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High open-circuit voltage single-layer polybithiophene-based photovoltaic devices

**Elinton L. Leguenza · Rodolfo L. Patyk ·
Regina M. Q. Mello · Liliana Micaroni ·
Marlus Koehler · Ivo A. Hümmelgen**

Abstract We report the construction of single-polymer-layer photovoltaic devices using polybithiophene thin films synthesized in propylene carbonate, using fluorine-doped tin-oxide as substrates. Polybithiophene films show high organization of molecular dipoles, leading to an open-circuit voltage of 2 V when photovoltaic devices with aluminum top contacts are constructed.

Keywords Photovoltaic devices · Polybithiophene · Electrochemical synthesis

Introduction

Organic photovoltaic devices based on both polymeric and small-molecular-weight semiconductors constitute a subject of intense research activity in recent years, aiming at the production of low-cost and high-efficiency devices. Among conjugated polymers, polythiophene and poly(3-methyl-thiophene) attracted attention for such applications for more than two decades [1]. Polythiophenes and its derivatives can be electrochemically deposited [1–7], constituting a potentially simple process for device preparation.

E. L. Leguenza · R. L. Patyk · M. Koehler · I. A. Hümmelgen (✉)
Departamento de Física, Universidade Federal do Paraná,
Caixa Postal 19044, 81531-990 Curitiba PR, Brazil
e-mail: iah@fisica.ufpr.br

E. L. Leguenza
Núcleo de Ciências Exatas e Tecnologia,
Centro Universitário Positivo,
81280-330 Curitiba PR, Brazil

R. M. Q. Mello · L. Micaroni
Departamento de Química, Universidade Federal do Paraná,
Caixa Postal 19081, 81531-990 Curitiba PR, Brazil

Electrochemical preparation of poly(3-alkylthiophene)s [8–10] and polythiophene [11] for photovoltaic applications using different substrates was also reported, but, similar to pioneering work, showed low open-circuit voltage, typically lower than 1 V. To improve device efficiency, heterojunction device strategies were also applied [12, 13], but with limited success concerning power conversion efficiency. Electro-chemically synthesized poly(3-methylthiophene) shows high exciton diffusion length when compared with most of the conjugated polymers, an important characteristic in the case of photovoltaic devices, which was attributed to a better organization of the layers grown at the beginning of the electrodeposition [9, 10].

It has been observed that polythiphenes obtained from galvanostatic polymerization of thiophene, bithiophene, and terthiophene in 0.5 M $LiClO_4$ in propylene carbonate present different conformation, depending on the starting compound. Polythiophenes films prepared from bithiophene and terthio-phene show a single band at 3,063 cm^{-1} [corresponding to aromatic beta-(C─H)-groups], which suggests a regular α,α'-linking of the monomeric units [14]. Bithiophene was cited as an excellent candidate for the preparation of high-quality polythiophene [15–17], and highly smooth and neutral polythiophene prepared by electropolymerization of bithiophene was also successfully used as hole injection contact in molecular light-emitting diodes [18]. The proposed regularity may positively influence the electrical behavior of polythiophene prepared from bithiophene, which will be denoted polybithiophene (PBT) throughout this text, justifying the investigation of the suitability of this prepara-tion route for photovoltaic devices.

In this work we report the preparation of PBT electro-chemically deposited on top of fluorine-doped tin-oxide (FTO) substrates, using bithiophene as monomer, for single organic-semiconductor-layer photovoltaic devices. FTO

substrates were selected because they constitute a substitute to the most usual indium–tin oxide (ITO). Due to the high demand and low production of indium, its price suffered a 10-fold increase since 2003 and now stands at the highest level since the Second World War [19]. Because the use of indium in coatings, mainly ITO, now accounts for 70% of total indium consumption [19], the substitution of ITO is desirable from an economical point of view.

