Color switchable polar polymeric materials

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Abstract

Spiropyran is an important mechanophore which has rarely been incorporated as a crosslinker in polar polymer matrices, limiting its applications in innovative mechanochromic devices. Here, three spiropyrans with two or three-attachment positions were synthesized and covalently bonded in polar poly(hydroxyethyl acrylate) (PHEA), to achieve color switchable materials, triggered by light and when swollen in water. The negative photochromism in the dark and mechanical activation by swelling in water were investigated. Measurements of negative photochromism were conducted in solution and crosslinked PHEA bulk polymers, with both showing color reversibility when stored in the dark or exposure to visible light. The force of swelling in water was sufficient to induce the ring-opening reaction of spiropyran polymers. It was found that tri-substituted spiropyran (SP3) was less influenced by the polar matrix but showed the fastest color activation during swelling. SP3 also showed accelerated ring opening to the colored state during the swelling process. Bleaching rates and color switchability were investigated under swollen and dehydrated conditions. The effect of cross-link density on the swelling activation was explored to better understand the interaction between the mechanophore and the polar environment. The results demonstrated that influences from both the polar environment and the mechanochromic nature of spiropyran had an impact on the absorption intensity, rate of change and the decoloration rate of the materials. This study

provides the opportunity to manipulate the properties of spiropyrans to afford materials with a range of color switching properties under different stimuli.

Introduction

Smart materials responsive to external stimuli, such as light, temperature, pH and force, have attracted a lot of attention due to their potential applications in packaging, ophthalmic lens, textiles, chemical diagnostics, force sensors and pressure sensitive coatings.[1-4] Mechanochromic polymeric materials, which change color under an applied force, have been well studied.[5-9] Spiropyran (SP) is one of the most promising mechanophores, which is colorless and undergoes a 6-π electrocyclic ring-opening reaction to form colored merocyanine (MC) under external force.[10, 11] SP based mechanochromic materials can be obtained by covalent [10-15] and non-covalent bonding to the matrix.[16] The concern for non-covalently bonded systems is that SP has the potential to leach from the matrix, especially in the presence of solvents and this limits their practical application. For SP covalently bonded systems, a diverse range of polymers have been utilized, including poly methyl (meth)acrylates (PMMA),[17] polystyrene (PS),[18] poly(ε-caprolactone) (PCL),[12, 19] and polydimethylsiloxane (PDMS).[13] These non-polar polymers are designed to stabilize the non-polar ring-closed SP before being subjected to external stimuli.

A polar environment will affect the SP $\leftrightarrow$ MC equilibrium due to the difference in polarity between SP and MC,[20] and the energy barrier of the isomerization, with a lower ground state energy of the MC in a polar environment.[21-23] This phenomenon has been defined as negative photochromism.[24] For SP linked hydrophilic polymer systems, the effect from the polar environment results in colored and more polar MC being the dominant form in the absence of visible light. As an example, it has been reported that SP conjugated with PEG as a soft segment in PU changed color without an applied force when kept in the dark.[25] To avoid the effect from

the polar environment for mechanochromism, SP has been protected in a non-polar environment within micelles in hydrogel systems, to ensure the SP remains in the colorless form prior to color triggering by an external force.[26] Manipulating the color switching of SP in hydrophilic matrices is important for applications such as for optical data storage.[20, 27] Efforts have been made to control the influence from polar environments, by adding electron withdrawing or electron donating groups to the SP molecule, or by using polar polymers with different functionalities, varying local electrostatic effects.[28] Additionally, the interaction between the polar components and MC not only affects the equilibrium of SP $\leftrightarrow$ MC, but also causes maximum absorbance wavelength (λ_{max}) shift.[22, 29] The polar effect can be induced from either a solvent or a polymer matrix.[20, 30] The negative photochromism cannot be neglected when hydrophilic polymers are employed in SP systems.[31] Although incorporation of SP into hydrophilic polymers for mechanochromism has barely been studied, the broad range of potential applications of hydrophilic polymers in coatings, food packaging, membranes and biomedical devices necessitates development of a range of polymer options for SP contained mechanochromic materials.

The forces induced by swelling of mechanochromic SP polymers in organic solvent and CO_2 are sufficient to activate SP to its colored MC form. Moore's group reported that crosslinked SP-PMMA can be activated by swelling in organic solvents.[32] It was found that the swelling rate was important to the color change behaviour, given that too slow a swelling rate could not trigger the ring-opening reaction, while too fast a swelling rate would cause sample damage. Microgels of 2-(diethylamino)ethyl-methacrylate (PDEA) with conjugated SP were developed by Zhu's group, which showed a color switching from pale yellow to pink due to the deformation caused by absorbing CO_2.[33] This implies that the efficient activation by swelling is attributed to the three-dimensional deformation, rather than uniaxial strain. Water is a widely used and non-toxic solvent, but cannot swell non-polar polymers to induce color change due to

the high polarity.[32] To date, water has not been used to swell hydrophilic polymers containing SP for mechanochromism. For the potential applications as mentioned earlier, it is important to see how the mechanical activation of SP to MC will behave differently in a hydrophilic polymer due to its interaction with such a polar environment.

As mechanochromic SPs have yet been crosslinked in pure swellable hydrophilic polymers, it is necessary to know the factors affecting the equilibrium of SP to MC, and how the mechanical swelling affects the chromism in a polar environment. In this article, we incorporated a series of spiropyrans into hydrophilic poly(hydroxyethyl acrylate) (PHEA), which act as a reversible sensor, switching color in response to the presence and absence of visible light and water. Herein the effect of a polar matrix on the color forming properties of these materials in the dark as well as the mechanochromic behaviour when swollen in water are investigated, with the presentation of a fully reversible switchable cyclic mechanochromic and negative photochromic materials.

