

Photo-response behavior of electrospun nanofibers based on spiropyran-cyclodextrin modified polymer†

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Tunable and durable photochromic materials are a rapidly expanding area of interest, with applications ranging from biomedical devices to industrial-fields. Here we examine electrospun poly (methacrylic acid) PMAA nanofibers covalently modified with the highly photochromic molecule, spiropyran (SP) or a derivate SP which is firstly coupled to a cyclodextrin molecule (β CD_{SP}). The photochromic properties of the starting materials and of the nanofibers were investigated. β CD_{SP}, PMAA_{SP} and PMAA- β CD_{SP} polymers exhibited a reverse photochromism. The kinetic results revealed a faster isomerization process for the β CD_{SP} molecule, than that for the PMAA- β CD_{SP} and for the PMAA_{SP}, the slowest one. The fastest isomerization is attributed to the presence of a large number of hydroxyl groups of the β CD which stabilizes the merocyanine form *via* hydrogen bonding, and the slowest isomerization is related to the PMAA chain structure that stabilizes the spiropyran form. Thus, combining the PMAA and β CD properties the photo-isomerization can be modulated. The photo-reversibility of this material was verified by UV-visible measurements cycling visible and UV light. Infrared spectroscopy and water contact angle were used for the nanofiber surface characterization, demonstrating the presence of the spiropyran on the mats surface and also showing a minimal effect on nanofiber size and shape when compared to PMAA fiber.

1. Introduction

Photochromic molecules undergo a color change on irradiation that can be reversed to the initial color either thermally or by subsequent irradiation.^{1,2} Spiropyrans are a group of light-switchable organic molecules, allowing reversible switching between a colorless closed spiro (SP) form and a strongly colored merocyanine (MC) open form,³ Scheme 1. The photochromic, thermochromic and solvatochromic responses of spiropyrans involve the cleavage of the spiro C–O bond.⁴ While the MC form has a large planar conjugated π -system and a high dipole moment due to its zwitterionic nature, the SP form is not fully conjugated and is neutral with a small dipole moment.^{5–7}

Spiropyrans have been incorporated into different organic and inorganic matrices in applications ranging from optical devices to biocompatible materials.^{3,5,8–10} The physical and chemical environment significantly changes the photochromic properties, such as switching rates or equilibrium state.⁵ In these materials, two types of photochromism have been observed; normal, in which the closed form is observed under dark conditions, and reverse, when the open form is the most stable one.^{11,12} Reverse photochromism has been attributed to the stabilization of the MC form *via* hydrogen bonding with the microenvironment around the molecule.^{11,13} A way to retain or adapt the physical-chemical properties of the spiropyrans can be by its molecular encapsulation in an appropriate matrix,¹⁴ by chemical structural modification or non-covalently doping of the molecule into appropriate matrices such as polymers^{15–17} or cyclodextrin (CD) cavity.^{5,12}

CDs have a rigid and well defined structure with a hydrophobic cavity. A variety of organic and inorganic guest molecules have been inserted into its cavity, resulting in the formation of

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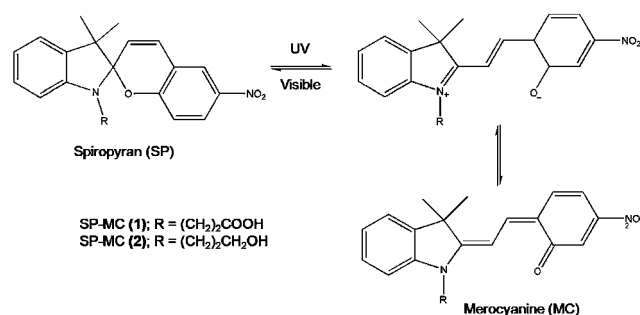
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† Electronic supplementary information (ESI) available: ¹H NMR spectra of β CD_{SP}, SP molecule and PMAA_{SP} polymer in DMSO-d₆, mass spectrum of the β CD_{SP} molecule, images of β CD_{SP}- β CD_{MC}, PMAA_{SP}-PMAA_{MC} and PMAA- β CD_{SP}-PMAA- β CD_{MC} aqueous solutions, water contact angle for PMAA- β CD_{SP} and PMAA- β CD_{MC} nanofibers and spin coating films of PMAA- β CD_{SP} and PMAA- β CD_{MC}. See DOI: 10.1039/c0jm01903h



Scheme 1 Spiropyran-merocyanine structures in equilibrium under UV-visible light irradiation.

inclusion complexes (ICs).^{18–23} The natural occurring CDs most commonly used are α -, β - and γ -cyclodextrin with six, seven and eight glucopyranose units, respectively. In these structures, the primary and secondary hydroxyl groups are responsible for the hydrophilic nature of the outer surface of the cyclic structure, making these CDs water-soluble.²¹ Combining the photochemical properties of the spiropyran molecules with polymer-CD based nanomaterials could expand their applications significantly. Once at a supramolecular level the specific interactions between the photochromic and the CD molecules may enhance or change photochemical properties of the guest molecule.²¹ In a micro or nano level, the polymer matrix could favor the assembly of this system in different ways.^{24,25} In particular, electrospun nanofibers can be used as building blocks of high-performance devices²⁶ containing the photo-responsive molecules. These light induced materials are of high interest for new applications such as a matrix for cell growth, light controlled drug delivery systems, biosensors and erasable optical memories.^{3,27–31} Electrospinning is a relatively easy and robust method that allows fabrication of continuous fibers with diameters ranging from 10 to 10 000 nm.^{24,32,33} Large specific surface area, high flexibility and superior mechanical performance have resulted in numerous applications in different areas of research, from biomedical applications to industrial-fields, using natural or modified polymers, loaded with nanoparticles as well as active agents.^{31,34–36}

