Spiropyran Based Hydrogels Actuators - Walking in the Light

Wayne Francis[†], *Aishling Dunne*[†], *Colm Delaney, Larisa Florea* and Dermot Diamond*

Insight Centre for Data Analytics,
National Centre for Sensor Research
Dublin City University,
Dublin 9, Ireland.

†Authors contributed equally to this work
*Corresponding author E-mail: larisa.florea@dcu.ie

Abstract

Herein we report on the synthesis of a bipedal hydrogel walker, based on *N*-isopropylacrylamide-*co*-acrylated spiropyran-*co*-acrylic acid p(NIPAAm-*co*-SP-*co*-AA). Due to the presence of the photochromic spiropyran molecule in the polymer structure, these hydrogels reversibly shrink and swell in aqueous environments when exposed to different light conditions. When placed onto a ratcheted surface, the actuation of the bipedal gel produces a walking motion by taking a series of steps in a given direction, as determined by the optimised design of the ratchet scaffold. We anticipate that such biomimetic hydrogel walkers could form the basis of light-actuated soft robots capable of more advanced functions such as autonomous migration to specific locations accompanied by triggered release of molecular cargo.

Keywords: Photo-Responsive, Hydrogel, Walkers, Biomimetic.

1. Introduction

The motile behaviour of life forms, from the most primitive to the more complex, has long fascinated scientists who remain captivated by their ability to navigate through challenging environments in response to external stimuli. The simple earthworm, for example, has been the focus of attention for scientific groups who attempt to achieve synthetic mimicry of its means of movement [1-3]. The earthworm's body is composed of cylinder-shaped segments which are filled with a fixed volume of incompressible fluid and its movement is attributed to the contraction of the circular and longitudinal muscle layers which run through the body of the worm. When the longitudinal muscles contract, the worm is made shorter and the liquid is forced into the sides of the cavity, causing the body to widen. Conversely, contraction of the circular muscles serves to elongate the worm's body. Sequential fine control over the length of individual segments allows the worm to move in one direction [4]. More advanced means of locomotion, as exhibited by humans and other large mammals, is controlled through interaction of both soft and hard materials. Many groups, studying soft and hard robotics, have looked to the human body for inspiration [5-7]. To date however, the hard robotics field has failed to produce devices that can match the functionalities offered by biology, such as flexibility, adaptability and self-repair observed in even the simplest living organisms (*e.g.* cells, bacteria, jellyfish and worms). These types of functionality cannot be offered by present robotics technologies, mainly because of the lack of mechanical compliance between the conventional robotics and the biological systems. For implantable devices this hard-soft material mismatch can lead to tissue damage and foreign body response, resulting in hypoxia, acidosis, thrombosis and implant rejection [8]. Great recent progress has been made at the macro-scale towards soft-fluidics by using soft elastomers with embedded pneumatic networks [9, 10]. These actuators contain inflatable channels fabricated in elastomeric materials which are configured to create specific movement when pressure is applied. Dielectric elastomers have also been proposed for the realisation of soft electro-actuators, however their main disadvantage remains the typically large actuation voltage needed [11, 12]. Currently, soft-robotics may offer actuators of modest complexity, which exhibit increased compliance with biological matrices. Biological inspiration has also led to the realisation of stimuli-responsive soft actuators through the use of hydrogels as a primitive mimic of biological tissue. Hydrogels comprise a broad range of polymeric materials which are capable of holding large volumes of water, due to their hydrophilic nature. Incorporation of stimuli-responsive compounds into the gel structure can be used to control the gel’s overall hydrophilic character. This offers a means to modulate the volume and shape of the hydrogel structure through the expulsion or absorption of water from the surrounding environment. A large number of stimuli-responsive mechanisms for these gels have been reported, including thermal [13, 14], pH [15], magnetic [16], glucose [17], antigen [18], electro [19], photo [20], and even multi-responsive hydrogels [21, 22]. Of particular interest is the development of hydrogels with biomimetic properties [23, 24], such as the ability to walk [25]. Yang *et al* [26] developed an arc shaped hydrogel based on poly(2-acrylamido-2-methylpropanesulfonic acid-*co*-acrylamide) (poly(AMPS-*co*-AAm), which was able to walk across a ratcheted surface upon electrical stimulation. The hydrogel contained cross-linked networks bearing bound negatively-charged sulfonic groups. In sodium chloride (NaCl) solutions, upon the application of an electric potential, the free ions of the NaCl electrolyte move towards their respective counter electrodes. Inside the hydrogel however, only the cations of the bound negatively-charged sulfonic groups are mobile and can move towards the cathode. This ion motion creates an ionic concentration gradient within the hydrogel and in turn an osmotic pressure difference within the hydrogel walker. This translates into a bending motion towards the cathode upon application of an electric field. Depending on the position of the electrodes, one side of the gel experiences a greater osmotic pressure difference, resulting in bending/deformation of the hydrogel. The bending behaviour is reversible and repeatable through successive "on/off " application of an electric field. When placed on a ratcheted surface and by repeatedly applying an electric field, a hydrogel arc can be made to “walk”. When the electric field is switched “on” the gel will shrink, resulting in the legs of the gel to come closer. Because of the shape of the ratchet, only one leg can move and the trailing leg will be “dragged” across the ratchet steps. When the electric field is removed the gel will expand, but as the trailing leg cannot expand back against the ratchet, the leading leg will be pushed forward.

