Synthesis of 3′,4′-Disubstituted Terthiophenes— Characterization and Electropolymerization. II. 3′-Bromo-4′-thienyl-2,2′:5′,2′-terthiophene and 3′,4′-diphenyl-2,2′:5′,2′-terthiophene in photovoltaic displays

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ABSTRACT: In a previous work 3′,4′-dibromo substituted polythiophene film was used to produce an electronic device with photovoltaic characteristic but only 0.006% yield was achieved. In an effort to understand the reason of this low-yield, we intend to elucidate the effect of substituents of terthiophene compounds on the morphological characteristics and conductivity of the electrochemical deposit. Thus, in this article we describe the electrochemical properties of thin films of poly(3′,4′-diphenyl-2,2′:5′,2″-terthiophene), and poly(3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene), the studies of electropolymerization using cyclic voltammetry, the determination of nucleation and growth mechanism using potential steps, and the morphology. Furthermore, a ZnO/Polymer/PTCDA/Li/Al photovoltaic cells have been devised and their I–V characteristics studied in the presence and in the absence of light. Incorporation of 3,4-9,10-tetra-carboxylic dianhydride, PTCDA, as acceptor, induces a wider absorption spectrum in the visible region. Study of the photovoltaic efficiency, that increased with a decrease of the polymeric coating thickness, which in turn, is related to the number of voltammetric cycles, was also accomplished, but the desired thickness was never obtained without missing the electronic properties. Thus, even if the polymeric layer had the appropriate structure, this study corroborates that, to prepare the deposit, the electrochemical parameters must be previously controlled so as to obtain the thickness and morphology that render the best response. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1722–1729, 2008

Key words: conducting polymers; conjugated polymers; diodes; electrochemistry; heteroatom-containing polymers

INTRODUCTION

Many polymers having an extensive conjugated π-electron system become conductive when doped[1] and display large nonlinear optical responses in their undoped form.[2] The field of conducting polymers started with the discovery of conductivity in doped polyacetylene films,[3] but polyacetylene is not an ideal conducting polymer because its conductive response is sensitive to the presence of oxidizing agents. These material limitations have aroused interest in more stable conjugated polymers such as polythiophenes.[4] Structural defects and solubility of polythiophene have drawn much attention during its investigation and interesting solutions have been put forward.[5–9] The extended conjugation in polythiophene is possible only in polymers bearing repeated bonds of thiophene with 2,5-bonds. Unfortunately, 2,4- and 2,3-couplings can also be found. These unwanted couplings are obtained when the polymers are prepared by (electro)oxidative polymerization. This is due to the fact that during polymerization both the absolute oxidation potential of the α position and the oxidative potential difference between the α and β positions decreases as the number of the rings increases.[1]

In organic semiconductors, the individual characteristic of the molecules and the structural order of the molecules in the film determine the macroscopic characteristic of the material. These features can be tailored using molecular engineering to synthesize the molecules with the best characteristics and

controlling the conditions under which the polymeric coatings are formed.[3–5]

The electrochromic properties observed in polythiophene deposits have drawn great interest from years.[10–12] Owing to its capacity of affording large photocurrents, generation of regular deposits with a minimum of impurities, are possible.[9]

One of the main features of heterocyclic conductive polymers is their trend to assume a planar geometry because this structure favor the maximum overlapping among p atomic orbitals (π conjugation) and, consequently, the existence of high energy donor bands and/or low energy acceptor bands. In (poly)heterocyclics bearing sulfur atoms, the extension of the π–π conjugation between adjacent rings is extensive and responsible for their electrical and optical properties. However, the likely distortion regarding the anticonformation angle that determine the relative orientation between adjacent rings and the subsequent molecular planar loss (torsional defect) would affect the electronic structure of the polymer, which might even determine its utility. Nevertheless, the addition of side groups to a terthiophene may bring about steric effects that decrease the torsion of the main chain, maintaining the π–π conjugation, or can alter, in a nondesirable fashion, other properties of the polymer. On the other hand, it is important to know the most favorable position in which such groups must be inserted as well as the tacticity the polymer will adopt.

The development of photovoltaic devices bearing a polymeric layer synthesized via electrochemical polymerization of 3′,4′-dibromo-2,2′:5′,2″-terthiophene, and a search for the most suitable conditions leading to a more uniform film with the desired thickness, was discussed and studied in a previous work.[13] Herein a comparison of the results obtained with devices fabricated with a polymeric layer, synthesized via electrochemical polymerization, of 3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene and 3′,4′-diphenyl-2,2′:5′,2″-terthiophene and their applications in the development of photovoltaic devices are described.

