Electrical and electrochemical measurements in nanostructured films of polythiophene derivatives

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A B S T R A C T

Thin films from polythiophene derivatives can be fabricated by some experimental methods, including the Langmuir techniques, which are particularly suitable if some degree of molecular control is required. In this study, electrical and electrochemical measurements in Langmuir-Schaefer and spin-coated films of polythiophene derivatives were carried out in order to compare the influence of the deposition technique in these properties. Through cyclic voltammetry and UV-visible absorption measurements it was possible to estimate the energy diagrams for all the polythiophene films. Besides, electrochromic effect in the polythiophene thin films was observed.

1. Introduction

The transport properties of conducting polymers are dominated by the disorder due to the partial crystallinity, non-homogeneous doping or by the disorder that is created during the synthesis and material processing [1]. In a polymer, the interaction between its chains leads to the formation of molecular orbitals, which are equivalent to the electronic bands in an inorganic semiconductor, where the HOMO (highest occupied molecular orbital) and the LUMO (lowest unoccupied molecular orbital) are the analogous to the valence and conduction bands, respectively. The energy difference between HOMO and LUMO levels, several times defined as the separation between π and π^* orbitals, is a forbidden energy scale (band gap) E_{gap} [2], which determines the intrinsic electronic properties of the material [3].

The electrical conductivity of polymeric materials can be tuned by changing some of its properties, such as morphology [4], which in the case of thin films, can be achieved by employing different deposition techniques [5]. Thin films from neat polythiophene derivatives can be fabricated by some experimental methods [6], including the Langmuir-Schaefer (LS) technique [7]. The difference between the LS to the well-defined Langmuir-Blodgett (LB) technique is the deposition orientation: horizontal lifting and

vertical dipping methods [8], respectively. Despite of their differences, both techniques provide nanostructured films with some morphological control down to molecular level [9,10].

The present study deals with the influence of the deposition technique in the energy diagram of four polythiophene derivatives in common electrical devices for direct current (DC) electrical measurements. The nanostructured thin films deposited by the LS technique are compared herein to the widely used spin-coated ones. Besides the electrical and electrochemical characterization, UV-visible absorption measurements were carried out in order to confirm the electrochromic effect in the polythiophene derivative thin films.

2. Experimental

The electrical transport and electrochemical properties of regioregular alkyl-substituted polythiophene derivatives (P3AT) were studied in its thin film form. The poly(3-butylthiophene) (P3BT), poly(3-hexylthiophene) (P3HT), poly(3-octylthiophene) (P3OT) and poly(3-decylthiophene) (P3DT) derivatives were obtained commercially from Sigma-Aldrich. The molecular weight for the repetitive units of P3BT, P3HT, P3OT and P3DT in increasing number of carbons in the side chain are 138, 166, 194 and 222 g mol^{-1}. The thin films were comparatively grown by the LS and spin-coating techniques. The Langmuir films were fabricated by spreading a solution of polythiophene derivatives in chloroform (0.2 mg mL^{-1}) onto ultra-pure water subphase (Millipore Milli-Q

system, resistivity $18.2\,M\Omega\,cm$) in a KSV 5000 Langmuir trough. The films were deposited using spin-coating and LS techniques onto ITO (indium-tin oxide) substrates (Asahi Glass Co., Japan) in order to carry out electrical, optical and electrochemical characterization.

The electrical characterization was carried out in the devices by deposition of the P3AT film onto ITO and then evaporation of the aluminum (Al) electrode on top, forming a diode-like structure ITO/P3AT/Al, and a Keithley model 238 SMU was employed as a voltage source (V) and current meter (I) in order to carry out DC electrical measurements. The thickness of the films were determined by a Veeco, Dektak 150 profilometer by scratching them with an aluminum tip, thus creating a step between the clean substrate and the film height. The thicknesses of the spin-coated films obtained by profilometry measurements for P3BT, P3HT, P3OT and P3DT in the ITO/P3AT/Al devices were approximately 101, 129, 96 and 133 nm, respectively. There were deposited 15 LS layers for P3HT, P3OT and P3DT onto ITO, and 10 layers for P3BT. The thicknesses of the LS films for P3BT, P3HT, P3OT and P3DT in the ITO/P3AT/Al devices, also obtained by profilometry measurements were 71, 190, 140 and 220 nm.

Cyclic voltammetry (CV) measurements were done using a Potentiostat/Galvanostat, model PGSTAT 30, coupled to a 10 mL electrochemical cell. The supporting electrolyte was a solution of $0.1\,mol\,L^{-1}$ tetrabutylammonium-perchlorate (TBAP) in acetonitrile (ACN). The cell was composed of an Ag/ACN with TBAP, $0.1\,mol\,L^{-1}$ as reference electrode, a $1.0\,cm^2$ platinum counter electrode and the working electrode (spin-coating and LS films of P3AT deposited onto ITO). The UV absorption spectra were obtained during the CV measurements using a Thermo Scientific Genesys 6 Spectrophotometer.

