

# Cellulose-Based Liquid Crystalline Photoresponsive Films with Tunable Surface Wettability

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**ABSTRACT**: We report on a new type of liquid crystalline cellulosic films with light controllable reversible wettability. The films are prepared from a thermotropic cellulose derivative functionalized with azo-containing groups. These groups exhibit dynamic changes in interfacial properties in response to UV irradiation. The UV irradiation induces trans-to-cis isomerization in the azobenzene moiety, which causes a conformational change in the upper molecular layers of the thin films. These changes originate a hydrophobic to comparatively hydrophilic transformation of the surface. The reversible wettability of the surface results from the cis/trans photo and thermal isomerization. The UV–vis absorption spectra, as well as contact angle measurements with UV irradiation, clearly support the understanding of the phenomenon. This type of surface design enables the amplification of molecular level conformational transitions to macroscopic changes in interface properties using the means of isomerism. This opens new opportunities in surface engineering using eco-friendly cellulose manipulation.



# ■ INTRODUCTION

The search for molecules having the ability to perform conformational switching upon the action of specific external stimuli has been an active topic of investigation for decades. Examples of those external stimuli are mechanical stress or optical signals of particular wavelength, among others. These characteristics are especially interesting when applied to surfaces in order to create interfacial tunable systems. Along with the engineering of the surface morphology, the wetting properties are among one of the most important interfacial features.<sup>1,2</sup> The control of the surface wettability has been seen as an attractive technique due to its application in industry.<sup>3-6</sup> The employment of the cis-to-trans isomerization is one of the most useful methods to control surface structure and physicochemical properties. Both azobenzene<sup>7,8</sup> and stilbene<sup>9</sup> derivatives can be reversibly switched between trans and cis forms using light irradiation. An important aspect of using this method is the fact that no permanent change in chemical structure is produced.

Several works have been done on the wettability of low molecular weight molecules containing photoresponsive chromophores and polymers containing azobenzene either in backbone or as a side chain group.<sup>10–15</sup> Although the roughness of the surface has a great influence on the wettability, the change in dipole moment in these two isomeric states is another important factor which also causes the change in this physical property.

Cellulose is the main constituent of plant cells and the mostly available polymer in nature. It is made up of  $\beta$ -D-glucopyranose, each of which has one primary and two secondary hydroxyl groups that can undergo esterification and etherification among other chemical reactions.

Introduction of substituents can make cellulose soluble in water due to the destruction of crystalline regions, which arise from the inter- and intra-hydrogen bonding among hydroxyl groups. It is very well-known that hydroxypropylcellulose (HPC) can generate aqueous liquid crystalline solutions, and some HPC esters were found to originate thermotropic and lyotropic phases.<sup>16–18</sup> Thermotropic cholesteric cellulose esters were referred to in the literature to undergo a cholesteric—nematic transition upon shearing.<sup>19</sup> Besides anisotropic mechanical properties, as seen in other liquid crystal (LC) polymeric materials, the cholesteric cellulose esters also present some remarkable optical characteristics.<sup>20</sup>

It has been reported in systematic studies<sup>21–23</sup> that isotropic solutions of cellulose and cellulose derivatives were successfully electrospun into fibers using different cellulose derivatives and different electrospinning parameters, where "electrospinning" or

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electrostatic fiber spinning is a process for drawing fibers with submicrometer diameters through the action of electrostatic forces. Recently, electrospun fibers made from liquid crystalline cellulose derivatives were obtained showing a very peculiar helical twisting.<sup>24</sup> These possibilities of electrospun fibers are increasing the chance of its usability in industry. Acetoxypropylcellulose (APC) is one of the known cellulose thermotropic cholesteric liquid crystalline materials. APC was found to present the pitch in the visible range, giving rise to a set of potential optical applications. The hydroxyl groups in APC enable some interesting chemical changes in the side chain allowing for the lateral functionalization of the polymer backbone. This modification can introduce additional flexibility to the molecular design.