The electronic device will be prepared using the electro-deposited polymeric layer of poly(3′,4′-diphenyl-2,2′:5′,2″-terthiophene) or (3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene), which corresponds to the electron-donor layer. The technique of thermal evaporation of thin films (a few nanometers) employed for the fabrication of semiconductors will be used to deposit the 3,4,9,10-perylene-tetra-carboxylic-dianhydride (PTCDA) film that corresponds to the electron-acceptor layer. PTCDA, besides being easily sublimable, is highly photostable and displays a wide absorption spectrum in the visible.

EXPERIMENTAL

Reagents and instrumentation

All chemicals and solvents were purchased from Aldrich and were utilized as received, except diethyl ether that was distilled over sodium prior to use. Grignard's reagent was prepared into a dried flask (flushed with N_2 before use) containing a 2-bromothiophene solution in diethyl ether and magnesium granules, under nitrogen.

FTIR spectra were measured on a Perkin-Elmer 1710 FT Spectrophotometer for solid dispersion with KBr pellets. ^1H and ^{13}C NMR spectra were recorded on a Bruker 200P Spectrometer using chloroform-d as solvent, and TMS as internal standard. Microanalysis was performed on a Fison, Model EA-1108, Elemental-Analyzer. Electrosynthesis and electrochemical characterization were accomplished on a Voltalab PGZ100, using a three-compartment cell, and dichloromethane as solvent. A polycrystalline platinum disk (0.07 cm^2 geometric area) was used as working electrode. All potentials quoted in this article are referred to a Ag/AgCl electrode in tetramethylammonium chloride to match the potential of a SCE at room temperature.[14] The auxiliary electrode was a helical platinum wire. SEM images were obtained on a JEOL, Model 6400 F, High-resolution Scanning Electron Microscope (HR-SEM).
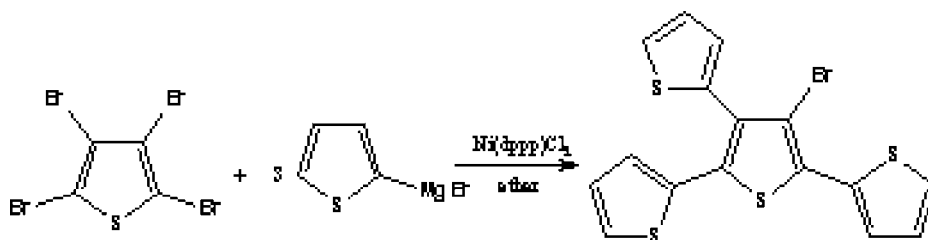
PROCEDURES

Synthesis of 3′,4′-diphenyl-2,2′:5′,2″-terthiophene

The synthesis of the monomer was accomplished according to methods described in the literature[15–17] and depicted in Scheme 1.
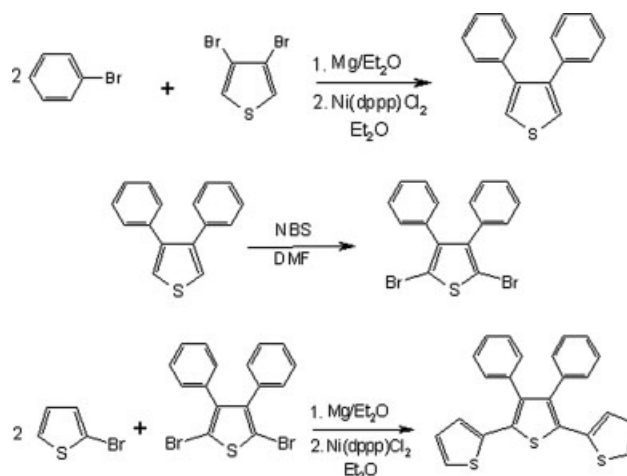
Scheme 1 Synthesis of 3′,4′-diphenyl-2,2′:5′,2″-terthiophene.