Experimental

The polymer films were prepared by galvanostatic deposition at a current density of 1.0 mA cm^{-2} on glass covered with FTO of sheet resistance in the range 10–15 $\Omega/\square$ supplied by Vidcon Ltda. Before deposition, the FTO was partially removed from the glass surface following established procedures [20]. The electrolyte was 0.5 M LiClO$_4$+0.1 M 2,2′-bithiophene in propylene carbonate, and samples batches were prepared using different deposition times: 40, 60, 80, 100, and 120 s, corresponding to 40, 60, 80, 100, and 120 mC.cm^{-2}, respectively. After synthesis, the films were polarized at 200 mV vs Ag pseudoreference electrode, for the same amounts of time used for deposition in each case. Pt was used as counter electrode. After film preparation, samples were washed in propylene carbonate and then dried at 50 °C in air for 30 min.

Devices were prepared evaporating Al at a pressure of 10^{-6} Torr on top of the PBT/FTO substrates, following the geometry schematically represented in Fig. 1. They were characterized measuring the current vs voltage I(V) characteristics under air mass 1.5 (AM1.5) spectral distribution, illuminated through the glass substrate, controlling the irradiance using neutral filters. For this purpose we used a 150-W Oriel solar simulator, a Keithley 230 voltage source and a Keithley 6485 picoammeter. PBT film thickness was estimated using a Dektak3 surface profiler.

Results and discussion

Devices with different PBT-film thicknesses were prepared following the procedure described above. The film thickness dependence on deposition time for the described conditions is presented in Fig. 2, indicating a faster growth at the beginning and arriving an almost linear growth after ~60 s.
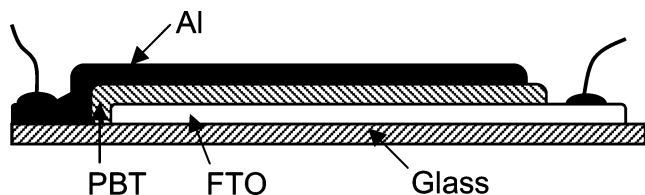
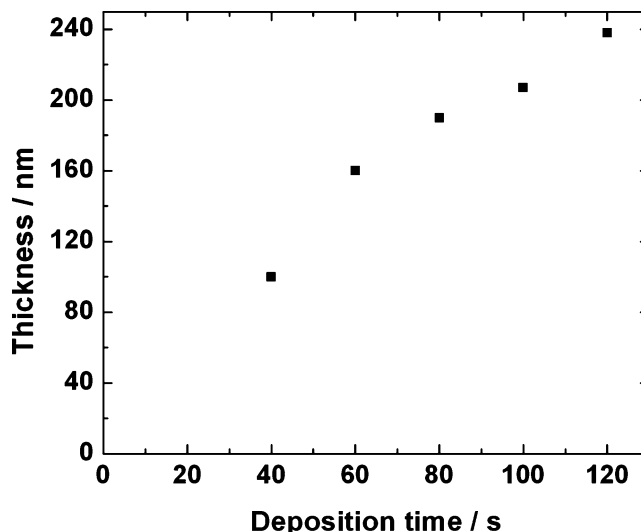

Fig. 1 Schematic structure of the photovoltaic devices

Fig. 2 Polybithiophene film thickness as a function of deposition time

The I(V) characteristics of devices with nominal PBT thicknesses of 100, 160, 190, 207, and 238 nm were measured in the dark and at irradiances of 7×10^{-2}, 3.3, and 6.6 W.m^{-2} (AM1.5 spectral distribution). In Fig. 3, we present such measurements for a 160-nm-thick PBT layer device. As can be observed, the curves measured with the device under illumination show photovoltaic effect, characterized by the points in the third quadrant of the plot. An unusual feature observed in Fig. 3 is the high open-circuit-voltage (V_{oc}), of the order of 2.2 V at an irradiance of 6.6 W m^{-2}.

In Figs. 4 and 5, we present the dependence of the photovoltaic relevant quantities, V_{oc}, short-circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (η) on the PBT layer thickness. V_{oc} corresponds to the potential value at I=0; J_{sc} is the device current density at V=0; the fill factor is given by

$$FF = \frac{V_p \cdot I_p}{V_{oc} \cdot I_{sc}}, \qquad (1)$$

where V_p and I_p represent the maximum-power-rectangle V and I values, respectively, and

$$\eta = \frac{V_{oc} \cdot J_{sc} \cdot FF}{E_{AM1.5}}, \qquad (2)$$

where $E_{AM1.5}$ is the total irradiance at AM1.5 spectral distribution. The most efficient devices (highest η) have a PBT layer thickness of 160 nm. It can be observed that the J_{sc} and FF dependence on PBT layer thickness is weak in the investigated range, so that the major factor determining the maximum of η is V_{oc}, which varies by a factor of ~2 for the investigated thickness range.

