

# Incorporation of acrylate based spiropyran monoliths in micro-fluidic devices for photo-controlled electroosmotic flow

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**Abstract.** Spiropyran photochromic compounds can be switched using light exposure between a non-polar spiro form (SP) and a zwitterionic merocyanine form (MC) that is subject to protonation (MC-H<sup>+</sup>). It has recently been demonstrated by Walsh *et al.* that, under acidic conditions, electroosmotic flow (EOF) generated in vinyl based spiropyran monoliths can be modulated using light irradiation [1].

In this paper, we report a spiropyran-modified acrylate based monolith which is particularly sensitive to protonation in the MC form, producing a positively charged surface that converts to the unpolar SP form by exposure to white light. When the MC-H<sup>+</sup> form is dominant, it produces a charged surface which enables a relatively high flow rate (up to 1.6  $\mu\text{l}/\text{min}$ ) to be generated under electroosmotic conditions. Upon exposure to white light, the concentration of MC-H<sup>+</sup> decreases due to the photo-conversion to the uncharged SP form, with up to 20% reduction of the EOF. The process is reversible, and removal of the light source results in a flow increase back to the original rate. The ability to alter flow rates in micro-fluidic channels using light has very significant implications, as it could dramatically simplify the manner in which micro-flow systems are controlled.

## Introduction

Photochromic molecules such as spiropyrans, which photoisomerise when exposed to light, can be incorporated into *adaptive materials* that have been exploited in a variety of applications. Of crucial importance is the possibility to operate an external light control of these materials at a molecular level, as this may imply a control of important behaviour such as: liquid movement across a surface [1], reversible control over binding of guest species [2, 3] or modulation of electrochemical properties [4]. Spiropyrans has the ability to reversibly switch between a charged merocyanine form (MC) and an unpolar spiro form (SP) by exposure to white light. The MC form presents a phenolate group that can be protonated (MC-H<sup>+</sup>) and the protonation stabilises the MC form, and in so doing creates a stable residual positive charge upon the molecular unit.

Exploiting this property, it has been demonstrated that the volume of a hydrogel copolymer of an acrylate spiropyran and poly(*N*-isopropylacrylamide) can reversibly expand and contract when the gel is alternatively exposed to light or kept in the dark [5]. When the hydrogel is placed in a slightly acidic environment and irradiated with visible light, the gel is overall largely neutral, because of the prevalence of the SP form. However, when kept in the dark, the gel becomes positively charged, because of the prevalence of the MC-H<sup>+</sup> form. Negatively charged fluorescent nanoparticles are preferentially adsorbed on the non-irradiated region, confirming the presence of an overall positive charge due to protonation of the photochromic compound [5].

Electroosmotic flow (EOF) as a means of driving liquid movement has attracted increasing attention in recent years, in parallel with the development of micro-fluidic systems [6]. EOF refers to the spontaneous movement of a fluid relative to a stationary charged surface when exposed to an externally applied electric field. This type of fluid movement offer a wide range of advantages compared to commonly used pumping systems (such as peristaltic pumps), as it creates a constant pulse-free flow in which the magnitude and the direction of the flow are easy to control without the necessity of moving parts, as in a conventional pump.

Polymeric organic monoliths (rigid macroporous polymers prepared by *in situ* polymerisation in a closed mould) provide an interesting platform for investigating EOF as they can be easily incorporated into microscale flow systems [7]. The copolymerisation of a vinyl spiropyran derivative with a divinylbenzene cross-linker to give a photochromic organic monolith has been shown to provide a route to the generation of a micro-flow systems with light tunable EOF under applied field up to 250 kV/m when the spiropyran moiety is switched between the charged MC-H<sup>+</sup> form and a unpolar SP form under white light exposure [1]. Flow rates for these systems reported previously were typically in the nl/min range.

In this paper we present a new acrylate based spiropyran monolith capable of flow rates in the  $\mu$ l/min range which can be reversibly photo-switched by up to 20% under white light exposure.