Scheme 2 Synthesis of 3′-bromo-4′-thienyl- 2, 2′:5′,2″-terthiophene

Step 1

Grignard's reagent, prepared from 2-benzyl bromide and 0.24 g magnesium granules in 20-mL diethyl ether, was slowly injected through a septum into a three-neck round-bottom flask containing 30 mg of $Ni(dppp)Cl_2$, 2.5 mmol of 3,4-dibromothiophene, and 20 mL of diethyl ether. The mixture was refluxed for 24 h under N_2. The reaction was terminated with methanol/water and the product was extracted with ether. The organic phase was washed with a saturated NaCl solution and dried ($MgSO_4$). After solvent removal, a dark liquid was obtained. The crude product was separated by column chromatography on silica-gel (hexane), followed by crystallization from methanol. After filtration, the product was vacuum dried.

Step 2

To the product obtained in step 1, dissolved in dimethylformamide (DMF), N-bromosuccinimide in DMF was added and the mixture was refluxed to obtain the brominated compound which was isolated by column chromatography on silica-gel (hexane), followed by crystallization from methanol. After filtration, the product was vacuum dried.

Finally, the brominated compound was placed into a three-neck round-bottom flask containing 20 mg of $Ni(dppp)Cl_2$ and 20 mL diethylether. To the resulting solution, Grignard's reagent was slowly injected through a septum. The final product was isolated and purified as described in step 1.

Synthesis of 3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene

Grignad's reagent, 2-bromomagnesium-thienyl prepared as in Step 1 of the abovementioned procedure, was slowly injected through a septum into a three-neck round-bottom flask containing 30 mg (0.075 mmol) of $Ni(dppp)Cl_2$, 1.0000 g (2.5 mmol) of 2,3,4,5-tetrabromothiophene, and 20 mL of diethylether (Scheme 2). The mixture was refluxed for 24 h under N_2. The reaction was terminated with methanol/water and the product was extracted with ether. The organic phase was washed with a NaCl saturated solution and dried ($MgSO_4$). After solvent removal, a dark liquid was obtained. The crude product was separated by column chromatography on silica-gel (hexane), followed by crystallization from methanol. After filtration, the product was vacuum dried for 24 h at 60°C.

Identification was carried out by elemental analyses and from spectroscopic data of the compounds.

Electrochemical polymerization of the monomers

Poly(3′,4′-diphenyl-2,2′:5′,2″-terthiophene) and poly (3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene) were prepared by anodic oxidation of the respective monomers $1 \times 10^{-3}M$ in HPLC grade dichloromethane as solvent and molecular sieves (4 Å) to ensure total exclusion of water from the electrolytic medium, under argon atmosphere. Tetrabutylammonium hexafluorophosphate, dried prior to use, was employed as supporting electrolyte ($10^{-2}M$). Cyclic voltammetry (CV) was used to determine the optimum working potential range for the subsequent electro-oxidation of the monomers to prepare the polymeric films by cyclic voltammetry and to carry out the electropolymerization and characterization at controlled potential. Deconvolution of the potentiostatic transients allows obtaining the nucleation and growth mechanism of the deposit, as described elsewhere.[13,14,18]

Solar cell preparation

The preparation of solar or photovoltaic cells, was accomplished following the ample bibliography available,[19] and the details were included in Part I.[13]

RESULTS AND DISCUSSION

As mentioned earlier, the monomers were synthesized, using a metal-catalyzed transition, coupled with the Grignard's reagent (Schemes 1 and 2) in the presence of nickel(II) dichloro propane-1,3-diylbis(diphenylphosphane) nickel(II). [$Ni(dppp)Cl_2$], as catalyst, which favors the substitution in positions 2 and 5 of the thiophene ring. Considering that the coupling of the thiophene ring in position 2 and 5 was
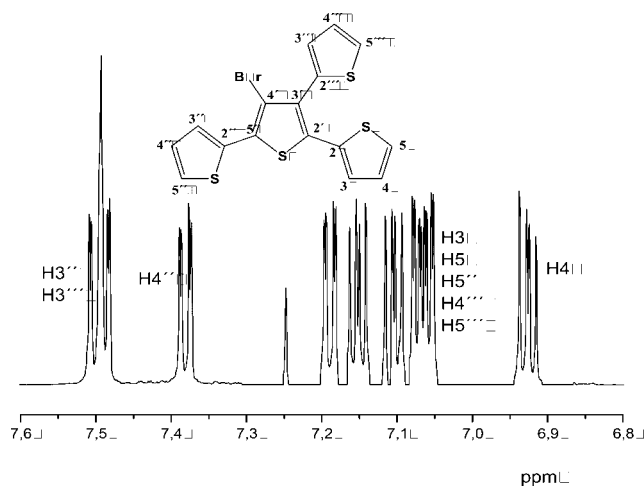
Figure 1 1H NMR spectrum of 3'-bromo-4'thienyl-2,2':5',2''-terthiophene.

