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# Achromatic Ellipsometry: Theory and Applications

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### Abstract

In the present chapter, the theory and some applications of Achromatic Ellipsometry, including transmittance, absorbance, and emission, are presented. The new methodology introduced here comprises the calculation of Stokes parameters using Fourier series analysis. Light polarization was determined by calculating the polarization degree, anisotropy, asymmetry parameters, and rotational and ellipsometry angles. The nematic liquid crystal E7™ doped with 4,7-bis{2-[4-(4-decylpiperazin-1-yl) phenyl]ethynyl}-[2,1,3]-benzothiadiazole (5A) within twisted and parallel structures, was used to illustrate the applications for this technique, that has been shown to be an innovative and versatile tool to correlate the photophysics with materials structure.

**Keywords:** ellipsometry, optical spectroscopy, Stokes parameters

## 1. Introduction

The understanding of light polarization from materials absorption, emission, and reflection can be addressed by matching one or more polarizers in the optical path of conventional photoluminescence and UV-vis spectrometers, called polarized photoluminescence and polarized absorbance, respectively [1–4]. These methodologies have been applied with the aim of acquiring information on the molecular arrangement (anisotropy and order factor) [3–6]. Besides that, Circular Dichroism spectroscopy has also been widely used to understand molecular organization based on their chirality [2, 6, 7]. Nevertheless, these techniques fail to identify all possible polarization states when applied separately. In the case of photoluminescence, for example, it is possible to get information from linear polarization states, but not from circular

ones. The polarized absorption, on the other hand, can elucidate the molecular order, but does not provide information on circular birefringence effects and Circular Dichroism. The last one consists in the difference between left and right circularly polarized light, thus resulting in the molecular asymmetry [6, 8, 9]. For instance, the study of energy transfer processes by means of the investigation of emitted polarized light can be very complicated when the polarized state is not completely described.

In this sense, Emission Ellipsometry (EE) is a technique that, combined with the Stokes theory, allows the complete description of the emitted light polarization states [6, 8, 9] being, in this manner, an excellent alternative in the study of energy transfer processes, mainly in polymeric materials [2, 5, 10, 11]. In addition, it is possible to obtain full information regarding molecular organization [2, 12], anisotropy [10], and asymmetry [13] factors in photoluminescent materials. All these studies and several applications in diverse materials lead to the development of a new method for Raman Optical Activity studies, named ellipsometric Raman spectroscopy (ERS) [14, 15]. In this new methodology, Basilio et al. [14] have been shown that EE combined with the Stokes theory can also be applied, not only for emitted but also for the scattered light. From this experiment, one can obtain meaningful information about materials optical activity even for easily photodegradable ones (both biological and polymeric) due to the limited exposition to exciting light.

This chapter aims a detailed review of Achromatic Ellipsometry from the appliance of Stokes theory on the determination of polarization parameters to its applications on materials studies.

## 2. Stokes theory

In the middle of the nineteenth century, the light polarization has had been mathematically characterized by Augustin Jean Fresnel (1788–1827) and Dominique François Arago (1786–1853), among others. Notwithstanding, the concept of partially polarized light was only formulated until the period around the year 1852, by Sir George Gabriel Stokes [12]. Fresnel and Arago used to describe polarized light in terms of its polarization ellipse. Such representation was incomplete, because it did not include partially polarized light. Stokes, on the other hand, solved the problem by demonstrating that it was possible to completely characterize any arbitrary polarization state from four experimental measurements (observables), in his work "On the Composition and Resolution of Streams of Polarized Light from Different Sources" [16]. Here and now, these observables are designated as Stokes parameters, which describe nonpolarized, partially, and complete polarized lights. Despite its fundamental contribution, his work was practically ignored by the scientific community for almost 100 years. In 1946, the Nobel laureate Subrahmanyan Chandrasekhar formulated the equations for radioactive transfer of partially polarized light [12], which was only possible due to Stokes' work. In addition to Stokes theory, new material developments for achromatic optical elements made possible the measuring of all polarization states as a function of wavelengths (optical spectrum), i.e., the necessary observables to enlighten the materials structure [2, 13, 14, 17, 18].

## 2.1. Polarization ellipse

Light description in terms of polarization ellipse, which is valid as long as the studied light is completely polarized, is very convenient. It allows the characterization of several states of light polarization using one equation [14, 18] and can result in forms interpreted as linearly and circularly polarized light. Beyond that, from the concept of polarization ellipse, it is possible to understand Stokes' description to identify all states of light polarization, including partially polarized beams [12]. In this sense, polarized light propagating along the $z$ direction, and the electric field in two orthogonal components propagating along $x$ and $y$ directions can be represented by the following equations:

$$E_x(z, t) = E_{0x} \cos(\tau + \delta_x) \tag{1}$$

$$E_y(z, t) = E_{0y} \cos(\tau + \delta_y) \tag{2}$$

where $E_{0x}$ and $E_{0y}$ are the maximum amplitude, $\delta_x$ and $\delta_y$ are the phase constants at $x$ and $y$ axis respectively, and $\tau = \omega t - kz$ is the diffuser. From Eqs. (1) and (2), one can obtain the equation for an arbitrary instant of time, $t$:

$$\frac{E_x^2}{E_{0x}^2} + \frac{E_y^2}{E_{0y}^2} - 2\frac{E_x E_y}{E_{0x} E_{0y}} \cos\delta = \sin^2(\delta) \tag{3}$$

where $\delta = \delta_y - \delta_x$. Equation (3) is named polarization ellipse [12, 19]. The ellipse described by Eq. (3) has its $a$ and $b$ axis rotated by an angle $\Psi$ relatively to the reference plan $xy$, as can be seen in **Figure 1**.

From the diagram above (**Figure 1**), it is possible to write the components $E'_x$ and $E'_y$ relatively to the components $E_x$ and $E_y$ and to the angle $\Psi$, in a way that:

$$E'_x = a\cos(\tau + \delta') \tag{4}$$

$$E'_y = \pm b\sin(\tau + \delta') \tag{5}$$

$$\frac{E'^2_x}{a^2} + \frac{E'^2_y}{b^2} = 1 \tag{6}$$

Equation (6) describes a standard ellipse, straight, where $a$ and $b$ are the major and minor axis, respectively [2, 12, 19]. It is important to note that, when the phase angle equals 90° and 270°, the angle $\Psi$ will be zero. This condition is only reached when $E_{0x}$ and $E_{0y}$ are zero, that is, for linearly polarized light along vertical ($y$-axis) or horizontal ($x$-axis) directions. Another important parameter is defined as ellipticity ($\chi$) [5, 12]:

