

Spectroscopy analysis of spiropyran-merocyanine molecular transformation

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Abstract. Spiropyrans materials are very studied for their application in transduction systems for biosensors. In this work the protocol of generation of multi and mono layers films and the efficiency of the transduction system are analyzed. The analyses were based on UV/Vis and Infrared vibrational spectroscopy in Attenuated Total Reflexion mode (ATR). The films were deposited in glass substrates, using (3-Aminopropyl) trimethoxysilano like linker. The UV/Vis spectra show that the deposition protocol allows the generation of a homogenous film from the first layer. Similar results were observed in ATR. The efficiency of the films, when analyzing them after light UV irradiation, is greater in the samples with two and three layers of deposit, since its absorption peaks are most intense in UV as in ATR. The efficiency falls from the fourth deposit layer. In ATR the efficiency is assumed by the vibration of the NO bond at 1338 cm^{-1} .

1. Introduction

Photochromism is the process of inducing color changes in a medium by incident electromagnetic radiation. Many different compounds have been found to exhibit photochromism; some of them are ones called spiropyrans, which have been the most extensively photochromic material studied over the past decades, since the discovery of the spiropyrans photochromic reactions in 1952 by Fisher and Hirshberg [1].

In particular, spiropyran (SP) has a great potential for application in optical devices, for example as data storage films and waveguides [2, 3] mainly, because of their physical and chemical properties could be controlled by illumination. More recently these molecules have been proposed for use in photoswitching of protein activity (biosensors transducers) [4,5].

When the SP is dissolved in solvents with low polarity, a colorless solution was obtained; when the solvent polarity is increased, colored solution was obtained. In fact solvents polarity not only affect to the color solution, the molecular structure is affected too [6]. Even in polar solvents certain spiropyrans in equilibrium with their trans-merocyanine forms were found.

In general, SP absorbs in the ultra violet (UV) region and not in the visible region. Upon UV illumination, the SP colorless isomer undergoes heterolytic cleavage of the NO bond to form the colored isomer (merocyanine). The coloration change (colorless to blue) in the sample is the physical

observation of the molecular transformation. This process can be reversed by visible illumination, see figure 1 [7].

The radical group NO would be changed to obtain different absorption peaks for the merocyanine state. The main feature of these materials is the several cycles of conversion and reconversion process that could be done. Each cycle limits or decreases the optical properties of the sample, by the photodegradation processes.

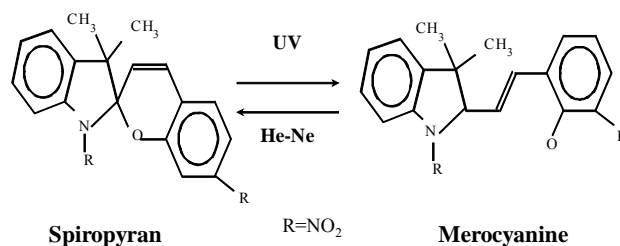


Figure 1. Schematic molecular structure of the sample before UV illumination (i.e. $\lambda = 355$ nm) and after isomerization. The process is reversible under visible illumination (i.e. $\lambda = 633$ nm).

Crucial for all the applications where the spiropyrans have found, it is a detailed understanding of the transitions kinetics between the spiropyran (SP) to merocyanine (MC) forms. The conversion of SP to MC occurs via a photochemical route involving ultraviolet photons. The transition from SP to MC has been studied and determined to occur on the picosecond to nanosecond time scale, but it depends of the source of transformation applied. For this, it is necessary to analyze the molecular behavior of these kinds of structures. In this context, vibrational spectroscopies would seem to be appropriated to study them, since they provide subtle details about molecular structure in liquids, gas or solid state. For example, Infrared [2, 7-10] and Raman [8,10] spectroscopic studies were done to observe the conformational and intermolecular interactions between the polymeric base and the spiropyran. Other works analyzed the solvent polarity effects into spiropyran molecule, using only the absorption spectrum of the structure [11-13].