Figure 2 Potentiodynamic response of 3',4'-biphenyl-2,2':5',2''-terthiophene in CH$_2$Cl$_2$, on Pt disc. $v = 50$ mV s^{-1}.

more difficult than expected, the use of palladium as catalyst plays a key role in the synthesis. Thus, the procedure leads first to a condensation in position 2, followed by condensation in position 5, affording the desired products, as corroborated from NMR and elemental analysis characterization. Elemental analysis of 3',4'-diphenyl-2,2':5',2''-terthiophene (yield: 19%; m.p. 89.0°C) was as follows: calculated: C: 71.96; H: 4.03; S: 24.17; found: C: 73.28; H: 4.01; S: 23.64. ^{1}HNMR (Fig. 1) showed the following: ^{1}HNMR (400 MHz, CDCl$_3$): δ = 7.16–7.22 ppm (6H, mp) ph-H2; ph-H4, ph-H6; δ = 7.12 ppm (2H,d) Th-H5, Th-H5''; δ = 7.10–7.12 ppm (4H, mp) ph-H3; ph-H5, δ = 6.98 ppm (2H,d) Th-H3, Th-H3'', δ = 6.90 ppm (2H,d) Th-H4, Th-H4''.

As for 3' bromo, 4'-thienyl-2,2':5',2''-terthiophene (yield: 29%; m.p. 90°C), elemental analysis: calculated, C: 46.94; H: 2.22; S: 31.32; found, C: 47.26; H: 1.91; S: 31.21. NMR analysis showed the following: ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.49 ppm (2H,dd) H3'', H3'''; δ = 7.38 ppm (1H,d) H4''; δ = 7.05–7.21 ppm (5H,mp) H3; H5, H5'', H4''', H5''', δ = 6.95 ppm (1H,d) H4.

Potentiodynamic electro-oxidation (CV) of these monomers showed that, when working within the optimum potential range, Figures 2 and 3, a current loop is observed right after the first sweep in the anodic limit, accounting for the modification of the electrode surface owing to deposit formation. This potential is higher for 3'4'-diphenyl-2,2':5',2''-terthiophene, whose symmetrical structure confer it a higher stability than that of 3'-bromo-4'thienyl-2,2':5',2''-terthiophene whose oxidation requires thus a higher overpotential. Successive cycling of both monomers exhibits an increase of the oxidation current after each cycle which has been ascribed to doping of the deposit taking place simultaneously to the increase of the polymeric film thickness. Along with
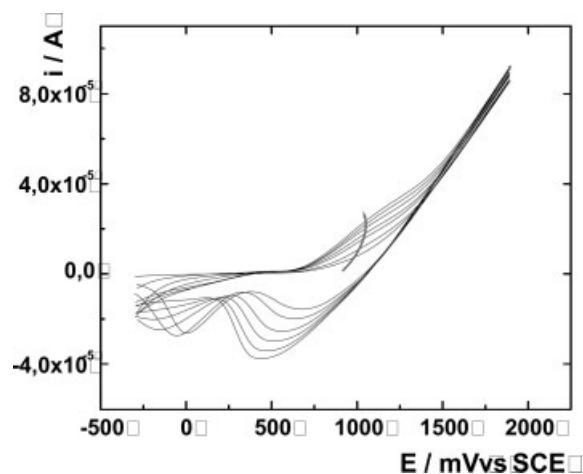
the increase of current, a shift towards more cathodic potential was observed too. This was attributed to that, due to conjugation increase as the length of the generated oligomer chains grow, the species become easier to be oxidized. Also, this would influence the band gap of the deposit demonstrating that the control of its thickness is essential regarding the fabrication of the photovoltaic devices. When CV is employed for the electropolymerization, this is accomplished by controlling the number of cycles.

