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Photo-responsive polymeric structures based on spiropyran

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Spiropyran is one of the most popular classes of photochromic compounds that change their optical and structural properties in response to external inputs such as light, protons and metal ions, making them ideal molecules for the fabrication of multifunctional stimuli-responsive materials. Nowadays, the emphasis in polymeric materials incorporating spiropyran units, focuses on the effectiveness of their reversible response to external photonic stimuli. Photo-control of a range of key characteristics for flow systems, such as wettability, permeability, photo-modulation of flow by photo-actuation of valves, photonic control of uptake and release of guests using films and coatings, and colorimetric sensing of various species, are highlighted and discussed.

Introduction

The photochromic properties of spirobenzopyrans were first discovered by Fischer and Hirshberg^[1] in 1952 where they observed that the irradiation of several solutions of spirobenzopyrans with UV-light (not exceeding 450 nm) produced colour modifications that could be reversed by exposing the same solutions to yellow light (containing no radiation below 500 nm). The photochromism of spiropyran is due to

the photo-cleavage of the C-O spiro bond upon irradiation with UV light^[2, 3]. This cleavage allows a conformational rearrangement between a closed, colorless spiropyran form and an opened, colourful merocyanine (MC) form^[3, 4] with an important absorption band in the visible spectral region (**Scheme 1**). In contrast, the exposure of the MC to visible light produces the reversion to its closed spiropyran form (SP); therefore, it is possible to modulate its conformation using light irradiation. These two forms are characterised by an important change of charge and dipole moment. The opened MC form is characterised by a conjugation between the two extremities of the molecule and is stabilised in the presence of polar solvents^[3, 4]. Another interesting property of the SP is its sensitivity towards pH^[5, 6]. By adding acid, the opened MC gets protonated forming the protonated merocyanine (MCH⁺) form (Scheme 1). A metal ions-binding centre can also be generated by a spatial rearrangement of the opened MC form thus spiropyrans present a high interest for photo-reversible metal ion-complexation (Scheme 1)^[7-10]. Since the spiropyran derivatives are sensitive towards many external agents, they became in the recent years compounds of choice for the development of a new generation of stimuli-responsive materials and sensors.

<Scheme1>

Since their discovery, photochromic spiropyrans have been incorporated into various materials *i.e.* surface bound monolayers^[7, 11-13], Langmuir monolayers^[14], Langmuir Blodgett films^[14], polymeric brushes^[9, 15-17], photocontrollable surfactants^[18], liquid crystalline materials^[19], polymeric matrices^[8, 15, 16, 20-36], organic/inorganic hybrid systems^[37], colloidal particles^[17, 38], ionic liquids^[39-43] and initiators for radical polymerisations^[44].

Materials with photochromic spiropyrans have the advantage of reversibly photo-induce changes in their properties such as conductivity^[24, 28, 45], wetting

behaviour^[9, 11, 22], optical properties^[9, 23, 27, 31, 32, 35, 44, 46], metal ion complexation^[7-10], cell adhesion^[25], surface morphology^[9], association/solubility^[29, 30], mechanical effects^[21, 36], colloidal system stability^[17, 38] and membrane permeability^[15, 16]. Therefore the possibility to photo-induce such a variation in their physical and chemical properties, has made spiropyran-based materials widely utilised in biological applications^[25], nonlinear optics^[47], reversible optical memory^[24, 48], optoelectronics^[49] and chemical sensing^[7, 10, 13, 46, 50]. The use of photo-stimulus is appealing because it can be applied precisely and in a non-invasive manner to different sections of a material or device, that otherwise, maybe unreachable. Stimuli-responsive polymers present all the advantages of polymeric materials, such as versatility, high response to weak stimuli, low cost, and compatibility with biological media. When photochromic spiropyran molecules are included in polymer matrices, new desired properties could be obtained. Stimuli-responsive polymers can introduce “on-demand” changes in volume^[51-54], optical properties^[23, 27, 31, 32, 34, 35, 44], permeability^[15, 16] and surface chemistry^[7, 55], which in turn activate different functions such as the capability of molecular recognition^[7, 56] (including capture, release and detection of analytes), autonomous flow rate^[52, 57], wettability switching^[22] among others.

Although spiropyran systems have shown to have multiple advantages for a wide variety of applications, they still suffer from issues like photofatigue, insufficient selectivity and lack of sensitivity, which in turn hinders their applicability at a larger level, for real-life applications. Several reports show that by immobilising the spiropyran moiety in a polymer matrix, photofatigue (often encounter due to the formation of aggregates between individual merocyanine moieties) can be dramatically improved. By entrapping (covalently or non-covalently) the spiropyran unit, its degree of motion is reduced and therefore the possibility of interaction between MC molecules (formed upon irradiation with UV light) is reduced, having beneficial effects on decreasing the photo-fatigue^[58]. Recent studies have shown that spiropyran fatigue resistance could be also improved by using light emitting diodes (LEDs) as light sources, most probably because they emit light in a narrow range of wavelengths that can be tuned to match the particular absorbance bands of the SP/MC forms of spiropyran^[58]. For the use of spiropyran systems in sensing platforms, researchers are well aware that the phenolate group in the MC moiety is mild binding center for metal ions, and it does not express exceptional sensitivity and selectivity.

However, several research groups have developed ligands based on the engineering of particular binding groups, typically in the 1' or 8 positions^[59, 60] of the spiropyran moiety (Scheme 1) finding new opportunities in sensing that in the past seemed only idealistic.

This paper focuses on the incorporation of spiropyran derivatives into polymer matrices. Specific examples are discussed in terms of the SP-incorporation techniques, influence of the SP's photochromic behaviour on the polymeric material and the applicability of these new-formed SP-containing polymers. Although there is a great amount of literature that covers the area of stimuli-responsive polymers based on SP, here, we illustrate the great versatility and potential of SP-based polymeric systems. The purpose of this paper is to present to the reader the vast possibilities of utilising spiropyran derivatives in polymeric materials emphasising the chemical design of the polymeric system and their applicability in many different areas of technology.