In this work, we report the preparation of photo-responsive nanofibers obtained using the electrospinning approach based on the modified polymer with a photochromic molecule, β CD-spiropyran. Firstly, monosubstituted β CD with spiropyran (β CD_{SP}, Fig. 1) was synthesized in a one step reaction. This modified β CD_{SP} was used to modify the poly (methacrylic acid) (PMAA) side chain. The association of supramolecular chemistry and

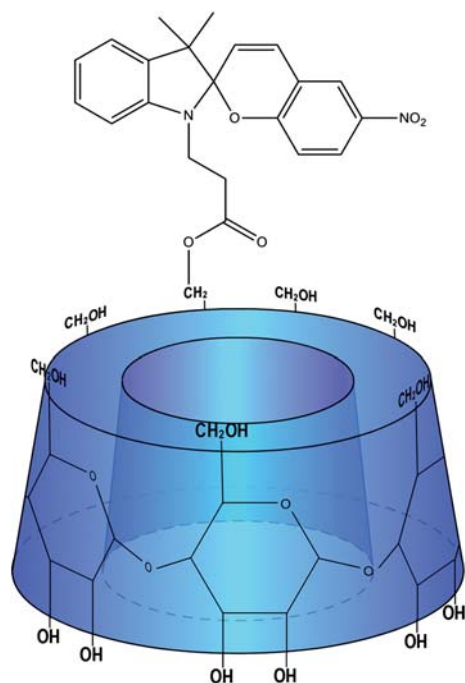


Fig. 1 Schematic representation of β CD_{SP} photochromic molecule.

polymer based material was to modulate the physical-chemical properties of spiropyran molecules, in solid and liquid phase. Additionally, direct modification of the PMAA side chain with spiropyran was also carried out to compare with the PMAA- β CD_{SP} material. Nuclear Magnetic Resonance (NMR) was used for structural characterization of the modified β CD_{SP} and both modified polymers PMAA- β CD_{SP} and PMAA_{SP}. Additionally, time-of-flight mass spectrum, MALDI-TOF, was used to confirm the monosubstitution of the β CD with spiropyran. UV-visible spectroscopy was used to characterize the photochromic properties of the β CD_{SP}, PMAA- β CD_{SP} and PMAA_{SP}. PMAA and PMAA- β CD_{SP} polymers were electrospun into fiber from a 15 wt% solution in *N,N*-dimethylformamide (DMF) and these materials were characterized by scanning electron microscopy (SEM). The surface properties were characterized by water contact angle measurements and also by infrared spectroscopy, using attenuated total reflectance apparatus (FTIR-ATR).

2. Results and discussion

2.1 Synthesis and characterization of β CD_{SP}, PMAA- β CD_{SP} and PMAA_{SP}

The reaction conditions using pyridine as solvent to synthesize the β CD_{SP} favored the substitution on the primary hydroxyl group of β CD molecule.³⁷ This observation is based on NMR results. The ¹H NMR spectrum of β CD_{SP} in DMSO-*d*₆ (Figure SI 1†) demonstrated all the hydrogen signals from β CD and spiropyran molecules, except the hydroxyl group of spiropyran at δ 12.2 (Figure SI 2†), indicating a covalent bond in the β CD macrocycle. The ratio between the aromatic singlet from spiropyran at δ 8.2 and CH 1 δ 4.8 and OH 6 at δ 4.4 from β CD is about 1 : 7 : 6, which indicated the monosubstitution on the primary hydroxyl group of β CD preferentially (Figure SI 1†). The molecular weight of β CD_{SP} was also verified by MALDI-TOF, $m/z = 1497.4$ (Figure SI 3†), confirming the monosubstitution in the β CD macrocycle.

The DCC strategy was also used to synthesize the PMAA- β CD_{SP} and this was efficient to obtain the modified polymer in

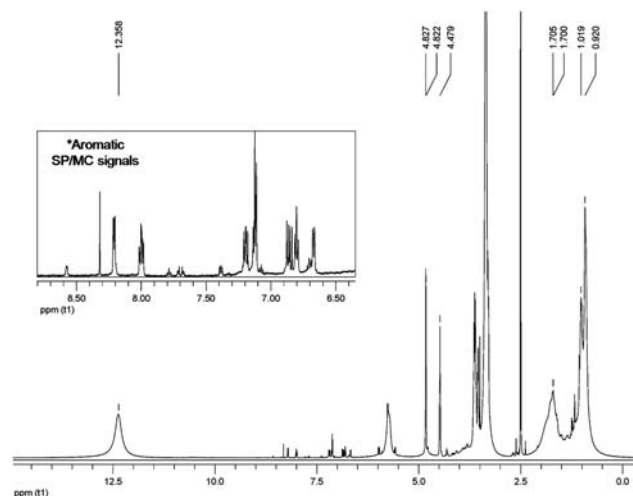


Fig. 2 ¹H NMR spectrum of PMAA- β CD_{SP} at 600 MHz in DMSO-*d*₆ at 30 °C.