Attempts to detect the main structural changes occurring in the ring-opening/closing process in spiropyrans, using IR vibrational spectroscopy, were reported by Schiele and Arnold for a series of indolinonitrospiropyrans [14] and later by Guiliano et al. for benzothiazolinonitrospiropyrans [15].

In this work, two spectroscopic techniques were used to study the ring-opening process of spiropyran to merocyanine in an acetone solution. The infrared vibrational analysis was done via the Total Attenuated Reflexion mode (ATR) whereas the UV/Vis spectroscopy was used as preliminary analysis of the opening process. The UV-Vis shows the changes in the visible region due to the molecular transformation. Infrared spectra show the conversion process from spiropyran to merocyanine in two ways: by the new peaks generation and by the changes in the line form of the peak form due to the opening process.

2. Materials and methods

2.1. Sample preparation

The spiropyran used in this work was 1',3'-Dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H) indole], 97%, which was dissolved in 40 ml of ethanol. The functionalized substrate was prepared in an aqueous solution with 1% mM of 3-Aminopropyltrimethoxysilane, silane is the linker between corning crystal and spiropyran molecule. Figure 1 show the spiropyran molecular structure used in this work and their corresponding merocyanine form after UV illumination. For multilayer generation, a solution of 10 ml of pyridine and 90 ml of dimethylformamide was used as linker between the spiropyran multilayers. The spiropyran was added to the functionalized substrate by substrate immersion with a frequency of 10 times/minute, into the spiropyran solution for two different times; a half and one hour. So for two layers generation, the substrate was immersed once in the pyridine/dimethylformamide solution and twice for a film of three spiropyran layers and so on.

2.2. UV/Visible spectroscopy

The absorption of spiropyran – merocyanine films, was performed in a Genesis UV/Vis spectrometer. First the spiropyran functionalized films were measured and after that the films were exposure for 10 minutes to UV irradiation inside a GelDoc Transilluminator with a 365 nm lamp; the power intensity of the 365 lamp was $500 \mu\text{W}/\text{cm}^2$. A functionalized substrate was used as baseline in all the measurements.

2.3 Infrared spectroscopy

An Infrared spectrometer FTIR Bruker Vertex 70 in Attenuated Total Reflexion (ATR) sampling mode was employed. A diamond ATR crystal of one reflection was used during the measurements. The silane spectrum was used as baseline and the acquisition time was 30 seconds to obtain the final vibration spectra. For the molecular transformation analysis, functionalized films were measured first and after the films were exposure for 10 minutes to UV irradiation inside a GelDoc Transilluminator. For the conversion kinetics analysis, the spiropyran films were irradiated during 20 minutes with a 4 watts Blacklight fluorescent tube used in billets identification, and 20 spectra were obtained.

3. Results and Discussion

3.1 UV/Vis Spectroscopy

Figure 2 shows the UV/Vis absorption spectra of the spiropyran functionalized films, prepared for a half and one hour. The spectra show a peak associated to the spiropyran state in the ultraviolet region at 370 nm and another less intense peak at 560 nm associated to the merocyanine state. The beginning of the ring-opening process in the colorless samples, could be due to two factors: the solvent polarity used in solutions and to the deposition protocol (mechanical movement at low frequency).

In both figures it is possible to observe that films with two, three and four layers have the more intense absorption peaks. The sample with five layers has the low intensity peaks; in fact the best sample, in both deposition times, is the sample with two layers. This behaviour could be associated to the molecular opening inhibition due to large films deposited.