Development of other forms of hydrogel stimulation offer more promising means of fine-tuning actuation. The use of photo-responsive hydrogels offers the possibility of accurately controlling irradiance, time, distance, position and wavelength of the light while offering non-contact stimulus that can be applied in a non-invasive manner. The incorporation of photo-responsive compounds in the modulation of hydrogels has been widely documented, most notably through the use of spiropyrans (SP), which also offer added sensitivity to pH, solvent polarity and metal ions [27-29]. Our group has been one of the pioneers in demonstrating that incorporation of spiropyrans into gel structures (hydrogels [30] and ionogels [31, 32]) can be used for the fabrication of photo-controlled liquid flow micro-fluidic manifolds [33], reversible microfluidic valves [34] and photo-programmable surface topographies [35]. The photo-responsive hydrogels used in these studies were typically composed of copolymers of *N*-isopropylacrylamide-*co*-acrylated spiropyran-*co*-acrylic acid (p(NIPAAm-*co*-SP-*co*-AA), in a molar ratio of 100:1:5. In an acidic environment SP is protonated, generating the more hydrophilic ($MC-H^+$) form. Absorption of water from the external environment thereby results in expansion of the hydrogel. Upon irradiation with white light ($\lambda_{max} = 422$ nm) $MC-H^+$ releases a proton causing it to isomerize back to the more hydrophobic SP form. This increase in hydrophobicity results in the expulsion of water and the contraction of the gel. The addition of acrylic acid into the hydrogel backbone provides an internal source of protons for reversible switching [20] removing the need for an external acidic environment and enabling the switching of SP to $MC-H^+$ to occur in neutral conditions. This allows for reversible photo-actuation to be performed in deionised water.

Expanding on this work, herein we present photo-responsive hydrogel walkers based on p(NIPAAm-*co*-SP-*co*-AA). These walkers can reversibly shrink and expand via on/off white light irradiation. When submerged in water and placed onto a ratcheted surface the walkers can achieve a unidirectional walking motion when exposed to different light conditions. These hydrogels offer a promising route for the development of directed locomotion in soft light robotics.

2. Experimental

2.1 Materials:

N-isopropylacrylamide 98% (NIPAAm), N,N’-methylenebisacrylamide 99% (MBIS), Phenylbis(2,4,6 trimethyl benzoyl) phosphine oxide 97% (PBPO), acrylic acid (180-200ppm MEHQ as inhibitor) 99% (AA), tetrahydrofuran 99% (THF), anhydrous dichloromethane (50-150 ppm amylene as stabilizer) 99% (DCM), ethyl acetate 99%, n-hexane 95%, were acquired from Sigma Aldrich, Ireland and used as received. 1’,3’,3’-Trimethyl-6-acryloylspiro(2H-1-benzopyran-2,2-indoline) (SP-A) was synthesised as described elsewhere [20].

2.2 Gel Preparation:

The hydrogel walkers were synthesised using a monomeric cocktail which consisted of 200 mg NIPAAm, 8 mg MBIS (3 mol% relative to NIPAAm), 6 mg SP-A (1 mol% relative to NIPAAm), 7 mg PBPO (1 mol% relative to NIPAAM) and 6 μL AA (5 mol% relative to NIPAAm) dissolved in 500 μL of the polymerisation solvent (4:1 vol: vol, THF: DI water). The arc-shaped hydrogel walkers were prepared by using a home-made cell consisting of a PMMA mask (**Figure 1**), a glass slide and a glass cover slide separated by a 500 μm high spacer made out of poly(methyl methacrylate)/pressure sensitive adhesive (PMMA/PSA). The cell was filled by capillary action with the monomer solution and subsequently exposed to white light through the mask (Figure 8). The polymerisation time was varied from 40 to 50 s, in order to compare polymerisation times with walker functionality. The white light source used was a

Dolan-Jenner-Industries Fiber-Lite LMI LED lamp with two gooseneck waveguides placed at a distance range of 1 to 2 cm from the platform. The light intensity measured with a Multicomp LX-1309 light meter was 310 - 320 kLux. After polymerisation, the hydrogel walkers were washed gently with ethanol and DI water to remove any unpolymerised material and allowed to swell in deionised water for 4-6 hours to ensure full hydration.

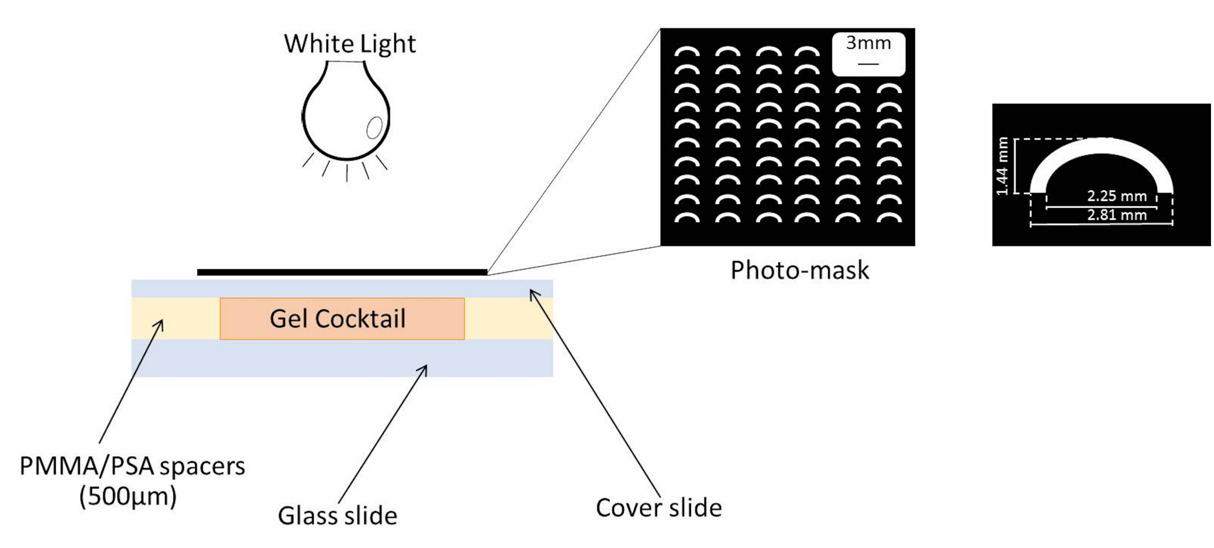

Figure 1: Side view of in-house made cell for gel polymerisation; insets show the photomask including specific measurements of a single arc-shaped walker.

