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Measurement of the Emitted Light Polarization State in Oriented and Non-Oriented PPV Films

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Summary: In this work we report the influence of the molecular orientation on the light emission polarization of poly (*p*-phenylene vinylene) (PPV) films. The oriented film was processed via the Langmuir-Blodgett (LB) technique while the non-ordered one was processed by casting technique. By means of an ellipsometry experiment, the information about the polarization state of the emitted light was obtained via Stokes parameters and the dissymmetry factor (g). The experiments were carried out at room and low temperature (10 K) and in the phonon-replicas range at 543 and 633 nm. We have observed a high dependence in the g factor and in the ellipticity of the emission spectra for LB films as function of the spectrum region, i. e., the phonon-replicas. This effect is attributed to the memory of the circular polarization that is lost by thermal disorder when the emission occurs distant from the zero- phonon peak.

Keywords: ellipsometry; Langmuir-Blodgett technique; luminescence; polarization; poli (*p*-phenylene vinylene)

Introduction

Conjugated polymers with non-localized π electrons are a new class of materials, called organic semiconductors, with great potential for technological applications. Their use as active layers, through their processing as thin films, allows us to fabricate electroluminescent devices like light emitting diodes (LED) and photovoltaic cells.[1,2] The semiconductors properties presented by conjugated polymers together with low fabrication and processing cost of their thin films permit both: their prompt application as devices and the study of their basics properties related to semiconductor physics. The emitted light from non-oriented amorphous materials as well as from surfaces made of organic materials partially crystalline is, in general, depolarized. The control of the polarization state of the emitted light in organic semiconductors is of great interest because of their possible technological applications. Active molecular devices, able to emit light with linear or circular polarization, are necessaries for industry of information (e.g. optical processing and storage, display). An intense research for the development of this type of technology is necessary yet in the way to integrate it to a production chain.[3] A possible immediate application is the use of the linear polarized light, emitted by these materials in association with liquid crystals displays, acting as light source. In the special case of light emitting polymers some questions, related to practical applications, are open yet. In this work we perform a study about the influence of molecular ordering on the polarization state of the light emitted by PPV films. By means of an ellipsometry experiment, the information about the polarization state of the emitted light was obtained via Stokes parameters and the dissymmetry factor (g).

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Experimental Section

The PPV chemical synthesis was performed via precursor route, of poly (xylylidene tetrahydrothiophenium chloride) (PTHT). Although the PPV route synthesis is extensively described everywhere[4] a few details of the route used in this work is described here. The PPV structure was synthesized according to Figure 1. It is has been accomplished substituting chloride anions of poly (xylylidene tetrahydrothiophenium chloride) (PTHT) by a dodecylbenzenesulfonate (DBS) anion. This step was introduced in PPV precursor route to obtain stable Langmuir films.[5] LB-PPV film with 40 monolayers was carried out after the thermal conversion from LB-PTHT/DBS film under atmospheric conditions at 110 °C. More details of this low thermal elimination route is present in Ref. 6. Casting film was synthesized spreading the PPV precursor into a substrate and thermal converted into PPV at 230 °C under vacuum after the solvent evaporation.

In the ellipsometry experiments the samples were pumped with a 458 nm argon ion laser. The emitted light was collected with a lens system and passed through a rotating quarter wave plate, varying from 0° to 360°. After the wave plate, a 0° polarizer was placed in front of a spectrophotometer and the spectra were recorded for different angles of the wave plate with step of 10°. The experiments were performed at room temperature (300 K) and at 10 K, using a quarter wave plate for two different wavelengths (543 and 633 nm).

Results and Discussion

A typical result of the ellipsometry measurement is shown in Figure 2; in which the arbitrary intensity acquired by the spectrometer at 633 nm (the emission wavelength probed was determined by the wave plate) is plotted as function of the angle of wave plate. This result was obtained for LB-PPV film at room temperature.

From the ellipsometry measurements we determine the polarization state of the emitted light through the Stokes parameters. These parameters are obtained fitting the ellipsometry measurements with the equation:[7,8]

$$I(\theta)=\frac{1}{2}[A+B\sin(2\theta)+C\cos(4\theta)+D\sin(4\theta)] \quad (1)$$

where : $A=S_0+\frac{S_1}{2}$, $B=S_3$, $C=\frac{S_1}{2}$ and $D=\frac{S_2}{2}$; being S_0, S_1, S_2 and S_3 the Stokes parameters.

The Stokes parameters are associated with the degree of polarization P, the

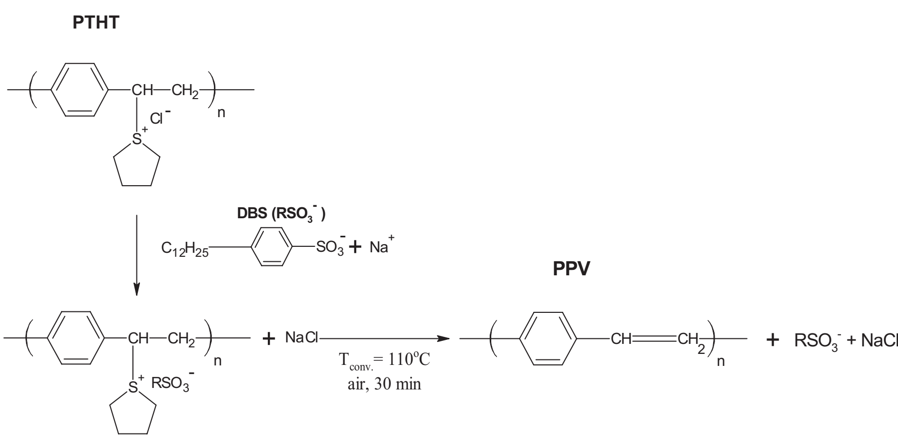

Figure 1.
Synthesis route of PPV/DBS films.