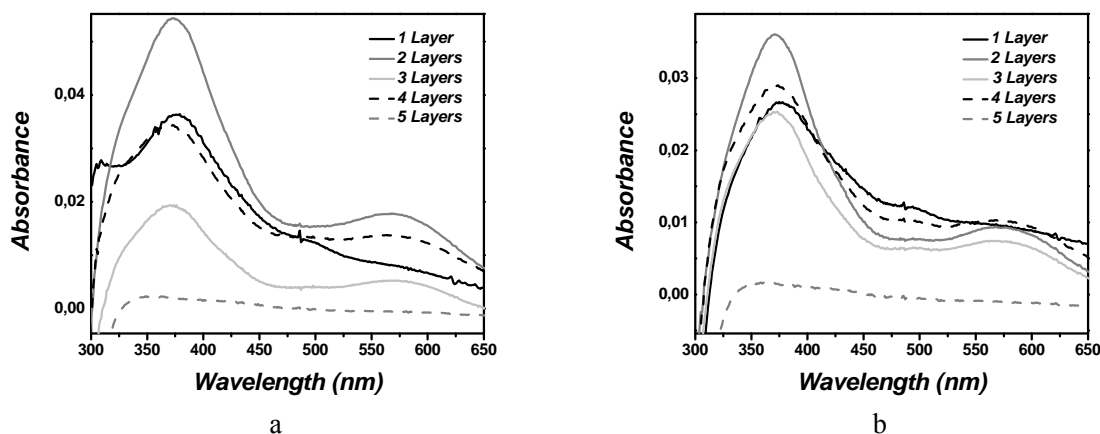


Figure 2. UV/Vis absorption spectra of samples at a).- half hour and b).- one hour; of immersing in the spiropyran solution.

After that, the spiropyran functionalized films were illuminated with UV radiation, by 10 minutes in the GelDoc Transilluminator. Even no colour is present in the samples due to the thickness of the deposited films, UV/Vis spectra show the increasing of the absorption peaks in the samples of two, three and four layers. Figure 3 shows this behavior for two and four layers films; the merocyanine spectra show a more intense absorption peak in the merocyanine state. In fact the presence of the peak at 560 nm is more evident. These results are in agreement with other works [3,8]. The intensity

increasing for the peak at 370 nm, is due to a better absorption efficiency when the conversion is induced.

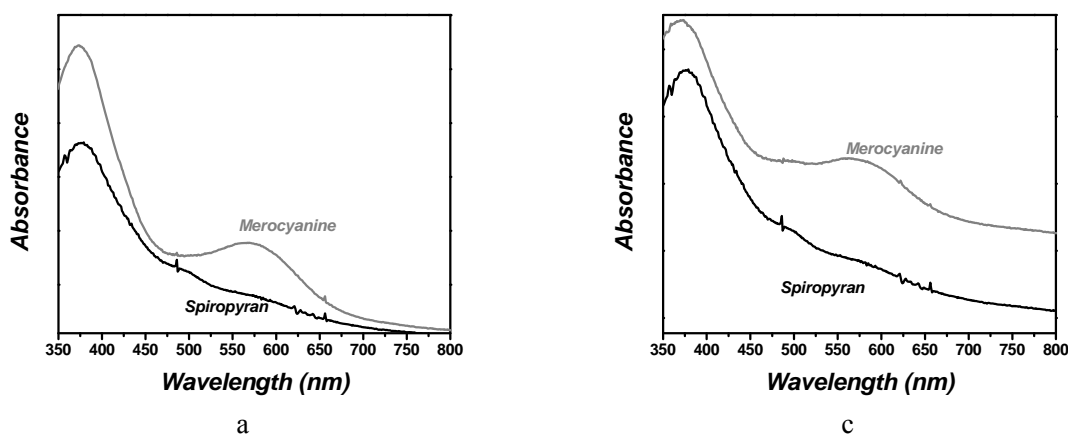


Figure 3. UV/Vis spectra of samples before and after UV irradiation.
a) Two layers, b) Four layers.

3.2 Infrared Spectroscopy

Figure 4 shows FTIR results in the finger print region ($1250\text{--}1650\text{ cm}^{-1}$). The peaks are associated to the molecular bonds for the merocyanine state. Infrared absorption presents an increase in the intensity of the peaks associated to the NO bond (at 1338 and 1520 cm^{-1}) and the generation of new peaks associated to the bonds: CN, CH bending (symmetric and asymmetric) and to the aromatic ring; when the ring-opening process occurs. In the CH region (data not showed), the mainly difference is the disappearing of the peak at 3025 cm^{-1} , which is due to the breaking of the CO or CN bond when the ring-opening process occurs.