2.3 Photo-Mask Fabrication:

The photo-mask used for gel polymerisation was firstly designed using AutoCAD 2014 and cut from a 1 mm thick sheet of black PMMA using a CO_2 laser ablation system (Epilog Zing Laser Series). The mask contained a 7 x 5 array of walkers of 1.44 mm height, 2.81 mm (outer) distance between the legs, and a width of 0.56 mm.

2.4 Ratcheted Channel Fabrication:

The ratcheted systems in this study were first designed using AutoCAD 2014 and a CO_2 laser ablation system (Epilog Zing Laser Series) was used to cut the required pieces out of black PMMA sheets. To assemble the ratcheted channel, a back PMMA layer, the ratchet layer and a glass slide were attached (**Figure 2**). The back layer and the main ratchet section were cut from 1 mm black PMMA. To avoid melting of the ratchet during laser cutting, 50 μm PSA was hand cut and applied to both sides after cutting. The back layer was joined with the main section first, then the glass slide was attached. Using clamps, the three sections were placed under pressure overnight. The ratcheted channel had a length of 45 mm, a 1 mm width and a height of 12 mm, while the ratchets had a height of 0.5 mm and a 7 mm distance between two consecutive ratchets.

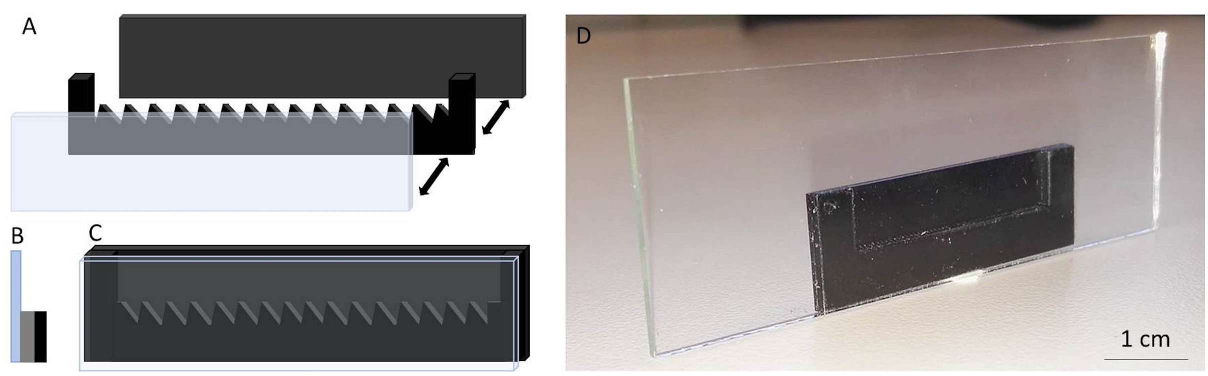

Figure 2: A) Schematic diagram showing the individual components of the ratcheted channel: glass slide, ratcheted channel bottom with side walls in black PMMA and PMMA back layer; Cartoon showing side (B) and front (C) views of the channel after assembly and D) Photo of the real ratcheted channel.

2.5 Hydrogel walker relative area and relative leg distance analysis:

The distance between the walker's legs and the area measurements of the freestanding hydrogel walkers were performed using Image J (1.47v) software. For each polymerisation time, three hydrogel samples were measured. The relative area %

(Eq. 1) and relative Legs distance% (Eq. 2) were calculated using the following equations (n=3):

$$Relative\ area\ (\%) = \frac{A_t}{A_o}\ x\ 100 \qquad \text{(Eq. 1)}$$

Where A_t = Measured area at time t and A_o = Area of a fully hydrated gel.

$$Relative\ leg\ distance\ (\%) = \frac{L_t}{L_0} x\ 100 \qquad \text{(Eq. 2)}$$

Where L_t = Measured inner leg distance at time t and L_0 = Initial inner leg distance of the fully hydrated walker.

2.6 Rheology:

Rheology curing measurements were performed on the unpolymerised cocktail. The measurements were carried out using an Anton-Paar MCR301 rheometer with a CP50-2 measuring tool with a diameter of 49.97 mm and a cone angle of 1.996° to measure the mechanical properties during polymerisation. The rheometer had a glass plate to which 900 µl of monomer mixture was placed and pressed with the CP50-2 tool with a space of 208 µm. A Dolan-Jenner-Industrie Fiber-Lite LMI white light was placed under the glass plate having a light intensity of 320 kLux, measured on top of the glass plate using a LX-1309: light meter. The curing and mechanical properties of the p(NIPAAm-*co*-SPA-*co*-AA) cocktail were measured over 15 minutes with data collected every second. White light curing was initiated after 60s and after the allotted time (40s, 45s and 50s, respectively) the light was turned off. The loss and storage moduli were analysed at 0.1% strain and 1Hz oscillation frequency against time. Polymer films of 500 µm thickness were polymerised for the specific times (40s, 45s and 50s) in the same manner as the walkers in the absence of the photomask with a light intensity of 318 kLux. After the polymer films were hydrated, circular disks of 15 mm diameter were cut using a manual puncher and used for further rheology analysis. The polymer discs from the various polymerisation times were placed under the PP15 rheometer tool (15 mm diameter) of the Anton Paar MCR 301 rheometer. Amplitude sweeps were carried out at 100 rad s^{-1} angular frequency, a normal force of 1 N with a gradual strain from 0.01 – 100%. The storage modulus was monitored with data being collected every 20 seconds.

