Structural Analysis of Spiropyran Polimers using ATR Spectroscopy

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Abstract. We have used infrared spectroscopy in attenuated total reflection (ATR) mode to analyze the interactions between the polymeric base and solvent with a photochromic material (spyropiran). We used cellulose acetate as polymeric base and the spyropiran; 1,3,3 trimethyl indoline-5-nitro benzopyrane. Thin films with different weight concentrations of SP were deposited in the polymeric base. The infrared spectra show bands whose frequencies are associated to several molecular bondings. It was observed a decreasing in intensity of absorbance for C=O stretching mode of the acetate group at 1720 cm\(^{-1}\) and for C=C stretching mode for the main chain at 823 and 982 cm\(^{-1}\) both associated to the presence of SP in polymeric films.

1. Introduction

Spiropyran (SP), have a great potential for applications in optical devices, for example as data storage films and waveguides\(^1\), principally because of their physical and chemical properties would be controlled by laser illumination. 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. Figure 1 shows this process, the cis-cisoid isomer is an intermediate process in this molecular transformation and it is associated to sample degradation\(^3\).

![Figure 1. Schematic molecular structure of the sample before UV illumination (i.e. \(\lambda = 355 \text{ nm}\)) and after isomerization. The process is reversible under visible illumination (i.e. \(\lambda = 633 \text{ nm}\)). The X isomer is an intermediate process in the conversion cycle between spiropyran to merocyanine.](image)

The radical group NO would be change to obtain different absorption peaks for the merocyanine state. The principal features of these materials are the several cycles of conversion and reconversion process that could be done. Otherwise each cycle generate a decreasing in the optical properties of the sample.

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For this reason, it is necessary to analyze the molecular behavior of these kind of structures. Infrared and Raman vibration techniques help us to visualize the interactions between molecules (SP, solvent and polymeric base). Infrared\textsuperscript{1,3-6} and Raman\textsuperscript{4,6} spectrometries studies have been used to observe the conformational and intermolecular interactions between the polymeric base and the spyropiran. Others works analized the solvent polarity effects into spyropiran molecule, using only the absorption spectrum of the structure\textsuperscript{7-9}.

In this work we used infrared spectroscopy in attenuated total reflection (ATR) mode to analyze the interactions between the polymeric base, solvent and SP.

2. Experimental work

2.1. Fabrication of thin samples

The samples were fabricated using the gravity-deposition technique, due to this our technique is simpler and cheaper. We use Cellulose Acetate (CA) as polimeric matrix and the spyro 1,3,3 trimethyl indoline-5-nitro benzopyrane. The fabrication process was as follow: we mixing 0.25\%, 0.5\%, 1\%, 2\% and 5\% of spiropyran (SP) in weight concentrations with 0.2 gr of CA dissolve in 10 ml of methylene chloride. The solution was deposited in a Petri covered box and dried at room temperature for 48 hrs. Our samples present a good optical quality and also optical defect-free was observed, see figures 2a and 2b.

![a. Spyropiran state. b. Merocianyne state.]

2.2. ATR Spectroscopy

The spectroscopy analysis was done using a Brucker Infrared Spectrometer Vertex 70 in Attenuated Total Reflectancy mode (ATR). Initially we obtained the ATR spectrum for CA in powder. This is our background spectrum, see figure 3.

![Figure 3. ATR spectrum of CA polymeric base.]

Figure 3, shows ATR spectrum of CA polymeric base intensity peaks for CH\textsubscript{3} molecular bonding in four different assignments and for the acetate group at 1720 cm\textsuperscript{-1}, which are the characteristic peaks for cellulose acetate. The infrared spectra shows the frequencies associated to each molecule bondings. This spectrum was obtained using polymeric chain in powder. In table 1, are enlisted the principal frequency peaks for CA polymeric base.

Figure 4, shows spyropiran interaction with methylene chloride used as solvent. The experiment was done as follow: initially was measured the spyropiran in powder, after that the solvent methylene chloride and finally we dissolvent 0.5 \% of spyropiran in 3 ml of methylene chloride.
Table 1. IR characteristic absorption frequencies for CA.

| Assignment                  | Wavenumber (cm\(^{-1}\)) | Assignment                  | Wavenumber (cm\(^{-1}\)) |
|-----------------------------|---------------------------|-----------------------------|---------------------------|
| OH Stretching               | 3400                      | C=O Stretching              | 1720                      |
| CH\(_3\) Asymmetric         | 2950                      | CH\(_3\) Asymmetric        | 1432                      |
| Stretching                  |                            | Deformation                |                           |
| CH\(_3\) Symmetric         | 2860                      | CH\(_3\) Symmetric        | 1370                      |
| Stretching                  |                            | Deformation                |                           |
| Acetate C-C-O Stretching    | 1235                      | Structural Factor           | 603                       |
| C-O Stretching             | 1050                      |                             |                           |

In the small plot we can observe an amplified view of the spectra for the 500-2000 region, in this plot we can observe the principal spyropiran peaks. Red line is methylene chloride absorbance, whereas green and blue lines correspond to spyropiran in powder and in solution (spyropiran dissolvent in methylene chloride) respectively. Absorbance spectrum of methylene chloride (red line) shows characteristic peaks of this solution: CH\(_3\) stretching (3048/2980 cm\(^{-1}\), asymmetric/symmetric), CH\(_3\) bending (1264/888 cm\(^{-1}\), asymmetric/symmetric) and C-Cl bond (724/700 cm\(^{-1}\), asymmetric/symmetric).