In this work azo-containing groups were chemically attached to the reactive hydroxyl sites of liquid crystalline APC molecules. The AzoAPC bulk material was characterized by means of differential scanning calorimetry (DSC), FTIR and <sup>1</sup>H NMR spectroscopy, polarizing optical microscopy (POM), and X-ray diffraction. In addition, thin flexible free-standing films (~60  $\mu$ m) were prepared and studied, using atomic force microscopy (AFM), X-ray diffraction, POM, and UV spectroscopy. Essays of the films wettability were also performed by measuring the contact angle of water droplets.

The study present herein concerns the synthesis, processing, and characterization of a new material based on a low-cost natural biocompatible polymer. The investigation of the system's bulk structure and its application in the production of polymeric films aims at the conception of new functional materials with surface reversible light responsive properties.

#### EXPERIMENTAL SECTION

**Materials and Reagents.** All chemicals were used as received without further purifications. The solvents (when needed) were dried by standard procedures.<sup>25</sup> HPC was purchased from Sigma-Aldrich (MW 100 000; MS = 3.5) and used as received.

**Synthesis of AzoAPC.** The starting material APC was synthesized according to Gray procedure, starting from commercially available HPC.<sup>18</sup> The average degree of substitution ( $\overline{\text{DS}}$ ) of the synthesized APC was calculated by <sup>1</sup>H NMR and was found to be  $\approx$ 2. The azobenzene derivative was obtained by a three-step synthetic route starting from commercially available *p*-aminoanisole to achieve the final azobenzene carboxylic acid derivative.<sup>26</sup> AzoAPC was synthesized by reacting an azobenzene derivative with APC previous synthesized by using a carbodiimide as coupling agent in dry THF and 4-DMAP as catalyst (Scheme 1). APC (1 g) was dissolved in dry THF (60 mL/g), and after total dissolution, 4-DMAP (21 mg) and azobenzene derivative (143 mg) were added to the reaction vessel. The resulting mixture was

cooled in an ice bath, and a solution of DCC (118 mg), in dry THF, was added dropwise. After addition, the reaction was allowed to warm to room temperature and carried overnight. The work-up was performed by evaporating the reaction solvent to 1/10 of its initial volume, and the final viscous oil was poured into a large volume of water. After 12 h in contact with water, the yellowish product was washed and dried to constant weight yielding 980 mg of AzoAPC, which was further purified. The final product was characterized by FTIR and <sup>1</sup>H NMR. The final average degree of azo substitution  $(\overline{DS})$  was found to be close to 0.2 (for further information go to Results and Discussion). It is important to stress that the purification of the AzoAPC was an issue that needed special attention due to the formation of ureas, a byproduct of the coupling agent carbodiimide, during the reaction. In the literature  $^{26-28}$ the cellulose derivative used was ethylcellulose (EC) which, after azo substitution, is precipitated in methanol. Because of its intrinsic solubility, APC is soluble in methanol (even after azo substitution) so the precipitation must be preformed in water. This change in the procedure altered the purity of the final azo cellulosic derivative. Both carbodiimides used (DCC and DIC) afford substituted ureas that are soluble in methanol but not in water. Moreover, they have similar behavior (solubility) as AzoAPC and, as a consequence, it was impossible to eliminate the compound during the standard reaction work-up. To circumvent this problem, a new "two-in-one" extraction/dialysis procedure was elaborated. A regular solid/liquid Soxhlet extractor was equipped with a dialysis membrane (Spectra/Por 4) with a cutoff of 12-14 kDa where the sample was loaded. After several days (typically 3 days) of refluxing in THF, the urea derivatives were accumulated in the bottom flask, and the pure polymer was trapped inside the dialysis membrane. The precipitation of the dialyzed polymer solution in water vields the pure AzoAPC. <sup>1</sup>H NMR (CDCl<sub>3</sub>; 400 MHz): 7.90 (sl, Ar-H); 7.96 (sl, Ar-H); 4.97 (sl, CH); 4.26-3.45 (m, CH); 2.01 (s, COCH<sub>3</sub>); 1.19–1.10 (m, CH<sub>3</sub>). IV (NaCl; cm<sup>-1</sup>): 3515 (OH), 2980, 2939, 2883, 1739 (C=O), 1603 (C=C arom), 1595 (C=C arom), 1506 (N=N), 1457, 1375, 1248, 1096, 849.

