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Tuning microfluidic flow by pulsed light oscillating spiropyran-based polymer hydrogel valves

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ABSTRACT

A method for microfluidic flow control based upon polymer hydrogel valves with rapid and reversible actuation properties is described. The platform allows for contactless optical flow control based upon pulsing light, resulting in a forced oscillating and control over the valve through photo-isomerisation of a spiropyran derivative, co-polymerised within an *N*-isopropylacrylamide (NIPAm) hydrogel. Application of pulsed light (450 nm) to the valves allows the valves to be held at an intermediate position for extended periods of time. Varying the extent of pulsing of the light source enables the flow rate to be regulated within a microfluidic flow rate range of 0–27 μL/min. Due to the pulsed light, a small period change in the flow rate is observed that corresponds to the pulse sequence as a corresponding oscillation in the hydrogel valves.

1. Introduction

The integration of stimuli-responsive materials within microfluidic devices as a mean of non-contact microfluidic flow control [1–6], has resulted in the development of novel in-situ, microscale mechanical components [7–16] with the potential to produce vastly simplified and highly efficient fluidic chip configurations. This requires less energy for operation and less dead volume between chips through elimination of significant amounts of tubing. The development of these biomimetic microfluidic flow systems; fluidic channels with integrated functionality similar to the human body such as the vascular system, allows for the production of microfluidic chips with in-situ generated valves, reducing the platform dimensions and complexity. This contrasts greatly with externally located mechanical valves, which are not readily scalable due to their large dimensions relative to the microfluidic platform, forcing fluidic handling to occur off chip.

Hydrogels within which a photochrome is covalently incorporated have been found to exhibit significant volume changes using light as the non-invasive power supply, resulting in potential uses in microfluidics [17]. A popular approach to the production of light responsive swell/shrink hydrogels has been the co-polymerisation of molecular photoswitches within poly(*N*-isopropylacrylamide) (pNIPAm) [4,18–22]. Several photochromes that exhibit light-induced isomerization have been investigated, particularly azobenzenes [21,23] and spiropyrans (Sp) [24–26]. Until now, the implementation of these light responsive gels for valve applications has been rarely reported [2,22]. Furthermore, tuning the flow control rather than an on/off function with these gel-based valves has not been reported. The latter is influenced by the fact that the photo-responsive molecules employed only has two states that are accessible by switching on/off a stimulus. Intermediate states, such as possible with mechanical valves, have been not reported. The ability to control flow, as well as stop/start flow *via* photoresponsive hydrogel valves having intermediate states would, however, be very appealing.

Recently we have reported a reversible light-responsive hydrogel valve that is inherently compatible with microfluidics, as the valve structures can be easily created in-situ after fabrication of the microfluidic platform [22]. In this self-protonating pNIPAm hydrogel, acrylic acid acts as a proton source in solution/polymer to stabilize the yellow coloured hydrophilic isomer merocyanine-H^+ (McH^+), which forms spontaneously in water (Scheme 1). This

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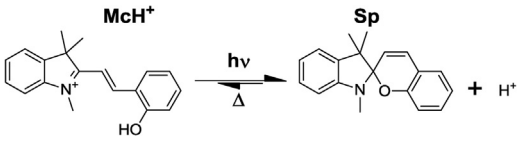

Scheme 1. The photoisomerisation of hydrophilic isomer merocyanine-H$^+$ (McH$^+$) to the ring-closed hydrophobic spiropyran using blue (450 nm) light, and its spontaneous back reaction in an acidic medium.

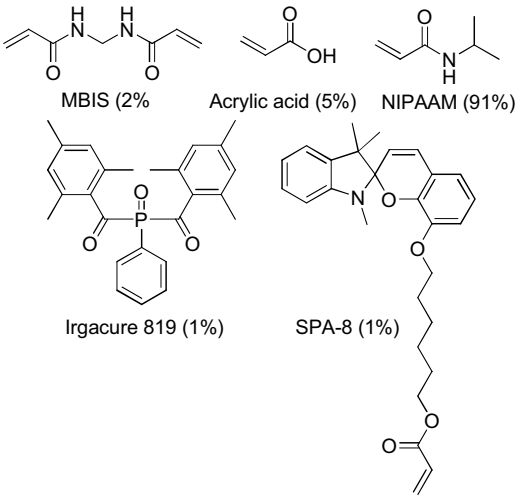

Fig. 1. Compounds used in the SPA-8 hydrogel formulation. Mole percentages of constituents in parenthesis.