Experimental Methods

Materials

Hydroxyethyl acrylate (HEA, 96%, Sigma) and ethylene glycol dimethacrylate (EGDMA, 98%, Sigma) were passed through basic aluminium oxide to remove the inhibitor monomethyl ether hydroquinone before use. Tetrahydrofuran (THF, Chem-Supply) was pre-dried over sodium, before being distilled from benzophenone and sodium under an inert atmosphere of nitrogen prior to use. 4-Dimethylaminopyridine (DMAP, ≥98%, Sigma), phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPOs, 97%, Sigma), methacrylic anhydride (94%, Sigma) were used as received. 3',3'-dimethyl-6-nitro-1'-(2-hydroxyethyl)spiro[chromene-2,2'-indoline]-5',8-diol was synthesized according to our previous work.[34] 1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5',8-diol, and 1'-(2-hydroxyethyl)-3',3'-dimethyl-6-

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nitrospiro[chromene-2,2'-indolin]-8-ol were synthesized according to literature procedures.[10,][13]

Synthesis of tri-methacrylate spiropyran (SP3): *3',3'-dimethyl-6-nitro-1'-(2-(methacryloyloxy)ethyl)spiro[chromene-2,2'-indoline]-5',8-diyl bis(2-methylacrylate)*
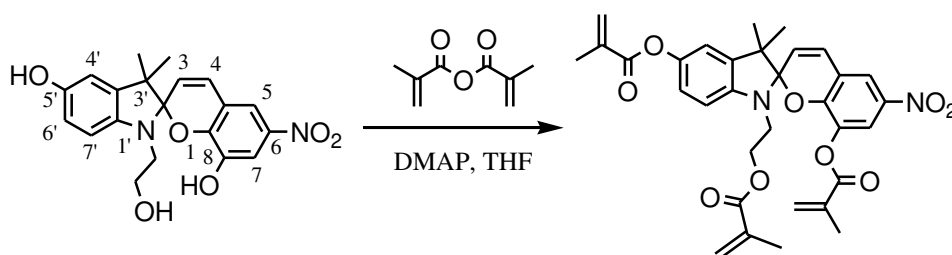

Scheme 1. Synthesis of tri-methacrylate SP3.

3',3'-dimethyl-6-nitro-1'-(2-hydroxyethyl)spiro[chromene-2,2'-indoline]-5',8-diol (0.20g, 0.52 mmol, 1.0 equiv) and DMAP (0.15 g, 1.23 mmol, 2.4 equiv) dissolved in THF (10 mL) was added methacrylic anhydride (0.28 mL, 1.87 mmol, 3.6 equiv). After stirring for 24 hr under Argon at room temperature, removed the solvent. The crude product was dissolved in minimal DCM, which was passed through basic alumina with DCM to obtain product **SP3** (0.20g, 0.34 mmol, 64% yield). ^{1}H NMR (400 HZ, CDCl$_3$): δ 7.96 (d, 1H), 7.92 (d, 1H), 6.98-6.96 (d, 1H), 6.87-6.85 (dd, 1H), 6.80 (d, 1H), 6.60-6.58 (d, 1H), 6.32 (s, 1H), 6.07 (s, 1H), 5.93 (m, 2H), 5.74 (s, 1H), 5.57 (s, 1H), 5.51 (s, 1H), 4.25 (m, 2H), 3.35 (m, 2H), 2.07 (s, 3H), 1.92 (s, 3H), 1.70 (s, 3H), 1.23 (s, 3H), 1.19 (s, 3H).

1',3',3'-trimethyl-6-nitrospiro[chromene-2,2'-indoline]-5',8-diyl bis(2-methylacrylate) (di-methacrylate spiropyran **SP1**), and 3',3'-dimethyl-6-nitro-1'-(2-(methacryloyloxy)ethyl)spiro[chromene-2,2'-indoline]-8-yl (2-methylacrylate) (di-methacrylate spiropyran **SP2**) were synthesized via the same method from the hydroxyl versions. **SP1**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.96 (d, 1H), 7.92 (d, 1H), 6.98 (d, 1H), 6.86 (dd, 1H), 6.79 (d, 1H), 6.45 (d, 1H), 6.32 (s, 1H), 5.91 (d, 1H), 5.89 (s, 1H), 5.74 (s, 1H), 5.51

(s, 1H), 2.64 (s, 3H), 2.07 (s, 3H), 1.69 (m, 3H), 1.24 (s, 3H), 1.21 (s, 3H). **SP2**: ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.95 (d, 1H), 7.90 (d, 1H), 7.12 (m, 1H), 7.00 (d, 1H), 6.96 (d, 1H), 6.83 (m, 1H), 6.63 (m, 1H), 6.07 (s, 1H), 5.93 (d, 1H), 5.87 (s, 1H), 5.56 (s, 1H), 5.38 (s, 1H), 4.24 (m, 2H), 3.36 (m, 2H), 1.92 (s, 3H), 1.61 (s, 3H), 1.24 (s, 3H), 1.17 (s, 3H).