**Differential Scanning Calorimetry.** DSC measurements were performed on a calorimeter from Setaram (model DSC 131) at a cooling or heating rate of 5  $^{\circ}$ C/min, ranging from -40 to 200  $^{\circ}$ C.

**Preparation of Thin Films.** The thin films were prepared using diluted solutions of AzoAPC in pure acetone. The solutions were poured into homemade cylindrical containers with inside lateral walls covered with a Teflon mold. Those cylindrical cells have a cover, which allowed the solvent to evaporate while the films were cast over the inside walls due to a controlled centrifuge motion (800 rpm) for 5 h. The films were dried for 2 h, until constant weight, in a vacuum chamber at room temperature, yielding homogeneous films with an average thickness of 60  $\mu$ m (measured with a Digimatic micrometer from Mitutoyo; average of 10 measurements in different areas of the films).

Polarized Optical Microscopy. The textures of both the bulk materials and corresponding films were observed using a polarizing



Figure 1. FTIR spectra of (a) APC and the corresponding (b) AzoAPC. The values of the wavenumber associated with the stretching of aromatic double bonds (1603 and 1500 cm<sup>-1</sup>) are indicated in the AzoAPC spectrum.

optical microscope Olympus BH2 coupled to a Casio EX-F1 Exilim Pro photo camera.

UV-vis Spectrophotometry. All the measurements were made using a Helios Gamma from Thermo Spectronic. A  $\sim 10^{-5}$  M of AzoAPC in chloroform was prepared for solution measurements. For AzoAPC film studies a drop of polymer in acetone was evaporated (until constant weight) to produce a film on the inside wall of the UV-vis measuring cuvette. The films were submitted to 20 min of UV-vis irradiation/relaxation cycles, with a 365 nm UV light (xenon source) and daylight, respectively. After each stage, an absorption spectrum was acquired.

**X-ray Diffraction.** Powder samples XRD patterns were collected using a PANalytical X'pert PRO diffractometer in Bragg–Brentano ( $\theta$ /  $2\theta$  coupled) geometry with graphite monochromated Cu K $\alpha$  (1.54 Å) radiation.

Atomic Force Microscopy. For the topographical characterization of the films surface, AFM data were acquired using a dimension 3100 spm with a Nanoscope IIIa controller from digital instruments (DI). All measurements were performed in tapping mode TM under ambient conditions. A commercial tapping mode etched silicon probe from DI and a 90  $\mu$ m × 90  $\mu$ m scanner were used.

Wettability. Wetting measurements (as a function of UV irradiation) were performed by placing water droplets on the AzoAPC films surface and taking close-up photograph with a Casio EX-F1 Exilim Pro in order to find the contact angle of the droplets. Snapshots of the drop were taken after periods of 20 min of UV irradiation (365 nm from a 4 W UV source and an intensity of  $1 \times 10^{-5}$  mW/cm<sup>2</sup> on the film surface) and after periods of 20 min relaxation under daylight. This procedure was repeated several times. Each picture was taken by using a new drop of water to ensure that the evaporation did not influence the measurements. The contact angle measurements were obtained from the snapshots using ImageJ 1.410 software. The results presented were obtained for different areas of the film and represent averages of three measurements.