can be switched using blue light, to the ring-closed, colourless hydrophobic spiropyran (SP) form, changing the overall character of a hydrogel *e.g.* from predominantly hydrophilic (swollen) to predominantly hydrophobic (contracted), allowing repeatable swelling and shrinkage of the material, due to accompanying water uptake and release [22]. Gel-valves integrated within microfluidic channels allowed reversible and repeatable operation, with opening and closing of the valve in minutes [22]. We now report on the application of this photoresponsive hydrogel valve for tuneable flow control within a microfluidic chip. By using a pulsing blue light source, an oscillating polymer hydrogel valve that can be maintained at intermediate sizes is obtained, enabling the microfluidic flow rate to be regulated.

2. Materials and method

2.1. Sample preparation

The hydrogel valves were produced using the following formulation (Fig. 1): 500 μL 2:1 dioxane and water mixture containing 229.8 mg solid content (0.45 mg/μl); consisting of 91 mol% *N*-isopropylacrylamide (NIPAm), 5 mol% acrylic acid (AA), 2 mol% *N*,*N*'-methylenebisacrylamide (MBAm), 1 mol% Irgacure 819 as white light photo initiator and 1 mol% of Spiropyran derivative SPA-8. All materials except SPA-8 were purchased from Sigma Aldrich and used without further purification. SPA-8 was synthesised using a previously published method [22].

2.2. Microfluidic chip design

Valves were polymerized in-situ within microfluidic channels created in polymethylmethacrylate (PMMA) chips. The two-layer chips were prepared using a 1.5 mm thick PMMA layer for inlets and channels and a 1 mm thick capping layer to seal the chip. The microfluidic channels, liquid inlet and an outlet, and a circular feature with central pillar (for housing the valve) were micromilled on the bottom layer and then sealed to the top capping layer using a solvent evaporation technique (7 min dichloromethane (DCM) exposure) [27]. The microchannel dimensions were 1 mm wide and 0.200 mm deep, while the circular valve chamber and pillar were 2.6 mm and 1 mm in diameter, respectively (Figs. 2, S1).

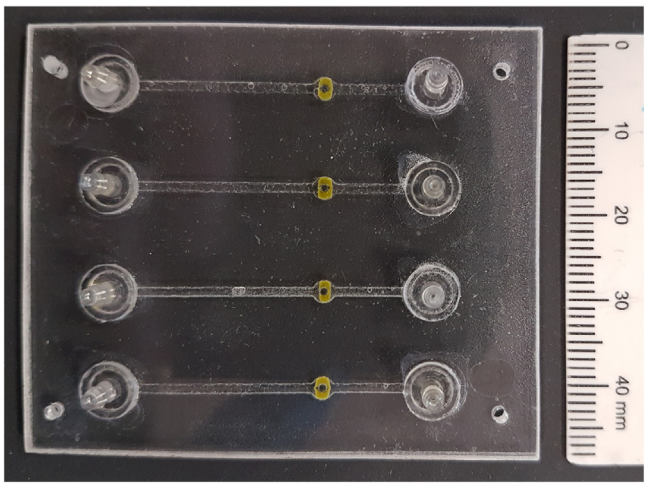

Fig. 2. Sealed microfluidic chip with inlet/outlet ports containing in-situ polymerised photo-responsive hydrogel valves (yellow gels surrounding pillars in valve chambers). One of these valves was used for the experiments in Figs. 4 and 5. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. Microfluidic valve preparation and performance

After completing chip fabrication, the microchannel was filled with the hydrogel formulation. The valve was created in-situ by irradiation of the solution with blue LED light (Kingbright HB Blue 450 nm (600 mW/4.5 lm/1.3 cd), 3.5 V) at 450 nm wavelength for 3 s, using an in-house fabricated LED illumination platform and mask to define the valve dimensions in the valve chamber. After polymerisation, the microfluidic system was rinsed using deionized water to remove any unreacted monomer and the valve was allowed to briefly swell to seal the channel (monitored using Fluigent S flow sensor). Following this, the gel was illuminated for a further 60 s to complete polymerisation. The valves were then left for 24 h prior to usage to ensure complete hydration and swelling.