Preparation of SP crosslinked PHEA film samples. For 1 mol % crosslinker density, HEA (0.4g, 1 equiv), SP3 (2.0 mg, 0.001 equiv), EGDMA (6.0 μL, 0.009 equiv), and photo initiator BAPOs (5.8 mg, 0.004 equiv) were mixed thoroughly in a vial. The mixture was injected into a glass mold (width: 1.6 cm, length: 5.0 cm, thickness: around 0.5 mm) with a silicone spacer sandwiched by two glass sheets, and exposed to white light (4W cool white light, 350 lumens) for 2 hr to polymerization. For 2.5% EGDMA crosslinked SP3-PHEA films, 15.1 μL EGDMA was added; for 5% EGDMA crosslinked SP3-PHEA films, 30.2 μL EGDMA was added; for 7.5% EGDMA crosslinked SP3-PHEA films, 45.2 μL EGDMA was added; for 10% EGDMA crosslinked SP3-PHEA films, 60.3 μL EGDMA was added. Regarding SP1-PHEA and SP2-PHEA, 0.1 mol % mechanophores and 0.95 mol % EGDMA were added respectively. To quantify the conversion ratio, crosslinked films were soaked in methanol for 2 days, which was changed regularly with fresh solvent, to remove the unreacted species, followed by drying under vacuum at ambient temperature until constant mass. The unreacted species for the samples were quantified to be less than 3 wt %; UV-Vis analysis of the extracted methanol solution, showed no detectable signals at 500-600 nm, confirming the mechanophores were conjugated in the polymer network.
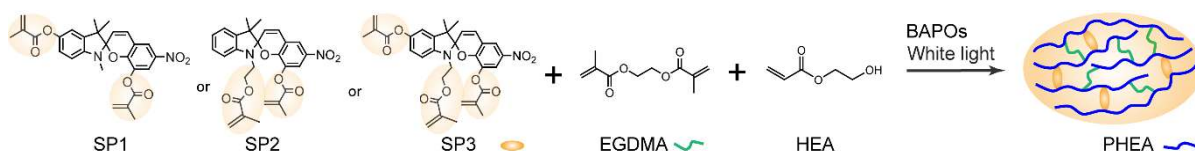
Scheme 2. Synthesis of SP-PHEA bulk materials via free radical polymerization under white light.

Characterization

^{1}H NMR spectroscopy was conducted on a Varian Unity 400 MHz spectrometer operating at 400 MHz, using deuterated chloroform ($CDCl_3$) as solvent and reference peak. UV−Vis spectrum was recorded on a Shimadzu UV−Vis Scanning Spectrophotometer (UV-2101 PC) with a fast scanning rate of 0.5 nm interval over a range of wavelengths 750-380 nm.

Swelling activation. Polymeric rectangular samples were cut to 7.5 mm × 20 mm. The samples were immersed in excess deionized water in vials fully covered with foil to avoid any light. Mass and dimensions were recorded during the swelling process. The ratio of size change ΔV was defined as $\Delta V=(V-V_0)/V_0$, where V and V_0 was calculated by *width × length × thickness*; the ratio of mass change Δm was determined by $\Delta m=(m-m_0)/m_0$.[32] Absorbance measurements were utilized to quantify the ring opening process from SP to MC.

MC reverting to SP under white light irradiation. Two decoloration processes were compared: swollen (hydrated) films or dehydrated films from the swollen state were exposed to white light. For measurement of the hydrated films, the colored samples activated by water swelling were exposed to white light until a constant absorption value was observed. For measurement of the dehydrated films, the colored swollen films were dehydrated under vacuum at room temperature until a constant mass, then irradiated with white light to force MC to return to SP until a stable absorbance was achieved.

Coloration-decoloration cycles. Two methods of coloration-decoloration cycles were conducted corresponding to the two decoloration processes. Colored swollen hydrated films were kept in water and placed under white light to force the MC ring close to SP until the stabilized absorbance was recorded; then the samples were covered with foil to block exposure to light, while recording the absorbance until it plateaued. The white light stimulated process was repeated 10 times. For the dehydrated films, the color saturated swollen films were dried

in the dark under vacuum at ambient temperature until a constant mass, and the absorbance was recorded; the dehydrated films were exposed to white light until a constant absorbance was observed, before being swollen in water again during which the mass and absorbance were recorded. The dehydration-hydration process was repeated 10 times.

Results and discussion

Methacrylated SPs were synthesized according to our previous work.[34] A series of spiropyrans with hydroxyl groups were treated with methacrylic anhydride to afford the methacrylate-SP (Scheme 1), which was polymerized with monomer HEA and co-crosslinker EGDMA via free radical polymerization under white light (Scheme 2). Thermal and UV polymerization techniques which are typical approaches to obtaining SP polymeric materials lead to incomplete ring-closed mechanophores, with the former approach requiring post bleaching with visible light, whereas the latter approach is affected by the formation of MC in situ, resulting in incomplete polymerization. Thus, using white light and BAPOs as an initiator avoided these issues and ensured the ring-closed form being dominant species.[26, 35] The obtained samples were used to study the effect of the polar environments on the coloration in the dark (negative photochromism) and activation by swelling in water (mechanochromism) (Scheme 3).


SP in HEA   SP-PHEA bulk polymer
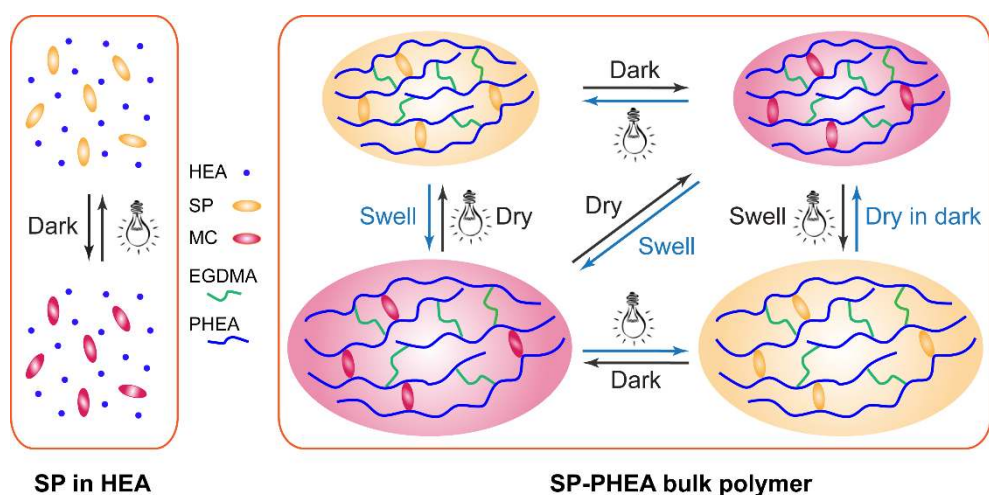
Scheme 3. Solutions of SP dissolved in HEA were used to study the thermodynamic equilibrium of free SP in a polar solvent, and SP-PHEA films were used to study their negative photochromic and mechanochromic properties in the solid state. The color reversibility is due to the isomerization between ring-closed SP and ring-open MC.

