

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

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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 observe. In ATR, the peak shift from 1487 cm^{-1} to 1510 cm^{-1} and two new peaks generation at 1568 cm^{-1} and 1595 cm^{-1} 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^{-1} , 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 indolinonitrosopyrans [14] and later by Guiliano et al. for benzothiazolinonitrosopyrans [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.