2.7 Hydrogel walker actuation:

To achieve the "walking" behaviour of the hydrogels, a single walker was placed on to one of the ratcheted channels. The channel was then carefully filled with deionised water. An Aigo GE-5 microscope (using a 60x objective lens and accompanying software) was placed facing the glass side of the ratcheted channels. Finally, the white light source was adjusted so both goosenecks were pointed at the walker and had an intensity of ~305 kLux. Once recording began the white light source was switched on. The walker was then monitored in real time and once the trailing leg had moved across at least one of the ratchet steps the light was removed. The gel was then monitored in the dark and once the leading leg had been pushed at least one ratchet step, the white light source was turned back on. This was continued until the hydrogel had walked a number of steps.

3. Results and Discussion:

3.1. Hydrogel walker:

The (p(NIPAAm-*co*-SP-coAA) hydrogels in this study were able to achieve reversible swelling and contraction through repeatable white light irradiation. In the absence of white light, the SP component of the gels underwent protonation to the more hydrophilic $MC\text{-}H^+$ form, due to protonation from the AA substituent (pKa ~ 4.5). Under these conditions, the gels expanded to the maximum capacity and had a yellow colour. When the hydrogels were illuminated with white light, the $MC\text{-}H^+$ was deprotonated back to the SP form (**Figure 3**).

This resulted in a rapid colour change towards white/colourless as the gel began to contract. This is due to the hydrophobic nature of SP which causes the polymer chains within the gel to collapse and water from the gel to be expelled to the external environment (Figure 3).

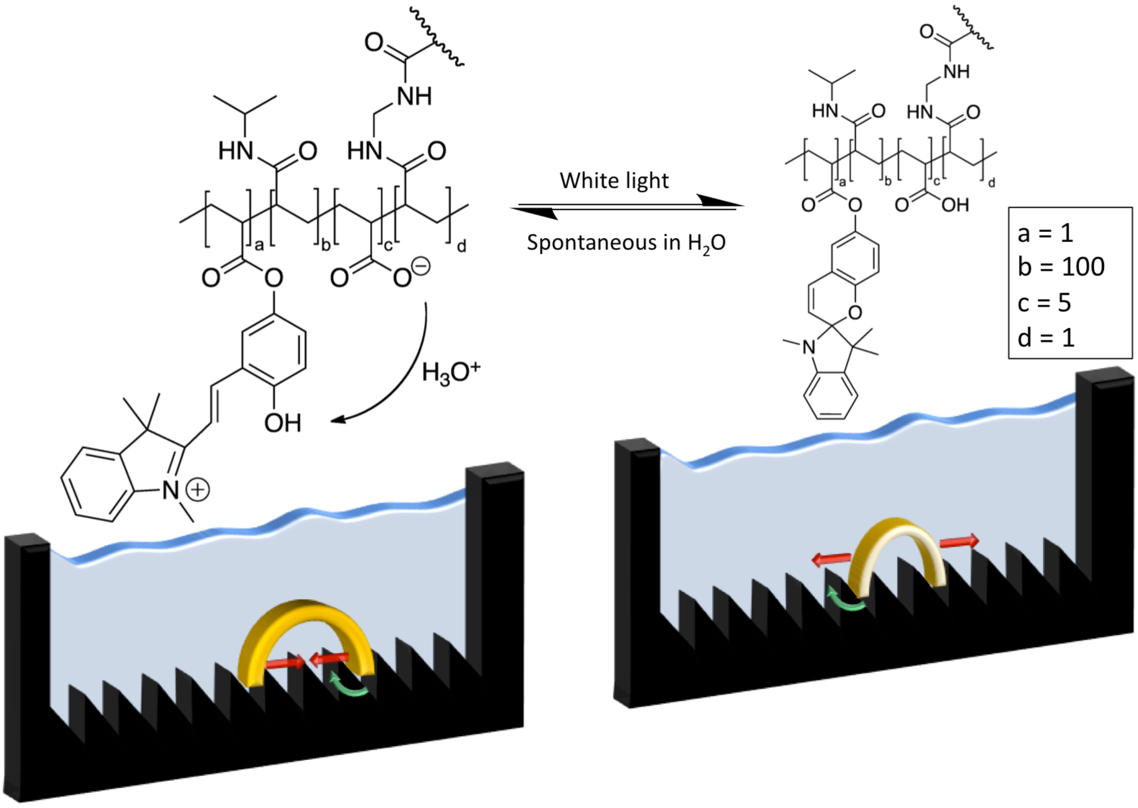

Figure 3: Chemical structure of the p(NIPAAm-*co*-SP-*co*-AA) hydrogel walkers under different illumination conditions and the physical effect it has on the gel morphology.

To achieve the walking motion this process was performed on a ratcheted polymethyl methacrylate (PMMA) surface, from right to left, as depicted in **Figure 4**. After a period of white light irradiation (5 min at ~305 kLux intensity), the gel began to contract, thereby causing deformation of the gel's structure. When the leading leg comes in contact with the vertical section of the ratchet step (Figure 4A), a gradual photo-induced reduction of the distance between the legs causes the trailing leg to be "dragged" over the bevel of the ratchet step (Figure 4 (B-D)).