Effect of polarity on SP coloration in solution and bulk polymer

The negative photochromism of different SPs in polar solvent were evaluated by dissolving SP in HEA. Samples of SP in HEA at 0.1 μmol % were prepared under ambient conditions and exposed to white light for 1 min to convert any MC to ring-closed SP, prior to being stored in the dark. The UV-Vis absorption peaks at around 550 nm attributed to ring-open MC were negligible in all the samples after white light bleaching (Figure S1), demonstrating the majority of mechanophores were in the ring closed form. The samples were kept in the dark under ambient conditions and measured for absorption regularly until they reached a plateau. The colour change was reversible by exposed to the white light and kept in the dark (Figure S1).

Figure 1 shows the saturated absorbance of the SP1-3 in HEA solution in the dark. The absorption intensity of SP3 was significantly lower than SP1 and SP2 (Figure 1b). This suggests that the interaction of SP1-3 with polar HEA differs (affecting the equilibrium between SP and MC) due to the different polarities of these three SPs. According to Tian *et al*, for the thermal competition between SP and MC in the absence of light, the energy for ring opening is mainly determined by MC conformational change.[22] In this case, the variation in the functionality position and number of SP1-3 may affect the equilibrium between SP and MC, resulting in different energies for stabilizing MC, leading to differences in absorption intensity. SP3 having all the different attachment positions has the least unstable coloured MC isomers. Additionally, a slight red shift of maximum absorption wavelength (λ_{max}) was observed from SP1 to SP3 (Figure 1a). It has been reported that red shift occurs with decreasing solvent

polarity for a specific SP.[27] Since the solvent was constant here, the λ_{max} shift in these three SP solutions was a result of the polarity difference of the chromophores. Both absorption intensity and λ_{max} differences revealed that the three SP had different extents of interaction with polar HEA.
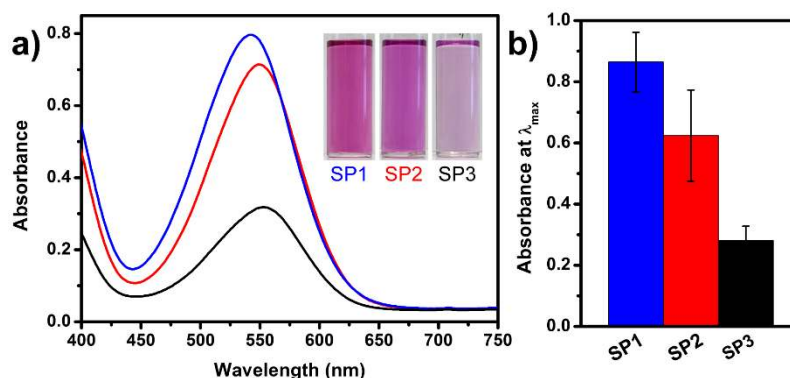

Figure 1. (a) Absorbance spectra of SP1-3 dissolved in HEA after absorption plateaued in darkness and the corresponding images, and (b) the absorption intensity at the maximum wavelength of 542nm, 549nm and 553nm respectively.

Next the negative photochromism of SP crosslinked in PHEA polymer was investigated. The prepared SP-PHEA films were pale yellow (Figure 2b) and characterized by UV-Vis spectroscopy showing no absorption peak in the visible range (Figure S2), indicating the ring-closed SP was the dominant form. The films gradually turned red in the absence of light, with λ_{max} at 537 nm, 544 nm and 549 nm for SP1, SP2 and SP3 respectively, indicating SP converted to ring-open MC. Over 10 days in the dark, the absorption of SP1 and SP2 films plateaued, while SP3 having a much lower absorbance still showed an increasing linear trend (Figure 2a). The overall absorption intensity curves of SP1 and SP2 showed non-linear increase. The saturated absorbance of SP3 was obtained after one month in the dark, with the absorbance of 1.35 ± 0.05. Since the absorption equilibrating time of SP3 was much longer than SP1 and SP2, the initial linear color change was used to determine the coloration rates. To show the color change more vividly, a "Yin-Yang" shaped SP1-PHEA/PHEA film was prepared by a three-

step curing polymerization process (Figure S7). In a dark environment overnight, the SP1-PHEA segments changed color (the inserted pictures in Figure 2a), while the pale yellow PHEA segments remained unchanged.

