



## Emission ellipsometry as a tool for optimizing the electrochemical synthesis of conjugated polymers thin films

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### ABSTRACT

Emission ellipsometry technique was used as a tool to optimize the electrochemical synthesis of luminescent poly 24 [3-alkylthiophenes] conjugated polymers. This methodology was applied to poly[3-octylthiophene] (P3OT) films. P3OT films were synthesized by the chronocoulometry technique, using tetraethylammonium tetrafluoroborate and lithium perchlorate, as supporting electrolytes to control empirically the polymer/polymer interaction. After excitation with polarized light, a partially polarized emission from these films was observed. The polarization degree of the light emitted by the polymer was calculated by Stokes theory. Emission of polarized light is attributed to the limitation of energy transfer and/or diffusion processes of the excited carriers. These energy transfer and/or diffusion processes are dependent on the concentration and on the chemical nature of the electrolyte in the polymer film. The best condition for synthesis of P3OT films is correlated with the maximum of the polarization degree. The proposed methodology can be applied to optimize the electrochemical synthesis of luminescent conjugated polymers.

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### 1. Introduction

Poly[3-alkylthiophenes] (P3ATs) have been studied as a promising active layer in organic electronic devices, mainly in solar cells [1]. Solvatochromism [2], electrochromism [3,4], thermochromism [5], electroluminescence [6], and photoluminescence [2,4–8] properties were also observed for these conjugate polymers. In solid state films, the emission efficiency, among other factors such as energy transfer processes or structural defects [8,9], depends on the chemical synthesis route, film processing, molecular packing, supra-molecular ordering and the polymer/polymer interaction. The solvent used [10], the regioregularity [11–14] or chemical doping [15] affects directly the P3ATs electronic structure (effective conjugation degree). A small bandgap and an enhancement in emission efficiency have been found in polymeric films processed with regioregular P3ATs [13,16,17]. Despite the progress in the chemical synthesis of regioregular P3ATs [16], the regioregularity does not ensure the supra-macromolecular order of polymeric films processed by using common techniques, such as spin-coating, casting or electrochemistry. Moreover, polymeric blends have been utilized to produce opto-electronic devices, such as organic field effect transistors

or light emission diodes [18,19]. Thus, the doping process and the polymer/polymer interaction are the most important physical parameters to enhance the electric or optical characteristics of the devices.

In general, P3ATs are obtained by chemical synthesis using 3-alkylthiophene monomer catalyzed by  $\text{FeCl}_3$  [2,4,5,7]. High regioregularity polymeric chains (~98% HT coupling) can be obtained using  $\text{Ni}(\text{dppp})\text{Cl}_2$  as a catalyst [12,14]. The advantage of the chemical synthesis is its ability to remove the dopant to obtain a pristine P3AT polymer. In the electrochemical synthesis process, however, the electrolyte used in P3ATs polymerization and film growth process remains in the film as a dopant. The spectroscopic features of polythiophenes depend strongly on film thickness, mainly because the doping level increases during the film growth [20]. It has been established that the ideal supporting electrolyte (SE) concentration for electrochemical techniques is about  $0.1 \text{ mol.L}^{-1}$  [21–24]. This paper deals with a quantitative method to determine the best electrochemical synthesis conditions for luminescent conjugated polymers. poly[3-octylthiophene] (P3OT) films were synthesized using the chronocoulometry technique to verify the proposed methodology. Tetraethylammonium tetrafluoroborate ( $(\text{C}_2\text{H}_5)_4\text{NBF}_4$ ) and lithium perchlorate ( $\text{LiClO}_4$ ) were used as supporting electrolytes. Emission ellipsometry measurements were carried out to quantify the polarization degree ( $P$ ) of the emitted light for P3OT films [25]. Considering the energy transfer processes and/or diffusion of photo-excited carriers and the polymer/polymer interaction, we correlated the parameter  $P$  with the electrochemical processing conditions.