## RESULTS AND DISCUSSION

The AzoAPC obtained by the coupling reaction between APC and the azo moiety was chemically characterized by FTIR and <sup>1</sup>H NMR. In the FTIR it is clearly visible the appearance of both the representative bands of the azo moiety (azo bond and aromatic double bonds) in the APC substrate (Figure 1a,b), indicating that the substitution was achieved. The stretching of the aromatic double bonds give rise to a duplet at 1603 and 1595 cm<sup>-1</sup>, and the weak peak at 1506 cm<sup>-1</sup> is assigned to the vibration of N=N bond. Both assignments are in accordance with the literature.<sup>29</sup> Another important datum is the weakening of the broad peak around  $3500 \text{ cm}^{-1}$  in the AzoAPC spectrum when compared with the APC's.

This is obviously due to the esterification of some of the available hydroxyl groups of the APC with the azo moiety yielding esters groups that vibrate at the same frequency as the "pre-existing" acetyl groups at roughly 1740 cm<sup>-1</sup>. The <sup>1</sup>H NMR data are coherent with the FTIR and give us even more information in terms of the extension of the esterification, e.g., the average degree of substitution of azo moiety in the starting APC ( $\overline{DS}_{AZO}$ ). From the NMR spectrum of APC a  $\overline{DS}_{AO}$  = 2.0 was calculated for the acetylation of HPC, <sup>30</sup> and using this value, it was possible to estimate the degree of acetylation of AzoAPC ( $\overline{DS}_{AZe}$  = 0.2) by using the following equation

$$\overline{\mathrm{DS}}_{\mathrm{AZO}} = \overline{\mathrm{DS}}_{\mathrm{AO}} \frac{3 \sum A_{\mathrm{A}\Gamma}}{8 A_{\mathrm{AC}}} \tag{1}$$

where  $\Sigma A_{A\Gamma}$  is the sum of the integrated areas of the aromatic protons (at ~7.9 and ~7.0 ppm) and  $A_{AC}$  is the integrated area of the acetyl groups.

The thermal properties of compounds APC and AzoAPC, as determined by DSC and POM, are presented in Figure 2a-c. Figure 2a represents the plots of the low-temperature thermograms of APC (dashed line) and AzoAPC (solid line). The observed glass temperature  $(T_g)$  and the profile of the corresponding second-order transition are similar for both compounds, which indicates that the azo substituent does not play a determinant role on the transition from glass to cholesteric phase in these materials. On the other hand, the DSC scan plots, at high temperatures, represented in Figure 2b, are significantly different for AzoAPC and APC. In the case of AzoAPC the firstorder cholesteric-isotropic temperature transition is about 40 °C lower than for APC. Moreover, the transition enthalpy is much higher for AzoAPC. The cause of these findings may be attributed to the stabilization of the isotropic phase of AzoAPC due to the fact that the substitution reaction was promoted in the isotropic phase.<sup>31</sup> The higher transition enthalpy may also be explained by a more significant difference in the order degree at the phase transition in the case of the AzoAPC.

The texture observed for AzoAPC at room temperature, presented in Figure 2c, indicates that a mesomorphic material was obtained. XRD results both for bulk and film materials, at room temperature, are presented in Figure 3a-d. By comparing parts a and b of Figure 3, it is possible to conclude that the local structures of bulk APC and AzoAPC are not significantly different. In both cases the diffraction pattern can be predominantly described by two broad peaks corresponding to the repeat distance between consecutive glucosidic units (11.3 Å) and the lateral packing distance of the cellulosic backbone (4.3 Å).

The fact that the inclusion of terminally linked azo moieties does not result in a major change to the X-ray diffraction pattern may be due to the similar length (11-12 Å) and lateral packing distances of the azobenzene rigid core (trans conformation) in comparison with the main-chain cellulose characteristic packing distances. These results are in agreement with those previously reported for other cellulose derivatives<sup>32</sup> and confirm the DSC and POM results obtained before, which indicate that AzoAPC is liquid crystalline at room temperature. In Figure 3c,d XRD results of APC and AzoAPC films can be compared. The local structures of APC and AzoAPC films are significantly different. As can be observed in Figure 2c, the diffraction pattern of APC



Figure 2. Thermograms of APC (---) and AzoAPC (---) (a) Glass transition temperature, upon heating (second cycle). (b) Chlolesteric to isotropic transition, upon cooling (second cycle). (c) Polarized light micrograph (between cross-polarizers) showing a characteristic texture of AzoAPC observed at room temperature.