The slopes of linearly fitted curves (Figure S3) were defined as the coloration rate in the absence of light, k_c, while $t_{1/2}$ was defined as the time to reach an absorbance at half maximum $Abs_{1/2}$ and are shown in Table 1. The coloration rate k_c of SP1&2 was an order of magnitude higher than SP3, and $t_{1/2}$ of SP3 was longer than SP1&2 by an order of magnitude. The much slower coloration speed of SP3 demonstrated that the majority of chromophores were still in the ring closed spiropyran form over a long period in the dark. The trend of absorption intensity is consistent with that observed for SP molecule dissolved in HEA solution, yet changed on a much longer time scale. The flexibility of SP in the crosslinked network was reduced compared to free SP molecules in solution, leading to a slower thermal ring-opening process. The λ_{max} of bulk samples showed the same trend as the solution samples, with SP3 having a higher λ_{max} followed by SP2 then SP1. SP2 and SP1 showed similar coloration rates and maximum absorbance behaviour in the dark, indicating the attachment number of SP in the polymer chains affects the thermal SP ↔ MC equilibrium. SP3 which exhibited a slower coloration speed and lower saturated absorbance is attributed to less flexibility (more conjugating positions) and polarity difference. The maximum absorbance of SP3 is around half that of SP1&2, which indicates that more than half of the SP3 mechanophore was still in ring-closed state. The incorporation of one more attachment point on SP effectively reduces the negative photochromism.
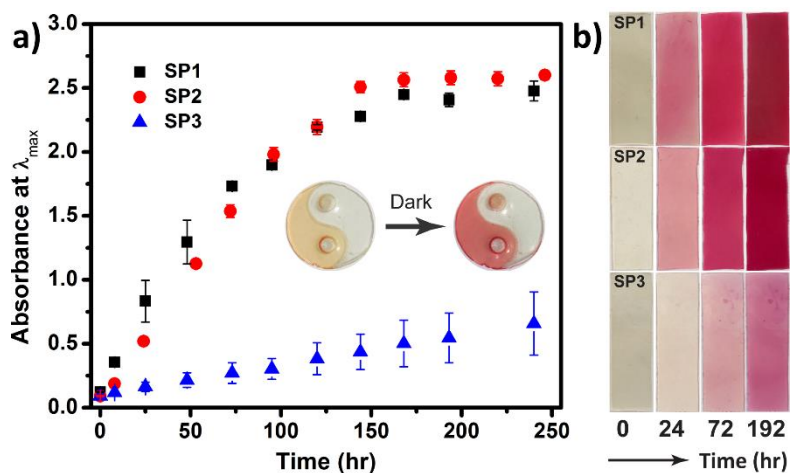
Figure 2. (a) Plot of absorbance at λ_{max} versus time in the dark for SP1-3 with 1 mol % crosslinkers (inserted pictures of SP1-PHEA/PHEA film in "Yin-Yang" symbol shape before and after being stored in the dark overnight, diameter: ~ 5 cm), and (b) images showing the color change of SP1-3 relative to time.

Table 1. Data calculated from Figure 2: Wavelength at maximum absorbance λ_{max}, coloration rate k_c, absorbance at half $Abs_{1/2}$ and the corresponding time $t_{1/2}$ for SP1-3 contained PHEA samples kept in the dark.

Sample	λ_{max}	$k_c \times 10^{-2}$ (R^2)	$Abs_{1/2}$	$t_{1/2}$
SP1	537	2.6 (0.999)	1.2	41.5
SP2	544	2.0 (0.998)	1.3	57.4
SP3	549	0.23 (0.998)	0.68	246

Color activation by swelling in water

To investigate the color activation by swelling in water, SP-PHEA films with 1 mol % crosslinker were immersed in water and subsequently swelled. Absorbance, sample size and mass change were measured as shown in Figure 3a-c. All samples became reddish pink as the size increased (Figure 3d, representative pictures not in scale), indicating spiropyrans were activated to ring-open MC. The inserted pictures in Figure 3b also showed the color change of

an SP3-PHEA/PHEA film in "Yin-Yang" shape after swelling in water for 1.5 hr; the four components of the symbol stuck well together even after swelling in water. The swelling ratios calculated by volume and mass expansion. These were identical for each of the samples although it was shown that the mass change calculation was more accurate (Figure 3c). To investigate how the dark environment affects the colouration during swelling, a control sample, a mono functionalized SP was also synthesized, which remained pendant (non-crosslinked) in the polymer network with 1 mol % EGDMA as crosslinker (Figure S4a). The control SP-PHEA specimen did not show a color change within 4 hours in water, although the swelling ratio was the same as the other SP samples (Figure S4b-e). This confirms that the SP1-3 ring-opening process within 4 hours was caused by the swelling force rather than the solvatochromism/negative photochromism from the hydrophilic environment. After the swelling ceased the absorbance continued to increase gradually over 40 hr (Figure 3). This differs from the swelling in organic solvents for SP in non-polar polymers as reported by Moore's group.[32] Here they observed an increase in absorbance at the same rate as the swelling. As with SP/non-polar samples mechanical force partially induces SP to MC color change,[36] however for our SP/polar samples the additional polar effect due to the polymer and water, continued to facilitate further ring opening of the SP to MC. A comparison of the time scale for color equilibrium of swelling in water with dry samples in the dark, the swelling force activating the mechanophore speeds up the color change. The polar effect induced by the hydrophilic environment was also observed for the control sample which was not affected by swelling. After 4 hr, the absorption peak at 519 nm began to appear on the control sample demonstrating the isomerization to ring-open MC; the absorption plateaued after 4 days (Figure S4c), a longer period than the mechanochromic SP1-3 samples (2 days). The study of non-polar polymer swelling in organic solvent by Moore *et al* assumed that an early plateauing of the fluorescence in THF was due to solvatochromism,[32] however here the swelling process of