From the results obtained by CV the suitable potential to perform the potentiostatic electropolymerization was selected. Thus, the nucleation and growth mechanism (NGM) was assessed using potentiostatic steps as described in the literature[18] and, as shown in previous works,[13,14,18,19] the NGM was described through mathematical equations obtained from kinetic studies realized with metallic
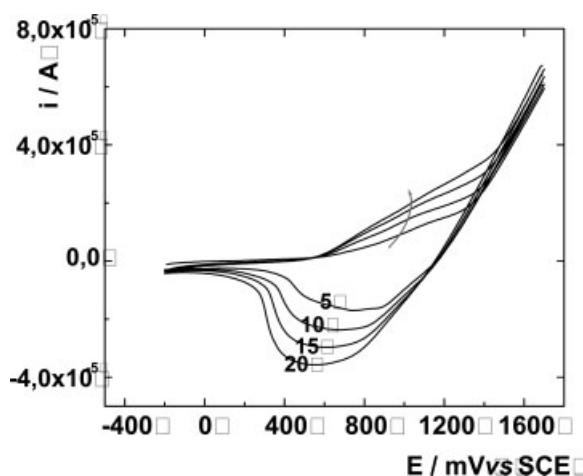

Figure 3 Potentiodynamic response of 3'-bromo-4'-thienyl-2,2':5',2''-terthiophene in CH$_2$Cl$_2$, on Pt disc. $v = 50$ mV s^{-1}.

deposits, although the polymerization process is not analogous to the electrodeposition of metals. It was found that for these monomers the NGM shows a predominance of instantaneous nucleation with bidimensional growth for very short times, whereas for longer electrolysis times tridimensional growth, controlled by diffusion or even by charge transfer, predominates, therefore, although these contributions to the NGM occur simultaneously and/or successively, they can be summarized according to the following equation

$$j = at\left[\exp\left(-bt^2\right)\right] + c[1 - \exp(-dt)]$$
$$+ et^{-0.5}\left[1 - \exp\left(-ft^2\right)\right] \quad (1)$$

where the first term corresponds to an instantaneous nucleation mechanism with bidimensional growth, IN2D; the second to an instantaneous nucleation with diffusion-controlled tridimensional growth, IN3Ddif; and the latter, to a tridimensional nucleation with charge-transfer controlled growth, IN3Dct and the constants a, b, c, ... , f have the same meaning as described elsewhere.[20–22]

As an example, deconvolution transients obtained for the studied monomers are exhibited in Figure 4 from which it can be appreciated, in the first place, that in both cases the addition of the three contributions corresponds exactly to the experimental transient, demonstrating an excellent agreement. Furthermore, for very short times the predominance of instantaneous nucleation with bidimensional growth is evidenced, while the other contribution(s) become important right after this time and, at longer times, the diffusional contribution prevails. Even in the case of 3′,4′-phenyl-2,2′:5′,2″-terthiophene, the charge transfer controlled contribution does not exist, which is consistent with the fact that the oligomerization process occurs very swiftly: the initial current drop, prior to nucleation, is much lower than in previous cases.[23]

Micrographs of the deposits obtained by CV and PM are depicted in Figure 5. It can be observed that, as usual, deposits obtained by CV produce more uniform surfaces during the potential sweep ordering of the deposit is favored. However, it is noteworthy that in both cases the surface is quite homogeneous, made of granules of identical size, which is consistent with that predicted from the NGM since only instantaneous nucleation was found, i.e., at the start up a determined number of nuclei are formed that grow as a function of the time of electrolysis, affording more homogeneous size. Consequently, an excellent agreement was found between the morphology predicted from the NGM and the one obtained by SEM, validating once more the feasibility of making this kind of correlation.
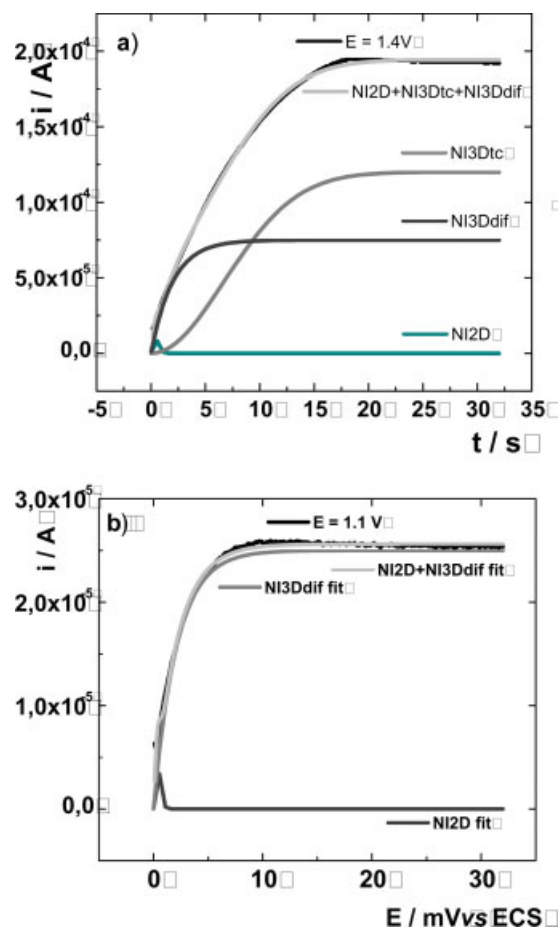
Figure 4 (a) Experimental potentiostatic transient of 3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene in CH$_2$Cl$_2$, on Pt disc (E = 1.5 V), and contributions to the global NGM. (b) Experimental potentiostatic transient of 3′,4′-diphenyl-2,2′:5′,2″-terthiophene in CH$_2$Cl$_2$, on Pt disc (E = 1.5 V), and contributions to the global NGM. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

