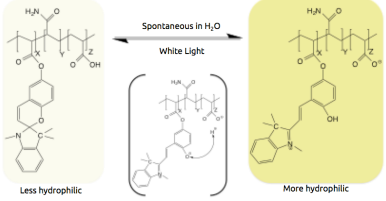

Figure 3: Chemical structure of p($(SP-A)_1$-$(Am)_{10}$-$(AA)_{10}$) in DI water under different illumination conditions.

When the hydrogel is immersed in DI water, in the dark, the AA dissociates and the proton is taken by the SP-A to form protonated merocyanine (MC-H^+)(yellow) resulting in hydrogel expansion. When exposed to white light, the MC-H^+ is converted back to SP-A (colourless) and H^+ is released causing reprotonation of some A^- sites that results in hydrogel contraction.

3. Photo-responsive hydrogels

The optimal composition used for the photo-responsive hydrogel was found to be AA: Am: SP-A in a 10:10:1 molar ratio.

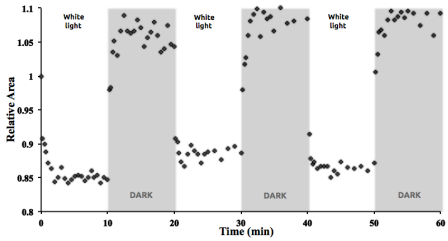

Figure 4: Repeatable photo-actuation of the photo-responsive p($(SP-A)_1$-$(Am)_{10}$-$(AA)_{10}$) hydrogels in DI water in real time.

The photo-actuation process was reversible, with the initial photo-contraction completed in about 120s and remaining at a constant value (~15%) as long as the white light was turned ON (10 min). After the white light was switched OFF the hydrogel reswelled to approximately its fully hydrated size in the first 60s in the dark and its size remained relatively constant until the next irradiation cycle. This process was repeated at least 3 times with no detectable hysteresis.

4. Conclusions

pH responsive hydrogels based on p(AA-Am) have been developed with significant shrinking/swelling capabilities. Introduction of a photo-acid generator, namely SP-A, inside the polymer backbone allowed for reversible hydrogel photo-actuation of over 15% in area in less than 2 minutes.

5. References

[1] L. Florea, D. Diamond and F. Benito-Lopez, *Macromol. Mat. and Eng.* **2012**, *297*, 1148-1159.
[2] H. Meng and H. Jinlian, *Journal of Intelligent Material Systems and Structures* **2010**, *21*, 859-885.
[3] J. Zhang and N. A. Peppas, *Macromolecules* **2000**, *33*, 102-107.