Valve performance was assessed using an in-house designed LED system for actuation of the valves. Valve opening was achieved *via* exposure to blue LED light (Kingbright HB Blue 450 nm (600 mW/4.5 lm/1.3 cd), 3.5 V) at full power for varying lengths of time, controlled by a Texas Instruments MSP430f5529 controller board. Closure of the valve occurred spontaneously when the LED light source was turned off. Flow rates were monitored using either a Fluigent S (range 0–7 μL/min) or M (range 0–80 μL/min) flow rate sensor connected to a Fluigent FRP Flowboard. It should be noted that the flow experiments reveal that these valves do not show fatigue after 10 h of operation with continuous switching.

To ensure a constant pressure was applied to the system to maintain regular liquid flow, a "constant head of pressure" method was employed using an in-house built platform. The set-up involved the use of two cylinder containers, henceforth known as reservoir 1 (R1) and reservoir 2 (R2). R1 was connected to the chip before the valve to provide the source of water and primary pressure for the flow through the chip. R2 was connected to the flow sensor and the chip after the valve. R2 acts as a means of regulating the pressure on the chip by providing a counter-pressure against R1. 500 mL (R1) and 300 mL (R2) water was added to the reservoirs

resulting in water column heights (water level to reservoir outlet port) of 62.75 mm (R1) and 29.80 mm (R2) allowing the valve to seal completely and block flow when in the swollen form, while also providing a flow rate range (0–5.5 μL/min) compatible with the Fluigent S sensor without failure of the valve in the contracted form. From Eq. (1) below it was estimated that for the simple fluidic system used in these experiments, the pressure was 3.23 mbar.

$$P = \rho gh \quad (1)$$

Where, P = pressure of the system, ρ = density of liquid (water @ 20 °C: 998.21 kgm^{-3}), g = acceleration due to gravity (9.80665 ms^{-2}) and h = difference in height of column of liquid (m). The wide (91.10 mm) diameters of the reservoirs ensure that the changes in liquid column heights in both reservoirs would be insignificant throughout the duration of the experiments. A total volume of 240.81 μL of water was calculated to have passed through the chip during the entire experimental run (5474 s; see SI Fig. S1) and based upon this volume, the associated height change is approximately 0.369 μm in each reservoir. This value was deemed small enough to have insignificant effect upon the overall pressures observed within the system throughout the experimental run.

2.4. Pulsed light experiments on hydrogel disks

The hydrogel disks generated to determine the effect of longer exposure of pulsed light were made by photopolymerizing the hydrogel monomer mixture between 150 um spaced glass slides using an Exfo Omnicure S2000 lamp. This results in a stronger crosslinked network than using the previously method described above, therefore less shrinking is observed. Subsequently, the formed film was swollen overnight in water, dried overnight (small amount of residual water is retained to prevent the material from becoming too brittle to handle) and small disks were manually punched using a 1.2 mm diameter hole puncher. Dimensional variations between disks used for the hydrogel size regulation experiments arises from variations in the amount of residual water being present in the gel during hole punching and therefore each disk must be individually characterised and the data normalised for comparison. The gels were swollen between two glass slides spaced 250 μm apart. The area of the gels was determined by a Leica M80 stereo microscope equipped with a Leica DFC420C camera. Images of the gel were taken after pulsing/constant illumination. The capture time of each image was 10–15 s. Images were taken every 5 min during illumination to ensure that the formation of McH$^+$ and resulting gel swelling when the light was off for image capture had minimal impact on the overall gel dimensions as the time required for gel imaging was far shorter than that of illumination during actuation. The images were analysed using Otsu Auto local thresholding with manual corrections in ImageJ software [28]. A light filter was used to block the blue light region of the spectrum to minimise shifts in the SPA-8 equilibrium (Scheme 1) and shrinking of the gel through generation of the SP form due to illumination required for microscope imaging, All microscope images were taken at 32× magnification.

3. Results and discussion

3.1. Regulating hydrogel size by pulsed light illumination

To investigate if it was possible to tune the size of the hydrogels by pulsed light, free standing hydrogel disks were exposed to a range of illumination conditions, using different pulse sequences, (1-1, 1-2 and 1-3) over longer time periods, whereby the first number denotes the time on, while the second number denoted the time off *e.g.* 1-1 stands for a sequence of 1 s illumination and 1 s darkness.