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## 2. Experimental section

### 2.1. Chemicals

The monomer 3-octylthiophene ( $C_{12}H_{20}S$ , 94%), the  $(C_2H_5)_4NBF_4$ , 99%, and the  $LiClO_4$ , 99% were purchased from Acros-Organics and were used without further purification. Acetonitrile (AN,  $CH_3CN$ , 99.5%, Vetec) was dried on molecular sieve (0.03 nm). Karl Fischer titration showed that the molecular sieve decreases the water content in acetonitrile to 0.05% or less.

### 2.2. Electrochemical polymerization

A standard three-electrode cell was used. The atmosphere was purged with argon before starting the electrochemical synthesis. Tin Oxide doped with Fluorine (FTO) substrates with conductivity of about  $19 \Omega m^{-2}$  were used as working electrodes, and a platinum plate as auxiliary electrode (AE). The potentials were determined in relation to the reference electrode  $Ag/AgCl/(0.100 mol.L^{-1} LiClO_4, AN)$ . The potential of  $Ag/AgCl/(0.100 mol.L^{-1} LiClO_4, AN)$  was measured as  $52 \pm 9 mV$  vs  $Ag/AgCl$  reference electrode. The monomer polymerization was accomplished by the chronocoulometry technique in potentiostatic method at 1.6 V finalized with the open circuit, using a potentiostat/galvanostat EG&G PAR 273A controlled by computer with M270 acquisition1 software. The polymer quantity was controlled by setting the electric charge to 80 mC. This charge generates films with appropriate characteristics for optical measurements. Films were grown using a monomer concentration equal to  $0.050 mol L^{-1}$  and concentrations of SE between  $0.025$  and  $0.175 mol L^{-1}$ , both dissolved in AN. Table 1 shows the SE concentration used for each sample. The films were rinsed with dry AN and dried with argon at room temperature. The rinsed films remain doped [15].

### 2.3. Spectroscopic characterization

The Fourier-transform infrared (FT-IR) spectra were recorded from  $3000$  to  $500 cm^{-1}$  after 128 scans, using  $4 cm^{-1}$  spectral resolution, with a Nicolet Nexus 470 FT-IR spectrophotometer. Samples were prepared by pressing the scraped P3OT films with KBr in disk form. The UV–vis absorption spectra were obtained by using a spectrophotometer FEMTO 800 XI in the range from  $300$  to  $1100 nm$ . Photoluminescence spectra (PL) were obtained by exciting the samples with the  $405 nm$  line of a diode laser (LaserLine-iZi), vertically polarized in relation to the laboratory reference, using a power of  $2.5 mW$ .

The emission ellipsometry experiment was performed using the setup described by Alliprandini-Filho et al. [25]. The samples were excited by the  $405 nm$  laser, and the emitted light was collected by a set of lenses and directed through an achromatic quarter-wave-plate (Newport 10RP54-1) as a compensator, and an achromatic polarizer (Newport 10LP-VIS-B). The emission was detected and analyzed by a USB 4000 Ocean Optics spectrophotometer. The experiment was performed by rotating the compensator around its own axis from  $0$  to  $360^\circ$ , with steps of  $10^\circ$ . All measurements were performed at room temperature ( $\sim 20^\circ C$ ) and under  $\sim 10^{-2} Pa$  vacuum.