Figure 3. X-ray diffraction pattern, at room temperature, of (a) bulk APC, (b) bulk AzoAPC, (c) APC film, and (d) AzoAPC film.

film is similar to those observed for bulk materials. In contrast to this, the pattern observed for AzoAPC film is far more complex, showing the presence of a large number of Bragg reflections in addition to the broad peaks characteristic of the mesomorphic state of APC and AzoAPC. This result indicates that the process used for producing the films induces a partial crystallization of



Figure 4. Two typical lamellar topographies of the free surface of a free-standing AzoAPC film. (a) and (b) represent the top view image of the height scan for two lamellas sizes. The AA' cross section was taken along the line marked on the (b) top view image.



**Figure 5.** (a) Photoimage of an AzoAPC film partially irradiated with UV (a.2) and with visible light (a.1 and a.3). (b1) and (b2) represent POM images of the same spot of an AzoAPC film before and after UV irradiation, respectively. (c) Absorption spectrum of AzoAPC for three cycles consisting of illumination with UV light for 20 min (Exp = exposure) followed by visible light irradiation for 20 min (Rel = relaxation) with the exception of the third cycle in which the film was allowed to relax for 2 h. The inset shows the isosbestic point (435 nm) and the 450 nm peak decrease. (d) Evolution of the absorption spectrum of AzoAPC film after being exposed for 20 min to UV radiation (t = 0 min). The absorption spectrum of AzoAPC not irradiated with UV is also given (No UV). The inset represents the absorption spectra of AzoAPC in a diluted acetone solution.

AzoAPC materials. The AFM observation of the AzoAPC films surface confirms the X-rays results in the sense that a layered structure can be the signature of the crystalline organization induced by the film preparation. The thickness of the lamellar structure was found to be in average of the order of 3.4 nm, irrespective of the size of the lamellas (see Figure 4a,b).

APC and also AzoAPC are not soluble in polar solvents like water. AzoAPC has even higher hydrophobicity, which can be



Figure 6. Scheme of the AzoAPC film surface undergoing a structural change upon exposure to UV light in addition to a reversible visible light isomerization. (a) Water droplet on the initial more hydrophobic (trans conformation) surface before UV radiation. (b) Water droplet on the less hydrophobic (cis conformation) surface after UV radiation. (c) Water droplet on the same AzoAPC film after one cycle of irradiation UV–vis light.

modified with UV irradiation. In addition, it can be expected that the linking of the Azo groups to the APC main chain will not significantly constrain the mobility of these side groups due to the liquid crystalline character associated with the flexibility of the polymer chain. Along with that characteristic, AzoAPC also responds to the UV light that produces a conformational change. The effect of UV upon the surface may be detected by means of simple macroscopic visual observation and also by POM, UV-vis spectrophotometry, and wetting studies. In Figure 5a, a photo of a partially UV-vis-irradiated film is shown. In that picture we can see the macroscopic optical difference between the irradiated section of the film (a.2) and the nonirradiated (a.1)and a.3) regions that were previously protected with a mask. POM images are shown in Figure 5a inside a2 and a3. In these pictures, the effect of UV irradiation may be observed due to slight changes in the birefringence of some areas of the film.