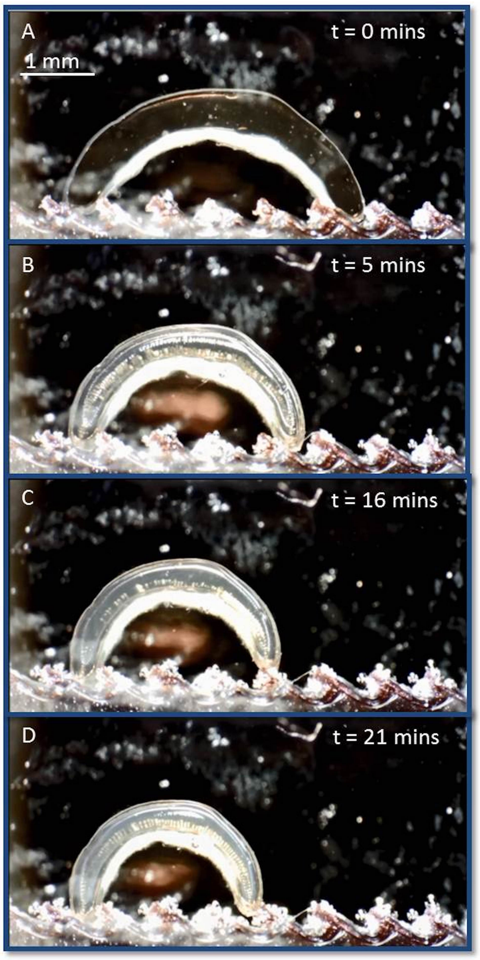

Figure 4: Series of snapshots showing the effect of light irradiation on the hydrogel walker. A) Light irradiation is initiated; B-D) Gradual reduction of inter-leg distance results in the trailing leg (right) being "dragged" over the bevel of the ratchet step.

When the light was removed the gel would gradually begin to re-swell and regain its original colour. Swelling continued until the trailing leg became lodged on a vertical section of a ratchet step, thus causing the leading leg to be pushed over the bevel of the corresponding ratchet step. By repeating this process, the p(NIPAAm-*co*-SP-*co*-AA walkers could be made walk in a single direction, determined by the direction of the ratchet (see **Figure 5**, **Figure S1**, **Video S1** and **Video 2**).

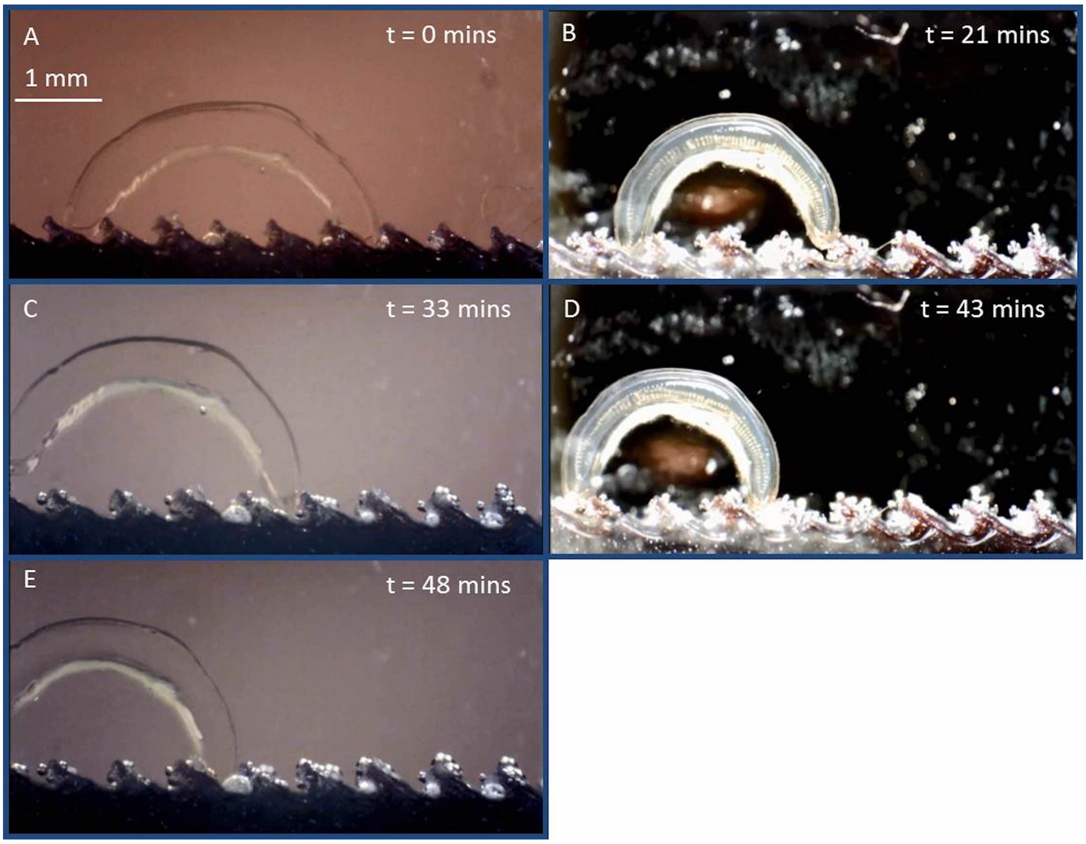

Figure 5: Series of snapshots showing the walking behaviour of the hydrogel (Video S1). A – B shows contraction of the trailing leg. C – Swelling in the dark results in the forward leg being pushed over the ratchet. D – E The sequence is repeated which results in the gel achieving a unidirectional walking motion (right to left).

3.2. Mechanical properties:

To design a hydrogel walker which can actuate over a series of predefined distances, it is necessary to have a comprehensive knowledge of the mechanical properties of the hydrogel walker. The elastic nature of a hydrogel can have a dramatic influence on its ability to actuate under a given stimulus. To best understand the effect of varied degrees of cross-linking, a rheology study was used to ascertain the most appropriate curing time. Three different polymerisation times were chosen (40s, 45s and 50s, respectively), during which the monomeric cocktail was exposed to white light irradiation and the storage modulus recorded (**Figure 6**). The storage modulus increases abruptly when the light is turned on (time = 60s) owing to significant growth of elastic structures due to the crosslinking. When the light is turned off (after 40s, 45s and 50s, respectively) no new radicals are formed by initiation, and therefore the increase in storage modulus is significantly slowed, as only the free radicals that are present when the light is turned off continue to propagate and terminate [36]. The hydrogels polymerised under 50s of light irradiation showed the highest storage modulus plateau at around 3700 Pa, and therefore exhibit the greatest elastic properties of the hydrogels studied (Figure 6). Polymerisation times longer than 60s were not suitable as polymerisation-induced diffusion, beyond the exposed areas of the photo mask, resulted in peripheral polymerisation.