Spiropyran-based Polymers

Most protocols for the incorporation of spiropyran units into polymer matrices generally involve polymerisation of derivatised spiropyran monomers or copolymerisation of these species with compatible monomeric units, where the spiropyran moiety can be introduced as side chain or as a part of the main polymer chain^[9, 10, 15, 16, 20, 33, 36, 50, 61-63]. Other methods include noncovalent doping/entrapment of spiropyran derivatives within various polymer matrices^[24, 32, 34, 35] or functionalisation of pre-formed polymers with spiropyran pendant groups^[45]. A number of examples of spiropyran based polymer most often present in recent literature are described in **Table 1** and comprise a series of homo- and co- polymers

obtained through various polymerisation techniques: radical polymerisation, atom-transfer radical polymerisation (ATRP), ring opening metathesis polymerisation (ROMP) and photo-polymerisation, among others. Other types of polymers in which the spiropyran is included as a pendant group post polymerisation or simply used as a dopant are also presented. Table 1 gives an overview of polymers containing spiropyran where the emphasis is on their structure. Spiropyran polymeric systems can be used for a variety of applications, showing that by combining the key advantages of the spiropyran moiety with the smart engineering of spiropyran based polymers, new materials with designed macroscopic properties can be obtained. Various types of spiropyran polymers have been designed in order to acquire photo-control over specific characteristics of the material like permeability towards different analytes, wettability, sensing behaviour, actuation and electrical properties or to visualise mechanical stress. The following sections will discuss specific spiropyran polymeric systems based on their photo-modulated properties.

<Table 1>

Photo modulated wettability

The wettability of surfaces depends on both, the surface chemistry and the surface morphology, in particular, on the micro-structures of the surface. Having the possibility to photo-control surface wettability has great implications in various fields as such micro-fluidics^[79], self-cleaning surfaces^[80, 81] and drug-delivery systems^[80]. In this context, a lot of effort has been put on functionalising surfaces with spiropyran polymeric materials. The photo-control wettability of SP-modified surfaces is based on the change in the dipole moment of the photo-generated merocyanine in

comparison with the closed spiropyran form (Scheme 1). If confined to an interface, this change in dipole moment affects the surface free energy, which gives rise to a switch in wettability^[9, 22, 61, 63, 77]. (Table 1 – No 1, 2, 7, 15).

In 2008 Samanta *et al.*^[9] synthesised a series of spiropyran functionalised norbornyl derivatives that were used to graft homopolymeric brushes using ROMP (Table 1 – No. 7) from silicon wafers and glass slides. The surface wettability was modulated using light as the external stimulus. The spiropyran-merocyanine photoinduced isomerisation gave a reversible contact angle change of 5-15°. The degree of wettability was amplified by irradiation in the presence of cobalt (II) ions obtaining a reversible contact angle variation of 35°. At that time it was the largest change in photoinduced surface wettability observed for a flat substrate. A few months later, the same group reported another technique to graft photochromic brushes from glass surfaces^[61] (Table 1 – No. 2) showing that in this conditions reversible contact angle variations as large as 70° when the films were irradiated in the presence of Fe²⁺ ions. Although impressive, these contact angle measurements were obtained under very specific conditions, involving a series of tedious processes such as:

- irradiation of the surface with UV light in the presence of 10 mM solution of metal salt in ethanol for 2 min;
- taking the contact angle measurement;
- irradiation (10 min) with visible light while immersed in toluene;
- drying and taking the second contact angle measurement.

Joseph *et al.*^[67] reported a photo-responsive surface consisting on thin layers of crosslinked poly(N-isopropyl acrylamide) functionalised with photochromic spirobenzopyran (Table 1 – No.3) grafted from cyclic olefin copolymer (COC)

substrate. The authors show that the wettability of the surface can be substantially decrease by white light irradiation and subsequently restore by storing the surface in an acidic solution (5mM HCl) for 10 minutes. The contact angle change of the flat COC surface functionalised with the SP-poly(N-isopropyl acrylamide) cross-linked was 24° and can be augmented by the introduction of surface micro-structures (79°) and even further enhanced by the incorporation of nanorods. The later showing a static contact angle change from 5° to 123° after irradiation with white light. This change in wettability upon irradiation with white light can be attributed to the synergistic effect between photoisomerization of the spirobenzopyran chromophore and the dehydration of the poly(N-isopropyl acrylamide) main chain can be explained as follow: light irradiation of the SP-poly(N-isopropyl acrylamide) cross-linked first induces photo- isomerization of spirobenzopyran chromophore to the hydrophobic SP closed-ring isomer causing the dehydration of the pNIPAAm polymer main chain. In the dark, in the presence of the acidic aqueous solution, the SP get protonated to MCH⁺ (Scheme 1), positively charged, and more hydrophilic. This phenomenon induces the re-hydration of the SP-poly(N-isopropyl acrylamide) copolymer. Even though the wettability of this type of surface can be repeatedly cycled with excellent reversibility for at least 5 cycles, still requires acidic treatment in between cycles in order to restore the surface hydrophilicity.

More recently, Wang *et al.*^[63] grafted SP polymeric brushes on silicon substrates by atom transfer radical polymerisation (Table 1 – No.1). They reported a remarkable contact angle change of approximately 96°, when the surface was exposed to cycles of UV (5 min) and visible light (20 min), with no intermediate surface treatment between measurements. The key point of this elevated wettability change

comes from the combination of the SP properties with a microstructured, laser-etched, silicon substrate (**Figure 1**).