The UV-vis absorption spectra of AzoAPC are shown in Figure 5c,d. The spectrum of AzoAPC very diluted in acetone is shown in the inset of Figure 5d. The absorption data of the solution show a preeminent peak at 354 nm and a weak band at 442 nm which are characteristic of the azo chromophore. It is known from the literature that both peaks are related with to  $\pi - \pi^*$  and  $n - \pi^*$  transition bands of the *trans*-azobenzene, respectively, and their relative populations provide information concerning the double-bond isomerization.<sup>33</sup> The films spectra

also show two peaks at 354 and 442 nm which are indicative that both in solution as in film the N=N bonds are in the trans conformation. Upon UV irradiation, the intensities of transition bands changes, lowering the intensity of 354 nm and increasing the intensity of 442 nm, which indicates the trans-to-cis isomerization. The widths of the trans state peaks in the film spectra are quite wide, in contrast to the spectrum of the solution. This may be attributed to the fact that most of the molecules are strongly bounded in the solid film.

Figure 5c shows the AzoAPC absorption spectra obtained for the same film exposed to UV and visible radiation for 20 min intervals, alternately. As mentioned previously, the trans-to-cis and the cis-to-trans isomerization can be followed by observing the relative intensities of peaks at 354 and 442 nm, especially the one with more energy. From the analysis of the spectra set (Figure 5c) it is possible to infer the existence reversibility of the isomerization of the azo moiety exists, since both "no UV" and "3 Rel 2h" show similar patterns. Moreover, 20 min UV irradiation of the AzoAPC film seems to be enough to saturate the trans-tocis isomerization. This is corroborated by the fact that after another cycle of excitation/relaxation the trans-to-cis state is recovered. Even starting from half of N=N bond trans conformation (e.g., 1 Rel and 2 Rel), the same trans-to-cis isomerization is achieved (e.g., 1 Exp and 2 Exp). From those results we can also infer that the relaxation time of the cis-to-trans conformation is



Figure 7. Contact angle changes for an AzoAPC film with or without UV irradiation for two different wavelengths. After several cycles of irradiation, the amplitude of the contact values increases (this is especially evident for the value of 365 nm wavelength). The experimental errors are estimated to be less than 2%.

close to 20 min (e.g., 1 Rel and 3 Rel 2 h). This value was calculated from the kinetics of cis-to-trans thermal isomerization using the data from Figure 5d and the model applied by Serra and Terentjev.<sup>34</sup> In order to follow the total relaxation of the cis-to-trans configuration, additional UV-vis spectroscopy experiments were performed and are shown in Figure 5d. In this case, the original nonirradiated film  $(\cdots)$  was exposed to UV light for 20 min and then left unexposed. Afterward, UV irradiation spectra were collected with time intervals of 20 min. As expected, the intensity of the band spectrum at 354 nm increases with time and after 12 h nearly matches the starting nonirradiated film spectrum. In the inset of Figure 5c the isosbestic point (435 nm) is shown as well as the 450 nm peak decrease. The cis-to-trans back-isomerization after 12 h can be interpreted by taking into account that the film layer/air interface is the main responsible for the photoisomerization mechanism. However, in the case of the film, the internal medium below the air/layer surface also plays a significant role. The effect is not present in the case of diluted solutions.

The possibility of controlling the wetting properties of the film surface is also a very important consequence of the phenomenon of trans-to-cis isomeric changes and their reversibility. Those phenomena can be observed by means of water droplets' contact angle measurements. The wettability of the AzoAPC films was tested by placing water droplets (around 20  $\mu$ L) on the film surface. The contact angle of the droplet shows a high degree of hydrophobicity of the nonirradiated AzoAPC surface (see Figure 6a). After UV irradiation, the film becomes less hydrophobic as shown in Figure 6 b. This might be due to the change in the dipole moment in the azo moiety. Because of its stereo arrangement symmetry, the trans isomer has a small dipole moment and a low surface free energy which make it more hydrophobic when compared to the cis isomer.<sup>1</sup> After the relaxation under visible light irradiation it can be seen that the film regains its hydrophobic character as shown in Figure 6c.