$$\tan(\chi) = \pm\frac{a}{b} \tag{7}$$

In this case, if $a = b$, which means that the light is left or right circularly polarized or even random, then the ellipticity became zero.
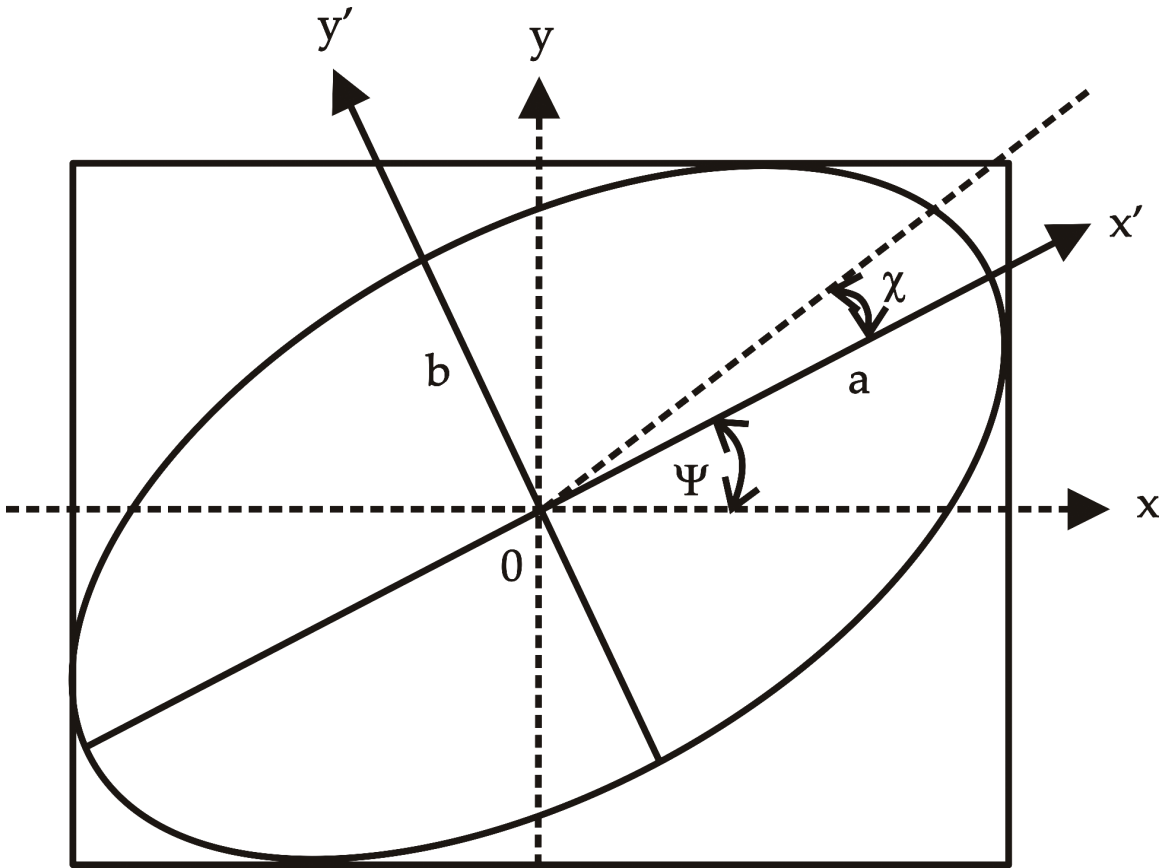
**Figure 1.** Polarization ellipse representation.

## 2.2. Stokes parameters

It is well known that the amplitude of the optical field cannot be observed [12, 15, 16, 19]. However, its intensity, derivative from the temporal average of square amplitude, can be observed. Therefore, one can obtain the polarization ellipse observables by taking the temporal average of nonobservables from the polarization ellipse. By doing that, it is possible to collect four parameters, the Stokes parameters [12, 16]. Consequently, Stokes parameters are a natural outcome of the wave theory of light, in a way that provide a complete description of any light polarization state [12]. More important, they are exactly the measured quantities.

Formerly, the Stokes parameters were used only for describing intensity measurements and polarization states of optical fields. Still, when these parameters are found in the form of column matrix (also known as Stokes vectors) they can lead to the study of spectroscopic observables [11–14, 17, 18]. Therein formalism, in Eq. (6), each term represents the temporal average, such as in Eq. (8) in its general form [19]:

$$\frac{E_x^2(t)}{E_{0x}^2} + \frac{E_y^2(t)}{E_{0y}^2} - 2\frac{E_x(t)E_y(t)}{E_{0x}E_{0y}} \cos\delta = \sin^2(\delta) \tag{8}$$

and the temporal average for each term is given by [12, 16]:

$$E_x^2(t) = \frac{1}{2}E_{0x}^2, \quad E_y^2(t) = \frac{1}{2}E_{0y}^2, \text{ and } E_x(t)E_y(t) = \frac{1}{2}E_{0x}E_{0y}\cos\delta \qquad (9)$$

Combining the equations (8) and (9), one can extract the Stokes parameters[1] from the following equation:

$$(E_{0x}^2 + E_{0y}^2)^2 - (E_{0x}^2 - E_{0y}^2)^2 - (2E_{0x}E_{0y}\cos\delta)^2 = (2E_{0x}E_{0y}\sin\delta)^2 \qquad (10)$$

arranged as follows:

$$\begin{aligned} S_0 &= E_{ox}^2 + E_{oy}^2 \\ S_1 &= E_{ox}^2 - E_{oy}^2 \\ S_2 &= 2E_{0x}E_{0y}\cos\delta \\ S_3 &= 2E_{0x}E_{0y}\sin\delta \end{aligned} \qquad (11)$$

Using the parameters above, Eq. (10) can be rewritten in terms of complete polarized light:

$$S_0^2 = S_1^2 + S_2^2 + S_3^2 \qquad (12)$$

The Stokes parameters, resulted from the definitions in Eq. (11), are real quantities expressed in terms of intensity. More than that, they are the observables from the polarization ellipse and, therefore, they represent the optical field.

The first parameter, $S_0$, represents the total light intensity. The following parameters describe the differences between: (i) horizontal or vertical linear polarization – $S_1$, (ii) linear polarization at $\pm 45°$ – $S_2$, and (iii) left or right circular polarization – $S_3$. For partially polarized light, using the Cauchy-Schwarz Inequality [12, 16], Eq. (12) can be rewritten as follows:

$$S_0^2 \geq S_1^2 + S_2^2 + S_3^2 \qquad (13)$$

where equality applies for completely polarized light and inequality for nonpolarized or partially polarized light. Since the Stokes parameters directly reflect the observables, one can represent the rotation angle ($\Psi$) and the ellipticity ($\chi$) using Eqs. (11) – (13) as:

$$\tan(2\Psi) = \frac{S_2}{S_1} \qquad (14)$$

$$\sin(2\chi) = \frac{S_3}{S_0} \qquad (15)$$

Finally, the degree of polarization ($P$) can be described using the Stokes parameters for any polarization state [2, 12, 19]:

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[1]Stokes parameters can also be obtained by means of plane waves. This solution can be found at Refs. [12, 16, 19].

$$P = \frac{I_{pol}}{I_{tot}} = \frac{(S_1^2 + S_2^2 + S_3^2)^{\frac{1}{2}}}{S_0} \tag{16}$$

where $I_{pol}$ means intensity of the sum of polarized components and $I_{tot}$ is the total intensity of the light beam. The value $P = 1$ corresponds to completely polarized light, whereas $P = 0$ corresponds to nonpolarized and $0 < P < 1$ to partially polarized light.