<Figure 1>

At present this is the highest and fastest contact angle variation reported for surfaces containing SPs and shows that the combination of a high amount of SP units (*e.g.* through the use of polymeric brushes) with surface morphology optimisation is essential to obtain effective photo-induced reversible hydrophobic-hydrophilic surfaces.

Photo modulated permeability

The use of membranes for drug-delivery via photo-modulated permeability is of great interest, and has been extensively investigated for a considerable time. For instance, Chung *et al.* ^[16] reported a polytetrafluoroethylene (PTFE) membrane grafted by conventional free radical polymerisation with a methacrylate-functionalised SP and acrylamide (Table 1- No. 3). Irradiation with UV light resulted in an increase in permeability of 125 % for a 10-volume % solution of water in methanol, suggesting that the pore sizes of the membrane are larger upon conversion to the MC form. The permeability of the membrane was reversed six times upon alternating exposure to UV and visible light with repeatable performances. In a similar manner, a photoresponsive membrane for organic solvents was produced by Park *et al.*^[15], in which methacrylate-functionalised SP and methyl methacrylate (MMA) copolymer (SP-MA-*co*-MMA, Table 1 – No. 2) was grafted from a porous

glass filter. Upon UV irradiation, the membrane was permeable to toluene, due to the collapse of the polymer chains (**Figure 2** - up). Since both the SP and MC non-grafted polymers are soluble in dimethylformamide (DMF), the polymer-grafted filter showed no change in permeability for DMF upon irradiation (**Figure 2** - bottom).

<Figure 2>

Photo actuation

Sugiura *et al.*^[82] synthesised a poly(*N*-isopropyl acrylamide) co-acrylated spirobenzopyran (pSPNIPAAm) (Table 1 – No. 3) cross-linked with *N,N*-methylene-bis(acrylamide) capable of photo-actuation in acidic media. Micro-valves were fabricated based on this material through in situ polymerisation at desired positions in micro-channels and later opened by local light irradiation. The opening of the valve is due to the photo-induced shrinkage of the pSPNIPAAm gels and can be explained as follow: when the copolymer was immersed in an acidic (0.5 mM HCl) solution, the spiropyran present in the copolymer changed to the open protonated merocyanine form (Scheme 1 - C). Then, when the polymer was irradiated with light at 422 nm, which matches the absorbance of the protonated merocyanine form, isomerisation of the chromophore to the closed-ring form takes place (Scheme 1 - A); as a result, the hydrophobic SP isomer induces dehydration of the main polymer chain and shrinkage of the gel occurs. This process was found to be rather fast, with each valve opening within 18 to 30 s of light irradiation.

A similar approach was presented by Benito-Lopez *et al.*^[65, 66], with the difference that in this case, an ionic liquid (IL) was incorporated within the

pSPNIPAAm polymer matrix (Table 1 – No. 3) to produce micro-fluidic valves. Using various IL components within the gels allowed the valve actuation kinetics to be controlled through IL mediation of the rate of protonation/deprotonation, and related movement of counter ions and solvent (water). Different ionogels (IL + polymer matrix) were photo-polymerised *in situ* in the channels of a poly(methyl methacrylate) (PMMA) micro-fluidic platform. After immersion for 2 h in 0.1 mM HCl aqueous solution, to convert the ionogel to the protonated swollen state, the rate of photoinduced shrinking due to dehydration of the ionogel was measured. Results showed that trihexyl-tetradecylphosphonium dicyanamide based ionogel produced the fastest valve-opening kinetics, opening after 4s light irradiation (**Figure 3**).

<Figure 3>

Recently, an improved reswelling time for spirobenzopyran-functionalised poly(*N*-isopropylacrylamide) hydrogels was reported by Satoh *et al.* [70] who used polymer type No. 6 (Table 1 - No. 6), with a SP unit which has a methoxy-group in position 8 (Scheme 1). The electron donating methoxy group in position 8 increases the electron density of the oxygen (position 1) which reduces the activation free energy (ΔG^\ddagger), accelerating the ring-opening rate constant $k_{\text{Sp} \rightarrow \text{McH}^+}$ up to 19.8 compared to the unsubstituted spiropyran. The increased ring-opening rate of the methoxy spirobenzopyran caused the gel to spontaneously reswell in an acidic environment (5 mM HCl) from the light-induced shrunken state in approximately 5 minutes.

Although these SP-containing polymeric valves have interesting potential for micro-fluidic devices, mainly due to the fact that they offer the possibility of flow

control by photo-opening of the valves, to date they present drawbacks in that the closing mechanism of the valves is still very long compared with opening, and the valves can only be re-swollen in an acidic environment.

Photo modulated electrical properties

Photo-control of electrical properties has been achieved by incorporating SP in conducting polymers through covalent bonding or doping, or by using SP containing polymers for polyelectrolytes multilayers.

Guo *et al.* [24] reported reversible photoswitchable proton-transfer processes between a molecular switch based on SP and the emeraldine salt form of polyaniline (SP-doped polyaniline Table 1 – No. 13) in the solid state and in solution. This process occurred as follows:

1) the MC form, generated by UV irradiation of SP (Scheme 1), abstracted the protons from the conductive emeraldine salt form of polyaniline, forming protonated merocyanine (MCH^+) and led to a reduction in the degree of protonation of polyaniline;

2) upon visible-light irradiation, the MCH^+ form released protons, which were captured by the polyaniline, to restore the degree of protonation. As the degree of protonation dictates the conductivity of the polymer, the electrical conductivity of the SP-doped polyaniline thin-film was reversibly controlled by light irradiation (UV and visible light). Although the drop in conductivity of the polyaniline film could be realised quite rapidly (10 min UV light irradiation), exposure to white light irradiation for 8 hours was required to restore about 95% of the initial conductivity. However, the authors suggest that this can be seen as an advantage if the material is used for

information recording (information can be written optically and read out electrically through conductivity measurements) as the slow conversion of MCH⁺ to SP inside the polymer allows the stored information to be retained for at least 2 h in the dark.

