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LED switching of spiropyran-doped polymer films

Shannon Stitzel · Robert Byrne · Dermot Diamond

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Abstract Spiropyrans are a well-known family of photochromic compounds that switch from uncoloured to highly coloured upon exposure to UV light with potential applications such as optical switches and memory storage devices. Typically the light sources used for controlling the state of the spiropyran are high power sources such as mercury lamps and lasers. Here we report the use of low power light emitting diodes (LEDs) to actuate the colour change in spiropyran-doped polymer films. The use of LEDs as an effective means of switching the dye expands the possible applications of these types of photochromic materials.

Introduction

Photochromism is the ability of a chemical species to reversibly change colour upon exposure to light [1]. During this process, photochromic compounds usually undergo a change in their molecular structure or conformation, which alters the absorption spectrum of the dye. An interesting photochrome is benzospiropyrans, which upon exposure to UV light undergoes a heterocyclic ring cleavage [2] to the open merocyanine form of the dye (Fig. 1). While the spiropyran or closed form of the dye is colourless, the open merocyanine structure has a strong absorption in the visible region due to the formation of an extended conjugated planar conformation.

There are many potential applications for photochromic materials such as control of the transmission of light in photochromic windows and eye-protection [3], in rewritable optical media [4, 5] and holigraphic recording [6], although their poor fatigue resistance is a limiting characteristic for spiropyrans. Other applications rely on the physical or chemical change that occurs in spiropyrans upon photoactivation. For instance, spiropyrans have been used as a means of directing fluid movement on glass surfaces [7, 8], as an optical switch in an immunosensor [9] and as molecular receptors for cations [2, 10–15]. Our main interest is in the photonic control of surface binding properties of spiropryan films in contact with liquids. We are particularly interested in developing applications based on switching spiropyran films immobilized on substrates using light emitting diodes (LEDs), as this will provide a very flexible and low power route the realizing many of the applications mentioned above. For example, LEDs could be used to modulate surface energy by switching between the charged (open) and the uncharged (closed) form. This in turn would facilitate control of liquid movement on surfaces, and relative attractiveness of polar/non-polar components for the surface. Binding of ions to the surface could also be turned off/on in a location specific manner that can be varied dynamically using LED arrays and simple masks.

However, to date, literature reports on spiropyrans switching has involved the use of high power sources such as mercury arc lamps or lasers. In this paper we report for the first time to our knowledge the use of LEDs as the means to induce the photochromic switching of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro [2*H*-1-benzopyran-2,2′-(2*H*)-indole] doped polymer films.

S. Stitzel · R. Byrne · D. Diamond (✉)
Adaptive Sensors Group, National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland
e-mail: dermot.diamond@dcu.ie

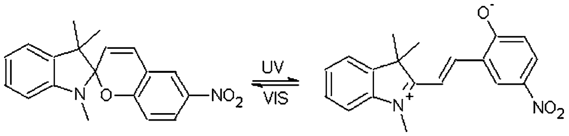

Fig. 1 The well-known photo-switching of benzospiropyran between the spiropyran (left) and merocyanine (right) forms

Experimental

Materials and instrumentation

Polymethylmethacrylate (PMMA) sheets (0.5 mm thick) (Goodfellows) were cut to size and washed with ethanol before use. Styrene, methacrylic acid, acetophenone, 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro [2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SP) were used as received from Sigma.

For the kinetic studies, spiropyran-doped polymer films were irradiated with a 380 nm LED (Digi-key) to activate the merocyanine form of the dye. A 525 nm LED (Stanley) was used to revert the dye back to the spiropyran form. The LEDs had an irradiance of approximately 1 mW/cm^2 measured with a Newport digital power meter (model 815). Both the colouring and bleaching processes were monitored in real time using a Perkin-Elmer photodiode array UV–Vis spectrometer. A schematic of the LED setup inside the UV–Vis spectrometer chamber is shown in Fig. 2. We followed the kinetics of the spiropyran/merocyanine photoswitching at 540 nm, which corresponded to the absorption maximum of the merocyanine form in the polymer films (Fig. 3). All kinetics data were collected at room temperature (20 °C).

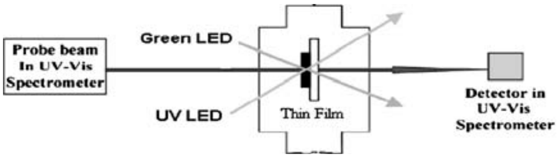

Fig. 2 Schematic of LED light source apparatus inside UV–Vis spectrometer chamber

Preparation of SP polymer films

A 0.5 mm thick PMMA slide (32 × 22 mm) was washed with ethanol to clean the surface and dried under a nitrogen stream. The slide was then placed in the spin coater using a tweezers, exposed side facing up, and 0.5 ml of the dye/monomer solution was placed on the slide and left for 10 min. The spin coater (Laurell Technologies, Model WS-200-4T2) was turned on for 30 s at 2000 rpm. The slide was then placed under a UV lamp (@254 nm) for 90 min to polymerize the film. Acetophenone was used as the free-radical initiator. The compositions of the monomer solutions are listed in Table 1.