the control SP in polar PHEA demonstrated that the polar effect slowed down the coloration process, compared to coloration of a dry sample kept in the dark (Figure S4e). This shows that the swelling force can accelerate the mechano-active SP ring-opening reaction. Additionally, Stretching can also induce ring-opening reaction of SP1-3 PHEA, however the activation ratio was too low to be measured. It's believed that the higher ratio of ring-opening triggered by swelling than that induced by stretching is due to the multi-direction expansion of swelling.
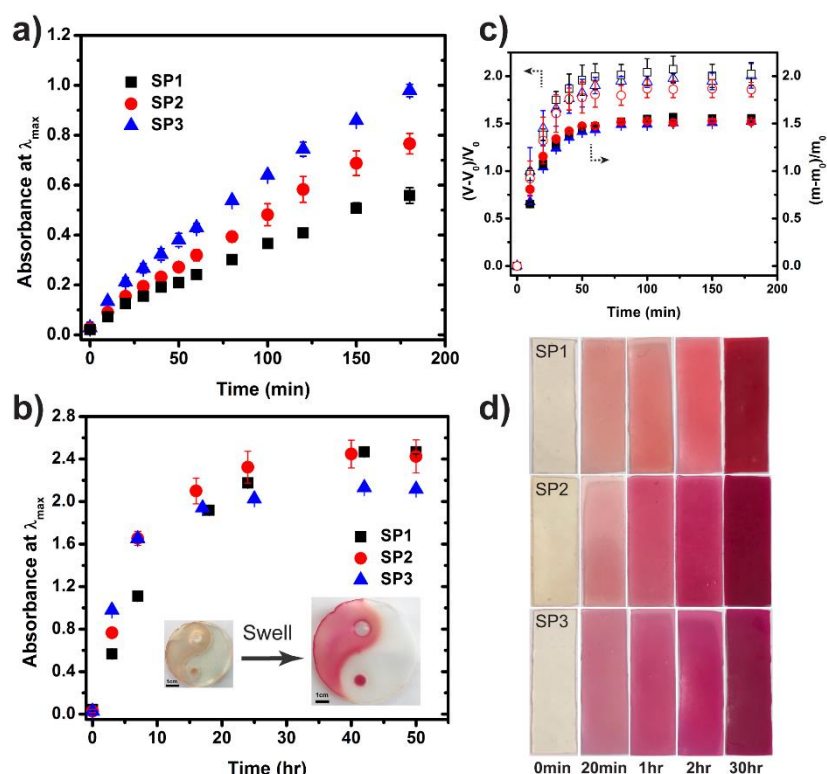
Figure 3. Absorbance as a function of the swelling time in water for SP1-3 samples with 1 mol % crosslinker (λ$_{max}$ of SP1 at 522 nm, SP2 at 532 nm and SP3 at 540 nm): (a) over 3hr and (b) over 50 hr (pictures of a SP3-PHEA/PHEA film in "Yin-Yang" shape before and after swelling in water for 1.5 hr as inserted, scale bar: 1 cm); (c) volume and mass change ratio of the three samples versus the immersing time in water; (d) the representative images showing the color change relative to the swelling time (images are not to scale).

Table 2 Summary of λ_{max}, k_c within 200 min, $Abs_{1/2}$ and $t_{1/2}$ for SP1-3 contained PHEA samples swelling in water.

Sample	λ_{max}	$k_c \times 10^{-3}$ (R^2)	$Abs_{1/2}$	$t_{1/2}$ (hr)
SP1	522	3.0 (0.996)	1.2	7.1
SP2	532	4.2 (0.997)	1.2	5.4
SP3	540	5.5 (0.993)	1.1	3.4

Differences in activation rate by swelling were observed for SP1-3, with SP3 > SP2 > SP1 (Figure 3a & Table 2). The faster swelling activation rate of SP3 film is influenced by the multi-axial deformation due to the increased crosslinking points in the polymer network. SP1 and SP2 differed in activation rate due to their attachment positions; the attachment points on *N*-position is more advantageous than on 5' position in force activation due to the bond cleavage distance, which is consistent with our previous study.[34] After two days immersed in water, the absorbance of SP1-3 samples plateaued, indicating an equilibrium of SP $\leftrightarrow$ MC toward MC was reached. SP1 and SP2 showed the identical absorbance within statistical error, slightly higher than SP3. This is due to SP1&2 being more influenced by the polar environment, as discussed earlier.

Decoloration studies

The colored films can revert to light yellow by exposure to white light leading to ring closure of MC to SP.[21, 28] The decoloration of colored SP1-3 films in swollen and corresponding dehydrated states were investigated by measuring the absorbance over time under white light. The color fading time (t_f) was determined by the intersection of the two tangent lines in both wet and dry conditions (Figure 4a-b). The swollen films were shown to bleach within 1-2 min, while all the dehydrated films took significantly longer time to decolor, in 30-110 min. This demonstrates that the stability of MC is poorer in the wet swollen state than the dry state. In

this case, water acts as a plasticiser in the swollen films [37], leading to an increase in free volume and flexibility, which facilitates the MC ring closure process. The difference of SP1-3 decoloration in the swollen state was minor with t_f summarized in Table 3.

It was noted that a large difference in the fading time t_f of SP1-3 polymer films was observed in the dehydrated state (Figure 4b), with the order of SP1 < SP2 < SP3. The color fading times t_f were 30 min, 62 min and 108 min for SP1-3 respectively. The decoloration rates (k_f) were determined by fitting the initial linear range (the first tangent line), resulting in 0.033, 0.016 and 0.0082 for SP1-3 respectively (Table 3). SP1 was shown to have a faster bleaching rate and is attributed to the attachment point at 5'-position speeding up the ring closure under visible light as previously reported.[38] The slow decoloration speed observed for SP3 is believed to be due to a higher number of cross-linkable points which reduces the flexibility of conformational isomerization of the mechanophore.