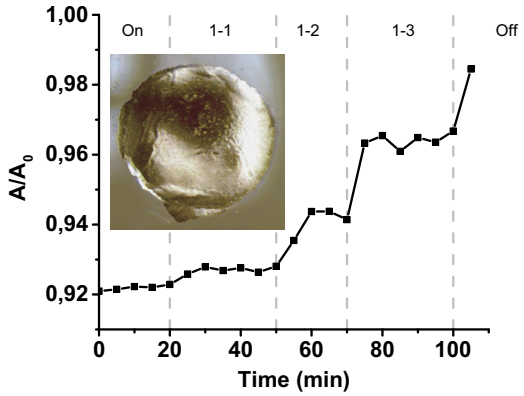

Fig. 3. Normalised effect of various pulse frequencies (on, 1-1, 1-2, 1-3, off) on hydrogel dimensions. Switching from constant illumination to a pulse sequence results in increased sized of the hydrogel. After switching off the LED, the gel recovers towards its initial size. Inset: visual enhanced photograph of the hydrogel in the shrunk state during constant illumination (on).

First, a fully swollen gel disk (surface area of 2,17 mm^2) was illuminated continuously with blue light to contract the gel to its minimal size (Fig. S2) and subsequently maintained at this size for 20 min. (Fig. 3, 92% initial area). After this period, various pulse sequences were used to create a gel of intermediate size (Fig. 3). The gel was first illuminated with a pulse sequence of 1-1 for 30 min. During the first 10 min of this period, the size of the gel increased slightly (93% initial area). For the remainder of this period, the area was relatively stable. Transitioning to the 1-2 pulse (after 50 min) produced a larger increase in the gel size and eventual stabilisation of gel diameter at 2.08 mm^2 (94% initial area). After switching to a 1-3 pulse sequence, a stable gel size of 2.12 mm^2 was generated (96% initial area). From this experiment it was clear that changing the pulse frequency from 1-1 to 1-3 leads to the establishment of an increasingly swollen gel, reflecting an increasing shift in the pseudo-equilibrium (Scheme 1) towards the McH$^+$ due to the longer light off period. The pulsed light sequence controls the light flux per unit time reaching the gel. This in turn controls the spiropyran equilibrium in the gel, which determines the degree of swelling. The pulse sequence creates a pseudo-equilibrium for the SP-McH$^+$ populations whereby the sequence is able to maintain a particular ratio of SP: McH$^+$ for an extended period of time. The result is that this maintains the gels dimensions in a somewhat fixed state (*vide infra*). These experiments show that the gel size can be controlled by a light pulse sequence and suggests that stable tunable flow rates can be achieved that relate to the pulse sequence employed.

3.2. Regulating microfluidic flow by (pulsed) light illumination

After generating the photo-responsive micro valve structure by photopolymerization of the monomer mixture inside a closed PMMA chip as previously reported [22], first the effect of various illumination methods was tested using a programmable LED platform. A Fluigent flow sensor S was used to keep the flow rates between 0 and 7 μL/min and the polymer valve was illuminated using four LED programmed sequences to induce varying degrees of valve actuation (a–d, Table 1). A continuous, single experimental run with the polymer valve illuminated using the four LED programme sequences for characterisation of the flow control properties was also performed (Fig. S3). Each programme was carried out in triplicate for statistical analysis and reproducibility tests (Figs. S4–S7).