Two main parameters influence the wetting properties of the material: one is the chemical composition of the surface, and the other is the surface roughness.<sup>35–37</sup> Two well-known models based on those two parameters can be employed to explain the wetting properties of surfaces. In the Wenzel model the liquid drop penetrates and follows the surface profile. The surface characteristics (either hydrophilic or hydrophobic) are enhanced by the surface roughness defined by the factor r.<sup>37</sup> In the Cassie–Baxter model,<sup>37</sup> applied to hydrophobic surfaces, the liquid drop does not follow completely the surface feature, and

part of the drop stays upon the air trapped in the roughness. If  $\varphi$  is the solid surface fraction in contact with the droplet, a combination of the Cassie–Baxter and Wenzel models leads to the more general expression

$$\cos \theta_{\rm c} = r\phi \cos \theta_{\rm Y} + \phi - 1 \tag{2}$$

where  $\theta_c$  is the macroscopic contact angle,  $\theta_Y$  is the Young contact angle corresponding to the solid fraction of the surface, and *r* is the surface roughness.<sup>2,38</sup>

The induction of reversible changes on the wettability of surfaces by photochemical rearrangement reactions, including cis-to-trans isomerization of azobenzene moieties by means of UV–vis irradiation, is also described in the literature.<sup>33,39–41</sup>

In this work, as schematically represented in Figure 6, the trans-to-cis isomerization of azobenzene moieties resulting from the effect of UV irradiation promotes the exposure of the azo dipole at the surface. As a consequence of the higher dipole moment of the cis isomer and its location precisely at the surface, the corresponding hydrophobic character is reduced. The contact angle measurements presented in Figure 7 are a clear indication of this effect. In the case of the isomer trans conformation (before UV irradiation) the surface is predominantly hydrophobic due to the apolar character of the terminal metoxy groups which demarcate the film/air interface. This is evidenced by the measurements of the contact angle of a water droplet on the surface, which is higher than  $90^{\circ}$  (close to  $120^{\circ}$ ), shown in Figure 7. As stated above, the surface becomes less hydrophobic when the cis conformation is promoted by UV irradiation. In that case the contact angle decreases, assuming values which approaches nearly 90°, shown in Figure 7.

Those findings may be interpreted according to the combination of the Cassie—Baxter and Wenzel models, considering that the conformational change from trans to cis corresponds to an increase of the hydrophilic area fraction of the surface described by a higher value of  $\varphi$  in eq 2.<sup>2</sup> The hydrophobic/hydrophilic surface character changes, due to UV irradiation, were found to be reversible as shown in Figure 7. Similar effects have been previously reported by other authors both in Langmuir— Blodgett and in solid polymer films.<sup>39,40</sup> The difference between the effect of the 254 and 365 nm wavelength radiation on the contact angle is due to the fact that the trans-to-cis isomerization absorption peak (354 nm) is closer to the 365 nm radiation wavelength. Therefore, the degree of isomerization produced by 365 nm radiation is significantly higher. The degree of isomerization is discussed above and shown in Figure 5.

In this work, the amplitude of the contact angle variations, due to the effect of UV irradiation cycles, increases with time for both wavelengths used. This is especially evident for 365 nm radiation. The increase of the hydrophilic surface area fraction given by the  $\varphi$  parameter with increasing number of radiation cycles may be due to a progressive alignment of the cis-azo moieties promoted by the successive trans-to-cis cycles as a kind of hysteresis effect.

# CONCLUSION

The preparation of novel cellulosic films with light stimuli responsive surface properties, associated with their reversible wettability, is presented. The hydrophobic—hydrophilic changes induced by light in the films show a very broad range as characterized by the contact angle measurements. The system described herein was prepared from a new cellulose azo-based material. This study is particularly relevant because, for the first time, as far as known by the authors, the properties of Azo cellulosic liquid crystalline materials were achieved at room temperature.

The kinetics of the cis/trans isomerization was accessed by means of UV spectroscopy and the corresponding relaxation time of  $\sim$ 20 min was measured. The system was characterized using different experimental techniques leading to a broad understanding of the underlying phenomena. The azo materials investigated in this work open new perspectives related to the opportunity of combining the liquid crystalline properties of the most abundant polymer in nature with the wide applications scope of functional materials.

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