a one step reaction. The presence of $\beta\text{CD}_{\text{SP}}$ molecule in the side chain of the PMAA was confirmed by the ^1H NMR spectrum, Fig. 2. In addition, the degree of substitution was evaluated using the integration ratio between PMAA hydrogens (CH_3 , δ 0.92; CH_2 δ 1.7) and those aromatic hydrogens from spiropyran molecule. These result based on relative amount of hydrogens suggests a substitution of 1.3% of the PMAA side chain with the $\beta\text{CD}_{\text{SP}}$ molecule. The ^1H NMR spectrum of the PMAA $_{\text{SP}}$ polymer (Figure SI 4†), synthesized to compare its photochromic properties with those observed for PMAA- $\beta\text{CD}_{\text{SP}}$, was also carried out, confirming the side chain modification. These three molecules synthesized presented a reverse photochromism behavior in aqueous solution (Figure SI 5†).

2.2 Photochemical properties of $\beta\text{CD}_{\text{SP}}$, PMAA- $\beta\text{CD}_{\text{SP}}$ and PMAA $_{\text{SP}}$

The photochromic activity under UV and visible light of $\beta\text{CD}_{\text{SP}}$ was evaluated by UV-visible measurements, Fig. 3a, and the results are in agreement with those reported previously.³⁸ The UV-visible measurements demonstrated that the MC form (open and color form) is more stable in aqueous solution under dark conditions than the SP form (closed, colorless form). This result in aqueous media demonstrates the reverse photochromism behavior.³⁸ The photo-reversibility from MC to SP forms and *vice versa* were observed by alternating the illumination from visible to UV light on the aqueous media, Fig. 3a.

The PMAA- $\beta\text{CD}_{\text{SP}}$ polymer also presented a reverse photochromic behavior in aqueous medium. Thus, the absorption band at λ_{max} (H_2O)/nm 514 related to the MC form in the UV-visible spectrum, is suppressed under visible light, Fig. 3b. The reverse isomerization process was also achieved for the PMAA- $\beta\text{CD}_{\text{SP}}$ polymer cycling visible and UV light in the aqueous solution, Fig. 3b. In aqueous solution the PMAA $_{\text{SP}}$ also presented a reverse photochromism as observed in both previous systems. This behavior in aqueous solution has been observed for different spiropyran molecules trapped in solid matrices and has been attributed to the stabilization of the zwitterionic form *via*

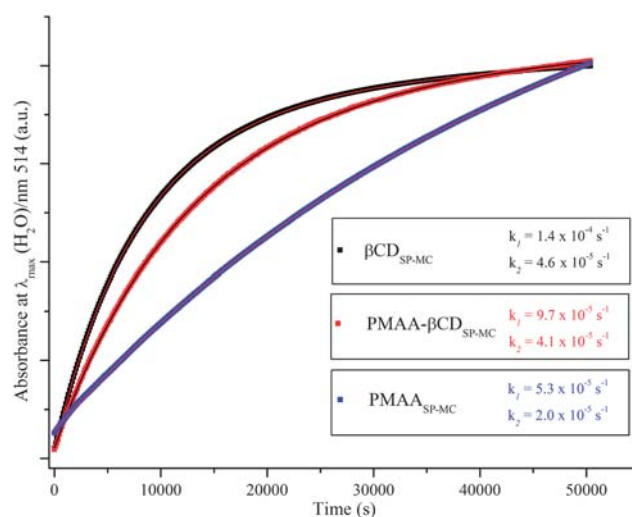


Fig. 4 Kinetic curves for $\beta\text{CD}_{\text{SP}}$, PMAA- $\beta\text{CD}_{\text{SP}}$ and PMAA $_{\text{SP}}$ at 25 °C.

hydrogen bond with the micro environment around the photochromic molecule.¹¹

Once all systems presented a reverse photochromism behavior, kinetic experiments were carried out for these samples to evaluate the color evolution. Fig. 4 shows the kinetic curves for $\beta\text{CD}_{\text{SP}}$, PMAA $_{\text{SP}}$ and PMAA- $\beta\text{CD}_{\text{SP}}$, evaluated for 14 h. These curves were fitted into a biexponential model, $A = B_1(1 - e^{-k_1 t}) + B_2(1 - e^{-k_2 t}) + C$, using Origin 7.0®. Where A is the optical density at λ_{max} , B_1 and B_2 are the contributions to the initial optical density, k_1 and k_2 are rate constants of the fast and slow components and C is the fade when time approaches to infinity.^{2,12}

The biexponential fitting model reveals that the $\beta\text{CD}_{\text{SP}}$ system presents the fastest color evolution with a $k_1 = 1.4 \times 10^{-4} \text{ s}^{-1}$ ($t_1 = 119 \text{ min}$), comparing to the PMAA $_{\text{SP}}$, the slowest isomerization process, $k_1 = 5.3 \times 10^{-5} \text{ s}^{-1}$ ($t_1 = 316 \text{ min}$) and the PMAA- $\beta\text{CD}_{\text{SP}}$ $k_1 = 9.7 \times 10^{-5} \text{ s}^{-1}$ ($t_1 = 172 \text{ min}$). The slow constant rates (k_2) for these three systems are $k_2 = 4.6 \times 10^{-5} \text{ s}^{-1}$ ($t_2 = 391 \text{ min}$), $k_2 = 2.0 \times 10^{-5} \text{ s}^{-1}$ ($t_2 = 839 \text{ min}$) and $k_2 = 4.1 \times$