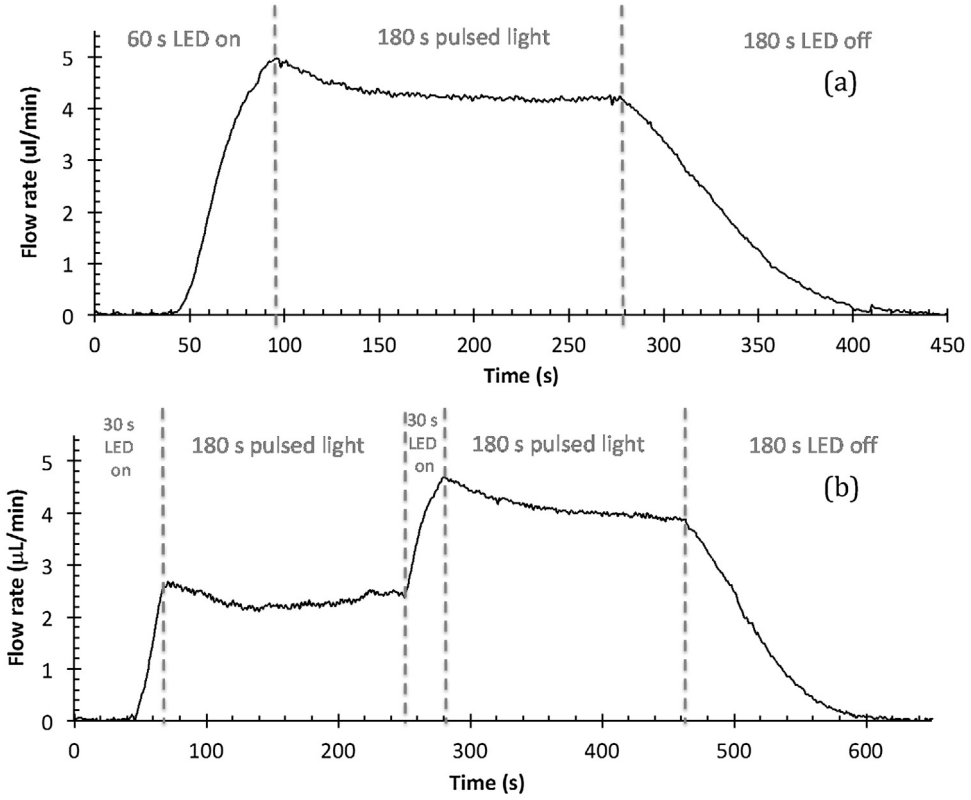

Fig. 4. (a) Flow profile of single rate flow control using SPA-8 hydrogel with LED programme c. (b) Flow profile of multiple flow rate control using SPA-8 hydrogel with LED programme d.

Table 1
Programs used to control the microfluidic flow rate.

Program	Description	Conditions
a	Valve flow range	LED on 180s, 360 s LED off
b	Valve actuation rate	LED on 60s, 180 s LED off
c	Single flow rate control	LED on 60s, LED pulse (1 s on-2 s off) 180s, 180 s LED off
d	Multiple flow rate control	LED on 30s, LED pulse (1 s on-2 s off) 180s, LED on 30s, LED pulse (1 s on-2 s off) 180 s, 180 s LED off

Initially, the flow range and limits of the valve was determined by illumination with blue light (450 nm) for 180 s (Fig. S4 and Table 2). A flow was observed after a short lag period after initiation of valve contraction (approx. 5 s). After approximately 55 s the initial rapid rate of valve opening began to significantly slow until the rate almost plateaued at 180 s. At this point, the light was switched off, and the valve re-swells leading to a decrease in flow rate. After a further 360 s the flow rate had returned almost to zero. Based upon these findings, it was proposed that illumination times during actuation would not exceed 60 s to ensure that the fastest actuation properties of the valves were exploited, as for efficient and practical valving, both opening and closing of the valves need to occur with relatively short time periods. To investigate this, the gel was illuminated with blue light for 60 s for valve opening, followed by darkness for 180 s for valve closure (Fig. S5). It was found that the opening of the valve occurs in less than 60 s under constant illumination and fully closes in 125 s. In addition, a highly reproducible and repeatable valving response was achieved (see SI; Table 3). A similar peak flow rate was observed during each valving event of approx. 4.76 ± 0.04 µL/min indicating that the valve opened to almost the same extent during each opening event. Additionally, a similar volume of water was found was passed (approx. 6.55 ± 0.4 µL) during each valving event. This reproducibility implies that the hydrogel valve exhibits sufficient precision to provide fluidic movement gating for microfluidic systems.

Following the successful application of the hydrogels as on-off valves, the ability to induce regulated flow by holding the polymer gels to intermediate states between 'fully open' and 'fully closed' for prolonged periods of time was investigated by pulsing of the light source (Fig. 4). It was found that under conditions of 1 s illumination and 2 s darkness (1-2 pulse sequence) a relatively stable flow rate could be maintained for the higher flow rates, as shown in Fig. 4a. The gel was first illuminated with 60 s of constant light followed by the 1-2 pulse for 180 s and finally 180 s of darkness to allow for valve closure (Fig. 4a, see SI; Table 4). In the first 60 s a similar increase in the flow rate was found as seen before (Fig. 4b). Upon changing the pulsed light exposure it was observed that while a stable, regulated flow rate was achieved (4.20 ± 0.05 µL/min), an initial relaxation period of approx. 90 s was required to reach this flow rate. The relaxation from peak flow rate to stable flow resulted in an average drop of 15.7% in flow rate. An oscillation in the flow rate with a small amplitude (0.05 µL/min, Fig. S8) and a frequency similar to the pulse sequence was observed (vide infra). After switching off the LED, the valve closed in a similar fashion as observed with programs a and b (Table 1).