## Experimental

### Materials and instruments

The acryl ester of (1',3',3' triimethyl-6-hydroxyspiro(2H-1)benzopyran-2, 2'-indole) (Acrylated SP, *Fig. 1*) was synthesised according to a previously reported procedure [5]. Brilliant Green, ethylene glycoldimethacrylate (EDMA), *t*-butanol and azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich (Ireland). Hydrochloric acid 32%, density 1.16 g/cm<sup>3</sup> was purchased from Fisher Scientific. Standard solutions of HCl 10<sup>-3</sup> M were prepared by dilution of 10<sup>-1</sup> M HCl stock solution. UV-transparent polytetrafluoro ethylene (PTFE) coated fused silica capillaries (100  $\mu$ m internal diameter, 375  $\mu$ m external diameter) were obtained from Polymicro Technologies (Phoenix, AZ, USA). Capillary flushing after the monolith synthesis was performed using an HPLC pump (Shimadzu, Japan). Subsequent HCl flushing was performed using a capillary fitting syringe. Monolith pictures were taken with a SVM-340 Synchronised Video Microscope (LabSmith, USA) while a S-3400N VP-SEM (Hitachi, Japan) was used for SEM imaging. Voltage control and current monitoring was achieved via a 0-30 kV high voltage power supply obtained from Unimicro Technologies (Pleasanton, CA, USA).

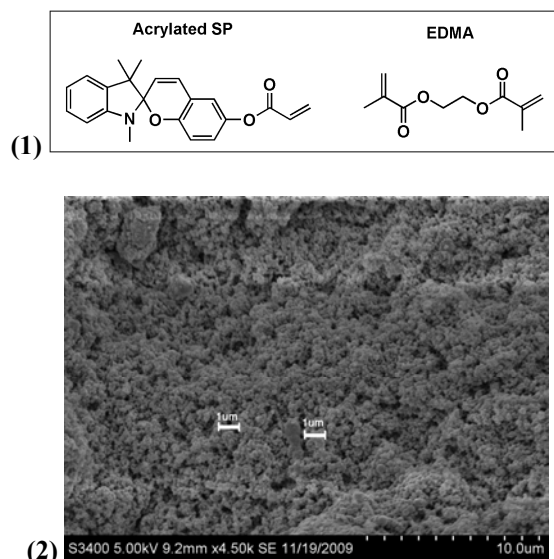
Inert acrylic pressure sensitive adhesive (PSA) polyester film (ARcare 8890) was purchased from Adhesives Research Ltd., Limerick, Ireland. Channels in the micro-fluidic chip were first designed using CAD 3D Excalibur software (Progressive Software Corporation, USA) and then fabricated by direct micro-milling (Datron 3D M6, Datron Technology Ltd., Milton Keynes, UK). Poly ether ether ketone (PEEK) tubing was obtained from Upchurch Scientific (Oak Harbour, WA, USA). PMMA sheets were obtained from Goodfellow Cambridge Limited (UK), and 5 min epoxy glue from Bondloc, Worcestershire, UK.

A 10 $\mu$ l glass syringe (SGE Australia Pty. Ltd.) filled with 10<sup>-3</sup> M aqueous solution of brilliant green was used to optimise the meniscus visualisation. White LEDs (430-760 nm) in a 3x3 array format were purchased from Lumitronix GmbH (Hechningen, Germany).

### Synthesis of spiropyran acrylate monolith

Prior to monolith synthesis, the walls of the PTFE coated fused silica capillaries were pre-treated with a silanising agent to ensure that the monolithic frit would be well anchored to the walls [8]. Acrylated SP and EDMA were chosen as the monomer and cross-linker, respectively. For the synthesis, a solution was made up consisting of 40  $\mu$ l EDMA, 6 mg of acrylated SP, 0.9 mg of

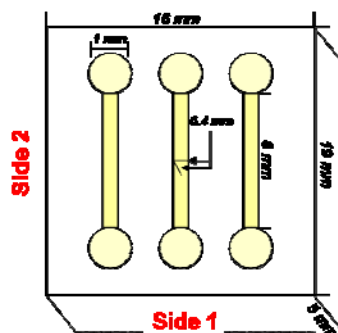
AIBN and 60  $\mu\text{l}$  of *t*-butanol as the porogenic solvent. The mixture was sonicated to dissolve the monomer and the initiator, purged to remove the dissolved oxygen and finally filled into pre-treated PTFE coated capillaries by capillary action. Using rubber septa to close both ends, a 10 cm length of capillary was placed on a water bath at 60°C for 90 minutes to initiate the *in-situ* polymerisation. The capillary was then flushed with methanol using a LC-10 AD HPLC pump, in order to remove any un-reacted components of the polymerisation mixture. The resulting polymer exhibits a macro-porous structure with globule size around 1  $\mu\text{m}$  (Fig. 1).