3. Results and Discussion

Fig. 1 shows the results of the DC electrical characterization for the ITO/P3AT/Al devices of P3BT, P3HT, P3OT and P3DT deposited by spin-coating and LS techniques. In order to compare the results for films with different thicknesses, d, the electric field moduli $F = V/d$ were calculated [11]. The I vs. F plots shown in Fig. 1 reveal a diode-like behavior, possibly due to the formation of a Schottky barrier [12], which is the result of the formation of defects in a metal-semiconductor interface [13,14]. For the ITO/P3AT/Al devices of spin-coated films, the current onset in direct polarization for P3BT and P3HT are at low F and close to each other, whereas the P3OT shows the less significant current increase. For the devices of LS films, the ITO/P3HT/Al stands before the others, once the current onset is at the lowest F.

The results for different polymers and deposition technique were also compared by means of the rectification factor of I vs. F plots, which is the ratio between the electrical current in direct and reverse polarization. The rectification factors calculated at $\sim$20 MV/m resulted in 1, 5500, 2100 and 17,000 for the ITO/P3AT(spin-coating)/Al devices and in 1, 790, 43 and 310 for the ITO/P3AT(LS)/Al devices of P3BT, P3HT, P3OT and P3DT, respectively. The ITO/P3AT/Al devices of spin-coated films showed higher rectification factors when compared to the LS ones, except for the P3BT in which both cases showed no rectifying signature.

Besides the Schottky barrier, the energy diagram also plays an important role on the charge transport in direct and reverse polarization, due to the work functions of the ITO electrodes (4.8 eV) [15] and Al (4.1 eV) [2], which promote different barriers for charge injection in the material [16]. By means of CV measurements, it was possible to determine the energy diagrams of the organic devices, since HOMO and LUMO are directly related to their ionization potential and electronic affinity, and thus allow an estimate of the interfacial barrier energy [17].

Fig. 2(a) and (b) shows the CV results obtained for the P3AT films deposited by spin-coating and LS technique, respectively, where two well-defined oxidation and reduction peaks were observed for all P3AT derivatives. It is also common to observe a single oxidation peak for polythiophene derivatives, caused by slow transport of counteranions [18]. The shape of the voltammogram of P3AT derivatives depends on several features, including the polymer molecular weight [19] and the monomer side chain length [20]. Before the first oxidation peak it was possible to estimate the oxidation potential onset, E'_{ox},[21,22] as observed in the Fig. 2(c) for the P3DT spin-coated film.

Since the measurements were carried out in solution and not under vacuum, the values must be corrected for each type of reference electrode and solution that was employed. The energy for the HOMO level can be calculated by the relation $E_{HOMO} = e\,E'_{ox} + 4.43$, where e is the electron charge and 4.43 eV is the correction for the Ag/ACN with TBAP $0.1\,mol\,L^{-1}$ electrode [23,24]. The HOMO values were calculated to be around 4.73, 4.71, 4.73 and 4.76 eV for the spin-coated films and around 4.68, 4.70, 4.73 and 4.77 eV for the ones obtained by the LS technique for P3BT, P3HT, P3OT and P3DT respectively. These HOMO values are similar to the ones found in literature for thin films of regioregular P3HT [25].

It was not possible to estimate the electronic affinity in the region of the anodic potential of the voltammograms (related to the LUMO of the considered material) due to the difficulty to accurately determine the potentials' onset for the second reduction peak. Instead, UV-visible optical absorption measurements were employed to determine the optical gap, which is usually close to the electronic gap, as shown by H. Eckhardt et al. for the poly (phenylene vinylene) [26]. Fig. 3(a) and (b) show the UV-visible spectra for the P3AT films deposited by spin-coating and LS films, respectively. The wavelength related to the optical gap is estimated
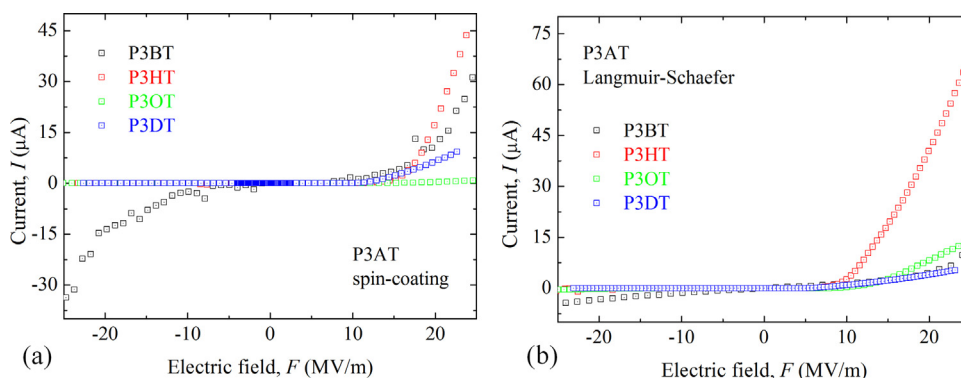

Fig 1. *I vs. F* plots for the ITO/P3AT/Al devices, where P3BT, P3HT, P3OT and P3DT were deposited by (a) spin-coating and (b) LS techniques.