Noticeably, λ_{max} of the corresponding dehydrated films shifted towards longer wavelength compared to that of the swollen films, with $\Delta \lambda_{max}$ of 17, 16 and 12 nm for SP1-3 respectively (Figure S6). This reflects the change in polarity due to the polar (water) environment. The polarity decreases with the removal of water, resulting in an increase of λ_{max} after dehydration. The λ_{max} of dehydrated SP1-3 PHEA samples was close to that of colored films in the dark (Figure 2 and Table 1), and is slightly longer due to the exposure to moisture.[37, 39] Utilizing the differences SP causes on λ_{max} shift in dissimilar environments, there is the potential for solvent sensors which respond to changes in the polarity.
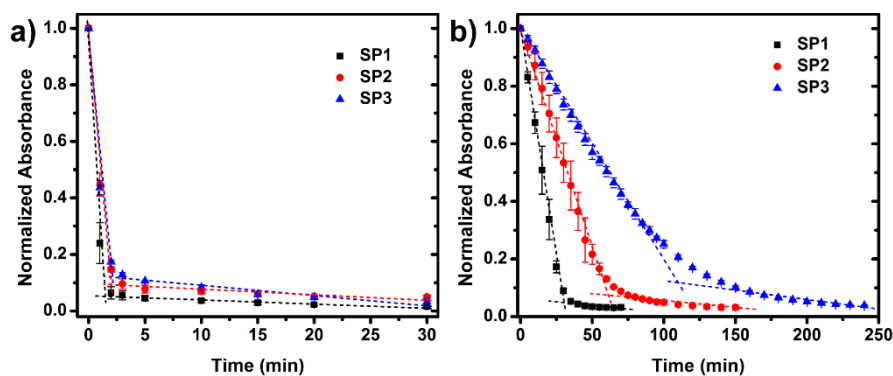
Figure 4. Decrease of absorbance at λ_{max} of SP1-3 PHEA (1 mol % crosslinkers) swollen films under white light irradiation in (a) swollen and (b) corresponding dehydrated states. Color fading time t_f is defined as the intersection of two tangent lines (dot lines).

Table 3. Summary of λ_{max}, color fading time t_f and decoloration rate k_f of SP1-3 samples in swollen and dehydrated states under white light, and the shift of λ_{max} from swollen to dehydrated state.

Sample	Swollen state			Dehydrated state			$\Delta \lambda_{max}$
	λ_{max} (nm)	t_f (min)	$k_f \times 10^{-1}$	λ_{max} (nm)	t_f (min)	$k_f \times 10^{-2}$	(nm)
SP1	522	1.5	- 5.3	539	30	- 3.3	17
SP2	532	2.0	- 4.5	548	62	- 1.6	16
SP3	540	2.1	- 4.4	552	108	- 0.82	12

Color switchability

Color switchability is essential when a sensor is required to be reused to track usage history. By turning white light on and off, the colored SP films switch between pale yellow and red color due to the isomerization between SP and MC. Based on the two decoloration conditions mentioned above, two cyclic tests were conducted, a) irradiating with white light then left in the dark while the sample was in the swollen state and b) swelling the sample in water, drying in the dark and then irradiating with white light as shown in Figure 5. The absorbance was

normalized based on the maximum value of the swollen state for a direct comparison of the two different switching modes.

For the tests irradiating white light on swollen films (Figure 5a), all samples showed color switchability over ten cycles. Upon white light irradiation, the ring-closed SP was the dominant form, and the MC signal after ten cycles stabilized at around 10% of original bleached value. The intensity of the sample due to MC, kept in the dark after swelling and white light irradiation was found to drop with increasing ring open-closure repetitions, with the absorbance of MC decreasing to 45-60% of the original intensity for SP1-3. This cyclic fatigue is due to the photodegradation of MC when irradiated by white light.[40-42] No significant difference in the absorption signal among SPs was observed (Figure 5a), which is expected since Figure 4a showed all three SPs had a similar rate of ring closure when exposed to white light. For the tests irradiating white light onto dehydrated films after swelling, similar trends of MC signal at bleached and colored states were recorded, with the degree of fatigue mainly dependant on the number of ring open-closure cycles. However, SP1 showed faster fatigue than SP2&3 after ten cycles especially in the dehydrated sample cycles (Figure 5b), although the time for SP1 ring closure was shorter than SP2&3 (Figure 4b).
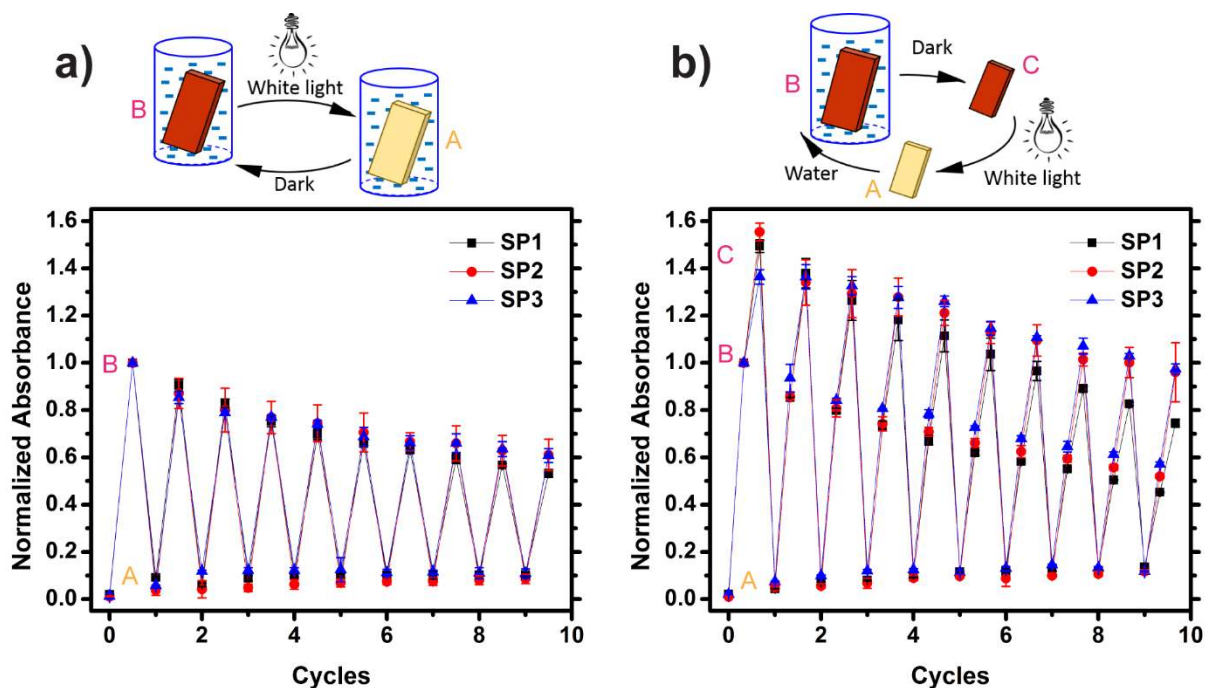
Figure 5. (a) Scheme of cyclic absorbance measurements between SP and MC by white light irradiation and subsequent storage in the dark for recovery, and the absorption plot of the SP1-3 films (1 mol % crosslinkers) in water; (b) scheme of cyclic absorbance measurements between SP and MC by swelling in water, dehydration in the dark at ambient conditions and white light irradiation, and the absorption plot of the SP1-3 films. The absorbance is normalized based on the maximum value in the swollen state.