On the other hand, analysis has been performed by determining the ATR FTIR spectra of the undoped polymers, i.e., applying the undoping potential, after generating the deposit by oxidation. The FTIR spectrum of thiophene ring exhibits specific Broadening peaks at 1050, 1095, 1630, 2935, and 2857 cm^{-1}, which indicates the formation of a polymeric bulk material, and suggests α-αo couplings of the thiophene rings. The strongest band arises around 1630 cm^{-1} was assigned to a Cα=Cβ stretching, those at 1050 cm^{-1} are due to C—H in-plane bending 2,5-disubstituted thiophene rings. All other main features in the polymer spectrum are similar to those appearing in the monomer spectrum.[13]

On the basis of thermal evaporation deposition techniques of thin layers (a few nanometers) of organic semiconductors bearing both types of doping,[24] a bilayer technology, in Figure 6, was
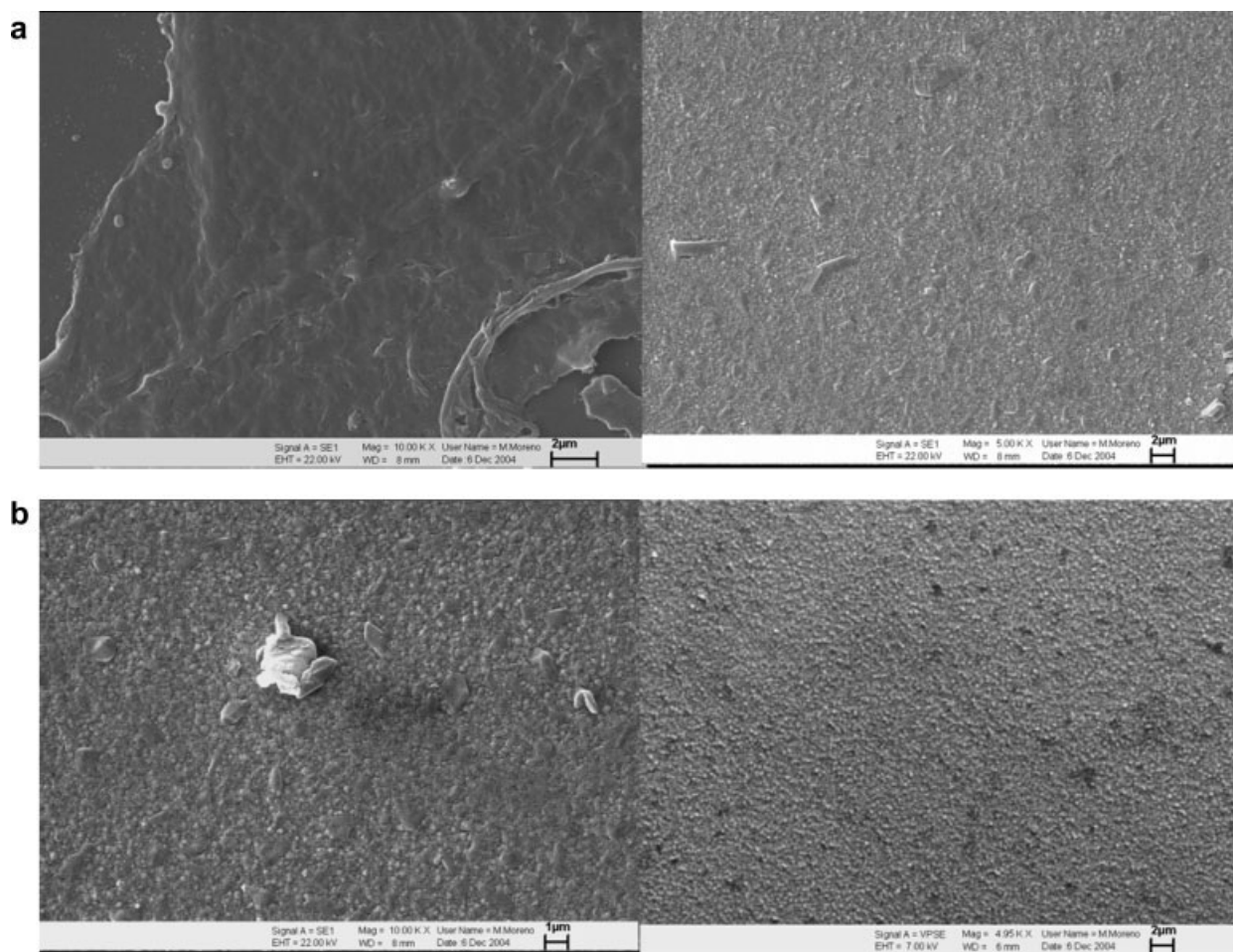
Figure 5 SEM micrographs of electrochemical deposits obtained by (a) CV, and (b) PM for 3'-bromo-4'-thienyl-2,2':5',2''-terthiophene (left) and 3',4'-biphenyl-2,2':5',2''-terthiophene (right).