**Table 1**  
Supporting electrolyte concentration for each sample.

Concentration ( $mol L^{-1}$ )	Sample	
	$(C_2H_5)_4NBF_4$	$LiClO_4$
0.025	BF025	Li025
0.050	BF050	Li050
0.075	BF075	Li075
0.100	BF100	Li100
0.125	BF125	Li125
0.150	BF150	Li150
0.175	BF175	Li175

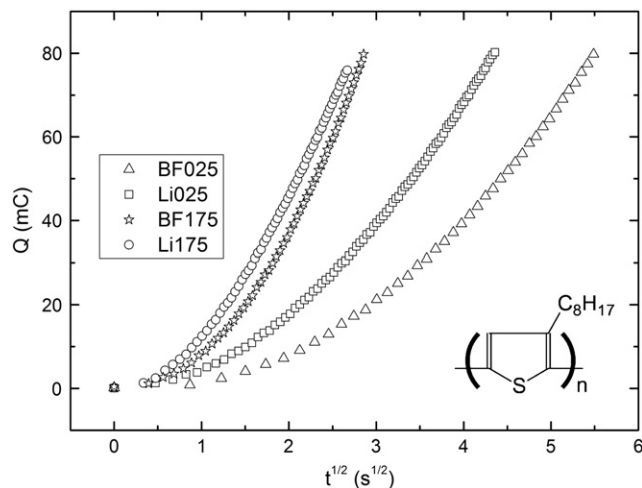
## 3. Results and discussion

Fig. 1 shows the electrochemical response of P3OT polymeric films during the single step potential chronocoulometry.  $Q$  is related to the highest ( $0.175 mol L^{-1}$ ) and the lowest ( $0.025 mol L^{-1}$ ) concentrations of  $(C_2H_5)_4NBF_4$  or  $LiClO_4$ , based on the integrated Cottrell Eq. (1) [26–28]:

$$Q = \frac{2nFACD^{1/2}}{\pi^{1/2}} t^{1/2} \quad (1)$$

where  $Q$  is the charge,  $n$  is the number of electrons,  $F$  is the Faraday constant,  $A$  is the electrode surface area,  $D$  is the monomer diffusion coefficient,  $C$  is the monomer concentration, and  $t$  is the time of electrochemical deposition. The curves are not linear at the beginning since Eq. (1) does not take into account the effects of migration current and ohmic resistance of bulk solution. A linear dependence is observed at longer times as, for example, 16 s for sample BF025. Another possible reason for the non linear dependence at the initial stage is the electrode surface modification, in which polymeric clusters could initially cover the electrode surface randomly, presenting pin roles [23]. As the time increases, the polymer covers the electrode surface, changes the growth speed and, consequently, the electrical current. Preliminary experiments indicated  $80 mC cm^{-2}$  as being enough to obtain P3OT films with appropriate physical characteristics to perform optical spectroscopy measurements such as absorbance, photoluminescence, and emission ellipsometry, in contrast to the  $300 mC cm^{-2}$  obtained by Micaroni and De Paoli [23]. Chronocoulometric data also show the necessary time to process films, which depends on the nature and concentration of the supporting electrolyte (see the total time in Fig. 1). As the concentration of SE increases, the synthesis time decreases, requiring 19.3 s for sample Li025 and 6.7 s for sample Li175. If the SE concentration is higher than  $0.1 mol. L^{-1}$ , film growth does not depend significantly on the SE nature. Probably, the ohmic resistance of the solution decreases and the process becomes controlled by monomer diffusion. Eq. (1) is satisfied for samples Li175 and BF175 if deposition time is approximately equal to 7.6 s.

Fig. 2 shows the UV–vis spectra of P3OT films obtained using the electrolyte  $LiClO_4$  and, for comparison purposes, the absorbance spectrum of sample BF175. The spectra were vertically shifted for better visualization. The typical absorption band in the spectral range  $350$ – $550 nm$ , due to the  $\pi \rightarrow \pi^*$  transition, for sample Li025 is blue-shifted (maximum at  $420 nm$ ) in comparison to those found in the literature [6,12,16]. The cause is the conjugation degree, which tends to be lower when the polymerization rate is high. This occurs in chronocoulometry technique due to the fact that initially the



**Fig. 1.** Electrochemical response curve of  $Q(mC)$  versus  $t^{1/2}(s^{1/2})$  for BF025, Li025, BF175, and Li175. The inset shows the P3OT chemical structure.

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