Effect of cross-link density on color activation in water

It has been reported that swelling activation of SP non-polar polymer in organic solvent is cross-link density dependant.[32] Here, a series of SP3-PHEA with 1-10% crosslinker density were prepared, varying EGDMA content with a constant concentration of SP3, to study the effect of cross-link density on color activation in a polar polymer environment. The absorbance with time immersed in water and the corresponding mass change were recorded and shown in Figure 6. All samples achieved maximum absorbance and mass after 50 and 2 hr respectively. The swelling ratio reduced with increasing cross-linking density, and consequently the absorption signal of MC also decreased. Although the SP chromophore would slowly form MC

without swelling, here the crosslinking density can be used to control the rate of color activation of SP3. This can be attributed to the reduced water content in the polymer network, causing a difference in the polarity of the matrix and free volume of the polymer chains. Interestingly, the absorption intensity in this instance due to the degree of crosslinking it does not follow the linear dependence reported for SP/non-polar polymer systems in organic solvent.[32]
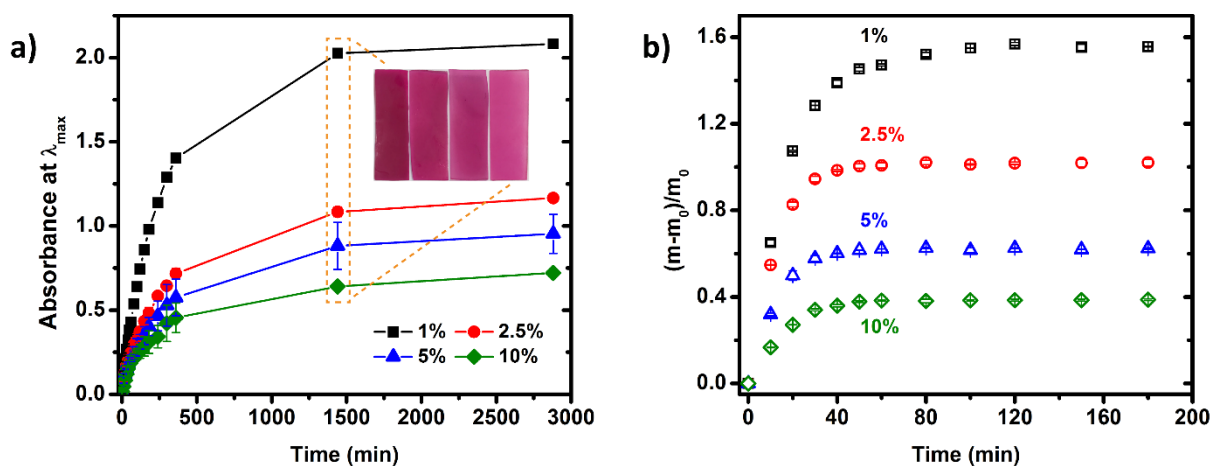
Figure 6. (a) Influence of crosslinking density on absorption intensity as a function of the swelling time for SP3-PHEA films (1 mol %, 2.5%, 5% and 10%), and the inset images of different crosslinked films swelling over 1 day; (b) swelling ratio of the SP3-PHEA films at different crosslinking density.

Conclusion

In summary, we have prepared three spiropyran molecules with two and three acrylate attachment positions which were subsequently covalently crosslinked with polar HEA monomer via white light induced polymerization. The effect of the polar environment on SP coloration (negative photochromism) was studied in HEA solution and crosslinked PHEA bulk materials, with the latter having a much longer activation time. SP-PHEA polymer films showed activation by swelling in water, due to mechanochromism, which was confirmed by incorporating a single functional SP into PHEA matrix which resulted in no color change during swelling. De-swelling in the dark, could not reverse the colored MC to colorless SP due

to the polar matrix. Under swollen conditions, the color reversibility can be achieved by exposure to visible light or stored in the dark, which was the same for dry bulk samples. It was determined that the tri-functional SP3 was least affected by negative photochromism, resulting in the lowest absorption intensity when stored in the dark, however it displayed the fastest color activation by swelling. SP3 also exhibited a significantly slower decoloration rate relative to SP1 and SP2 once dehydrated after swelling. The color switchability was dependent on the number of cycles, with 45-60% remaining in the MC form after 10 cycles. The cross-linking density affected the rate and degree of SP ring-opening, with the absorption results showing that the lowest cross-linking density presented the highest absorption intensity. These results demonstrated that SP3 in PHEA has a greater resistance to the polar environment in switching to colored MC, and that the absorption can be regulated by controlling the degree of cross-linking. The switchable color triggering by swelling in water and light offer opportunities to tailor polar hydrophilic swellable films with color changing properties suitable for biomedical applications such as biosensors or optical storage devices.

ASSOCIATED CONTENT

Supporting information

Absorbance spectra, linear fitting curves of absorption plots and a control SP sample.

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Notes

The authors declare no competing financial interest.

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