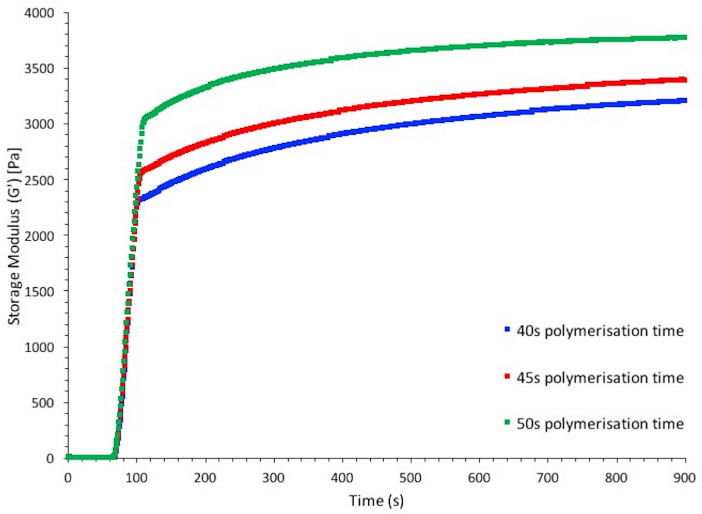

Figure 6: Photo-curing of hydrogels produced under different light irradiation times (40s, 45s and 50 s, respectively). White light polymerisation was initiated at t=60 s.

Mechanical studies of the hydrogels were also performed after hydration, as detailed in the experimental section. It was revealed that upon hydration, the storage modulus of the hydrogels polymerised under different polymerisation times (40s, 45s, and 50s, respectively), although increasing with the polymerisation time, does not vary significantly (Figure S1).

However, amplitude sweeps reveal that the linear viscoelastic range (LVE) is significantly different and decreases with increased polymerisation time. This could be due to the fact that crosslinking density is increasing with the polymerisation time, also causing an increase in chain entanglement. Therefore, when an increase shear stress is applied, physical interactions and entanglements will be destroyed prior to covalent bonds. As a result, the sudden decrease in G' (indicating the end of the LVE) occurs at lower shear stress for the hydrogels polymerised under a longer polymerisation time, which implies that there are more physical crosslinks and chain entanglements in these sample networks [37].

3.3. Relative area and relative leg distance analysis:

Extending our knowledge of these materials to fabricate a simple hydrogel walker required not only an insight into the mechanical properties but also greater understanding of the volume change of the material during actuation cycles. On a stepped surface, it is important to fully understand both the swelling of the respective legs and maximum bipedal distance, during actuation. To determine the actuation properties of the hydrogel walkers polymerised under different polymerisation times, a study was performed to examine the effect on both the relative area of the entire gel and the distance between the legs upon irradiation with white light. Polymerisation time is an important parameter when synthesising hydrogels as it affects the crosslinking density of the hydrogel, thus its mechanical properties (Figure 6) and its ability to absorb and expel water and the material's shape memory [38-41]. **Figure 7** shows the relative area of each of the gels when exposed to three cycles of white light irradiation. It confirms, as expected, that polymerisation times plays only a minor role in the extent of swelling or contraction exhibited by the resulted hydrogel, in these particular conditions (polymerisation times of 40s, 45s and 50s, respectively). The 50 second polymerised gels showed the greatest repeatability and were better able to swell close to their original size when compared to the shorter polymerization times. Relative area change is $A_{rel.}$

$_{\text{change}}$ = 24.14 ± 7.43% (n=3) for the hydrogels polymerised under 40s of light irradiation, $A_{\text{rel. change}}$ = 23.11 ± 9.24% (n=3) for 45s polymerisation time and $A_{\text{rel. change}}$ = 25.87 ± 2.35% (n=3) for 50s polymerisation time, respectively. For the hydrogel polymerised under 40s of white light irradiation, there is a clear gradual decrease in the size of the hydrogel both under light and dark conditions (**40s: 2nd cycle** 62.28 ±5.41% (contracted); 78.98 ±6.04% (expanded) and **3rd cycle** 56.94 ±6.41% (contracted) 75.17 ±7.75% (expanded). This is most likely due to the decreased crosslinking density and physical entanglements present in these hydrogels, which may impede the hydrogels from returning to their original size.

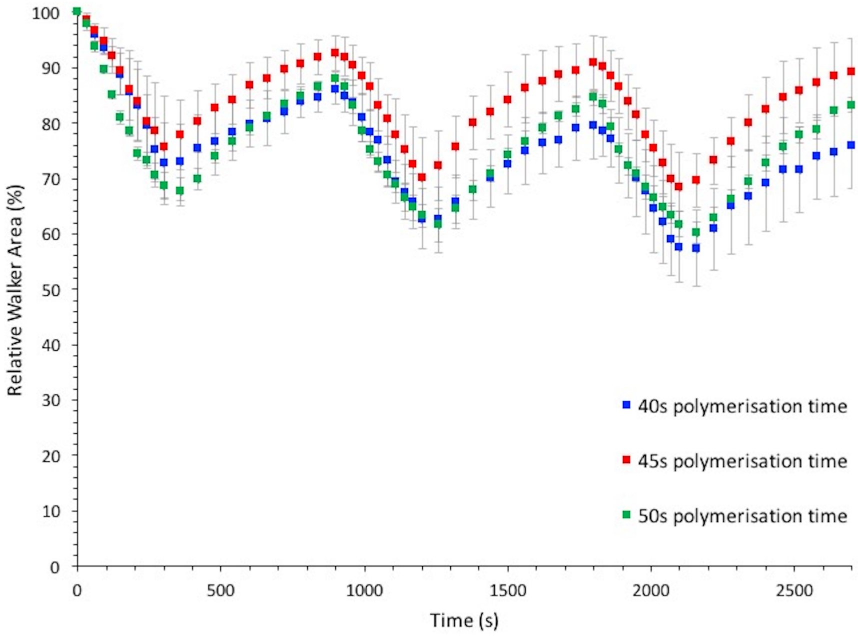

Figure 7: Three photo-actuation cycles of hydrogel walkers produced after 40s, 45s and 50s of light irradiation, respectively, showing the relative changes in walker area when exposed to different illumination conditions. The measurements have been done in triplicate and the error bars represent standard deviations.