## 2.3. How to measure Stokes parameters

As described in earlier sections, the Stokes parameters are real observables. To measure them, it is necessary at least two optical components with which the light must interact to be analyzed successfully. Generally, these elements are polarizers and quarter-wave plates that can be set up in several ways in order to acquire the Stokes parameters. These optical components can be mathematically represented as a Muller matrix [2, 12], and, from the mathematic relations, the Stokes parameters can be obtained (see Eq. (18)).

There are several available methods to get the Stokes parameters. Collet describes diverse optical configurations and measurement modes to calculate them [12]. Although, one must be careful with systematic errors, alignment and intensity corrections that can be introduced in the system depending on the chosen experimental assembly, mainly on those which the exchange of optical elements during the experiment is required. One way to avoid this problem is to keep the optical elements fixed, reducing a significant amount of errors from alignment and problems from light intensity corrections due to reflections or absorptions. This is the main proposal of this chapter: keeping the optical elements fixed, the observables will be decomposed by Fourier series. This method also provides the advantage of using achromatic optical elements that work in a broad spectral range, especially at visible spectrum.

The representation of light polarization states as Stokes parameters in the form of column matrix (Stokes vector) can be seen below:

$$S = \begin{pmatrix} S_0 \\ S_1 \\ S_2 \\ S_3 \end{pmatrix} \tag{17}$$

In this matrix formalism, the effects on the light polarization from any beam due to optical components can be mathematically represented also by matrix, in this case, the Muller matrix [12, 14]. Concerning the fixed optical components, the analysis method via Fourier series employs a quarter-wave plate and a fixed linear polarizer, as can be seen in **Figure 2**.

From the arrangement shown in **Figure 2**, it is possible to correlate the intensity of emerging field ($E'_x$ and $E'_y$) with the Stokes parameters from incident field ($E_x$ and $E_y$) through Eqs. (5), (14), and (16):

$$I(\theta) = \frac{1}{2}[A + B.\sin{(2\theta)} + C.\cos{(4\theta)} + D.\sin{(4\theta)}] \tag{18}$$
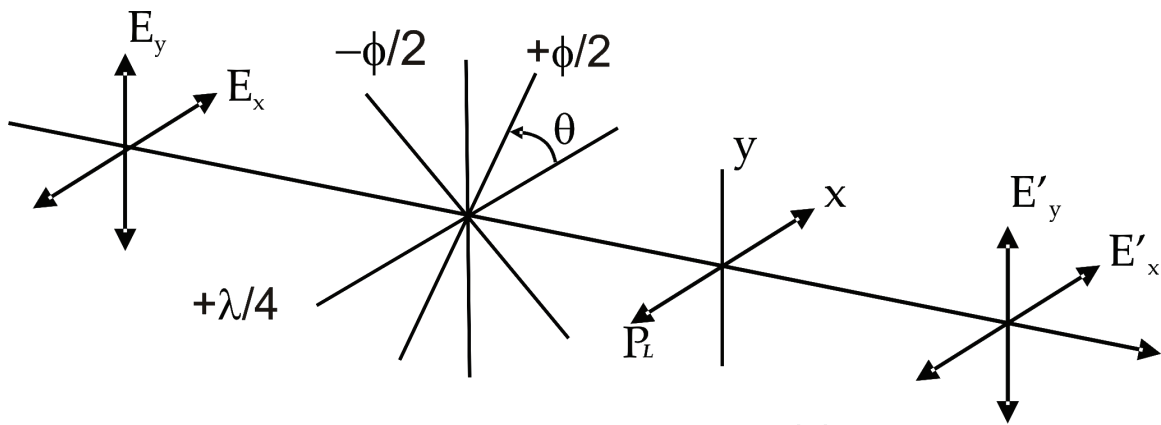
**Figure 2.** Diagram of an electromagnetic wave propagating through a quarter-wave plate, rotated by an angle θ, and a linear polarizer $P_L$ (horizontal) for the measurement of Stokes Parameters.

where for a polarizer with transmission axis along the horizontal direction (*x*-axis): $A = S_0 + \frac{S_1}{2}$, $B = -S_3$, $C = \frac{S_1}{2}$, and $D = \frac{S_2}{2}$; or a polarizer with transmission axis along the vertical direction (*y*-axis): $A = S_0 - \frac{S_1}{2}$, $B = S_3$, $C = \frac{-S_1}{2}$, and $D = \frac{-S_2}{2}$.

Eq. (18) is a truncated Fourier series, with a constant term *A*, a term with double frequency (*B*), and two more terms with quadruple frequencies (*C* and *D*). As a Fourier series, this equation admits only one solution for parameters *A*, *B*, *C*, and *D*; thus resulting in a very precise way to obtain Stokes parameters. It is also likely to obtain the polarization degree (*P*) for the emerging light, from Eq. (18). In addition, Alliprandini-Filho [2], describes the asymmetry factor (*g*) and Circular Dichroism acquired from Stokes parameters, providing more complex information about the chirality of the molecules that compose the studied material. One can see that the technique described here is a powerful tool in the understanding of material conformations and structure.

### 2.3.1. Anisotropy

Similarly to the new approach as presented at previous sections, Therézio et al. [10] outlined a new method to determine anisotropy using Stokes parameters. In this methodology, the Stokes parameters are firstly rewritten as a function of electric field intensities, as described in Eq. (18). Then, the *y* component is considered in the same direction as the laboratory frame of reference, and *x* in the horizontal direction at the same reference. Besides, $E_{ox}^2 = I_{0x}$ and $E_{oy}^2 = I_{0y}$, where $I_{0i}$ is the beam intensity at *i* direction. Then, considering that a sample is excited by a beam at *y* direction is possible to obtain $E_{ox}^2 = I_{\parallel, \perp}$ and $E_{oy}^2 = I_{\parallel, \parallel}$, where $I_{\parallel, \perp}$ refers to the emission at perpendicular direction (⊥) due to parallel excitation (∥). Hence, the first and second equations from Eq. (11) set can be expressed as:

$$\begin{cases} S_0 = I_{\parallel, \perp} + I_{\parallel, \parallel} \\ S_1 = I_{\parallel, \perp} - I_{\parallel, \parallel} \end{cases} \quad (19)$$

From the conventional equation that determines the anisotropy factor, *r* [1, 10]:

$$r = \frac{I_{\parallel,\parallel} - I_{\parallel,\perp}}{I_{\parallel,\parallel} + 2I_{\parallel,\perp}}. \tag{20}$$

combined with Eq. (11), the anisotropy factor as a function of Stokes parameters is given by:

$$r = \frac{-2\frac{S_1}{S_0}}{3 + \frac{S_1}{S_0}}. \tag{21}$$

Perhaps the most advantage of Eq. (21), besides the obvious application as efficient technique for the studies of photophysical properties of luminescent materials, is the useless of corrections related to optical components, such as diffraction grade and slits when compared with the traditional methods as the one described by Eq. (20).