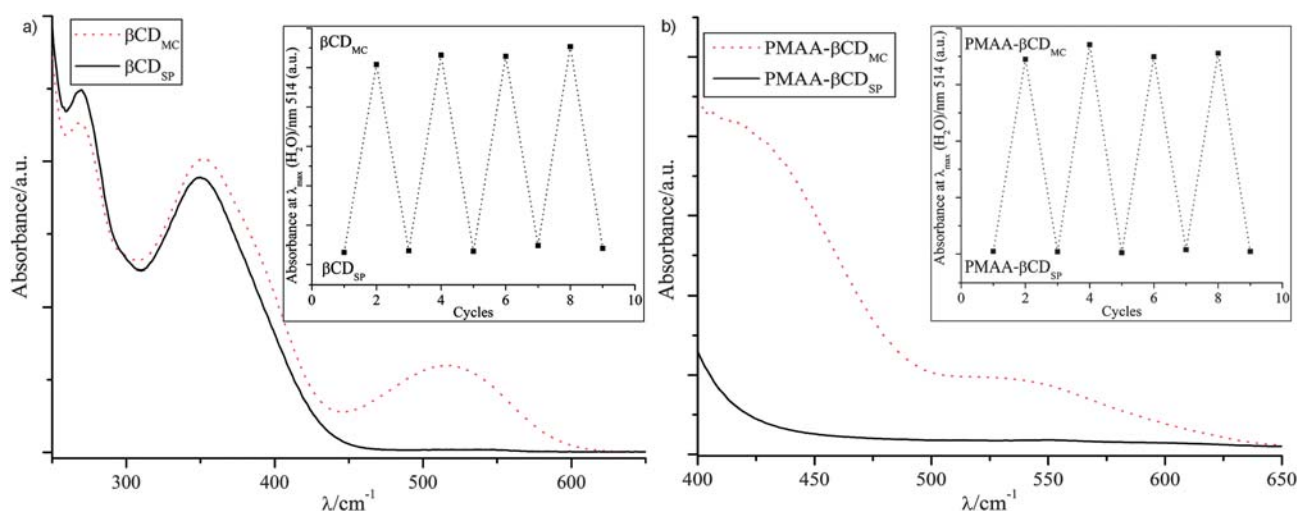


Fig. 3 (a) UV-visible absorption spectra of the $\beta\text{CD}_{\text{SP-MC}}$ and the reversibility process (insert box) and (b) UV-visible absorption spectra of the PMAA- $\beta\text{CD}_{\text{SP-MC}}$ and the reversibility process (insert box).

10^{-5} s^{-1} ($t_2 = 404 \text{ min}$) for $\beta\text{CD}_{\text{SP}}$, PMAA_{SP} and $\text{PMAA-}\beta\text{CD}_{\text{SP}}$, respectively.

The microenvironment around the photochromic molecule is responsible for the MC stability and also for the interconversion rates.^{11,39} These kinetic results reveal an interesting point about the photochromic behavior for the polymer-cyclodextrin material. The hydroxyl groups from the βCD molecule lead to a stabilization of the MC form, in a more efficient way than those hydroxyl groups from PMAA polymer. This may occur because of the hydrophobic groups in the PMAA side chain ($-\text{CH}_3$) or because of the lower mobility of the spiropyran in the polymer system,² which stabilizes the colorless form. This result can be confirmed by the slowest coloration rate observed in the PMAA_{SP} system.

In this sense, combining properties from both molecules (PMAA and βCD) led to an intermediate photochromic switching rate, mediated by the hydrophilic moieties of the βCD and the polymer chain. The cause of slowest switching speed observed for PMAA_{SP} is the rotational mobility of the molecule in the host matrix,² which was not affected or reduced by the conjugation of the spiropyran with the βCD molecule in the $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ polymer. These results confirm the importance of the hydroxyl groups from βCD in the MC form stabilization. Thus, combining the βCD molecule with the spiropyran is useful to increase the isomerization rate in the PMAA polymer matrix.

2.3 Nanofiber characterization

In an attempt to make use of this novel photochromic polymer, $\text{PMAA-}\beta\text{CD}_{\text{SP}}$, we successfully fabricated it into nanofibers using electrospinning. The SEM images of the electrospun $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ nanofibers are presented in Fig. 5a and 5b. These nanofibers are beads-free and have a relatively narrow distribution of fiber diameters. The PMAA nanofibers SEM images, electrospun in order to compare with those obtained using $\text{PMAA-}\beta\text{CD}_{\text{SP}}$, are depicted in Fig. 5c and 5d. These nanofibers present a similar morphology of those prepared with the $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ polymer and no beads were observed, however, a significant difference was observed in the nanofibers diameter

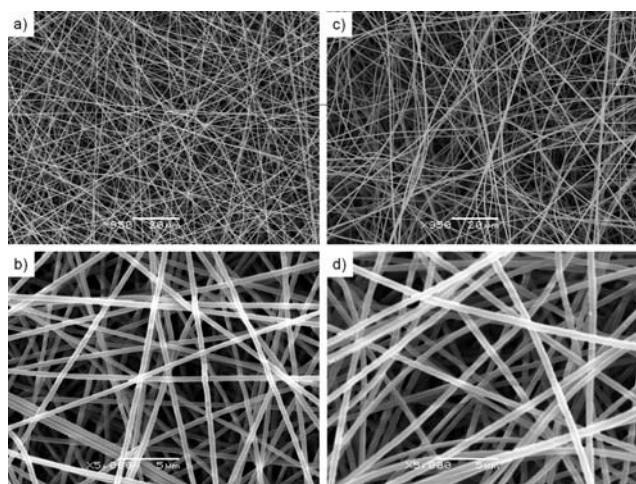


Fig. 5 SEM images of: (a) $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ 15 wt% (950 \times), (b) $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ 15 wt% (5000 \times), (c) PMAA 15 wt% (950 \times) and (d) PMAA 15 wt% (5000 \times).