Another example of a polymeric system comprising both polyaniline and spiropyran, but this time linked via a covalent bond (Table 1 – No. 14), was presented by Bardavid *et al.*^[45]. When the spiropyran pendant group was switched to the merocyanine form, the change in the dipole moment of the molecule led to a substantial (*ca.* 2 orders of magnitude) increase in conductance of the photochromic polyaniline nanowires. The transformation was found to be fully reversible with no significant signal loss.

Reversible changes in the dipole moment of SPs upon light irradiation (UV and visible light) were also exploited by Li *et al.*^[78] who recently reported an organic field-effect transistor (OFET) that contains a spiropyran doped poly-(3-hexylthiophene) polymer (Table 1 – No 16) as the active layer. In this OFET, the photo-induced, SP to MC and MC to SP conformational changes caused two distinct interaction strengths at the organic/organic interface and therefore the channel conductance could be reversibly modulated in a noninvasive manner.

A relatively new approach is the utilisation of spiropyran functionalised polymers for building polyelectrolytes multilayers. Pennakalathil *et al.*^[33] recently showed that a stratum composed of poly(acrylate, merocyanine) (PMC) (Table 1 – No. 1) and poly-(diallyldimethylammonium chloride) (PDADMAC) bilayers can be easily disassembled in water upon irradiation with white light by converting the MC to SP (**Figure 4**). This phenomenon was ascribed mainly to the vanished electrostatic attractive interaction between the layer pairs, but also to the increased hydrophobicity of the PSP due to the photoisomerisation of zwitterionic ionic PMC to neutral PSP.

<Figure 4>

Sensing capabilities

In the area of sensing with spiropyran polymeric systems, a significant amount of research has focused on metal ion sensing, due to the ability of MC to employ the negatively charged phenolate group of the zwitterionic form in the binding of metal ions (Scheme 1).

Controlled free radical polymerisation reactions, such as ATRP, have been used to graft copolymers of SP monomers with MMA (Table 1 – No. 2) onto surfaces to obtain photoswitchable planar substrates and colloids^[17, 61]. An interesting example is the work of Fries *et al.* where polymer brushes were grafted^[61] (or spin-coated^[10, 50]) onto glass surfaces to create reversible photoswitchable optical sensors by utilising the complexation of the open MC zwitterion with metal ions (Scheme 1). The irradiated polymers were exposed to 25 mM metal ion solutions and were air-dried^[50, 61]. Upon complexation with different metal ions, the MC absorbance decreased, with an accompanying significant blue shift in the lambda maxima, which is metal ion dependent (**Figure 5**). When the complex was irradiated with visible light in a non-polar solvent, the metal ion was dissociated, and the ring closed to the inactive SP isomer. The system was reported to be reversible for at least three cycles, with good reproducibility of the contact angles. Using a similar type of polymer (Table 1 – No. 2) the same group also showed the possibility of detecting multiple divalent metal ions in binary solutions^[50]. Several binary metal ion combinations of Sn^{2+} , Cu^{2+} , Fe^{2+} , Zn^{2+} , Co^{2+} , and Ni^{2+} were prepared at different concentration ratios and it was shown that depending on the binding affinity of the MC towards each

individual metal ion, MC is capable of identifying one or both metal ions simultaneously (**Table 2**).

<Figure 5>

<Table 2>

A similar polymer with potential for metal ion sensing was produced by Connal *et al.*^[68] (Table 1 – No. 4) using highly ordered honeycomb materials (**Figure 6**). They demonstrated that palladium ions could be integrated into the SP polymer chain, in solution, using the MC binding abilities and then incorporated into honeycomb films. Furthermore, by reducing the palladium in the film, palladium-based micro-ring structures were obtained, showing the potential of using SP-honeycomb films as templates for building hybrid organic/inorganic porous films.

<Figure 6>

Although the poor selectivity of the SP-polymers is still considered as a drawback on these systems, good selectivity was reported in the case of Cu^{2+} when a sulfobetaine - methacrylate-functionalised SP copolymers, linear or covalently cross-linked (Table 1 – No. 5) were used^[69]. However, even in this case, NaCl concentration in the system was found to play an important role, since high NaCl concentrations results in inefficient metal ion sensitivity. This effect could be due to the fact that the electrostatically cross-linked networks of the zwitterionic sulfobetaine units may be loosened by NaCl addition, resulting in easy entry of metal ions into the network.

Several photoswitchable fluorescent cyanide anion sensors based on SP-polymers, a copolymer consisting of *N*-isopropylacrylamide and coumarin-conjugated spiropyran units^[64] (Table 1 – No. 3) and a spiropyran–polythiophene conjugate^[72] (Table 1 – No. 8), were recently reported. It was shown that the cyanide ion could be selectively detected (in the presence of anions such as F⁻, Cl⁻, Br⁻, I⁻, AcO⁻, H₂PO₄⁻, HSO₄⁻, NO₃⁻ and ClO₄⁻) by monitoring the formation of an adduct, derived from the nucleophilic addition of cyanide anion to the ring-opened MC form of the spiropyran (**Figure 7**).

<Figure 7 >

Another possibility of utilizing SP-polymers as sensors relies on the solvatochromic properties of the MC form. The colour of the MC form depends on the difference in polarity between the photo-excited MC form and the conjugated zwitterionic ground state. By utilising this property, we recently reported photochromic capillary coatings^[71, 83] (Table 1 – No. 7) capable of detecting solvent of different polarities that are passing through a chemically modified capillary in continuous flow mode. In polar solvents, the ground state of the MC form is stabilised relative to the excited state, leading to a blue shift in the visible absorption band. In non-polar solvents, the energy difference between the ground and the excited state is much lower, because of the high energy level of the ground state. As a result, as the polarity of the solvent increases, the absorbance λ_{max} shifts to shorter wavelengths, (*hypsochromic* or blue shift), manifesting as a change in colour of the capillary coating (**Figure 8**).