### 2.3.2. Anisotropy and Circular Dichroism

Despite the fact that Therézio et al. [13] had originally described this methodology for the study and characterization of a cholesteric liquid crystal, the dissymmetry and Circular Dichroism can be measured and studied with this method for any material of interest, since the material presents the measurable physical characteristics, as symmetry, for example.

Here the asymmetry factor, $g$, is defined by:

$$g = -2\frac{I^R - I^L}{I^R + I^L} \tag{22}$$

where $I^R$ and $I^L$ are the light intensities with excitation from right (R) and left (L) circularly polarized light. It is also related to parameter $\Delta$, the difference between the two circularized lights, and is expressed by:

$$\Delta = \frac{-g}{2} \tag{23}$$

The asymmetry factor becomes a Circular Dichroism measurement when the absorption of linearly polarized light across a sample is analyzed.

In the formulation presented here, $g$ can be determined from Stokes parameters. It can be noticed, in Eq. (19), that the Stokes parameter $S_3$ represents the difference $I^R - I^L$ and $S_0$ the sum of intensities $I^R + I^L$. As the linearly polarized light can be decomposed into the sum of two circularly polarized light beams (left and right), the Stokes parameters $S_3$ and $S_0$ can be directly related to $g$ parameter [13] by the following equation:

$$g = 2\frac{S_3}{S_0} \tag{24}$$

### 2.3.3. Ellipsometric Raman Spectroscopy

The Raman Optical Activity (ROA) has been provided numerous information about chiral molecules conformation. Those molecules have fundamental relevance in many areas of

knowledge including Biology and Medicine. Basilio et al. [14] present details of a new technique to measure the Raman of chiral carbon: the ellipsometric Raman spectroscopy (ERS). The technique ERS quantifies the vibrational optical activity through measurement of small differences in intensity of Raman scattering for chiral molecules, when the impinging light is right and left circularly polarized. In other words, ERS is the application of Achromatic Ellipsometry to measure the Raman scattering. That is for say, through the technique of Ellipsometry one can measure the Stokes parameters, thus describing the complete light polarization states. The exciting light in ERS is a laser source which can be decomposed into two circular polarizations: right and left. Similarly to ROA experiments, the parameter $S_3$ describes the amount of light when normalized. ESR technique was validated by the successful characterization of the chiral alcohol (S)-(−)-1-phenylethanol (1-PhEtOH).

## 3. Applications

In this section, applications of Achromatic Ellipsometry will be briefly presented: the utilization of Emission Ellipsometry for studying a luminescent dye into a nematic liquid crystal. In this example, the importance of using the right optical elements will be noticed.

### 3.1. Nematic Liquid Crystal E7™ doped with a benzothiadiazole derivative dye

Samples were prepared using nematic liquid crystal E7™. Basically, it consists of a mixture of LC 5CB (47%), 7CB (25%), 8OCB (18%), and 5CT (10%), doped with a luminescent dye 4,7-bis {2-[4-(4-decylpiperazin-1-yl) phenyl]ethynyl}-[2,1,3]-benzothiadiazole (5A) at 0.025% of molar concentration [20]. Cells were prepared by superimposing two BK7 glass substrates coated with Poly(vinyl alcohol) (PVA) films separated by 20 mm thick Mylar spacers. The PVA films were previously rubbed with soft velvet to induce a specific aligning direction to the liquid crystal molecules. In this work, three different configurations were investigated considering the aligning direction induced in each glass plate of the cell: S00, S45 and S90 represent the rotation angles between the two substrates of the cells at 0° (parallel configuration), 45° and 90° (twisted), respectively. The alignment direction 0° was determined to be parallel with the vertical direction of lab reference. The scheme of the cells is presented in **Figure 3**.
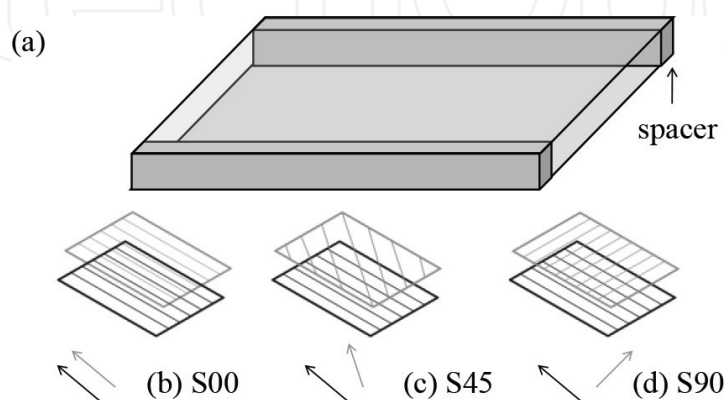


**Figure 3.** (a) Scheme of the liquid crystal cell. Rows indicate the alignment direction of each substrate of the cells (b) S00 – parallel axis (0°), (c) S45 – axis rotated in 45° and (d) S90 – perpendicular axis (90°).

Optical absorption (OA) measurements in UV-Vis-NIR were made in a FEMT O 800XI spectrometer. In the measurements of polarized optical absorption (POA), calcite polarizer Mugta10™ was inserted in the optical pathway of incident light, generating linear horizontally polarized light (LHP) and vertically polarized light (LVP). Photoluminescence measurements were made with an incident light of argon laser from Spectra Physics Inc. Stabilite 2017, with excitation wavelength at 457 nm. The emitted light from the sample was collimated by a set of lenses and detected by the Ocean Optics USB 2000 spectrometer. PL measurements were made on the two faces of the samples and the light was recorded on the same face.

Samples also followed EE and TE measurements. For the TE measurements, polarized light was analyzed by the Fourier series decomposition. The incident light was polarized vertically, right and left circularly. In the experimental set up, in the optical way of the transmitted light, an achromatic quarter-wave retarder was used, and a fixed calcite polarizer was placed before the spectrometer. In this case, a power meter of the OPHIR laser measurement group was used as a detector. The argon laser from Spectra Physics Inc. Stabilite 2017 at 457 nm and the He-Ne laser at 633 nm were used as light source. In this experiment, the quarter-wave retarder rotates around the propagation axis of transmitted light from 0 to 360° in steps of 10°.