**Fig. 1:** (1) Structure of SP acrylate monomer and EDMA cross-linker used to synthesise the spiropyran acrylate based monolith. (2) Scanning electron micrograph of a cross-section of the porous structure of the SP acrylate monolith.

### Micro-fluidic chip for electro-osmotic flow measurement

The spiropyran modified monolith was incorporated into a micro-fluidic chip for EOF measurement. A micro-fluidic chip 16 mm x 19 mm x 5 mm with channels 8 mm x 0.4 mm x 0.4 mm was fabricated by direct micro-milling as described by Nie *et al.* [7] (Fig. 2). After milling, the PMMA sheets were washed thoroughly with ethanol to remove traces of dust and excess PMMA, and the 8 mm long spiropyran monoliths encased in the channels. The capillaries were held in place in the channels using a drop of 5 min epoxy resin before the channels were covered with a layer of PSA followed by a second, unmilled sheet of 0.5 mm thick PMMA. The so-assembled microchip was then placed in a vice for several minutes to ensure complete sealing of the chip. 1 cm lengths of PEEK tubings were used as inlet and outlet tubing and were connected to 1.5 ml plastic vials which served as solvent reservoirs.

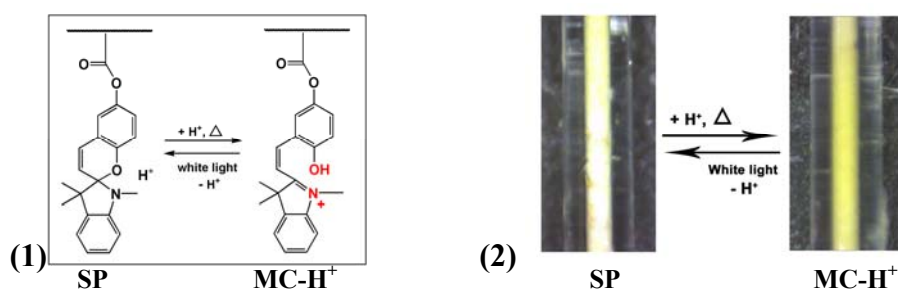


**Fig. 2:** Schematic representation of the top view of the micro-fluidic chip which incorporates three 8 mm long monoliths for EOF measurement.

## Results and discussion

### Photochromic properties of the spiropyran acrylate monolith

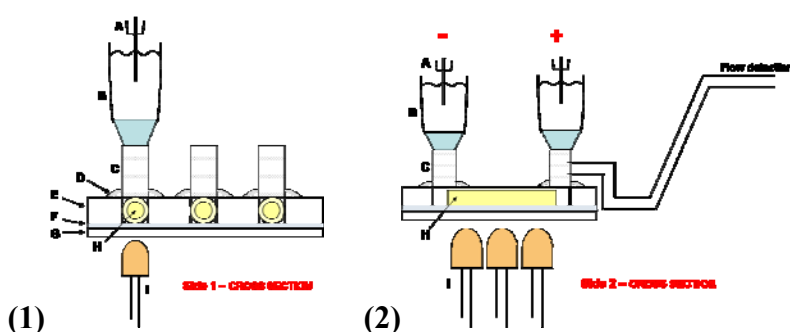
The spiropyran acrylate monolith can be switched in the presence of acid ( $10^{-3}$  M HCl) between a  $\text{MC-H}^+$  form and an uncharged SP form (Fig. 3). In an acidic environment, the protonation of the phenolate group is highly favoured and the formation of the  $\text{MC-H}^+$  form occurs spontaneously, accompanied by the appearance of a characteristic yellow colour. Irradiation with white light causes reconversion to the SP form, with associated release of protons.