Following the successful control of a single flow rate, it was demonstrated that the valves can also act as reproducible variable flow rate regulators during continuous operation *i.e.* changing flow

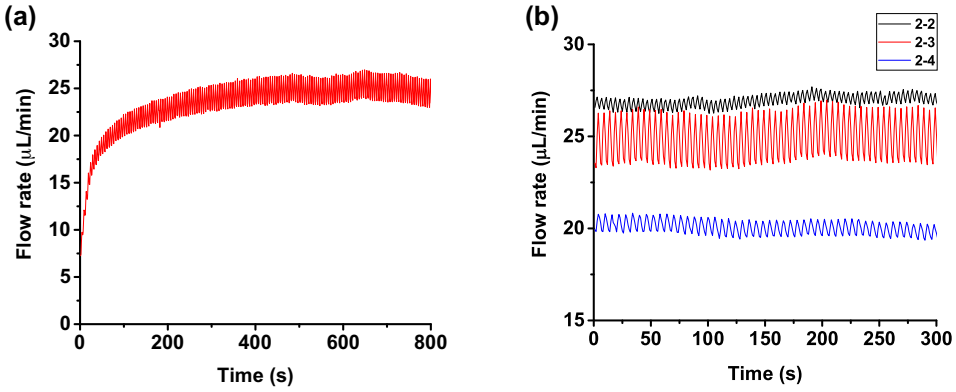

Fig. 5. (a) Effect of pulsed light (2-3 sequence) on the measured flow speed of a hydrogel valve, showing a stable flow speed of 25 μL/minute. (b) Arbitrary selected part in time of the flow speed for pulse sequences of 2-2, 2-3 and 2-4. In all cases, the oscillation follows the pulse sequence used.

rates during operation (Fig. 4b) using program d (See Tables 1 and 5 in SI). During the first flow rate control event, the 30 s constant illumination resulted in a peak flow rate of 2.61 ± 0.08 μL/min. This is, approximately 50% of the maximum flow that can be achieved, which was as expected since the illumination period was half that of the single flow control event (Fig. 4a). When switched to 1-2 pulsed light, a slight decrease in flow is initially observed in the first 90 s, which becomes more stable but with a gradual increase in flow over time. After a period of time (approx. 90 s), the flow rate begins to stabilise. However, since the pulsed light sequence maintain the pseudo-equilibrium further towards the McH^+ than the condition at 90 s, the flow rate is seen to slowly increase, and this would continue to increase over time towards the steady-state flow rate, which is ca. 4 μL/min according to Fig. 4a. Nevertheless, since the time to create the equilibrium is larger than the time used in this experiment, repeatable and relatively stable plateau's can be formed. Following the initial 1-2 pulsed light sequence a further 30 s of light was applied to the valve to further increase the flow rate. A peak flow of 4.66 ± 0.08 μL/min was generated following this illumination phase with a gradual reduction to 3.99 μL/min ±0.03 during the 1-2 pulsed light sequence. Once again, similar effects were found during this second flow control phase whereby 30 s constant illumination resulted in rapid opening of the valve followed by reduction in flow rate to a more stable flow. In this case however, after the 90 s reduction towards the steady-state condition (ca. 4.0 μL/min). Hence, these experiments show that the flow depends on the pulsed light sequence and in the case of short exposure, also on the initial value.