**Figure 4a** presents absorbance and PL spectra normalized at maximum intensity of S00, S45 and S90 samples. Optical properties of the 5A dye did not change the electronics-vibrational transitions $\pi \rightarrow \pi^*$ e $\pi^* \rightarrow \pi$ significantly due to guest-host interaction in different cell configurations. The PL measurements were also performed with the wavelength excitation at 488 and 514 nm, and the emission did not show changes in the line shape or in the band position. In **Figure 4b–d**, polarized absorption spectrum, parallel, and perpendicular polarization are presented for S00, S45, and S90 samples, respectively. With these measurements, it was possible to observe that the 5A dye molecules are oriented in the same direction of the liquid crystal [21, 22]. An important fact is that S45 and S90 samples did not present the same line shape for the polarized absorption optical spectrum when the light interacted firstly in the different faces of samples. This clearly shows an asymmetry in the molecular ordering along the optical way, induced by liquid crystal molecular alignment, the exception in this case being the S00 sample. As a result, there are changes in the light polarization transmitted by this type of system [23].

**Table 1** shows $S_1$, $S_2$ and $S_3$ parameters normalized by $S_0$ obtained during EE measurements and its polarizations. In general, data of **Table 1** show that the change in the excitation wavelength does not change either the Stokes parameter and the degree polarization for each sample dramatically, mainly at 457 and 488 nm, due to absorption intensity (**Figure 4a**) is very close ($A_{457nm}/A_{514nm} = 0.91$). This means that the average orientation of molecules closer to the surface is what contributes the most to the emission. In the S00 sample, the emitted light is LPV due to the high value of $S_1$ with a negative signal. This is due to molecular alignment at 0° direction (or parallel to the y axis), and consequently, the LPV light is emitted. The high value of $S_2$ module shows that molecules are not fully oriented to the vertical direction. For this reason, a linear +45° polarized light is observed. This type of polarization does not change significantly in relation to the wavelength and polarization of excitation source. This result is corroborated by the different value of zero in the OA for perpendicular direction as shown in
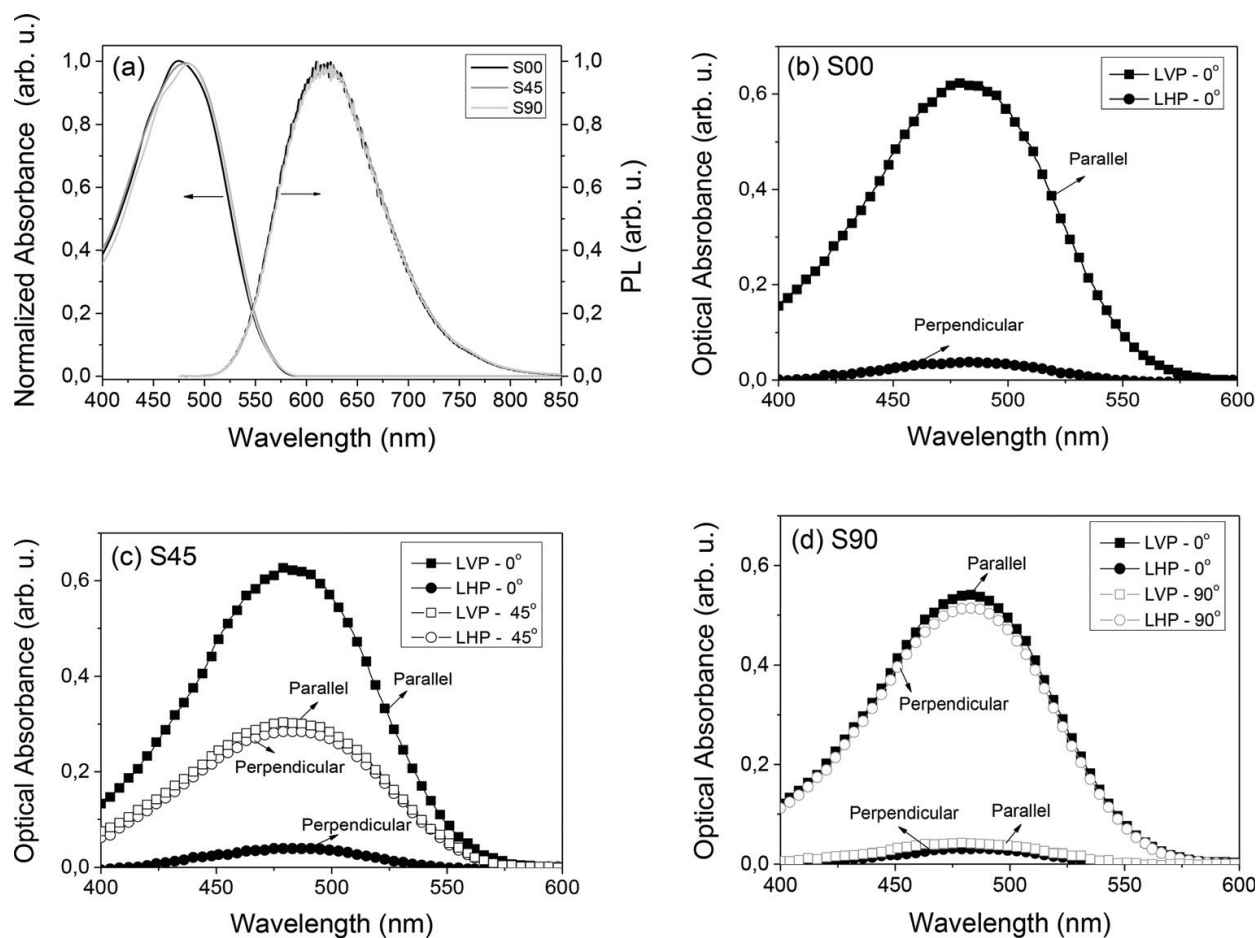
**Figure 4.** (a) OA and PL (excitation light at 457 nm) spectrums of S00, S45, and S90 samples. POA in parallel (vertical) and perpendicular (horizontal) direction of S00 (b), S45(c), and S90 samples (d). The direction at 0° of PVA films is considered parallel in relation to the vertical direction of laboratory.