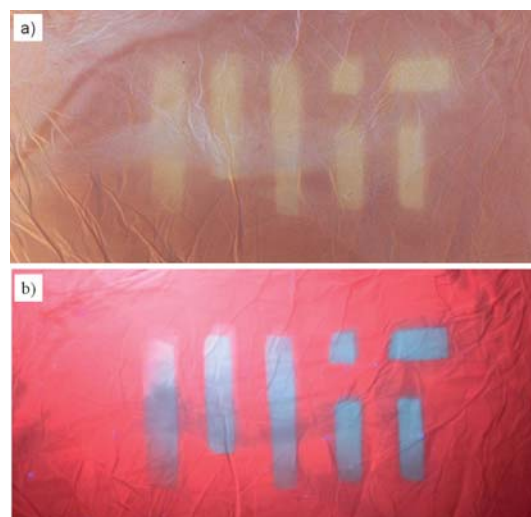


Fig. 6 Electrospun nanofibers of $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ heated at 80 $^{\circ}\text{C}$ and then (a) shined with visible light through a shaped mask and (b) exposed under UV light to demonstrate the fluorescence behavior of merocyanine form incorporated in the polymer matrix.

comparing the PMAA ($526 \pm 24 \text{ nm}$) with that prepared with the $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ polymer ($422 \pm 40 \text{ nm}$).

The photo-responsive or thermal properties under UV and visible light or heat, based on SP-MC isomerization, was verified in the nanofibers obtained by the electrospun approach, as depicted in Fig. 6a and 6b. The electrospun nanofiber, shown in Fig. 6a, was heated at 80 $^{\circ}\text{C}$ for 12 h and exposed to visible light during this period through a mask. After this period the covered $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ nanofiber presented a light red color associated to the MC form and the masked portion irradiated with visible light presented a white color related to the SP form, demonstrating the photochromic property of the nanofibers. Additionally, the nanofiber was placed under UV light, Fig. 6b, and the difference between these isomers were intensified by the fluorescence property of the MC form.

The chemical composition of the starting materials (βCD , SP-MC and $\beta\text{CD}_{\text{SP-MC}}$) and the surface chemistry of the nanofibers (PMAA and $\text{PMAA-}\beta\text{CD}_{\text{SP}}$) were also characterized by FTIR-ATR. The infrared spectra of βCD , SP-MC and $\beta\text{CD}_{\text{SP-MC}}$ are depicted in Fig. 7a (zoom in to a better visualization of the bands from 4000 to 2000 cm^{-1}) and 7b (bands from 2000 to 500 cm^{-1}). The FTIR-ATR spectrum of βCD presents those characteristic bands: $\nu_{\text{max}}/\text{cm}^{-1}$ 3300 (OH stretching), 2930 (CH symmetric and asymmetric stretching) and that one around 1027 (C–O–C stretching).^{40,41} SP-MC infrared spectrum demonstrates its characteristic bands; $\nu_{\text{max}}/\text{cm}^{-1}$ 1707 (CO stretching), 1605–1575 (C=C) and (C=N), and those bands at 1329 and 940 (CN) and (OCN).^{42–44} In the FTIR-ATR spectrum of $\beta\text{CD}_{\text{SP-MC}}$, it is possible to observe bands from both molecules, βCD and SP-MC, confirming the structure proposed by NMR and MALDI-TOF.

In Fig. 7c, are depicted the FTIR-ATR spectra for the PMAA and the modified $\text{PMAA-}\beta\text{CD}_{\text{SP}}$ polymers. The PMAA polymer spectrum shows its characteristic signal, $\nu_{\text{max}}/\text{cm}^{-1}$ 1387 ($-\text{C}(\text{CH}_3)$), 1702 (CO stretching), 2985–2930 (CH symmetric and asymmetric stretching) and 3000 (OH), a broad stretching band.^{45–47} Even in a small intensity, once the degree of substitution