An analysis of the relative inter-leg distance for a set of walkers of varied polymerisation time was also performed. Figure 6 shows the effect polymerisation times had on the actuation of the hydrogel structures, and in particular the relative changes in leg distance when the gels were exposed to different illumination conditions. As seen from Figure 6, polymerization times of 40s and 45s, respectively, resulted in gels with a lower storage modulus. Upon actuation, this failed to show an appreciable change on the centre angle of the arc-shaped walker. When exposed to white light all of the hydrogel walkers were able to expand and contract (Figure 7 and Figure 8), however the ones polymerised for 40s and 45s, respectively, couldn't maintain their shape and became flat when irradiated on a ratcheted surface.

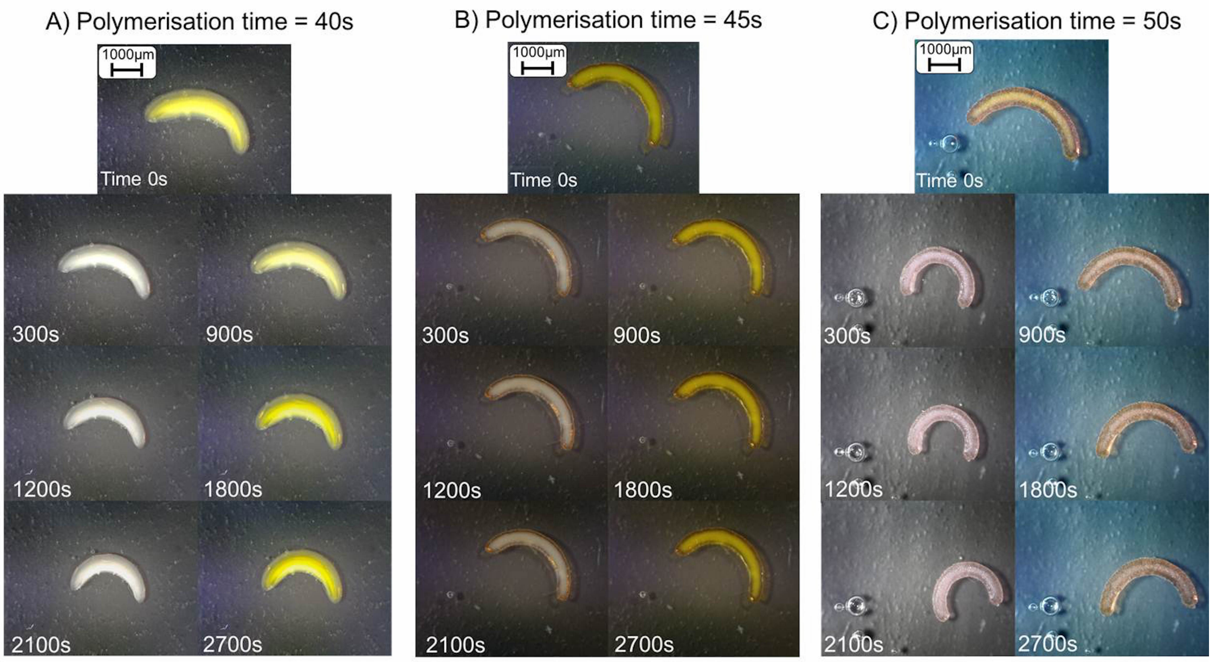

Figure 8: Three photo-actuation cycles of hydrogel walkers produced after 40s, 45s and 50s of light irradiation, respectively, showing the relative changes in legs distance when exposed to different illumination conditions.

The results of this assessment of actuation behaviour, in particular inter-leg distance, are summarised in the plots shown in **Figure 9**. This clearly demonstrates that the gels synthesised using a 50 second polymerisation time had the greatest reduction in distance between the legs when exposed to white light. The 40 and 45 second gels showed minor and irreproducible inter-leg distance changes and therefore limited movement. Knowledge of the extent of change in the centre angle of the arc-shaped walker/ inter-leg distance is integral to the design of the ratcheted surface on which the walker moves. By assessing the distance between the legs before and after actuation it is possible to design ratchets of optimal dimensions to maximise the potential for unidirectional movement. These results had a direct influence on the width of ratchets used for further studies, as outlined in the experimental section.