**Figure 3b**. For the S45 sample, it can be seen by the $S_1$ value that on the face of 0° alignment, the light emitted is mostly linear vertically polarized as in the S00 sample. However, for the face with 45° alignment, this parameter decreases significantly. On the other hand, that face presents a significant increase in the $S_2$ parameter, which shows the emission of polarized light linear at 45° caused by the molecular ordering at 45°. Still for the S45 sample, the change in the wavelength and polarization of the excitation source does not cause a significant change in the Stokes parameter. Therefore, the emitted light remains with the same type of polarization. For the S90 sample, the light interacts first in the face with 0° alignment, independently of polarization and wavelength of excitation source, the emitted light is LVP as in the other samples. However, in the face with 90° alignment, the sample exhibits the emission of LHP light because the signal of $S_1$ is positive. This was expected due to molecules that, on this face, are horizontally oriented in relation to referential. An important point is that in the face with 0° alignment, this sample does not show linear polarized light at 45°, whereas on the face with 90° alignment, the emitted light presents a percentage of linear 45° polarized light. For the same face, when the wavelength of excitation source is at 514 nm, there is emission of circularly polarized light. This shows that molecules are rotating inside the liquid crystal cell and the emission of

| | | | $S_1/S_0$ | $S_2/S_0$ | $S_3/S_0$ | $P$ | $r$ |
|---|---|---|---|---|---|---|---|
| **Sample S00** | | | | | | | |
| $\lambda_{exc}$ = 457 nm | RCP | Face 00° | −0.67 | −0.33 | 0.09 | 0.75 | 0.58 |
| | LVP | Face 00° | −0.74 | −0.41 | 0.09 | 0.86 | 0.65 |
| $\lambda_{exc}$ = 488 nm | RCP | Face 00° | −0.55 | −0.33 | 0.07 | 0.68 | 0.45 |
| | LVP | Face 00° | −0.64 | −0.35 | 0.09 | 0.73 | 0.54 |
| $\lambda_{exc}$ = 514 nm | RCP | Face 00° | −0.47 | −0.47 | 0.05 | 0.67 | 0.37 |
| | LVP | Face 00° | −0.52 | −0.40 | 0.10 | 0.67 | 0.41 |
| **Sample S45** | | | | | | | |
| $\lambda exc$ = 457 nm | RCP | Face 00° | −0.85 | −0.11 | 0.03 | 0.86 | 0.79 |
| | | Face 45° | −0.25 | 0.73 | 0.02 | 0.78 | 0.18 |
| | LVP | Face 00° | −0.84 | −0.10 | 0.05 | 0.85 | 0.77 |
| | | Face 45° | −0.25 | 0.76 | 0.04 | 0.81 | 0.18 |
| $\lambda exc$ = 488 nm | RCP | Face 00° | −0.86 | −0.12 | 0.04 | 0.87 | 0.80 |
| | | Face 45° | −0.31 | 0.87 | 0.03 | 0.92 | 0.23 |
| | LVP | Face 00° | −0.87 | −0.12 | 0.03 | 0.88 | 0.81 |
| | | Face 45° | −0.32 | 0.86 | 0.03 | 0.92 | 0.23 |
| $\lambda exc$ = 514 nm | RCP | Face 00° | −0.80 | −0.16 | 0.03 | 0.81 | 0.73 |
| | | Face 45° | −0.34 | 0.83 | 0.02 | 0.90 | 0.26 |
| | LVP | Face 00° | −0.85 | −0.18 | 0.13 | 0.88 | 0.79 |
| | | Face 45° | −0.32 | 0.82 | 0.02 | 0.89 | 0.23 |
| **Sample S90** | | | | | | | |
| $\lambda exc$ = 457 nm | RCP | Face 00° | −0.79 | 0.03 | −0.06 | 0.79 | 0.71 |
| | | Face 90° | 0.80 | 0.20 | −0.05 | 0.82 | −0.42 |
| | LVP | Face 00° | −0.74 | 0.06 | 0.03 | 0.74 | 0.65 |
| | | Face 90° | 0.53 | 0.16 | −0.04 | 0.55 | −0.30 |
| $\lambda exc$ = 488 nm | RCP | Face 00° | −0.80 | 0.03 | 0.02 | 0.80 | 0.73 |
| | | Face 90° | 0.74 | 0.16 | −0.07 | 0.76 | −0.40 |
| | LVP | Face 00° | −0.85 | 0.03 | 0.00 | 0.86 | 0.79 |
| | | Face 90° | 0.58 | 0.11 | −0.10 | 0.60 | −0.32 |
| $\lambda exc$ = 514 nm | RCP | Face 00° | −0.85 | −0.04 | 0.12 | 0.86 | 0.79 |
| | | Face 90° | 0.78 | 0.20 | −0.12 | 0.81 | −0.41 |
| | LVP | Face 00° | −0.81 | −0.03 | 0.01 | 0.81 | 0.73 |
| | | Face 90° | 0.56 | 0.12 | −0.11 | 0.59 | −0.31 |

**Table 1.** Normalized Stokes parameter and polarization degree of S00, S45, and S90 samples.

LHP light occurs by molecules that are preferably oriented in the horizontal direction (**Figure 2d**), but have components in the vertical direction. For this reason, there is linear horizontally polarized emitted light even when the excitation source is LVP. The circularly polarized light can be easily observed when the excitation wavelength is at 514 nm. This happens because the length of penetration in the sample for this wavelength is higher ($A_{457nm}/A_{514nm}$ = 1.29) than the other wavelengths.

**Figure 5** shows two EE measurements performed in the S45 sample using the excitation light at 488 nm and LVP. By the fitting of EE data and using Eq. (18), Stokes parameters of samples' emitted light in function of the different excitation wavelengths and the type of the light polarization could be obtained. These measurements were performed on the two faces of the cell. Thereby, the molecular orientation within the liquid crystal cell by the emission of the dyes could be seen.

In order to verify the transmitted light properties, TE measurements were made at two wavelengths: 457 and 633 nm. Optical absorption of the 5A dye is present at 457 nm. For 633 nm changes in the polarization of transmitted light are caused only by the refractive index of the system, as there is not absorption. **Figure 6** shows two TSE measurements of the S45 and S90 samples.

By TE measurements, Stokes parameters were obtained and the polarization state of transmitted light was described. **Table 2** shows the Stokes parameters and the polarization degree of samples' transmitted light.

The first important point to discuss in these results is the polarization values higher than one. This occurs in three measures and it is due to the measurements' error that is around 5%. However, these values are not higher than recommended. From TE measurements, it could be seen that samples change the polarization of transmitted light and that this variation occurs even when the wavelength is not in the OA spectrum range of 5A dye. This is due to system birefringence [23]. Based on **Table 2**, it is clear that for the S00 sample, when the incident light
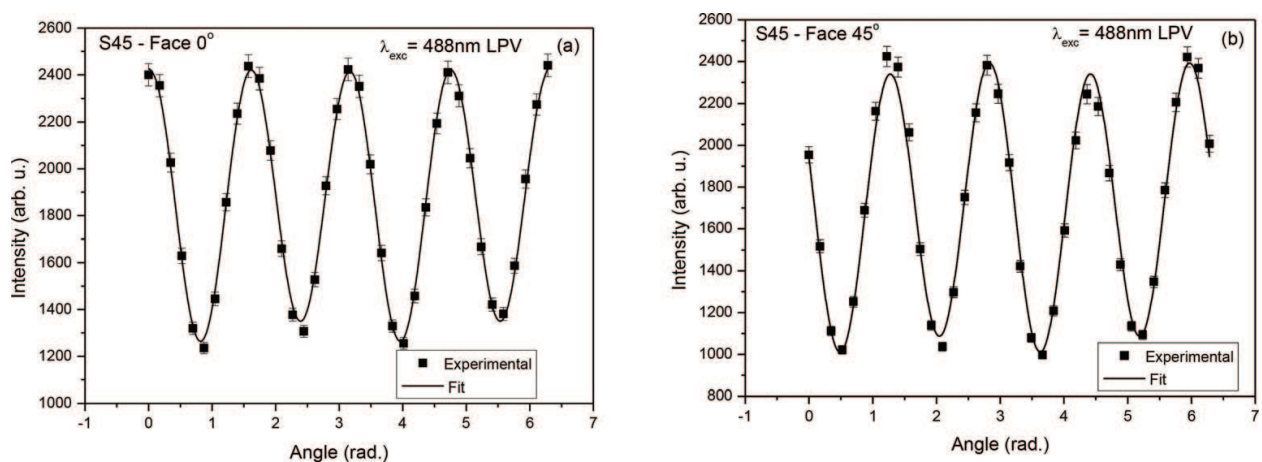