Finally in order to show that the flow rate is controlled by the pulsed sequence and that this concept is more general, as well as amplifying the oscillation, a set of experiments was performed, in which the hydrogel valve was illuminated using a 2-2, 2-3 and 2-4 pulsed light sequences for an extended period. During these experiments, the flow was measured using a Fluigent M flow sensor which has a much larger flow range, ranging from 0 to 80 μL/min. When starting the illumination using a 2–3 pulse, it takes roughly 300 s to reach a constant flow of 25 μL/min (Fig. 5a) that can be maintained for at least 10 min. Superimposed is a smaller oscillation in the flow rate with an amplitude of roughly 3 μL/min (Fig. 5b). This amplitude is largest when the flow rate reaches a pseudo equilibrium state. The frequency of the oscillation corresponds to the pulse sequence with an increase in the flow rate during illumination and a decrease when not illuminated. This reveals that during the pulsed light irradiation, an oscillation in the corresponding dimensions of the hydrogel valve occurs. Interestingly when the pulse sequence is changed the flow rate also changes. A shorter light-off period (2-2) leads to a higher flow of 27 μL/min while a longer light-off period (2-4) produces a flow rate of 20 μL/min, with the oscillation flow rate frequency the same as the pulse frequency. The longer light-off period leads to an increasing shift in the pseudo-equilibrium (Scheme 1) towards the protonated merocyanine McH^+. This results in more swollen gel valve, and a corresponding decrease in flow rate. It should be noted, however, that there is no systematic change in amplitude of the flow oscillation when the pulse sequence is changed. The amplitude at these higher flow rates is more pronounced than for the experiments in Fig. 4, due to the larger size of the flow sensor, which has less restriction on the flow, as well as the larger time between the pulses.

4. Conclusions

We have shown that reproducible actuation for flow control within practical timescales can be achieved using a photoresponsive polymer hydrogel formulation. By using a pulsing blue light source an oscillating polymer hydrogel valve with intermediate steady-state size related to the pulse sequence is formed that can be used to regulate the flow rate in a microfluidic channel, similar to fully controllable mechanical valves. These hydrogel materials demonstrate the initial steps towards the creation of truly biomimetic fluidics platforms whereby the entire regulatory processes of the system are fully integrated, enclosed from the external environment and inherently scalable. In contrast to existing mechanical valves, whose integration on chip is limited by size and arrays of which must be located off-chip requiring extensive interconnectivity and producing significant dead volumes, the production of chips with integrated valves, addressable externally using light, clearly provides the foundation for the development of chips with much more sophisticated fluid handling capabilities. The use of millimetre dimension surface mounded LEDs in combination with similarly sized gel valves creates the opportunity to create arrays of valves without any significant increase in platform dimensions, to perform more complex functions, such as multi-stage chemical processes or large scale arrays of "single shot" assays while remaining compact and portable. Our results not only demonstrate the potential application of these gels within microfluidic platforms as microscale valves for the production of low-cost flow control but also characterise the properties of controlling photoresponsive hydrogel dimensions using pulsed light.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2017.01.112.

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Biographies

Simon Coleman received his B.Sc in Analytical Science in 2006 at Dublin City University and his PhD in 2010 under Prof. Dermot Diamond investigating the physicochemical properties of ionic liquids. He is currently a postdoctoral Research Fellow at the National Centre for Sensor Research (NCSR) with research interests in ionic liquids, polymer synthesis, microfluidics and stimuli responsive materials for sensor applications within the personal sensing, wearables, medical and environmental sectors.

Jeroen ter Schiphorst received his Bachelor's degree from Fontys University of Applied Science in 2011. Afterward, he started a Masters in Chemical Engineering: Molecular Engineering at Eindhoven Universiy of Technology. He received his Masters of Science degree in 2014. In March 2014 he joined the Functional Organic Materials and Devices (SFD) group for a PhD under the supervision of A.P.H.J Schenning. He is currently working on light switchable materials in microfluidics for the NAPES project

Aymen Ben Azouz has worked with Caterpillar as an Electrical Engineer before joining Dublin City University to work on the development of new sensing techniques for automatic milking systems as part of his masters degree. He subsequently completed a PhD in 2013 with a focus on laser processing of materials for the purpose of fabrication of microfluidics. He is now working on the NAPES project within Insight centre. His interests include the development of an automated platforms for the purpose of environmental sensing.

Sterre Bakker is a B.Sc student at the Eindhoven University of Technology. She did her internship at the Fuctional Organic Materials and Devices (SFD) group under the supervision of Jeroen ter Schiphorst and A.P.H.J. Schenning.

Albertus P.H.J Schenning is professor at the Eindhoven University of Technology. He received his Ph.D degree at the University of Nijmegen in 1996 on supramolecular architectures based on porphyrin and receptor molecules with Dr. M.C. Feiters and Prof. R.J.M. Nolte. His research interests are focused on functional organic materials.

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 has been 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).