employed to evaluate poly(3',4'-biphenyl-2,2':5',2''-terthiophene) and poly(3'-bromo-4'-thienyl-2,2':5',2''-terthiophene), respectively, as the polymeric layer in the preparation of photovoltaic devices. The insertion of a thin layer of LiF underneath the Al metallic negative electrode stabilizes high open-circuits voltages.[25] On the other hand, PTCDA is a crystalline organic semiconductor particularly interesting because of its excellent properties and electronic potential, useful to device optoelectronic mechanisms.
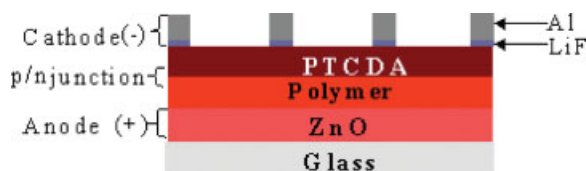

Figure 6 Structure of a plastic solar cell. The active layer comprises a thiophene derivative polymer and a perylene derivative, PTCDA, used as hole-injection layers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The efficiency of the devices is related, among other factors, to the thickness of the comprising layers,[26] glass/ZnO (180 nm)/PTCDA (200 nm)/polymer/LiF (<15 nm) Al (100 nm). The thickness of all deposits, except that of the polymer, can be controlled by thermal evaporation techniques, whereas the thickness of the polymer is controlled by the number of voltammetric cycles (CV) or the time of application of the deposition potential (PM).

Devices of different thickness were prepared. No photovoltaic effect was achieved for the devices built from polymers obtained by using a small number of cycles. This was not the case for a cell prepared with a 20-cycles film, wherein the thickness was much greater than the recommended one; and probably this is the reason why its efficiency was not sufficiently high.

Typical current-voltage characteristics (I-V) and electroluminescence-voltage (EL-V) for layers of polymers obtained after 10 voltammetric cycles are displayed in Figure 7.