**Figure 5.** EE Measurement made in the S45 sample at face 0° (a) and 45° (b).
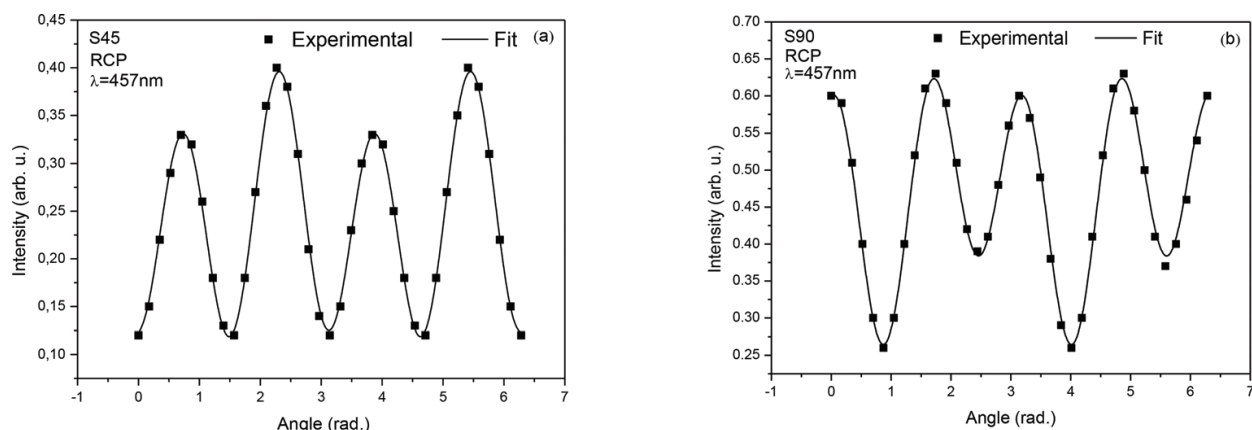
**Figure 6.** (a) Transmittance Ellipsometry measurements of the S45 sample, the light interacting firstly in the face with molecules oriented at 45° and the source at 457 nm is right circularly polarized. (b) Transmittance Ellipsometry measurements of the S90 sample, the light interacting firstly in the face with molecules oriented at 0° and the source at 457 nm is right circularly polarized.

is at 457 nm and right circularly polarized, the transmitted light is linear horizontally polarized due to the high value of $S_1$ with positive signal. There is also a significant amount of linear +45° polarization because of the value of $S_2$ and a small percentage of light is left circularly polarized. It is important to observe that the incident light is right circularly polarized, and the S00 sample changes the type of polarization of transmitted light for the small percentage of left circular polarization. In case of the incident light is left circularly polarized, the transmitted light through the sample is linear +45° polarized by the high value of $S_2$. There is also an amount of the linear horizontally polarized light due to the value of $S_1$, the transmitted light presents a small percentage of right circular polarization. When the incident light is linear vertically polarized, the transmitted light is linear vertically polarized by the $S_1$ value, and there is a small part of transmitted light that is right circularly polarized. Therefore, in this case, there are practically no changes in the polarization of incident light. Still for the S00 sample, when the incident light is right circularly polarized and the wavelength at 633 nm, the transmitted light changes its polarization for the linear −45°. There is a small percentage of light that is linear horizontally and right circularly polarized. For the measurement performed with the left circularly polarized incident light, a similar behavior of that when the incident light is right circularly polarized was shown. However, the transmitted light is linear +45° polarized, which is the majority of transmitted light polarization. When the incident light is linear vertically polarized, the sample does not change the polarization of transmitted light, which occurs in the same way when the wavelength is at 457nm and there is not optical absorption of dyes.

For the S45 sample, the same measurements as those of the S00 were obtained. However, in this sample, the incidence of light was carried out in the two faces of the sample, and it allows the verification of whether the polarization of transmitted light changes with molecular ordering. When the incident light has right circular polarization and wavelength at 457 nm, it can be observed that when the light interacts first in the face with 0° alignment, the transmitted light is linear +45° polarized, and a part of light is linear horizontally polarized, which should be

|  |  |  | $S_1/S_0$ | $S_2/S_0$ | $S_3/S_0$ | $P$ |
|---|---|---|---|---|---|---|
| **Sample S00** | | | | | | |
| $\lambda$ = 457 nm | RCP | Face 00° | 0.62 | 0.36 | −0.16 | 0.74 |
| | LCP | Face 00° | 0.44 | −0.82 | 0.20 | 0.95 |
| | LVP | Face 00° | −1.00 | 0.03 | 0.13 | 1.01 |
| $\lambda$ = 633 nm | RCP | Face 00° | 0.11 | −0.79 | 0.09 | 0.80 |
| | LCP | Face 00° | −0.08 | 0.79 | 0.06 | 0.80 |
| | LVP | Face 00° | −0.95 | 0.06 | −0.03 | 0.95 |
| **Sample S45** | | | | | | |
| $\lambda$ =457 nm | RCP | Face 00° | 0.19 | 0.53 | 0.02 | 0.56 |
| | | Face 45° | 0.66 | −0.13 | 0.08 | 0.68 |
| | LCP | Face 00° | 0.05 | 0.63 | 0.03 | 0.63 |
| | | Face 45° | 0.69 | −0.02 | 0.08 | 0.69 |
| | LVP | Face 00° | −0.38 | −0.93 | 0.00 | 1.01 |
| | | Face 45° | 0.48 | −0.12 | −0.03 | 0.50 |
| $\lambda$ = 633 nm | RCP | Face 00° | 0.57 | 0.04 | 0.11 | 0.59 |
| | | Face 45° | 0.30 | −0.52 | 0.03 | 0.60 |
| | LCP | Face 00° | −0.22 | 0.03 | 0.45 | 0.50 |
| | | Face 45° | 0.22 | 0.11 | 0.55 | 0.61 |
| | LVP | Face 00° | −0.35 | −0.97 | 0.00 | 1.04 |
| | | Face 45° | −0.02 | −0.27 | −0.14 | 0.30 |
| **Sample S90** | | | | | | |
| $\lambda$ = 457 nm | RCP | Face 00° | −0.82 | −0.32 | 0.18 | 0.90 |
| | | Face 90° | 0.56 | 0.52 | −0.15 | 0.78 |
| | LCP | Face 00° | −0.53 | 0.37 | −0.52 | 0.84 |
| | | Face 90° | 0.63 | −0.39 | 0.42 | 0.85 |
| | LVP | Face 00° | 0.94 | −0.14 | 0.17 | 0.97 |
| | | Face 90° | 0.98 | −0.02 | −0.01 | 0.98 |
| $\lambda$ = 633 nm | RCP | Face 00° | −0.02 | 0.84 | 0.05 | 0.84 |
| | | Face 90° | 0.44 | −0.67 | 0.23 | 0.84 |
| | LCP | Face 00° | −0.37 | −0.68 | −0.42 | 0.88 |
| | | Face 90° | 0.24 | 0.80 | 0.00 | 0.84 |
| | LVP | Face 00° | 0.87 | −0.42 | −0.25 | 1.00 |
| | | Face 90° | 0.98 | −0.12 | −0.07 | 0.99 |