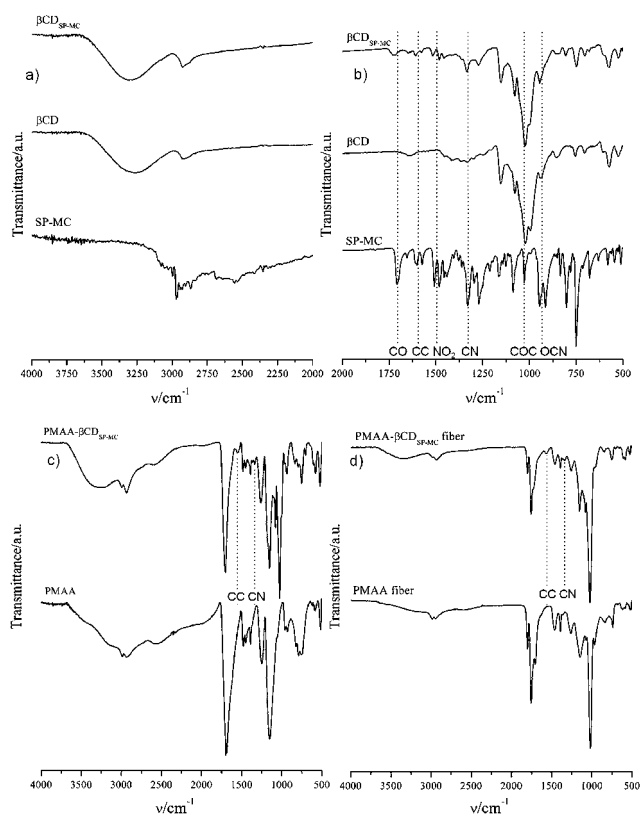


Fig. 7 FTIR-ATR spectra for the β CD, SP-MC and β CD_{SP-MC} starting materials (a) zoom in from 4000 to 2000 cm^{-1} , (b) from 2000 to 500 cm^{-1} , (c) PMAA and PMAA- β CD_{SP-MC} polymers and (d) PMAA and PMAA- β CD_{SP-MC} nanofibers after annealing process.

was about 1.3%, the $\nu_{\text{max}}/\text{cm}^{-1}$ 1575 (C=C) and 1337 (CN) band of the SP-MC molecule was observed in the spectrum for the PMAA- β CD_{SP}, indicating its presence in the polymer.

Surface analysis of the electrospun nanofibers was also carried out. The spectra for the PMAA and PMAA- β CD_{SP} nanofibers, after the annealing process, are shown in Fig. 7d. The infrared spectrum for the PMAA nanofibers presents three distinguishable signals $\nu_{\text{max}}/\text{cm}^{-1}$ 1802, 1756 and 1701 (CO), in which these last two were attributed to the free C=O (1756 cm^{-1}) and those interacting by hydrogen bond (1701 cm^{-1}).⁴⁸ Moreover, the presence of a new band at $\nu_{\text{max}}/\text{cm}^{-1}$ 1017 was observed, as an effect of the annealing process, in which the cross-linking between carboxyl groups occurred. The infrared spectrum of the PMAA- β CD_{SP} nanofibers presents those bands at $\nu_{\text{max}}/\text{cm}^{-1}$ 1575 (C=C) and 1337 (CN) from the SP-MC molecule. This result suggests the presence of the SP-MC photochromic moieties in the nanofibers surface.

Fig. 8 presents the water adsorption process for the PMAA and PMAA- β CD_{SP} nanofibers as a function of time. The nanofibers stability under water conditions was tested for both, PMAA and PMAA- β CD_{SP}, after the annealing process. As result of the cross-link process and the chemical modification of the PMAA with the photochromic molecule, the PMAA- β CD_{SP} nanofibers demonstrated an increase in the surface hydrophobicity, while the PMAA adsorbed water after 420 s.

Surface analysis of the modified electrospun fibers was also performed by water contact angle measurements. The water

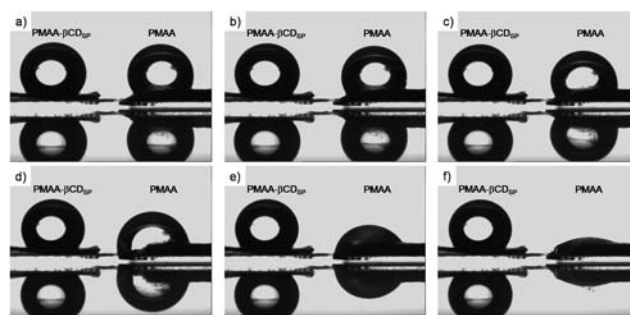


Fig. 8 Electrospun nanofibers of PMAA- β CD_{SP} (left) and PMAA (right) at time: (a) zero, (b) 180, (c) 360, (d) 370, (e) 420 and (f) 480 s.

contact angle on electrospun nanofiber mats is related to both, the roughness of the mats and the chemistry on the fibers surface.⁹ Two samples of PMAA- β CD_{SP} were prepared, one which was exposed to UV light during 24 h and the other sample that was exposed to visible light for the same period of time. The water contact angle measurements after these 24 h of UV irradiation was $138 \pm 2^\circ$ and for the one exposed to visible light was $155 \pm 5^\circ$ (Figures SI 6†). The decrease in the water contact angle for that nanofiber exposed to UV light might be related to photochromic properties of the SP-MC isomerization present in the electrospun nanofibers surface.⁷ The large change in the dipole moment between the two isomer states of the spiropyran might be able to modify the surface chemistry on the nanofibers, leading to the differences in the water contact angles modulated by the UV and visible irradiation. The 15° change for the water contact angle is in agreement with other systems containing SP molecule in the polymer matrix, reported previously in the literature.^{49,50} This result is in agreement with those obtained by FTIR-ATR, in which SP-MC infrared bands were observed in the PMAA- β CD_{SP} nanofibers spectrum. This light induced modification on the surface of the nanofiber can be useful as a matrix for cell growth, in which light might be able to induce cell detachment. Thin films based on these suitable materials have been used as support and switching between UV and visible light has been able to modify the cell adhesion properties.⁵¹⁻⁵³