<Figure 8>

An interesting approach of utilising the solvatochromic properties of the MC unit was reported by Shiraishi *et al.*^[62], who showed the possibility of utilising a polymer consisting of poly-*N*-isopropylacrylamide (NIPAM) and SP units (poly-(NIPAM x -*co*-SP y) (x/y) 15/1), Table 1 - No. 3) as a colorimetric thermometer in the range of 10-34 °C. The change in temperature induces a polarity change in poly-NIPAM from a more polar character at low temperature (coil conformation) to a less polar domain inside the polymer associated with polymer aggregation (globule), when temperature is increased. This change in polarity can be accurately sensed by the MC, present in the polymer matrix and interrogated by UV irradiation (**Figure 9**).

<Figure 9>

Mechanochromic mechanophores

Mechanochromic mechanophores are mechanophores that change colour with the application of an external force. In the recent years, SPs have been incorporated into a range of polymeric materials and it was shown that they can provide visible detection and mapping of mechanical stresses through their mechanically induced transformation from SP to MC (**Figure 10**). The spiro C–O bond is the critical point for mechanically induced activation, and to ensure stress over the C-O junction, polymerisable groups or polymeric chains have to be placed on the SP unit on opposing sides of the spiro-junction. Mathematical modeling shows that positions 5' or 6' of the indole side and positions 7 or 8 of the benzopyran side (Scheme 1),

preferentially stresses the spiro C–O bond over the spiro C–C bond, suggesting that these positions are the ideal linkage points between the SP and the polymer matrix for the production of mechanochromic materials. In this context, bifunctionalised SP units with polymerisable groups in these positions have been incorporated into poly-(methyl acrylate) (PMA) and poly-methylmethacrylate (PMMA) chains^[73-75] (linear or crosslinked), polyurethanes^[36] and polycaprolactone^[76]. It was shown that, in all the above-mentioned examples, the C-O bond can be broken via a mechanical stress, resulting in a change in colour of the polymer before polymer failure. These results showed that 5', 6'- and 7,8 bifunctionalised SP units have great potential to produce smart polymers with self-sensing capabilities, damage detection and visual reporting of catastrophic failure prevention.

<Figure 10>

Conclusion

The examples presented in this review undoubtedly demonstrate the versatility of spiropyrans with respect to routes for incorporation into polymeric matrices, and great potential of the resulting switchable materials for many applications. For example, polymers can be doped or functionalised with SP post-polymerisation or directly linked during the polymerisation process. Moreover, derivatisation of SP with monomeric units at the 6, the 8- or at the 1'- position (see Scheme 1) can be achieved through the use of a spacer/linker group. Polymerisation of these SP-monomeric units or their copolymerisation with compatible monomeric units have produced a wide array of designer-polymers with tuneable properties. Smart engineering of SP-

polymeric materials allows photo-modulation of the physical and chemical properties of these materials, ranging from photochromic behaviour, to wettability, permeability, and electrical properties, to “on-demand” sensing behaviour (*i.e.*, that can be turned on or off using light). It seems to us that no other photochromic unit is capable of producing “stimuli-responsive” polymeric systems for such a wide variety of applications and we believe that these materials could form the basis of the new types of autonomous microfluidic based analytical devices that are much more biomimetic in nature.

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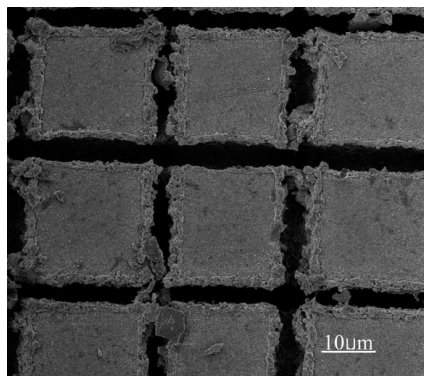


Figure 1. SEM image of the photo-responsive poly (SP) thin films on roughly etched silicon substrates. Reproduced with permission from ref^[63].

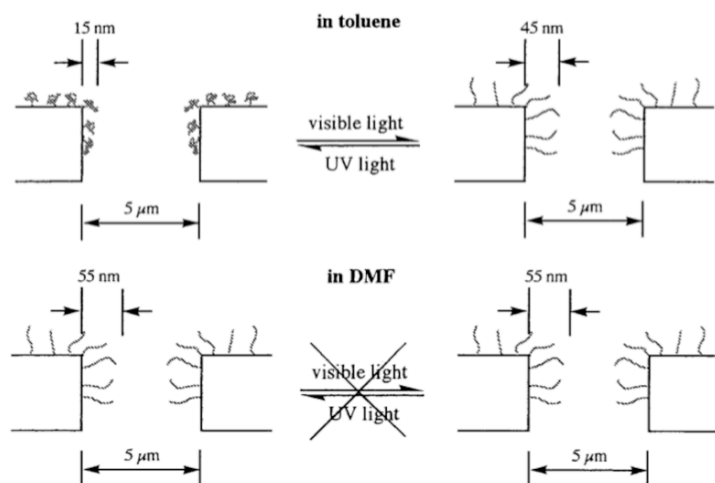


Figure 2. Schematic representation of the thickness of a (SP-MA-co-MMA) grafted layer. The shrunk grafted chains open pores to increase permeation, and extended chains cover pores to decrease permeation. Reproduced with permission from ref. ^[15] Copyright (1998) American Chemical Society.

