

# ATR-FTIR Spectroscopy and their Applications in the Ring-Opening Reaction of Spiropyran Polymers

\*R. Delgado Macuil<sup>1</sup>, M. Rojas López<sup>1</sup>, M. Bibbins Martinez<sup>1</sup>, V. Camacho Pernas<sup>2</sup>.

<sup>1</sup>*Centro de Investigación en Biotecnología Aplicada del IPN, Tepetitla, Tlaxcala, México.*

<sup>2</sup>*Universidad Politécnica de Puebla, México.*

\*Contact author e-mail: [rdmacuil@yahoo.com.mx](mailto:rdmacuil@yahoo.com.mx)

**Abstract.** In this work we applied FTIR vibrational spectroscopy in Attenuated Total Reflectance mode, to observe the transient species, in an acetone solution at very low weight concentration, due to the molecular transformation from spiropyran to merocyanine form, in four different spiropyran types. In UV/VIS spectroscopy a new peak generation in the visible region was observed. In ATR, the peak shift from 1487 cm<sup>-1</sup> to 1510 cm<sup>-1</sup> and two new peaks generation at 1568 cm<sup>-1</sup> and 1595 cm<sup>-1</sup> are associated to the ring. Also, due to the C-O break down bonding when the molecular transformation was done, the peak associated to the O-C-N bond diminished in intensity and the new peaks generations between 900 to 1000 cm<sup>-1</sup>, are associated to this molecular transformation.

## INTRODUCTION

With the development of the electronics and information industries, the importance of functional dyes with high optical properties has increased. Since the discovery of the spiropyrans photochromic reactions in 1952 by Fisher and Hirshberg [1], the interest in the use of spiropyran dyes, for photoelectric and photoelectrochemical devices, has been increasing. Due this, these materials have been the most extensively photochromic materials studied over the past decades.

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 orientation is affected too [6].

Photochromism is the process of inducing color changes in a medium by incident radiation. For example, SP absorbs in the ultra violet (UV) region. Upon UV illumination, the SP colorless isomer undergoes heterolytic cleavage of the NO bond to form the merocyanine colored isomer (MC), the radical group NO would be changed to obtain different absorption peaks for the merocyanine state, see Fig. 1, the process can be reversed by visible illumination. The coloration change in the sample is the physical observation of this molecular transformation. The SP most features are that several cycles of conversion and reconversion process could be done; even each cycle limited or decreases the optical properties of the sample, by the photodegradation processes.

Crucial for all the applications where the spiropyrans have found, it is a detailed understanding of the transitions kinetics between the spiropyran (SP) and 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. For this, it is necessary analyzing 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 [2,6-9] and Raman [7,9] spectrometries studies were applied to observe the conformational and intermolecular interactions between the polymeric base and the spiropyran. Others works analyzed the solvent polarity effects into spiropyran molecule, using only the UV/VIS absorption spectrum of the structure [10-12].

Attempts to detect the main structural changes occurring in the ring-opening/closing process in spiropyrans (in solid state), using IR vibrational spectroscopy, were reported by Schiele and Arnold for a series of indolinonitrosopiropyrans [14] and later by Guiliano et al. for benzothiazolinonitrosopiropyrans [15]. In the latter study, the photochromic conversion was performed by UV – irradiating the spiropyrans, dispersed in a solid matrix.

In this work, two spectroscopies techniques were used to study the ring-opening process of spiropyran to merocyanine in an acetone solution (a polar solution). The vibrational analysis was done by the Total Attenuated Reflexion mode (ATR). 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 peaks forms due to the ring-opening process.

## EXPERIMENTAL WORK

### Sample fabrication

All the solutions were prepared of the following way: spiropyrans were weighed in an analytical balance; 0.1g of SP1 and 0.1mg of SP2, SP3 and SP4, were diluted in 4 milliliters of acetone. The dilution was favoured by means of solely manual agitation. After that the spiropyran form was analyzed, all solutions were exposing to the sun light for different time interval. The spiropyrans used in this work are summarized in the table 1, the table shows too, the expose time to sun irradiation and the final colour of the solution after that.

TABLE 1. Spiropyrans photochromic materials analyzed.

Name	Molecular formula	Expose time (Hours)	Colour after Sun irradiation
SP1	1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]naphth[2,1-b][1,4]oxazine]	72	sky blue tenuous
SP2	1',3'-Dihydro-8-methoxy-1',3',3'-trimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(2H)-indole]	2	brown
SP3	1,3-Dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]phenanthr[9,10-b](1,4)oxazine]	2	dark blue
SP4	1',3'-Dihydrospiro [cyclohexane-1,2'-[2H]imidazo[4,5-b]pyridine]	24	dwell

In Fig. 1, we show the molecular structures of the spiropyrans and merocyanines (when ring opening process occurs after sun irradiation) of the photochromic materials used in this work.