Additionally, water contact angle for thin films based on PMAA- β CD_{SP} polymer prepared by a spin-coating technique, using DMF solution at 15% wt (see SI 7† for preparation method), was measured and compared with those values obtained for nanofiber mats. The water contact angle for the thin film exposed under UV ($59 \pm 4^\circ$) was smaller than that one irradiated with visible light ($68 \pm 2^\circ$). The decrease in the water contact angle for the MC form is in agreement with previous results obtained for the nanofibers, demonstrating the presence of spiropyran on the film surface. Additionally, these angles measured for the thin films are similar to those observed for a modified poly (methyl methacrylate) with spiropyran.⁵¹ The water contact angle for the free glass slide was also measured ($23 \pm 1^\circ$), confirming the presence of the film in the glass slide.

3. Materials and methods

3.1 Materials

All reagents were used without further purification: β -cyclodextrin, (β CD) *N,N'*-dicyclohexylcarbodiimide (DCC),

trimethylindolenine, 3-iodopropanoic acid, 2-hydroxy-5-nitrobenzaldehyde, piperidine, 2-butanone, 3-iodo-1-propanol, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF) and pyridine were purchased from Sigma-Aldrich, dichloromethane and chloroform were purchased from OmniSolv® and poly (methacrylic acid), 100 KDa, was purchased from Polyscience, Inc.

3.2 Synthesis and characterization of mono- β -cyclodextrin-spiropyran

Spiropyran (**1**) was synthesized as described previously.⁵⁴ Mono- β -cyclodextrin substituted with SP was synthesized in one step reaction.^{55–57} SP (0.76 g, 2.0 mM) and DCC (1.03 g, 5.0 mM) were dissolved in 40 mL of dry pyridine and the solution was stirred for 10 min. β CD (2.3 g, 2.0 mM) was dissolved in 50 mL of pyridine and poured in SP/DCC solution after being cooled in an ice bath. The mixture was stirred for 12 h in ice bath and for 24 h at room temperature under argon atmosphere. The solution was filtered to remove dicyclohexylurea (DCU) as precipitated. The resulting solution was evaporated under reduced pressure to give a dark purple powder, which was washed with dichloromethane to remove remaining DCC, DCU and SP-DCC. The resulting solid material was purified dissolving in 200 mL of water at 50 °C and then precipitating in THF to remove the free β CD. The solid was filtered and the solution was evaporated under reduced pressure. This procedure was repeated several times and then the resulting dark red water solution was frozen and lyophilized to give pure monosubstituted β CD_{SP} (yield 25%).

Structure was confirmed by NMR obtained on a Bruker DRX 600 – AVANCE spectrometer at 30 °C, operating at 600 MHz. Chemical shifts are reported in parts per million (ppm) on the δ scale, and were referenced to residual protonated solvent peaks. Spectra were obtained in dimethyl sulfoxide (Cambridge Isotope Laboratories, Inc – 99.9% of isotopic purity) referenced to DMSO-*d*₆ at δ H 2.50.

Mass spectrum was obtained on a Bruker Daltonics Omnicflex MALDI-TOF mass spectrometer. 2,5-Dihydroxybenzoic acid (2,5-DHB) was used as matrix for the β CD_{SP} (20–25 mg of 2,5-DHB into 1 mL of 60 : 40 MeOH–H₂O). β CD_{SP} stock solution was prepared by dissolving 1–2 mg in 1 mL of MeOH; 10 μ L of the stock solution was added to 100 μ L of matrix solution. Mass spectrum was calibrated using an external reference (Proteo-Mass™ Peptide MALDI-MS Calibration standards, Sigma-Aldrich) with α -cyano-4-hydroxycinnamic acid as matrix.

3.3 Synthesis and characterization of poly (methacrylic acid) with mono- β -cyclodextrin-spiropyran

PMAA (1.5 g) and DCC (0.32 g) were dissolved in 20 mL of dry pyridine. β CD_{SP} (1.5 g) was dissolved in 30 mL of dry pyridine, and this solution was poured into first one under argon atmosphere. Solution was stirred at room temperature for three days. After this period, 5.0 mL of NaOH 0.25% w/v water solution was added and after additional three days DCC was removed as DCU. The resulting solution was dried under pressure and solid was washed with dichloromethane. The resulting material was dissolved in water and dialyzed (Slide-A-Lyzer dialysis cassettes MWCO 20 KDa, Pierce) against water for 5 days. Solution was

frozen and lyophilized to obtain PMAA- β CD_{SP} (yield 70%). In order to compare the photochemical properties of PMAA- β CD_{SP} spiropyran (**2**) was synthesized as described previously⁵⁸ and was covalently bonded to PMAA, using 0.37 g of (**2**) and the same reaction conditions used for the PMAA- β CD_{SP}. The structure of PMAA- β CD_{SP} and PMAA_{SP} were confirmed by ¹H NMR spectrum on a Bruker DRX 600 – AVANCE spectrometer at 30 °C, operating at 600 MHz. in DMSO-*d*₆.