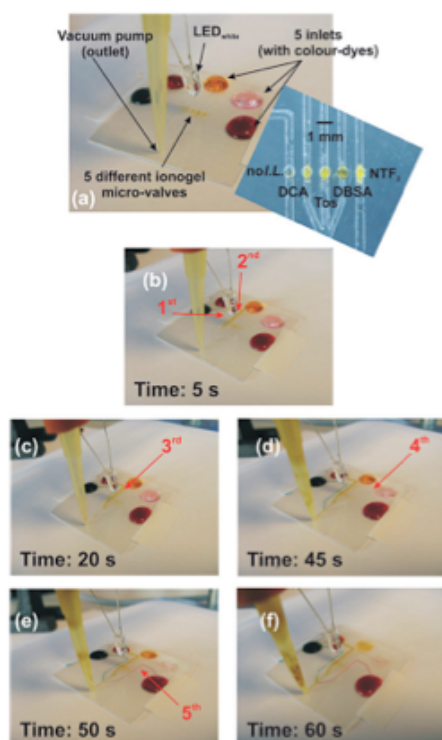


Figure 3. Performance of ionogel micro-fluidic valves: (a) micro-valves closed; the applied vacuum is unable to pull the dyes through the micro-channels. White light is applied for the time specified in each picture (b). ‘No I.L.’ valve is first to actuate followed by ionogels incorporating [dca]⁻ (c), [tos]⁻ (d), [dbsa]⁻ (e), [NTf₂]⁻ (f), all valves are open. Numbers and arrows indicate when the channel is filled with the dye because of micro-valve actuation^[66]. Reproduced by permission of The Royal Society of Chemistry.

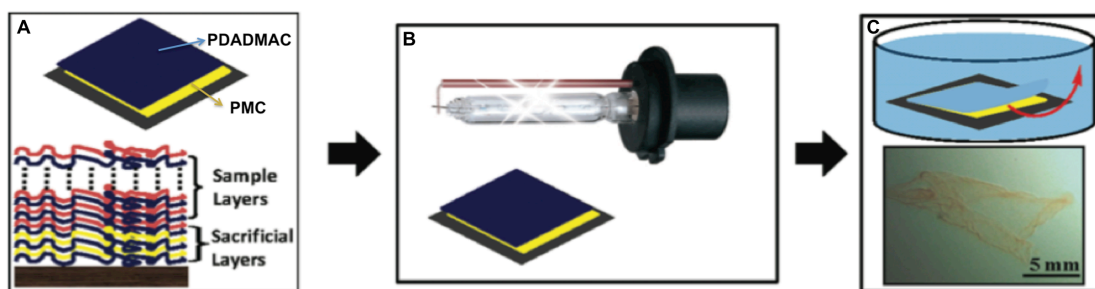


Figure 4. A- Schematic view of the sacrificial layer and the sample layer; B - Irradiation with white light; C - disassembly of the sacrificial layer in water after irradiation with white light. Reproduced with permission from ref.^[33] Copyright (2011) American Chemical Society.

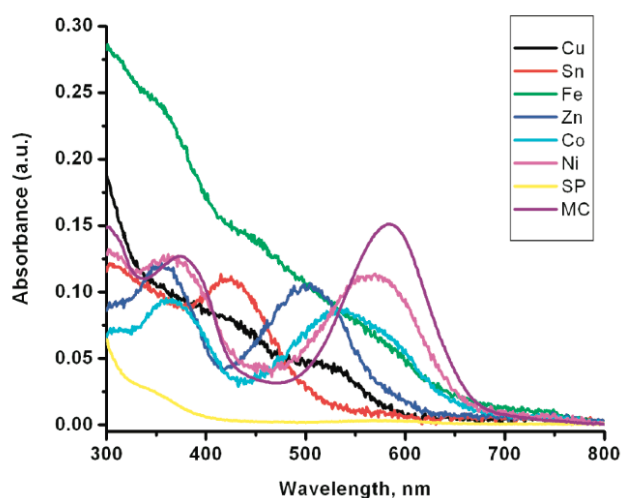


Figure 5. Absorbance spectra of SP-polymer layers (Table 1 – No. 2) in the presence of different metal ions. Reproduced with permission from ref.^[50] Copyright (2011) American Chemical Society.

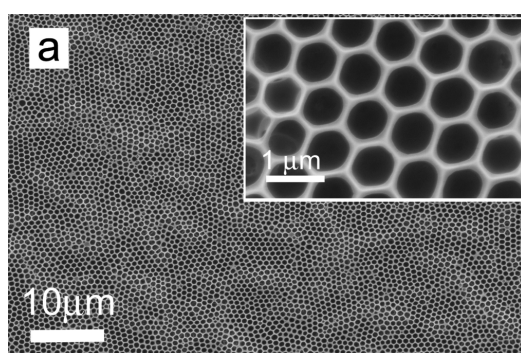


Figure 6. Scanning electron micrographs of photochromic honeycomb structures: (a) a low-resolution image of a honeycomb structure, with the inset showing a high-magnification image of the honeycomb structure. Reproduced with permission from ref.^[68] Copyright (2010) American Chemical Society.

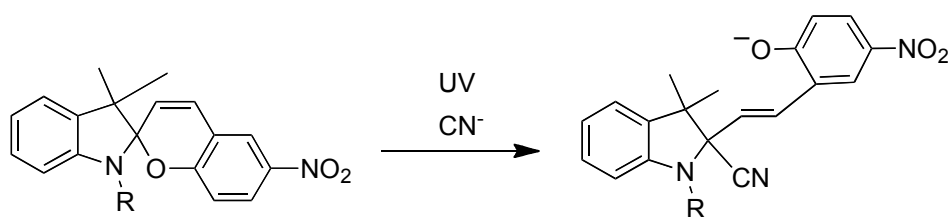


Figure 7. Scheme showing the reaction between the spiropyran and cyanide.