Results and discussion

Three different SP-doped polymer films were coated onto PMMA substrates. The PMMA substrate was chosen for its optical transparency in the visible spectrum. Thin films (~1 μm thick) were spun on the PMMA to create a PMMA slide with a photochromic surface. Depending on the polarity of the polymer film, the merocyanine form had a different absorption maximum as seen in Fig. 3. This shift in the absorbance spectrum is due to the solvatochromic nature of the dye, as previously been reported [12, 16]. The dye exhibited a red shift as the polymer matrix became more non-polar, with the polymethacrylic acid (PMAA) film having an absorbance maximum at 540 nm (curve A), while the more non-polar polystyrene (PS) film had an absorbance maximum at 553 nm (curve C). This demonstrates that the absorbance of the dye can be tuned by controlling the polarity of polymer matrix, or conversely,

Fig. 3 UV–Vis spectra of merocyanine form of dye entrapped in a thin film of (**A**) polyacrylic acid, (**B**) 50/50 polyacrylic acid/polystyrene and (**C**) polystyrene

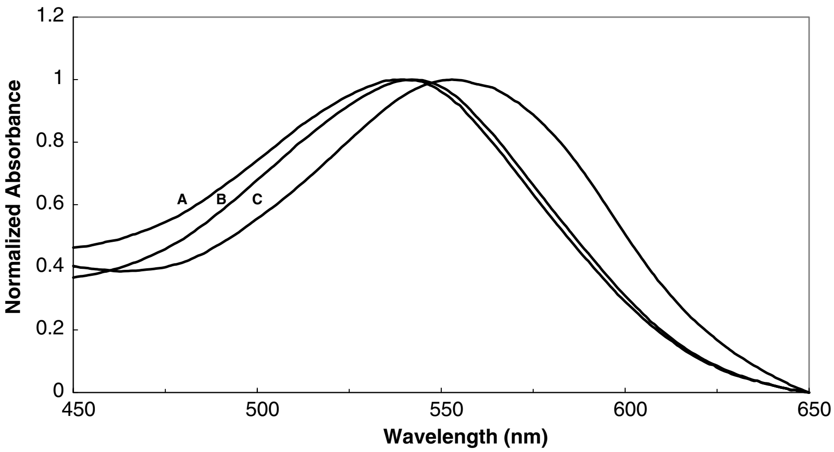

Table 1 Monomer solutions for preparation of SP containing polymer films

Solutions	Acetophenone (mmol)	Methacrylic acid (MA) (mmol)	Styrene (Sty) (mmol)	Spiropyran dye (mmol)
100% MA	25.0	25.0	0.0	0.025
50(MA):50(Sty)	25.0	12.5	12.5	0.025
100% Sty	25.0	0.0	25.0	0.025

Table 2 Dye opening and closing kinetics for different polymer films $n = 4$

Polymer film composition	k_{UV} (s^{-1})	k_{Vis} (s^{-1})
100% Polymethacrylate	$(2.6 \pm 0.1) \times 10^{-2}$	$(1.2 \pm 0.1) \times 10^{-2}$
50/50 Polymethacrylate/ polystyrene	$(2.5 \pm 0.2) \times 10^{-2}$	$(1.7 \pm 0.1) \times 10^{-2}$
100% Polystyrene	$(2.2 \pm 0.3) \times 10^{-2}$	$(1.4 \pm 0.1) \times 10^{-2}$

that the dye can be used to measure the polarity of its environment.

In any dynamic system, kinetics is important, and in moving to a LED based approach, we were concerned that the kinetics of the switching process would be adversely affected. First-order rate constants for the opening and closing of the spiropyrans-doped polymers were determined using Solver (Microsoft Excel), by fitting the absorbance data to the following equation

$$y = ae^{-kt} + b \tag{1}$$

where y is the absorbance value, a is the absorbance at $t = 0$, k is the rate constant, t is time and b is asymptotic value [17]. The photochromic rate constant k is subscripted UV and Vis to denote the opening and closing processes, respectively. Figure 4 shows an example of the k_{UV} (Fig. 4a) and k_{Vis} (Fig. 4b) data obtained from a 50/50 PMAA/PS spiropyran-doped polymer film. As seen in Fig. 4a, the absorbance value increases rapidly as soon as the UV LED is switched on, indicating efficient opening of the spiropyrans into the merocyanine form. The photostationary state was reached after only 3 min of UV irradiation compared to 10–30 min reported by others [6, 18]. Upon exposure to a 525 nm green LED, the dye closed again as seen in Fig. 4b, returning to the baseline absorbance value within 5 min. The models obtained fit the data well as demonstrated by having less then 2% error for most data points (insets Fig. 4a, b show residual error plots). The k_{UV} and k_{Vis} rates for the different polymer matrixes are reported in Table 2. The rate constants obtained in these polymer films (2×10^{-2} s^{-1}) are slightly larger than those previously reported (2×10^{-3} s^{-1}) by Tork et al. [6], probably due to differences in the film casting methods. Interestingly, although the different ratios of methacrylic acid and styrene in the polymer films led to changes in the absorbance maximum of the dye (Fig. 3), the switching kinetics of the films seemed to be relatively unaffected by this polarity change as seen by the rate constants obtained in Table 2.

