pH AND PHOTO-RESPONSIVE HYDROGEL ACTUATORS

A. Dunne, S. Mac Ardle, J. Hennessy, L. Florea*, and D. Diamond
Insight Centre for Data Analytics, National Centre for Sensor Research,
School of Chemical Sciences, Dublin City University, Dublin 9, IRELAND

ABSTRACT

In this study, pH responsive hydrogels were developed using copolymers of acrylic acid (AA) and acrylamide (AAm) in different molar ratios. At pH above the pKa of AA (pH>4.5) the AA dissociates to the more hydrophilic acrylate (A^-) ion, 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, promoting release of water from the gel. Incorporation of spirobenzopyran-acrylate (SP-A) as a photo acid generator (p(AAm-co-AA-co-SP-A)) translates this pH-response in to a rapid and reversible photo-response.

KEYWORDS: pH-responsive, Hydrogels, Photo-responsive, Spirobenzopyran

INTRODUCTION

Hydrogels constitute a group of hydrophilic polymeric materials, capable of holding large amounts of water in their three-dimensional networks. By incorporating stimuli-responsive units in their structure, hydrogel actuators can be developed, that respond to a variety of stimuli such as light, pH, electric or magnetic fields, among others. Polymers containing acidic or alkaline functional groups which respond to changes in pH form pH-sensitive polymers. A pH change around the pKa value of the functional groups (*e.g.* carboxylic acid or amine) results in the ionization of the groups and the generated electro-static repulsive force leads to an increase in the hydrodynamic volume of the polymeric hydrogel (*i.e.,* swelling).

Some of the most popular pH sensitive materials are copolymers of acrylic acid (AA) and its derivatives. In pH conditions > 4.5, the carboxyl group is deprotonated (COO^-) and it is protonated in acidic conditions of pH < 4.5 (COOH). Varying the concentration of the pH sensitive material in the polymeric hydrogel matrix will affect the degree of hydrogel actuation.

Conversion from a pH-responsive to a photo-responsive material can be achieved through the integration of a photo-acid generator in the polymer matrix[1]. Photo-acid generators are molecules that can release a proton upon light exposure enabling a localised pH change. Herein we propose the use of spiropyrans as reversible photo-acid generators for the fabrication of photo-switchable pH responsive actuators *via* photo-induced pH jump. In the dark, in the presence of available protons, the spiropyran (SP) will transform to the more hydrophilic protonated merocyanine ($MC\text{-}H^+$). Contrary, upon exposure to visible light the $MC\text{-}H^+$ will convert back to the SP form, releasing a H^+ in the process[2].

In this study, pH responsive hydrogels were developed using copolymers of acrylamide (AAm) and acrylic acid (AA) in different molar ratios (70:30, 50:50 and 30:70, respectively). Using the pH responsive composition 50:50 AAm: AA, the pH response was converted in to a photo response by incorporating a spiropyran-acrylate into the backbone as an internal photo-acid generator. This allowed for the development of a photo-responsive hydrogel capable of shrinking and expanding upon white light irradiation via a localised pH jump reaction.

EXPERIMENTAL

Gel Preparation

For hydrogel synthesis, the pH-responsive monomeric cocktail consisted of AAm (30, 50 and 70 mol%, respectively), AA (70, 50 and 30 mol%, respectively), PBPO (1 mol%) and PEG-258 (1.5 mol%) dissolved in 500 µL of the polymerisation solvent (1:1, vol: vol, THF: DI water). 5 mol% SP-A was added to the Am:AA 1:1 molar composition, to obtain the photo-responsive (p(AAm-co-AA-co-SP-A)) hydrogel.

pH induced actuation

pH actuation studies were carried out on three different hydrogels for each pH solution used. The imaging was done with an Aigo GE-5 microscope using a 60x objective lens with the accompanying software.

Photo-induced actuation

For white light irradiation shrinking and reswelling measurements, the hydrogels were placed in a custom-made cell and exposed to different light conditions. An image was taken every 30s.