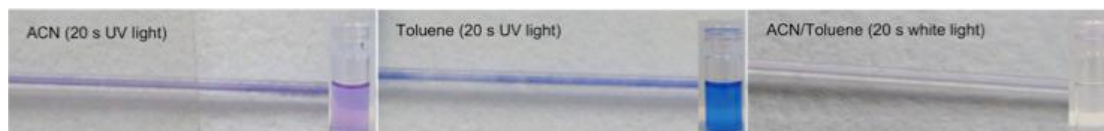


Figure 8. Photographs of the spiropyran monomer solutions and the spiropyran polymeric brushes (Table 1 – No. 4) functionalised capillary in acetonitrile (ACN) and toluene, respectively, after irradiation with UV and white light. Reproduced with permission from ref. ^[71] Copyright (2011) Elsevier.

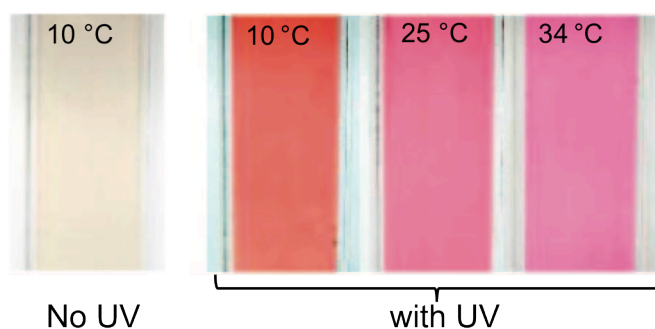


Figure 9. Photographs of the polymer solutions in different conditions. Reproduced with permission from ref. ^[62] Copyright (2009) American Chemical Society.

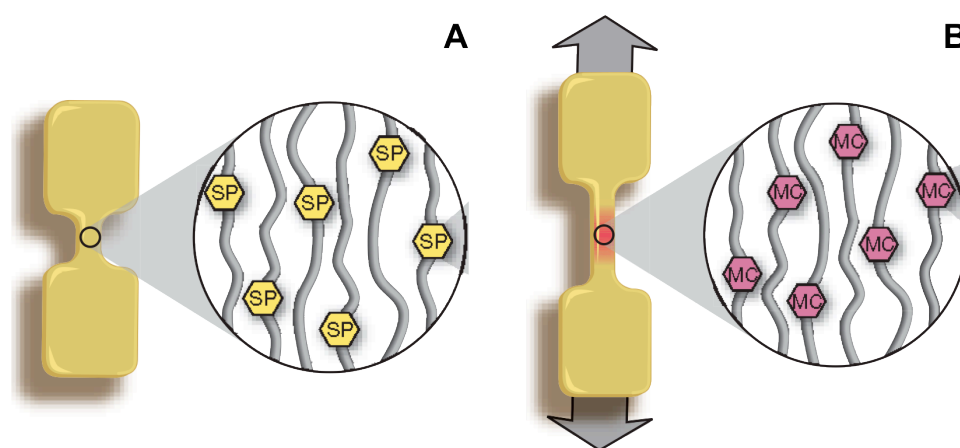
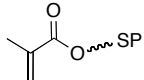
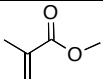
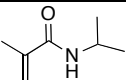
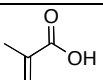
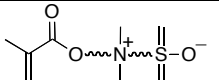
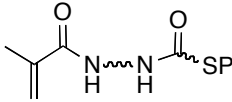
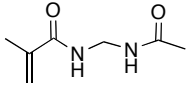
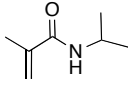
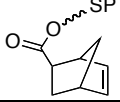
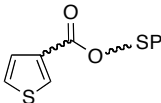

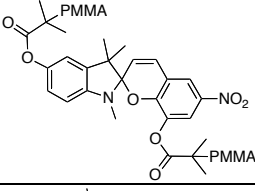
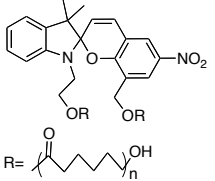
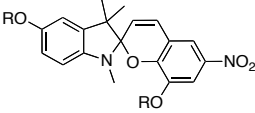


Figure 10. Schematic diagram of ‘dog bone’ specimens prepared from SP mechanochromic polymers. A: shows the initial state of the polymer; B: Upon application of tensile force, the conversion between the colourless spiropyran and coloured merocyanine forms of the mechanophore occurs. Reproduced with permission from ref. ^[75] Copyright (2009), Rights Managed by Nature Publishing Group.

Table 1. Polymers containing spiroopyran.