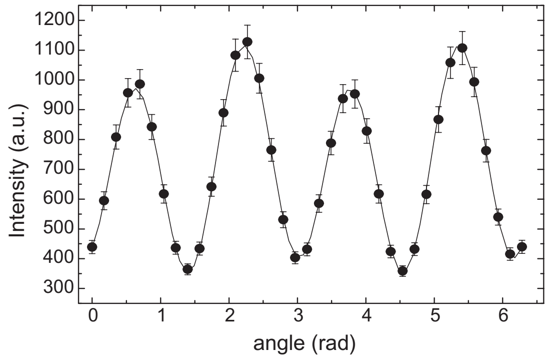

Figure 2.
Ellipsometry measurement for LB-PPV at 300 K. The full line represents the theoretical fitting obtained with equation 1.

azimuth angle φ and the ellipticity χ, which characterize the elliptical light, by the following equations:

$$P = \frac{(S_1^2 + S_2^2 + S_3^2)}{S_0}, \quad (2)$$

$$tg(2) = \frac{S_2}{S_1}, \quad (3)$$

$$\sin(2\chi) = \frac{S_3}{S_0} \quad (4)$$

With the parameters of the ellipse defined in the Figure 3.

The polarized light is also characterized by the g dissymmetry factor that reveals the difference between the right- and the left-hand circular polarization. This factor can be calculated by:

$$g = 2\frac{I_L - I_R}{I_L + I_R} \quad (5)$$

where I_L and I_R are the light intensity obtained for (φ + 45) and (φ − 45), respectively. In the Table 1, we summarize the ellipse parameters from the emitted light of the PPV films.

From Table 1 we conclude that at room temperature the LB-PPV film emits a more polarized light than casting-PPV. Considering an estimated error of about 5%, we verify that the polarization degree for ordered film almost does not modify at different temperatures. In the other hand, for casting-PPV, the polarization degree decreases when the temperature is lowered. We conclude from other experimental tests that this behavior is completely arbitrarily, depending of the pump position on film surface. This could be a consequence of the

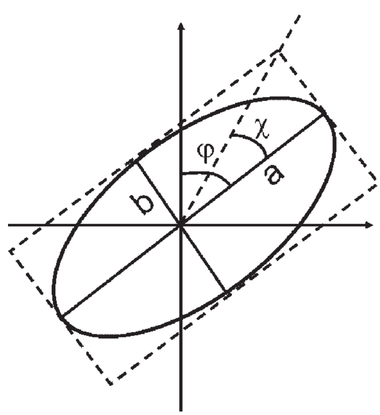

Figure 3.
Parameters that defines an elliptically polarized light.[7,8]

Table 1.
Ellipse parameters obtained from the emitted light of the LB-PPV and Casting-PPV samples.

Sample	T(K)	λ (nm)	P	χ	φ	g
LB	300	543.5	0.67	2.2°	−16°	0.13
	10	543.5	0.66	3.0°	−16°	0.17
	300	633	0.69	0.8°	−18°	0.04
	10	633	0.71	1.1°	−13°	0.06
Casting	300	633	0.14	0.1°	−41°	−0.009
	10	633	0.10	0.1°	−41°	−0.018

random distribution of the conjugation length, usually presented by casting films. It is also worth noting that the LB-PPV film presents a higher dissymmetry value than casting film. The positive value for g factor in LB film reveals that the emitted light is more left-hand circularly polarized, while the negative g value in the non-ordered film represent a more right-hand circular polarization emitted light. As can be observed in table 1 for LB-PPV, the dissymmetry g, as well as the ellipticity χ, decreases about three times when the 543.5 nm wave plate is replaced by the 633 nm wave plate and about 25% when the temperature is raised to 300 K. The dissymmetry changes can also be observed in casting-PPV, where the g value decreases 50% at room temperature. This effect occurs much probably because the emission polarized light has a memory that is lost in the vibrational states. Consequently, the g values tend to diminish for more distant wavelength from the zero-phonon peak. In the case of the LB-PPV film, the photoluminescence spectrum presents the zero-phonon emission peak near to 525 nm at 10 K that is blue shifted to 510 nm at room temperature.[5]

Conclusions

In summary, from the measured stokes parameters we conclude that the ordered film presents much higher degree of polarization than the non-ordered. We also observed that the factor P almost does not modify for LB-film when the temperature is changed. However, for the casting-PPV it decreases when the temperature is lowered. The g value and ellipticity analysis reveal that the circular emitted light possibly has a memory effect that can be lost in the vibrational states.

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