**Table 2.** Stokes parameters and the polarization degree of S00, S45, and S90 samples.

noticed for the $S_1$ value. This value increases significantly when the incidence occurs in the other face. On the other hand, the amount of linear at 45° polarized light decreases and changes the signal for negative. When the incident light is left circularly polarized, the transmitted light through the sample has the same state of that when the incidence occurs with the right circularly polarized light. However, the smallest part of polarized light ($S_1$ for the face at 0° and $S_2$ for the face at 45°) becomes practically zero. When the incident light is linear vertically polarized and the light interacts firstly with the face with 0° alignment, the polarization of transmitted light was changed to linear −45° polarization, there is still a small percentage of linear vertically polarized light. When the incidence occurs firstly in the face with 45° alignment, the transmitted light has linear horizontal polarization. However, the value of linear 45° polarized light that in the other face (0° alignment) is very high, decreases significantly. Measurements were made with the wavelength at 633 nm, and in this case, there is not OA of dye. The incident light is right circularly polarized and interacting first in the face with 0° alignment, the transmitted light has the linear horizontal polarization, and a small part of light is right circularly polarized. Nevertheless, when the light interacts first in the face with 45° alignment, the transmitted light is linear −45° polarized, there is still a part of the transmitted light that has the linear horizontal polarization. When the incident light is left circularly polarized and interacts first in the face with 0° alignment, the transmitted light has right circular polarization. There is still a part of the transmitted light that is linear vertically polarized. In the case of light interacting firstly with the other face (45° alignment), it can be verified that the majority of transmitted light is right circularly polarized, There is still a significant part of linear horizontally polarized light and a small part of linear +45° polarized light. When the incident light is linear vertically polarized, it can be observed that when the light interacts initially with the face with 0° alignment, the greater part of transmitted light has linear +45° polarization. There is also a percentage of linear vertically polarized light for the measurement performed when the light interacts first in the other face (45° alignment) of the sample. The transmitted light has very little polarization and the main polarization is linear −45°.

In the S90 sample, measurements were made in the same way as those of the S45 sample. For the incident light with wavelength at 457 nm and the right circular polarization, it can be seen that when the light interacts firstly with the face with 0° alignment, the transmitted light is linear vertically polarized. There is still a part of the light that is linear −45° polarized and a small part that is right circularly polarized. When the incident light interacts initially with the other face (90° alignment), the transmitted light has linear horizontal polarization, linear +45°, and a small part of light is left circularly polarized. When the incident light has left circular polarization, it could be verified that when the light interacts first in the face with 0° alignment, the transmitted light has a significant value of linear vertically and left circularly polarized light. There is also a small amount of linear +45° polarized light. When the light interacts initially with the other face (90° alignment), the transmitted light changes the signal of Stokes parameters in relation to the face with 0° alignment. Moreover, the transmitted light has linear horizontal polarization and it also has right circular polarization and a small percentage of linear −45° polarized light. When the incident light has linear vertical polarization, the transmitted light is practically linear horizontally polarized. There is only a small part of linear −45°

and right circularly polarized light when the incidence is performed firstly in the face with 0° alignment.

Like the other samples, measurements in the S90 were also made with the wavelength at 633 nm. When the incident light has right circular polarization, if the incident light interacts firstly in the face with 0° alignment, the transmitted light is linear +45° polarized. If the incidence occurs firstly in the other face (90° alignment), the transmitted light is mainly linear +45° polarized, in this case there is still a small amount of linear horizontal polarization and right circular polarization. When the incident light has left circular polarization, what happens is a similar process when the incident light is right circularly polarized? However, there is an inversion of the main polarization state of light between the face with 0° and 90° alignment. Measurement was also made with the incidence of linear vertically polarized light. For the two faces, the transmitted light is linear horizontally polarized. Therefore, the transmitted light changes completely its type of polarization. It is possible to observe that when the incident light interacts initially in the face with 0° alignment, the transmitted light has a percentage of linear −45° and left circularly polarized light. For the incidence performed in the other face (90° alignment) a percentage of this polarization state for the transmitted light is much smaller in relation to the incidence achieved firstly in the face with 0° alignment.

With EE and TE measurements, a complete molecular ordering inside the doped liquid crystal cell could be verified. It is important to observe that the EE measurements, in general, allow characterization of the molecular ordering onto the substrate surface. It can be changed by the excitation wavelength and molecules along the cell. With TE measurements, results allow the presence of an effect that occurs in the molecular ordering along of the doped liquid crystal cell. This can be related to the birefringence of system only when the light is transmitted by the sample and there is no optical absorption of 5A dye, or it can be related to the optical absorption and the birefringence simultaneously.

## 4. Conclusion

In this work, we illustrated a new methodology for measuring Raman Optical Activity [14] and the application of achromatic Ellipsometry in the study of benzotiadiazol derivative dye doped in the E7 nematic liquid crystal. Emission and transmittance Ellipsometry experiments were used to verify its molecular ordering within a liquid crystal cell. The obtained results showed that chromophores were ordered in the same direction of the E7 molecules. In addition, due to the change in the excitation wavelength, penetration depth in the sample could be verified, enabling the analysis of molecules ordering within a liquid crystal cell. Ellipsometry experiments also indicate that the molecular orientation inside the cells somehow changes the polarization of transmitted light. This effect can be due to system birefringence (both liquid crystal and dye) or due to combined process between dyes optical absorption and system birefringence. It is important to emphasize that changes in light polarization occur differently for one process (birefringence) or two processes simultaneously (birefringence and optical absorption). Finally, achromatic Ellipsometry was demonstrated to be a complete spectroscopic technique that enables the analysis of bulk and interfacial molecular ordering.

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