The electrodes used in this device have similar work functions φ: φ_{Al} is expected to be around 4.3 eV [21] and φ_{FTO} was reported to be between 4.4 and 4.9 eV [22–24].
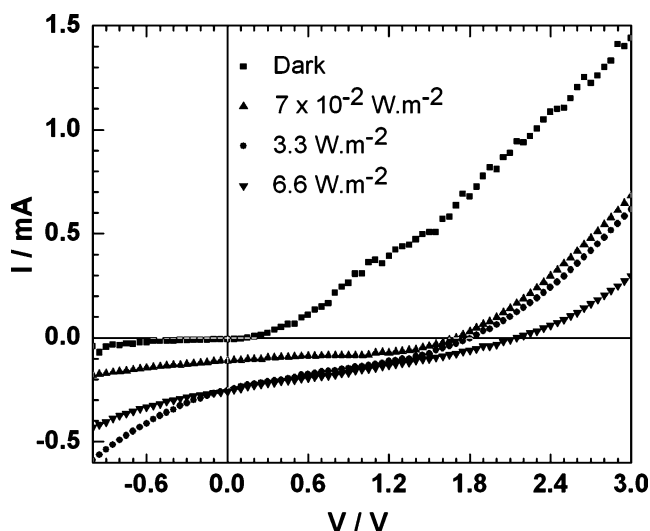
Fig. 3 Current–voltage characteristics of a FTO/PBT(160 nm)/Al device in the dark and under different irradiances. Device active area: 4.3 mm^2; spectral distribution AM1.5

Therefore, the high value of V_{oc} can hardly be attributed solely to the built-in electric field due to the difference of electrodes work function. Additionally, FTO/polythiophene/Al devices electrochemically prepared following a different route present usual V_{oc} values, around 0.7–0.8 V [11], the same occurring with TiO$_2$/poly(3-undecyl-2,2′-bithiophene)-based devices [7].

The high V_{oc} values observed in our devices prepared from bithiophene units suggest that conformation of the polymer and its organization during deposition leads to organization of the dipoles, to some extent influenced by the used solvent, propylene carbonate. Organized dipoles would be responsible for a polarization built-in electric field giving rise to the open-circuit potential. Because the dipole moment of the bithiophene lies parallel to the rings, this high V_{oc} suggests again that polythiophene electrodeposited using bithiophene following the described procedure has significant portions of the macromolecules organized with
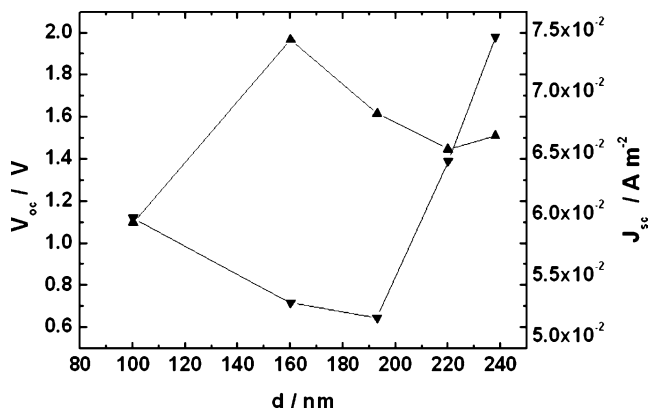
Fig. 4 Open-circuit potential (*up triangles*) and short-circuit current density (*down triangles*) dependence on PBT thickness of FTO/PBT/Al devices at 6.6 W.m^{-2}, spectral distribution AM1.5
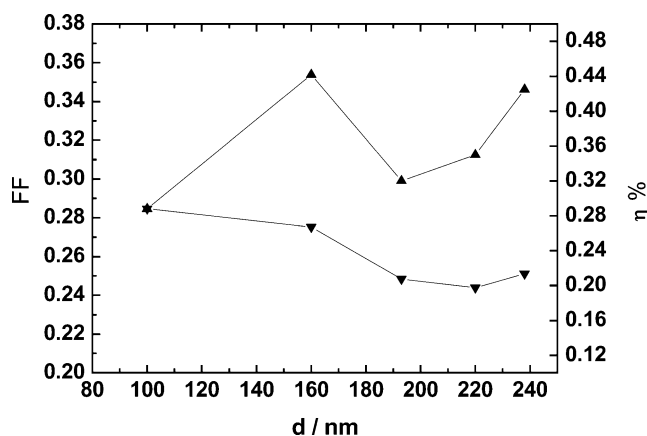
Fig. 5 Fill factor (*down triangles*) and power conversion efficiency (*up triangles*) dependence on PBT thickness of FTO/PBT/Al devices at 6.6 W.m^{-2}, spectral distribution AM1.5