RESULTS AND DISCUSSION

In the case of the 50:50 AAm:AA p(AAm-co-AA) (Figure 1A), circular hydrogels were polymerised that show an area of 0.72 mm^2 at pH 3 compared with 3.56 mm^2 for the same hydrogel at pH 11. This dramatic increase of 396.14% in area is due to the greater amount of hydrophilic acrylate ions being present in the polymer backbone in basic conditions (Figure 1B).

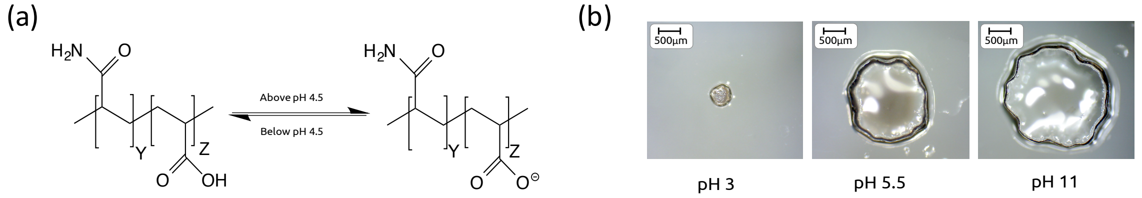

Figure 1: Chemical structure (A) and images (B) of p(AAm-co-AA) hydrogels in different pH conditions.

For the p(AAm-*co*-AA-*co*-SPA) hydrogel, the SP-A unit serves as a reversible photo-acid (Fig. 2A). This ensures a localised pH change under different illumination conditions, determining the ratio of AA/A$^-$ present, and therefore the hydrophilic character of the polymer backbone. In this case, photo-contraction of over 15% in diameter was achieved within 90 s of white light irradiation followed by reswelling to ~95% of its fully hydrated size after further ~30 s in the dark (Fig.2B)

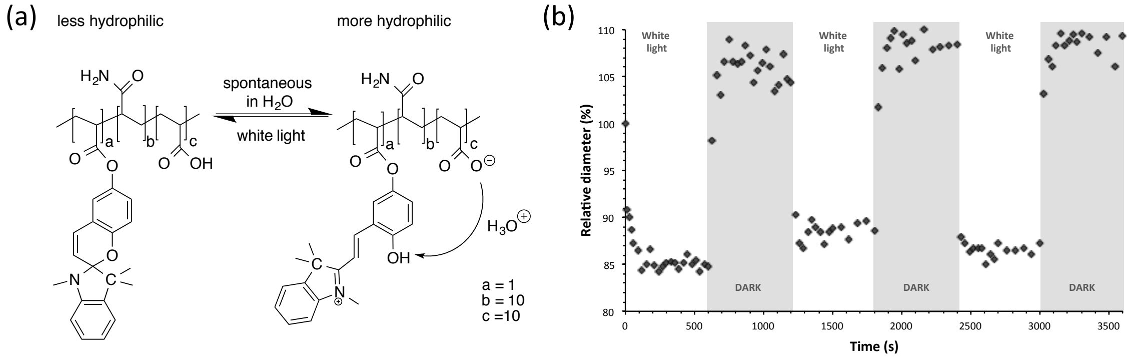

Figure 2: Chemical structure (A) and three actuation cycles for the p(AAm-co-AA-co-SPA) hydrogel under different illumination conditions.

CONCLUSION

In both cases (pH and photo-responsive hydrogels) the stimuli-induced contraction/reswelling processes were reversible and repeatable over at least 3 cycles with no detectable hysteresis. The fast actuation of the p(AAm-*co*-AA-*co*-SPA) hydrogels demonstrates great potential for their incorporation in microfluidic systems as reversible photo-controlled micro-valves.

ACKNOWLEDGEMENTS

Science Foundation Ireland under the Insight initiative, grant SFI/12/RC/2289.

REFERENCES

[1] Liang, D., Hongrui, J., 2007. Autonomous microfluidics with stimuli-responsive hydrogels. *Soft Matter* 3, 1223–1230.

[2] Kimio, S., Toshiyuki, T., Taku, S., Toshiyuki, K., 2013. Photo-induced reversible proton dissociation of spirobenzopyran in aqueous systems. *J. Photochem. A Chem.* 261, 46–52.

CONTACT

* Larisa Florea, tel: +353-1-7006009; larisa.florea@dcu.ie