While most papers report using 50–100 W white-light power sources equipped with bandpass filters to provide an irradiance in the mW/cm^2 range [6, 16, 19], in this work we use a low-power UV LED but which still provides an irradiance of approximately 1 mW/cm^2. Despite the drastic difference in current and voltage requirements of LEDs relative to arc lamps, clearly the LEDs are still able to effectively switch the spiropyran-doped polymer films.

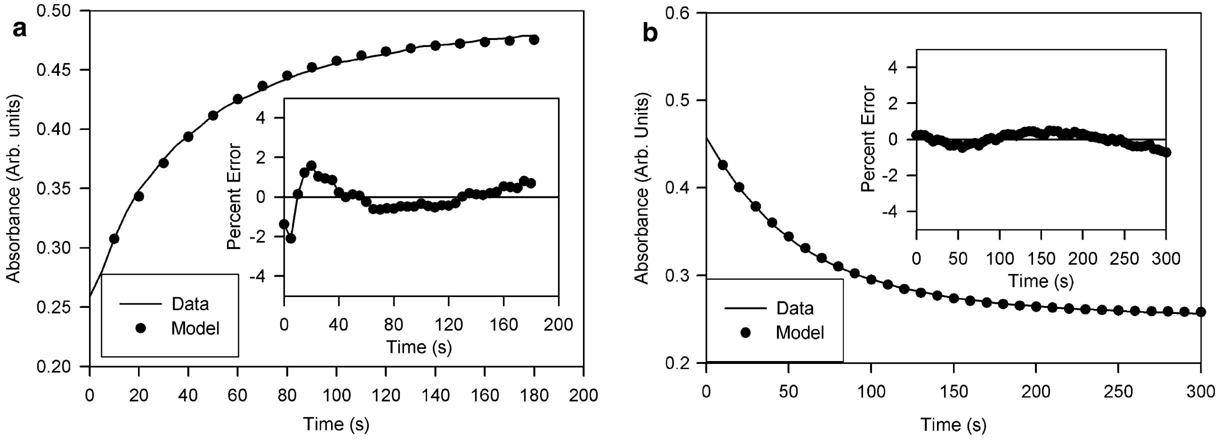

Fig. 4 Kinetics (absorbance versus time) plots of a 50/50 polyacrylic acid/polystyrene film at 540 nm and 20 °C for (a) ring opening using a UV (380 nm) LED and, (b) ring closing using a green (525 nm) LED. In both cases, the fit to a single exponential (first order) model is shown, with a residuals plot of percent error for the single exponential model as an inset

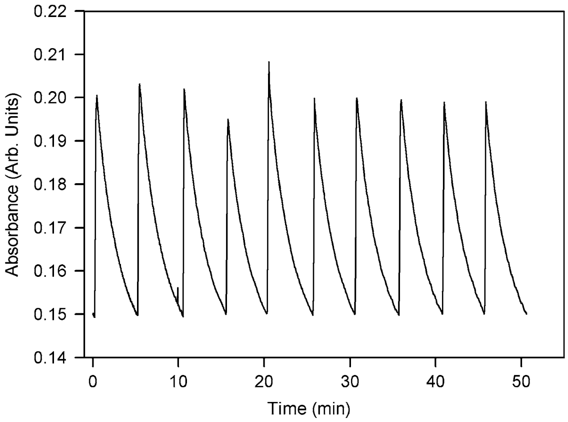

Fig. 5 Light emitting diode switching of photochromic PMAA/PS polymer film; first 10 switches between coloured (high absorbance) and uncoloured forms (low absorbance) of the dye

Using the LED set-up shown in Fig. 2, a 50/50 PMAA/PS film was switched between the coloured and uncoloured forms of the dye 100 times by alternating exposure between the UV and green LEDs. The films were coloured using a 10-second exposure of UV light, and then uncoloured by exposure to the green light for the length of time required for the film to return to the baseline absorbance (approximately 5 min). The 10 s exposure led to approximately 25% of the steady-state absorbance (see Fig. 5). Photo-fatigue of the film was observed during the course of the 100 exposures, resulting in an approximate 11% loss in the maximum absorbance value at 540 nm. Despite this gradual reduction in absorbance, the effectiveness of using LEDs as photoactuators for spiropyrans is clearly demonstrated. We are currently developing pulsed-mode measurements and more photostable analogs as means for reducing the effect of photo-fatigue.

Conclusion

The use of LEDs as an effective light source for switching spiropyran-doped polymer films is reported. Light emitting diode light sources require significantly less power and are inexpensive alternatives to sources such as the arc lamps typically reported. The small size of LEDs compared to arc lamps is also appealing, enabling devices combining the photochromic nature of spiropyrans with LEDs to be envisioned. Future work will be aimed at applying spiropyran-doped polymer films to solid state sensing devices using clusters of LEDs for switching and sensing the spriropyrans. We will also investigate the use of LEDs for controlling liquid position and movement on spiropyrans films immobilized on transparent substrates.

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