The same figure shows a 10 cm\(^{-1}\) frequency shift between the spyro in powder and spyro plus methylene spectra. This shift is due to the solvent effect on the spyro [7-9]. As we can observe in figure 4, some peaks of spyropiran molecule are covered by solvent peaks, for example, peaks for frequencies lower than 750 cm\(^{-1}\). Table 2 enlist all the frequencies associated to the spyropiran molecule (with and without shift) observed between 760 and 1750 cm\(^{-1}\).

Table 2. ATR characteristic absorption frequencies for syropiran dissolved in methylene chloride.

| Stable wavenumbers (cm\(^{-1}\)) | Shifted wavenumbers (cm\(^{-1}\)) |
|----------------------------------|-----------------------------------|
| 744                              | 813 shifted to 823                |
| 1024                             | 971 shifted to 982                |
| 1587                             | 1279 shifted to 1289              |
| 1610                             | 1512 shifted to 1522              |
| 1642                             | 1642 shifted to 1654              |

Finally ATR spectra of spyropiran deposited in CA polymeric base was measured, using methylene chloride and dried at room temperature for 48 hrs. This was done for different weight concentrations (0.25%, 0.5%, 1%, 2% and 5%). In figure 5, fundamental vibration modes of spyropiran molecule are
indicated, where: CH in plane stretching at 744 and 2937 cm$^{-1}$, O-C-N stretching at 934 cm$^{-1}$, CH out of plane stretching at 1118 cm$^{-1}$, C-N stretching at 1303 cm$^{-1}$, for the ring at 1488, 1517, and 1587 cm$^{-1}$, C=C and C=N stretching at 1642 cm$^{-1}$.

To make more noticeable the observation of the intensity peaks at: 1334, 1488, 1517, 1562 and 1587 cm$^{-1}$, figure 6 shows the amplified region between 1250 and 1700 cm$^{-1}$. Such peaks are associated to the spiropropan concentration into polymeric matrix. In this form, it is noticeable the systematic increasing of the SP intensity peaks with the concentration variation of spiro in CA polymeric base.

![Figure 5. ATR spectra of spiropropan deposited in CA polymeric base dissolved with methylene chloride at several SP concentrations.](image1)

![Figure 6. Amplified plot of the ATR spectra of fig. 5 to show the generation or increasing of the intensity peaks associated to spiropropan presence.](image2)

3. Conclusions
We have applied infrared ATR spectroscopy to study polymeric films constituted by: a polimeric base, a solvent and a photochromic material. The samples analyzed were prepared with several concentrations of SP. ATR technique was sensible to the absorption peaks associated to the polimeric base and to SP molecule. Absorbance peaks associated to SP were detected between 1300 and 1600 cm$^{-1}$ and the increases in intensity with SP concentration were observed principally for the ring at 1517 cm$^{-1}$ and to 1587 cm$^{-1}$. Absorbance intensity peaks are almost 10 cm$^{-1}$ shifted, for the polimeric films, due to the solvent effect.

References
[1] Bobrovsky A, Boiko N and Shibaev V 1999 *Advanced Materials* **11** 1025.
[2] Ramos García R, Delgado Macuil R, Iturbe Castillo D, González de los Santos E and Soriano Corral F 2003 *Optical Quantum Electronics* **35** 641.
[3] Crano R Guglielmetti 1999 *Organic Photochromic and Thermochromic Compounds Vol 2* (New York: Kluwer Academic) Chapters 1-2.
[4] Takayanagi M, Nakata M, Ozaki Y, Iriyama K and Tasumi M 1997 *Journal Molecular Structure* **407** 85.
[5] Hoon L, Jaung Y and Jeong S 2002 *Bulletin Korean Chemical Society* **23** 1045.
[6] Takayanagi M, Nakata M, Ozaki Y, Iriyama K and Tasumi M 1997 *Journal Molecular Structure* **407** 239.
[7] Chibisov A and Gorner H, 1997 *Journal of Physics Chemistry A* **101** 4305.
[8] Khimenko V, Chibisov A and Gorner H, 1997 *Journal of Physics Chemistry A* **101** 7304.
[9] Wojtyk J, Wasey A, Kazmaier P, Hoz S and Buncel E 2000 *Journal of Physics Chemistry A* **104** 9046.