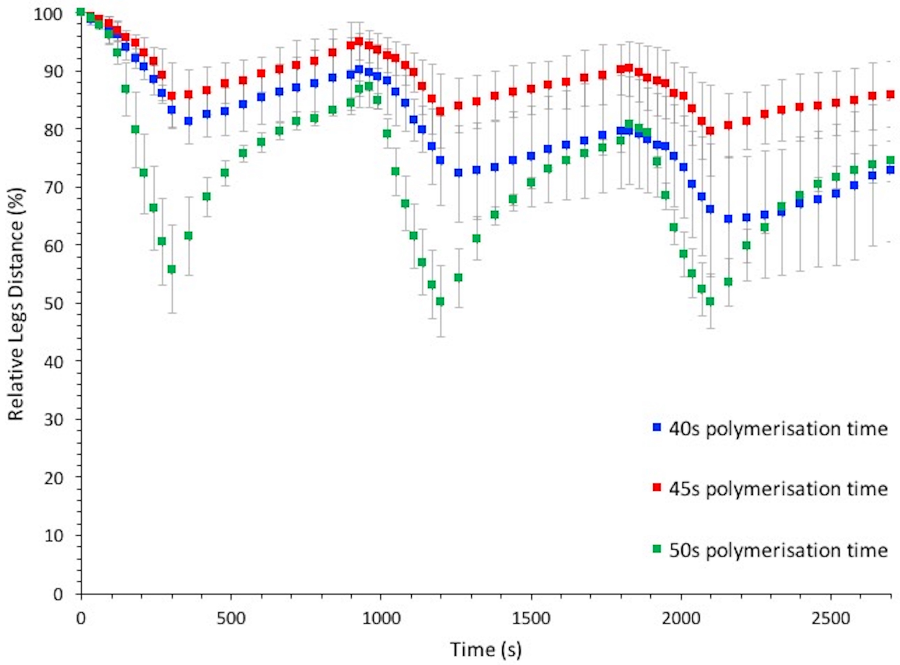

Figure 9: Three photo-actuation cycles of hydrogel walkers produced after 40s, 45s and 50s of light irradiation, respectively, showing the relative changes in legs distance when exposed to different illumination conditions.

As the actuation behaviour (swelling, contraction) in hydrogels is essentially diffusion controlled, the reduction of the scale of these structures can dramatically increase the rate at which these effects occur [42]. Improved kinetics of the actuation could also be realised by increasing the pore density of the hydrogel structure [43] as this can substantially reduce the overall diffusion pathlength for water uptake and release. Furthermore, modification of substituents on the photoswitch molecule produces dramatic improvements in the switching kinetics, which also contributes to the overall effectiveness of the gel actuation effect [44, 45]. This in turn will allow for the realisation of soft micro-robots, capable of various forms of locomotion on a significantly reduced timescale. In addition, photo-switchable dynamic ratchet structures that emerge /disappear can be created, and linking this behaviour with the 'walkers' offers the intriguing possibility of externally switching between 'on' (ratchet features present, directed movement turned on) and 'off' (smooth surface restored, directed movement turned off)[35].

4. Conclusion

In conclusion, we have synthesised a hydrogel walker based on p(NIPAAm-*co*-SP-*co*-AA) which can reversibly swell and contract when submerged in water and subjected to cycles of white light irradiation. The hydrogel is able to achieve unidirectional walking when placed onto a ratcheted surface. These results show that photo-responsive hydrogels make promising candidates for the development of biomimetic soft robots which could exploit their reversible and repeatable actuation. This study opens the possibility for development of more advanced biomimetic walking soft robots which can perform tasks such as cargo transport, sensing and targeted drug delivery. The ability to control on-demand uptake and release, with porous materials of this nature, offers the possibility of localised triggered reactions upon secondary stimulation at desired destinations [46, 47]. The combination of these processes could be used to achieve targeted transport, delivery and release within fluidic systems.

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Vitae

Wayne Francis is a PhD student in Professor Dermot Diamond's research group, in Dublin City University. Wayne received his B.Sc. (Ord) in Analytical Chemistry from Institute of Technology Tallaght and his B.Sc. (Hons) in Chemical Sciences with Medicinal Chemistry from Dublin Institute of Technology. Wayne's research interests include the design, synthesis and applications of stimuli-responsive materials and his PhD is focused on the development of synthetic biomimetic micro "vehicles".

Aishling Dunne received her B.Sc. (Ord) in Pharmaceutical Chemistry with Chemical sciences from Dublin Institute of Technology in 2012 and received her B.Sc. (Hons) in

Chemical Sciences with Medicinal Chemistry from Dublin Institute of Technology in 2013. Aishling is currently pursuing her PhD degree under the supervision of Professor Dermot Diamond and Dr. Larisa Florea in NCSR, Dublin City University. Aishling's research interests include the synthesis of novel photo-responsive materials and application in micro-fluidic devices.

Dr. Colm Delaney studied chemistry at Trinity College Dublin (TCD) and graduated with a B.A. Mod (Hons.). He subsequently carried out a research MSc. in Materials Chemistry on the topic of organic light-emitting materials. In 2015 Colm completed his PhD. in Organic Chemistry with Prof. Sylvia M. Draper in TCD, on the synthesis and application of novel materials for fuel-cell applications. He then joined the Adaptive Sensors Group, lead by Prof. Dermot Diamond, as a Postdoctoral Researcher. His research focuses on the design and synthesis of sensing materials for the earlier detection of disease and monitoring of wellbeing.

Dr. Larisa Florea studied organic chemistry and chemical engineering at University "Politehnica" from Timisoara, Romania (B.Sc. Hons 2009). In 2009 she joined the Adaptive Sensors Group at Dublin City University where she earned her Ph.D. under the supervision of Prof. Dermot Diamond and Dr. Fernando Benito-Lopez. Since 2013 she has carried out her postdoctoral research with Prof. Dermot Diamond in the INSIGHT Centre at Dublin City University, where she is currently Team Leader in smart materials and microfluidics. Her research interests include the design, synthesis and applications of stimuli-responsive polymers as novel sensing and actuating materials in microfluidic devices.

Prof. Dermot Diamond received his Ph.D. and D.Sc. from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was Vice-President for Research at Dublin City University (2002–2004). He has published over 300 peer-reviewed papers in international journals, is a named inventor in 18 patents, and is co-author and editor of four books. He is director and founding member of the National Centre for Sensor Research (www.ncsr.ie) at Dublin City University, and an SFI-funded investigator in the INSIGHT Centre (http://www.insight-centre.org).