the rings plane perpendicular to the interfaces with FTO and/or Al.

A rough quantitative analysis can be made taking the molecular mass of the bithiophene units and assuming a PBT density of the order of 1 g cm^{-3}, leading to a molecular density of ~4×10^{27} m^{-3}. Assuming a constant polarization (P) along the PBT film in the direction perpendicular to the interfaces of the electrodes, one can write [25]

$$P = \frac{1}{3}(\varepsilon + 2)N\mu_0\langle\cos\theta\rangle, \tag{3}$$

where ε is the dielectric constant, μ_0 the permanent dipole moment, and θ the angle between P and μ_0. In writing Eq. 3, it is assumed that no dipole reorientation is allowed, which means that ε is the macroscopic dielectric constant [25]. The relation between the polarization and the macroscopic electric field is $P = (\varepsilon - 1)\varepsilon_0 F$. Substituting this relation in Eq. 3, we obtain,

$$N = \frac{3(\varepsilon - 1)}{\varepsilon + 2}\frac{\varepsilon_0}{\mu_0\langle\cos\theta\rangle}\frac{V_{OC}}{d}, \tag{4}$$

where we assume $F = V_{oc}/d$; ε_0 is the permittivity of vacuum, d the thickness of the PBT film, and N the density of permanent dipoles. Taking an arbitrary but reasonable value of $\varepsilon = 3$ and $\mu_0 = 1.4$ D, which corresponds to an average twisting dihedral angle between the thiophene rings of 135° [26], for $d = 160$ nm, $\langle\cos\theta\rangle \sim 1$, and $V_{oc} \approx 2$ V, one obtains $N \approx 3 \times 10^{25}$ m^{-3}. This simplified analysis suggests that the high value of V_{oc} is produced by a polarization that corresponds to around 1% of the bithiophene units lying with dipole vectors oriented parallel to each other and perpendicular to the interfaces of the electrodes.

We have submitted samples to an annealing at 80 °C for 10 min in air, before Al contact deposition. In these samples, V_{oc} was reduced to almost zero, which is

consistent with a random distribution of dipoles and the work functions of the selected electrodes, showing that at this temperature the preferential orientation of dipoles is lost.

The values of power efficiency achieved by our devices are low, far from those belonging to the best reported among organic photovoltaic cells (>3%) [27, 28]. But the remarkable high open-circuit voltage achieved in our single-active-layer devices indicates a high degree of molecular organization, which, from a practical point of view, is interesting for photodetection via potential measurement. Such high potential values may easily achieve a quite favorable condition of the signal-to-noise ratio, simplifying electronic detection circuitry.

Furthermore, the insertion of polarized layers constitutes a new promising strategy for open-circuit voltage and power conversion efficiency increase in organic semiconductor-based devices, which is not restricted to single-active-layer devices. Such polarized layers may be used in heterojunction devices, which incorporate additional layers with good charge dissociation and collection features, potentially allowing further efficiency improvements. For photovoltaics, certainly materials whose dipoles remain oriented even at higher temperatures are highly desirable.

Conclusions

We demonstrate that polythiophene thin films synthesized from bithiophene in propylene carbonate onto FTO substrates show high polarization, leading to remarkable high observable open-circuit voltages when photovoltaic devices with aluminum top contacts are constructed.

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