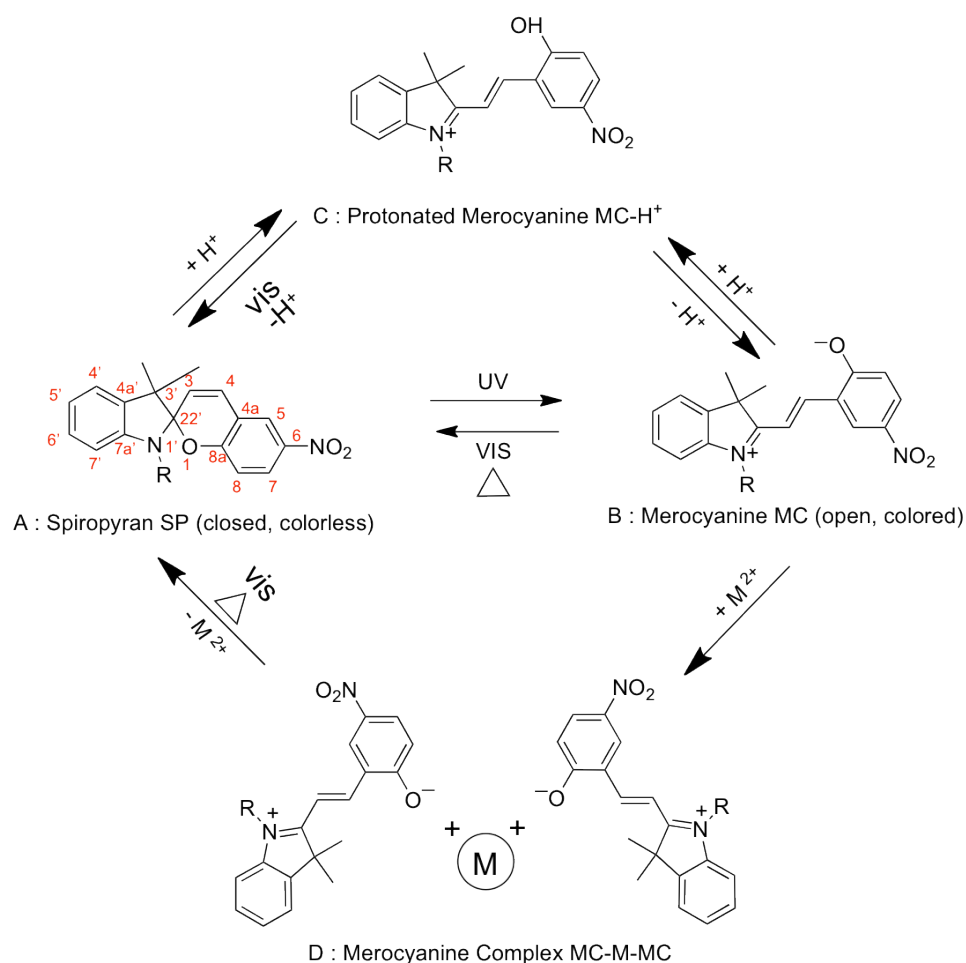
No.	Homo- & Co- polymers of SP		Application
	SP monomer	Co-monomer	
1		-	Photo-controlled Wettability ^[63] , Photo-modulation of Electrostatic Interactions ^[33]
2			Metal Ions Sensing ^[61] , Photo-controlled Wettability ^[61] , Photo-controlled Permeability ^[15]
3			Cyanide Anion Sensing ^[64] , Photo-actuator ^[65, 66] , Photo-controlled Permeability ^[16] , Photo-controlled Wettability ^[67]
4			Metal Ions Sensing ^[68]
5			Selective Cu ²⁺ Sensing ^[69]
6		 	Photo-actuator ^[70]
7		-	Photo-controlled Wettability ^[9] , Solvent Sensing ^[71]
8			Cyanide Anion Sensing ^[72]
9			Mechanophore ^[73-75]
10			Mechanophore ^[76]
11			Mechanophore ^[36]
	SP-functionalised polymers		

12		Photo-modulated conductivity ^[45]
	SP-doped polymers	
13	SP +	Photo-modulated conductivity ^[24]
14	SP +	Photo-actuation ²² Photo-controlled Wettability ^[22, 77]
15	SP +	Photo-modulated conductance ^[78]

* Unless specified SP monomeric units consist of a SP unit having the polymerisable group attached in position 1', 6 or 8 (Scheme 1); ~~~~~ - denotes an alkyl chain having from one to eight carbon atoms.

Table 2. Table showing the selectivity of the binding of spiropyran polymer in different binary metal ion solutions. Reproduced with permission from ref. ^[50] Copyright (2011) American Chemical Society.

Metal Ion Mixtures	Ratios		
	10-90	50-50	90-10
Sn-Co	Sn	Sn	Sn
Sn-Ni	Sn	Sn	Sn
Sn-Zn	Sn	Sn	Sn
Sn-Fe	Sn	Sn	Sn
Sn-Cu	both	both	both
Ni-Zn	Zn	Zn	Zn
Ni-Fe	Fe	Fe	Fe
Cu-Co	both	both	both
Cu-Ni	both	both	both
Cu-Fe	both	both	both
Cu-Zn	both	both	both
Co-Ni	both	both	both
Zn-Fe	both	both	both
Zn-Co	both	both	both
Co-Fe	both	both	both



Scheme 1. Reversible structural transformations of spiropyran derivatives in response to external inputs such as light, protons, and metal ions.



Larisa Florea studied organic chemistry and chemical engineering at University “Politehnica” from Timisoara, Romania (BSc Hons 2009). In 2009 she joined the Adaptive Sensors Group at Dublin City University where she is currently pursuing her PhD degree under the supervision of Prof. Dermot Diamond and Dr. Fernando Benito-Lopez. Her research interests include the development of stimuli- responsive polymers as novel sensing materials in micro-fluidics.



Dermot Diamond received his PhD and DSc from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was VP for Research at Dublin City University (2002–2004). He has published over 200 peer-reviewed papers in international journals, is a named inventor in 13 patents, and is co-author and editor of three books. He is currently director of the National Centre for Sensor Research (www.ncsr.ie) and a Principle Investigator in CLARITY (www.clarity-centre.com/), a major research initiative focused on wireless sensor networks. In 2002 he was awarded the inaugural silver medal for Sensor Research by the RSC, London.



Fernando Benito López studied chemistry at the Universidad Autonoma de Madrid and completed his master studies in the Department of Inorganic Chemistry in 2002. He obtained his PhD at the University of Twente, The Netherlands, under the supervision of Prof. David N. Reinhoudt in 2007. He carried out his postdoctoral research in the group of Prof. Dermot Diamond at Dublin City University, Dublin, Ireland. In 2010, he became Team Leader in polymer microfluidics at CLARITY: Centre for Sensor Web Technology, Dublin City University. Currently he is Senior Scientist in CIC microGUNE: Microtechnologies Cooperative Research Center in the Basque Country, Spain.

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Photo-responsive polymeric structures based on spiropyran

The development of new synthetic routes to produce photo-responsive spiropyran (SP) - polymeric structures has achieved great attention over the past decade due to the potential applications of these materials. Smart engineering of

SP-polymeric materials allows photo-modulation of their physical, chemical and electrical properties, ranging from their phototchromic behaviour, to the wettability and permeability of surfaces to “on-demand” sensing behaviour.