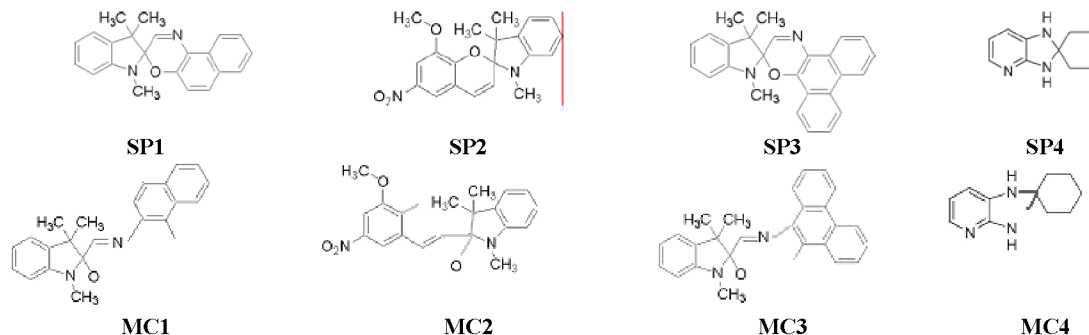


FIGURE 1. Spiropyran and Merocyanine forms (ring-opening process).

### UV-VIS spectroscopy

The absorption of acetone-spiropyran solutions, were performed in a Genesis UV/VIS spectrometer. First the solution without sun irradiation was measurement and later the solution after sun irradiation. Acetone was used as baseline in all the measurements.

### Infrared spectroscopy

Attenuated Total reflexion mode of the Infrared spectrometer Bruker Vertex 70 was used. The spectrum of acetone was used as background in all the measurements; the crystal used was a diamond crystal of one reflection. And the exposure time was 30 seconds for each sample.

For a better discussion the infrared spectra were divided in two regions, the CH region and the finger print region.

## RESULTS AND DISCUSSION

### UV-VIS spectroscopy

Figure 2 shows the absorption spectra for the four different spiropyrans used in this work and their correspondent merocyanine form. In the figures, black dot line is acetone (just for reference), continuous black line is spiropyran and grey continuous line is merocyanine. In Fig. 2 the transformation from spiropyran to merocyanine is observe by: the shifted to higher frequencies (from 600 nm to 514 nm) and also the increase of the absorption peak in SP1, the shifted to higher frequencies (from 590 nm to 545 nm) in SP2, the absorption increase in almost three times for SP3 and the generation of a new broad peak in the visible region in SP4 (between 390 to 615 nm).

According to the analysis done, the SP1, SP3 and SP4, are who could be handled of effective form for any kind of applications (for example in biosensors like transducers), due to their photochromic phenomenon is bigger.

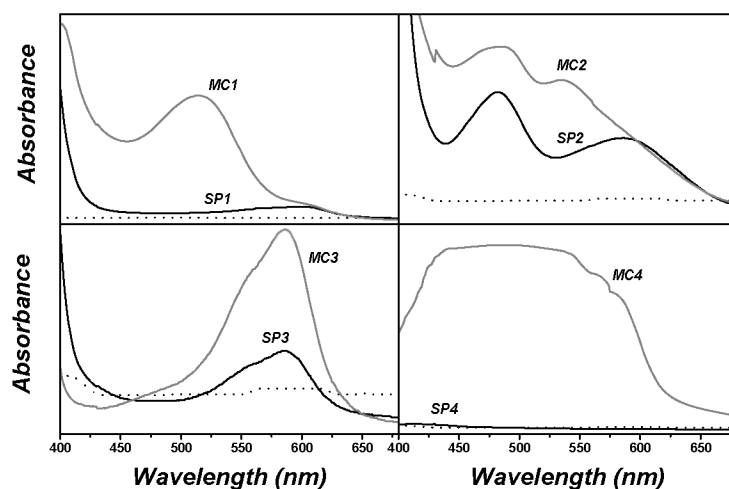


FIGURE 2. UV/Vis absorption for the spiropyran and merocyanine state, for the four samples used in this work, the black dot line is the acetone spectrum.