**Fig. 3:** (1) SP acrylate switching in acidic environment between the  $\text{MC-H}^+$  form (right) and the SP form (left) when irradiated with white light. (2) Picture of the spiropyran acrylate monolith flushed with HCl  $10^{-3}$  M switched between the  $\text{MC-H}^+$  form, in the absence of light exposure and the SP form when irradiated with white light.

### EOF evaluation

For protection, 8 mm lengths of SP acrylate monolith filled capillaries were encased in a PMMA micro-fluidic platform with channels 8 mm x 0.4 mm x 0.4 mm (Fig. 4). Additionally to reduce the occurrence of electrolysis of the buffer within the channels, the micro-fluidic platform was equipped with two comparatively large buffer reservoirs at the chip inlet and outlet. At the two ends of each channel two pieces of tubing were placed as an inlet and outlet for the HCl solution. Each piece of tubing was connected to a 1.5 ml reservoir containing  $10^{-3}$  M HCl. The working electrodes were then placed inside the reservoirs. This platform also makes EOF measurement very simple as the electrodes are placed directly into the buffer reservoirs and the measurements can be taken immediately. The spiropyran acrylate monolith was irradiated using a 3x3 square array of 9 white LEDs (430-760 nm) placed on the bottom of the chip where the thickness of the PMMA is lower and the light irradiation is more efficient. LEDs were chosen as they are relatively low-power light sources with negligible heating effect when compared to conventional lamps. LEDs present ca.  $1 \text{ mW/cm}^2$  power compared to the power of arc lamp light sources reported in most papers, which are typically 50-100 W. Despite this much lower power, LEDs have shown to effectively switch the  $\text{MC} \leftrightarrow \text{SP}$  system with minimal photo-bleaching [9].



**Fig. 4 (1 and 2):** Schematic representation of the cross section of the microchip side 1 and 2 (Fig. 3). A) Electrode; B)  $1.5 \text{ ml } 10^{-3} \text{ M HCl}$  reservoir; C) PEEK tubing; D) epoxy glue; E) PMMA sheet 5 mm thickness; F) layer of PSA; G) second sheet of PMMA (0.5 mm thickness); H) SP acrylate monolith 8 mm length; I) white LEDs (430-760 nm) 3x3 square array of 9 LEDs.

The EOF effect was measured in the presence of the SP form, which was induced by irradiating the monoliths with white LEDs, and afterwards in the presence of the MC-H<sup>+</sup> form, generated spontaneously under acidic conditions (10<sup>-3</sup> M HCl).

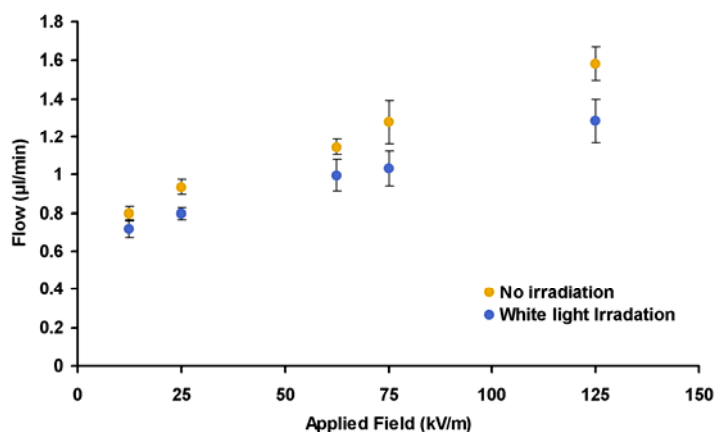
The EOF measurement was carried out according to the procedure reported by Nie *et al.* [7, 10]. The microchip was filled with 10<sup>-3</sup> M HCl solution and connected through a capillary outlet to a 10  $\mu$ l glass syringe filled with an aqueous solution of 10<sup>-3</sup> M brilliant green leaving an air gap between the HCl liquid front and the front of the brilliant green solution. The flow rate was calculated by tracing the working fluid/air meniscus and timing its movement. The choice of a highly coloured green solution greatly enhances the visualisation of the meniscus. The absence of a downstream load pressure was ensured by the outlet being directly open to the atmosphere and being placed at the same level of the 10<sup>-3</sup> M HCl reservoirs.

Once the monolith, tubing and reservoir were filled with working liquid and connected to the syringe for flow measurements, the system was left for one hour before measurements were made in order to ensure the system was at equilibrium before an electric field was applied.