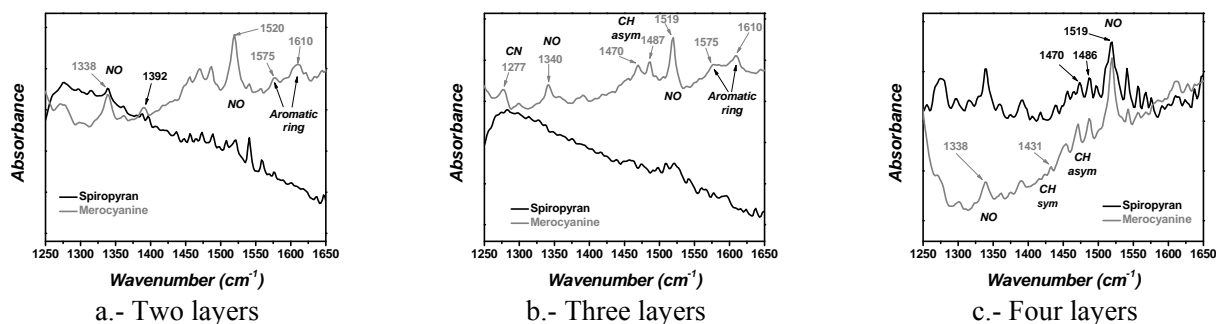


Figure 4. Infrared spectra of samples before and after UV irradiation.

Finally in figure 5, the FTIR absorption associated to the kinetics of the ring opening process is presented. The spiropyran films were irradiated in a continuous way during 20 minutes with a 4 watts Blacklight fluorescent tube. The samples were measured by ATR mode and the spectra were acquired on real time ever minute. This figure shows only seven spectra of the all kinetics for a clear lecture. The generation or transformation of the peaks observed at 1 minute is very clear, especially in the region 1300 to 1700 cm^{-1} . Due to the low intensity of the source of irradiation, changes are more notorious after 10 minutes of sample irradiation.

Table 1 summarizes the frequency values of the FTIR peaks and their assignment, observed in figure 5 when the ring-opening process occurs.

The FTIR kinetics analysis could be performed when another UV source, with large power.

Table 1. Frequency values of the FTIR peaks observed in the kinetics of the ring opening processes.

Figure number	Wavenumber	assignment	Figure number	Wavenumber	assignment
1	1338	NO	4	1527	NO
2	1376 and 1395	CH bending sym.	5	1558 and 1618	Aromatic ring
3	1456 and 1473	CH bending asym.	6	1650	C=C

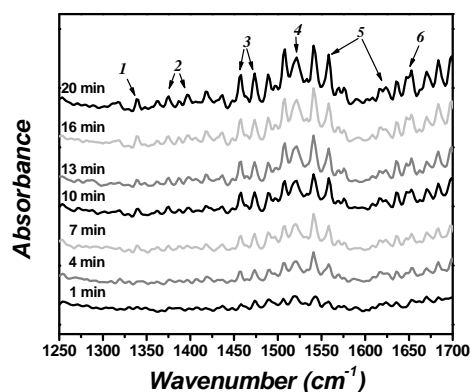


Figure 5. Kinetics of the ring opening process by FTIR of the sample with three layers.

4. Conclusions

In this work an analysis of the ring-opening process of spiropyran to merocyanine state was done by UV/VIS and Infrared spectroscopies. UV/VIS shows that the spiropyran functionalized films with two and three layers present the best response. A peak at 560 nm associated only to merocyanine appears. The vibrational response confirms these results obtained by UV/VIS. In the finger print region, infrared spectra show changes in intensity of the peaks associated to the bonds: NO, CN, CH and to the aromatic ring; when the ring-opening process occurs. The FTIR kinetics analysis show how the ring opening process is done, the increasing and generation of peaks could be observed better after 10 minutes of UV irradiation.

5. References

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