### Infrared spectroscopy

**C-H region.** In Fig. 3, the vibrational response for the spiropyran and merocyanine form is displayed. The spectrum of each sample were obtained separately, initially being in the spiropyran state at the moment that the SP-acetone solution was prepared, and later when the solution was exposed to sun irradiation, as it were mentioned already previously. For the case of the SP1, when SP1 transform into MC1, the molecule is now oriented in the space with single radicals  $\text{CH}_3$  in the end of the molecule, whereas in SP form the radicals  $\text{CH}_3$  was in the middle, see Fig. 1. That is why in merocyanine form the peak at  $3025 \text{ cm}^{-1}$  present in SP1 disappears for merocyanine state. And also the band at  $2850 \text{ cm}^{-1}$ , associated to the CH stretching symmetric bond, decreased in intensity.

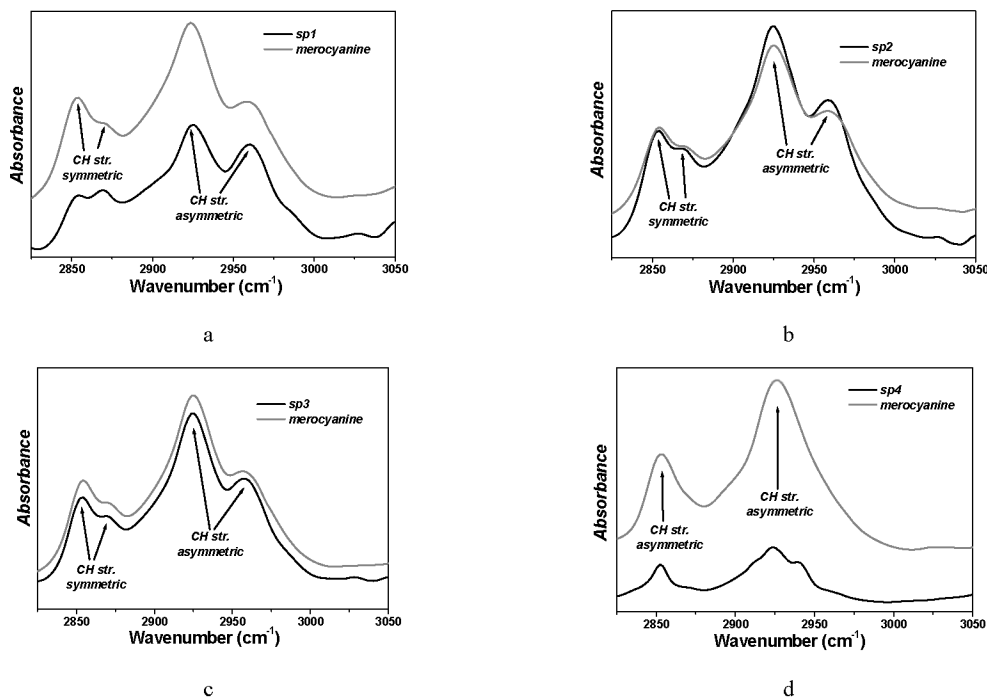


FIGURE 3. Infrared spectra for the spiropyran in the CH region.

For the SP2 and their MC2 form, significant difference between two spectra is not observed. Maybe this is because when the ring-opening process occurs the radicals  $\text{CH}_3$  keeps their position in the middle of the molecular structure, see

Fig. 1. And except for a diminishing in the asymmetric stretching vibrational mode and the  $3025\text{ cm}^{-1}$  peak disappears, the spectra are very similar.

In the merocyanine molecule of the SP3, it presents the same direction characteristic of the SP1 form, the  $\text{CH}_3$  is in the end of the molecule, see Fig. 1. The MC3 spectrum only shows the peak disappear at  $3025\text{ cm}^{-1}$ .

In the case of the SP4, similar to SP1, also presents a great difference in the intensity of the CH vibrational bands. Also, in MC4 form, the peak located at  $2925\text{ cm}^{-1}$  begins to narrowed, on the other hand, the peak at  $3025\text{ cm}^{-1}$  in the SP4 it does not appear, case in opposition to the others three previous spiropyrans.

**Finger print region.** In the finger print region, from  $800$  to  $1800\text{ cm}^{-1}$ , see Fig. 4, are present the principal changes associated to the ring opening process. In each figure the open circles shows the principal changes and the arrow shows peaks characteristics only to the merocyanine form.

Due to the C-O break down bond when the ring-opening process is done, two things must be occur: the peak associated to the O-C-N bond must to diminish in intensity and new peaks must be present in the spectra.

Also due to the orientation changes when the ring-opening process is done, peaks associated to the  $=\text{C-O}$ , C-N, ring and C-H bonds must changes in their form.

In the spectra of SP1 and MC1, the remarkable differences are in the O-C-N bond when the spiropyran peak now changes to a broad peak with two peaks inside in merocyanine state. The same occurs to the peak associated to the C-H bending vibrational mode, in SP state the symmetric peak is bigger in intensity but in MC state the asymmetric peak is now the most intensity peak.