EOF is generated as a consequence of the formation of an electrical double layer at the liquid-solid interface. In an acid environment (10<sup>-3</sup> M HCl) the surface of the spiropyran monolith is positively charged because of the presence of the MC-H<sup>+</sup> form. As a consequence there is the formation of an electrical double layer and when an electric field is applied the mobile ions move in response to the electric field, dragging the bulk solution and generating the EOF. In this case, as the surface is positively charged, overall the EOF moves from the anode to the cathode.

The EOF generated increases proportionally to the applied field (*Fig.5*) from ca. 0.7  $\mu$ l/min (at 12.5 kV/m) to 1.6  $\mu$ l/min (at 125 kV/m). When the same measurement is performed while exposing the monolith to white light, the EOF decreases by 15% on average. It reaches a maximum at 125 kV/m where a decrease of 20% is observed (*Table 1*) due to disruption of the charged double layer by partial formation of the uncharged SP isomer. The experiments were repeated in triplicate and the statistics shows reproducibility and a consistent decrease in the EOF when the monolith is exposed to white light irradiation. We can therefore conclude that, as expected, the EOF (and therefore the flow rate) increases when an external field is applied, but in addition, that the flow rate is always lower when under illumination with white light, compared to that obtained at the same applied field in the dark.

The fact that the EOF cannot be completely suppressed is most likely due to inability of the light irradiation to reach the entire thickness of the monolith homogeneously, as a result of its non-transparent nature, leaving the spiropyran close to the central core predominantly in the MC-H<sup>+</sup> form. In comparison with the recently submitted work by Walsh *et al.* [1], where the EOF was evaluated using a vinyl based spiropyran monolith, the hereby reported SP acrylate monolith generates relatively faster flow rates probably due to higher stability of MC-H<sup>+</sup> form.



**Fig. 5:** Graph showing the EOF increase as an effect of the application of an increasing electric field both for the SP acrylate monolith in the MC-H<sup>+</sup> form (no irradiation) and in the SP form (white light irradiation). Statistics shows that the EOF generated with or without white light irradiation is substantially different (n=3).

Flow rate variations when applying white light exposure and increasing electric field			
Applied Field [kV/m]	No Irradiation (mean flow rate value) [ $\mu\text{l}/\text{min}$ ]	White light Irradiation (mean flow rate value) [ $\mu\text{l}/\text{min}$ ]	EOF DECREASE (%)
0	0	0	0
12.5	0.80 ( $\pm 0.03$ )	0.72 ( $\pm 0.04$ )	10.0
25	0.94 ( $\pm 0.04$ )	0.80 ( $\pm 0.02$ )	14.9
62.5	1.15 ( $\pm 0.04$ )	0.99 ( $\pm 0.08$ )	13.9
75	1.28 ( $\pm 0.11$ )	1.03 ( $\pm 0.09$ )	19.5
125	1.60 ( $\pm 0.08$ )	1.28 ( $\pm 0.10$ )	20.0

**Table 1:** Table showing the mean flow rate values ( $\mu\text{l}/\text{min}$ ) recorded when increasing the applied field on the spiropyran functionalised monolith. The experiments were carried out exposing and not exposing the monoliths to white light irradiation. On the left the % of EOF decrease when the monolith is irradiated with white light irradiation is reported.

## Conclusions

Acrylate based spiropyran monoliths have been synthesised and characterised in terms of photoswitchable EOF behaviour. Under acidic conditions, the SP acrylate monolith surface is preferentially in the MC-H<sup>+</sup> form, which can be readily converted to the SP form through exposure to white light. When an external electric field is applied in the presence of  $10^{-3}$  M HCl, EOF in the 0.7  $\mu\text{l}/\text{min}$  to 1.6  $\mu\text{l}/\text{min}$  range is generated. Under constant applied field, white light irradiation leads to a decrease in the EOF. Removal of the light source results in a flow increase. Clearly this spiropyran monolith can act as an electro-osmotic pump, in which the flow can be modulated through the presence or absence of light. This ability to profoundly alter such properties using light has very significant implications for science as it could lead to the development of micro-fluidic platforms where the liquid flow can be externally modulated using light irradiation.

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