3.4 Photochemical properties of β CD_{SP}, PMAA- β CD_{SP} and PMAA_{SP}

The photochemical properties of the β CD_{SP}, PMAA_{SP} and PMAA- β CD_{SP} were evaluated by UV-visible spectrophotometer measurements. The reversibility of the isomerization process for β CD_{SP} and PMAA- β CD_{SP} were evaluated by cycling UV and visible light for 5 min in a stock solution of β CD_{SP} (0.2 mg mL⁻¹) and PMAA- β CD_{SP} (20.0 mg mL⁻¹) at 40 °C. During this process, aliquots were evaluated using Varian Cary 50 UV-Visible Spectrophotometer and absorbance measured at $\lambda_{\max}(\text{H}_2\text{O})/\text{nm}$ 514. The kinetic isomerization process (reverse photochromism) for β CD_{SP}, PMAA_{SP} and PMAA- β CD_{SP} were taken in a SpectraMax Plus³⁸⁴, Molecular Devices, at 25 °C. Aqueous solution of 3.0 mg mL⁻¹ of β CD_{SP} and 15.0 mg mL⁻¹ for PMAA_{SP} and PMAA- β CD_{SP} were used. Solutions were irradiated with visible light for 10 min and then absorption at $\lambda_{\max}(\text{H}_2\text{O})/\text{nm}$ 514 were taken every 2 min during 14 h for each solution.

3.5 Electrospinning

Solutions of PMAA and PMAA- β CD_{SP} were prepared at 15% wt in DMF with overnight stirring. The solution was electrospun onto a plate-to-plate assembly. The electrical potential about 20–25 kV were used for PMAA and PMAA- β CD_{SP} solution. Solution flow rate (0.02 mL min⁻¹) and capillary tip to collector distance (25 cm) for both solutions were kept the same to obtain a stable electrospinning. Nanofibers from PMAA and PMAA- β CD_{SP} were annealed in oven at 170 °C for 12 h.⁵⁹

The fibers morphologies were observed by a JEOL-6060SEM (JEOL Ltd., Japan) scanning electron microscope (SEM). The fibers were sputter-coated with a 5–8 nm layer of gold for imaging using a Desk II cold sputter/etch unit (Denton Vacuum LLC, Moorestown, NJ). The fiber diameters were determined using AnalySIS image processing software (Soft Imaging System Corp., Lakewood, CO).

FTIR-ATR spectra were obtained in a Bruker Alpha-E using a ZnSe crystal, in transmission mode. Samples were placed directly in the ZnSe surface, and 512 scans were used to acquire the all spectra and background (ZnSe crystal), in a resolution of 4 cm⁻¹. The spectra were processed using OPUS version 6.5, and then final figures were made in Origin 7.0® from Microcal.

Contact angle measurements were carried out using the sessile drop method in DSA 10 (Kruss) equipment. Ten drops of distilled water, 10 μ L, were placed in the nanofibers surface and six measurements were taken for each. Two nanofibers samples were prepared, one was kept under UV irradiation (365 nm) for 24 h and the second one was placed under visible light (510 nm), before contact angle measurements.

4. Conclusions

In this work, a photochromic β CD_{SP} molecule, PMAA_{SP} and PMAA- β CD_{SP} polymers were successfully synthesized using DCC strategy. The structures of these molecules were confirmed by NMR and MALDI-TOF. All three molecules presented photochromic properties based on the spiropyran–merocyanine isomerization, with reverse photochromism in aqueous solution. A repeatable photo-isomerization process of the β CD_{SP} and the PMAA- β CD_{SP} was observed, switching between UV and visible light irradiation in their aqueous solution. The kinetic curves for the isomerization process were fitted into a biexponential equation and the constants k_1 and k_2 were obtained. The β CD_{SP} presented the fastest isomerization process ($k_1 = 1.4 \times 10^{-4} \text{ s}^{-1}$ and $k_2 = 4.6 \times 10^{-5} \text{ s}^{-1}$) and the PMAA_{SP} the slowest one ($k_1 = 5.3 \times 10^{-5} \text{ s}^{-1}$ and $k_2 = 2.0 \times 10^{-5} \text{ s}^{-1}$). The fastest rate constant for the β CD_{SP} is most likely due to the presence of several β CD hydroxyl groups around the spiropyran molecule, which stabilizes the merocyanine form. In the PMAA_{SP} polymer, the PMAA polymer chain was responsible for the slowest rate constant observed. Thus, combining of the β CD and the PMAA structures in the PMAA- β CD_{SP} polymer led to an intermediate photo-isomerization process ($k_1 = 9.7 \times 10^{-5} \text{ s}^{-1}$ and $k_2 = 4.1 \times 10^{-5} \text{ s}^{-1}$).

PMAA- β CD_{SP} polymer was electrospun into fibers and the photochromic properties based on the spiropyran isomerization was observed in solid state. The PMAA- β CD_{SP} nanofibers ($422 \pm 40 \text{ nm}$) present a hydrophobic surface after the annealing process, while those electrospun using PMAA ($526 \pm 24 \text{ nm}$) were hydrophilic. The presence of the spiropyran on the nanofiber surface was confirmed using FTIR-ATR, in which vibrational modes of the photochromic molecule were detected in the nanofibers material. The water contact angle measurements showed a decrease in the water contact angle for the nanofiber previously irradiated by UV light, comparing to that one irradiated by visible light. Similar results were obtained for thin films prepared by the spin coating approach, demonstrating that the change in the water contact angle is due to the presence of spiropyran on the materials surface. The photochromic properties of the PMAA- β CD_{SP} demonstrated in this work open new possibilities for light-driven nanomaterials with microenvironment controlled isomerization rates.

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