Also the peaks  $1204$ ,  $1248$ ,  $1317$ ,  $1572$  and  $1595\text{ cm}^{-1}$ ; appears in the spectrum of merocyanine, due to the new orientation of the  $=\text{C-O}$  bond and the ring.

In the spectra of SP2 and MC2, the significant changes, also occurs in the O-C-N bond and in the C-H bond; and new peaks associated to the  $=\text{C-O}$  bond ( $1204$  and  $1247\text{ cm}^{-1}$ ) and to the ring ( $1564$ ,  $1574$  and  $1596\text{ cm}^{-1}$ ) appears in merocyanine state.

In the spectra of SP3 and MC3, the significant changes, also occurs in the O-C-N bond and in the C-H bond; and new peaks associated to the  $=\text{C-O}$  bond ( $1204$  and  $1247\text{ cm}^{-1}$ ) and to the ring ( $1564$ ,  $1574$  and  $1596\text{ cm}^{-1}$ ) appears in merocyanine state.

Finally in SP4 and their merocyanine state, the remarkable differences are in the C-N bond and to the ring ( $1555$ ,  $1577$  and  $1595\text{ cm}^{-1}$ ) when the ring-opening process occurs.

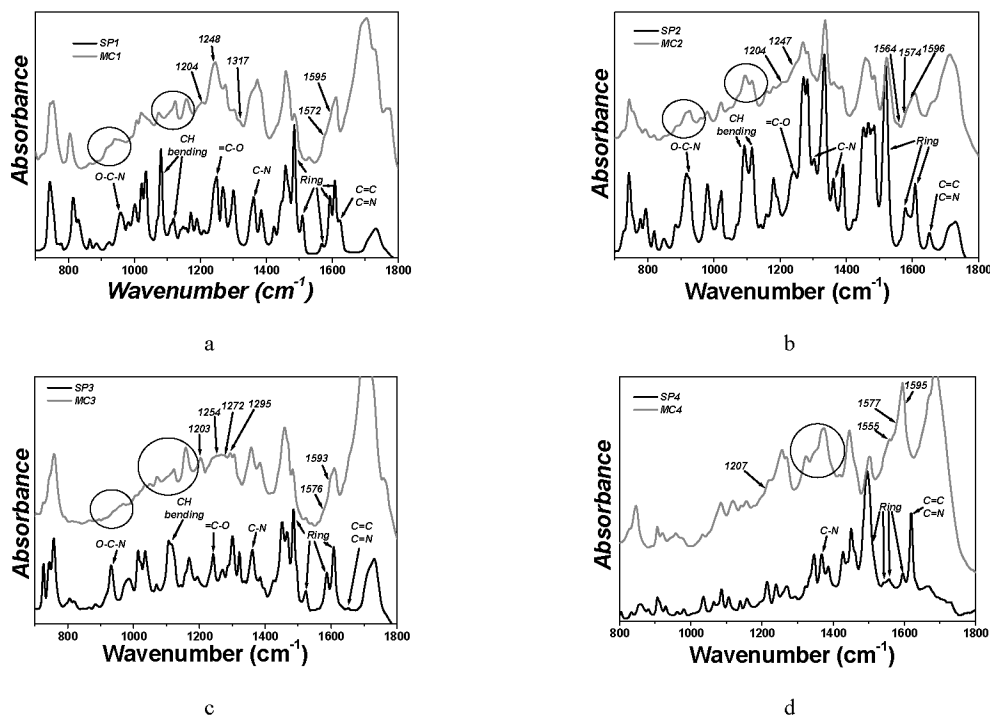


FIGURE 4. Infrared spectra for the spiropyrans in the finger print region.

## CONCLUSIONS

In this work an analysis about the ring-opening process of spiropyran to merocyanine state is done by UV/VIS and Infrared spectroscopies.

UV/VIS shows that the spiropyrans with oxazine and pyridine groups are the most adequate to any kind of applications, due they present the biggest changes in absorption. The group indole is the spiropyran that present the lower changes in absorption. Even the SP1 is the molecule that shows the lower physical changes.

The vibrational results confirm these obtained by UV/VIS for the SP1 and SP3 both from oxazine group. In the C-H region, the mainly difference is the disappearing of the peak at  $3025\text{ cm}^{-1}$ , which is due to the break of the C-O or C-N bond when the ring-opening process occurs. In the finger print region, infrared spectra present diminish in intensity of the peak associated to the O-C-N bond and the orientation changes in the peaks associated to the bonds: =C-O, C-N, C-H bending and to the ring; when the ring-opening process occurs.

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