These responses correspond to devices that behave as diode, therefore it is impossible to compare them
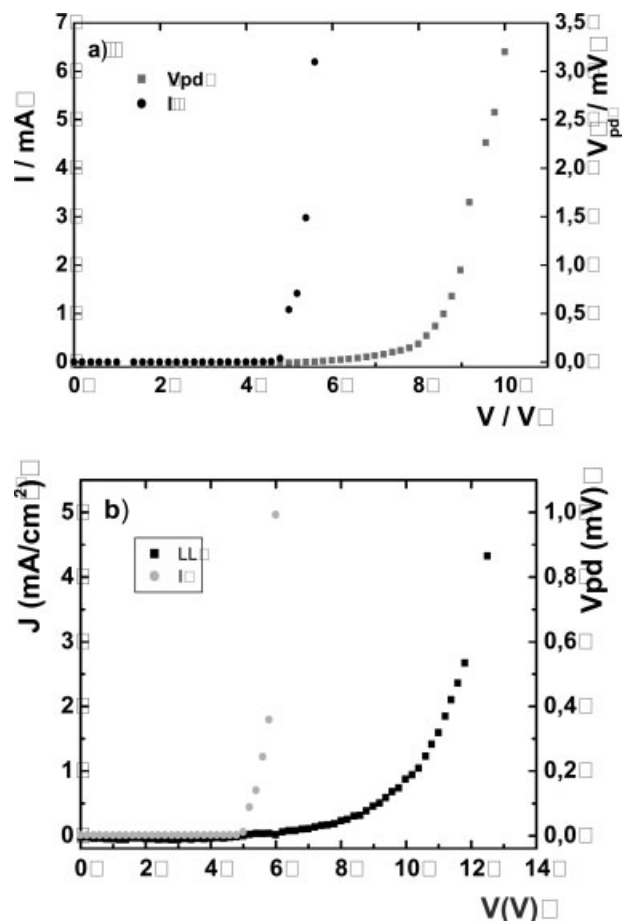
Figure 7 Response of a device Glass/ZnO/PTCDA/polymer/Al/LiF. (a) poly(3′,4′-diphenyl-2,2′:5′,2″-terthiophene), and (b) poly(3′-bromo-4′-thienyl-2,2′:5′,2″-terthiophene).

with those reported in the previous work, Part I,[13] as initially proposed because this behavior is unpredictable and, as demonstrated in the present work, only can be proved by experimental means since the current literature lacks of theoretical bases that support such predictions.

The first threshold voltage, injection threshold, V_{ITH}, occurring at 5 V, corresponds to a strong increase of hole injection, since the organic layer usually is p-type. The second threshold voltage, threshold voltage for light emission V_{ELTH}, at 8 V, which corresponds to the appearance of light emission, pertains to a balanced injection of electrons. The difference between V_{ITH} and V_{ELTH} is a function of the band mismatch at the anode and at the cathode. For $V > V_{\text{ELTH}}$ the luminance increases proportionally to the current density, indicating that the quantum efficiency is almost constant over a wide range of current.

Thus, even though the behavior of these devices cannot be directly compared with the behavior of the previous ones, it was demonstrated that, as before,[13] the thickness and morphology of the poly-

meric film must be optimized to improve the device yield. As indicated earlier, this may be realized using electrochemical techniques to prepare the polymeric layer by varying the number of voltammetric cycles or the electrolysis time. Besides, modulation of the other parameters that control the electropolymerization process, e.g., monomer concentration, solvent, etc., and that influence the morphology of the deposit can be carried out to enhance the yield of the device. Consequently, even if the yields obtained thus far are low, the use of these monomers for the preparation of polymeric layer for photovoltaic devices must not be disregarded before undertaking a systematic survey about its electropreparation.

CONCLUSIONS

The method employed for the synthesis of the monomers, as postulated in the previous work, Part I, is suitable for the preparation of monomers of 3′4′-disubstituted terthiophens aimed at improving the properties of the respective polymers. In the absence of water in the electrolytic medium, it is likely the obtention of poly(3′,4′-biphenyl-2,2′;5′,2″-terthiophene) or poly(3′,4′-disustituted-2,2′;5′,2″-terthiophene) using either potentiodynamic or potentiostatic techniques, leading to deposits whose thickness and morphology can be regulated by controlling the number of cycles or the electrolysis time, respectively. This allows the obtention of polymers useful for the fabrication of photovoltaic devices.

The NGMs of the surveyed tetrasubstituted polymers showed a predominance of instantaneous nucleation, with bi or tridimensional growth, controlled by diffusion or charge transfer. In addition, a good agreement was found between the morphology predicted from NGM and the one obtained by SEM. Thus, the direct obtention of the NGM during the electropolymerization is a suitable tool to predict *in situ* the morphology of the generated deposit.

Poly(3′,4′-biphenyl-2,2′;5′,2″-terthiophene) displayed diode properties of low capacity. Among other factors, the efficiency of the devices depends upon the thickness of the comprising layers. The thickness of all the layers but that of the polymer can be controlled by vacuum thermal evaporation. The polymer thickness, on the other hand, can be controlled by the number of voltammetric cycles or electrolysis time. Thus, although the monomeric structure employed to prepare the polymeric layer is suitable concerning the band gap, this study corroborates that, previously, the electrochemical parameters for the preparation of the deposit must be optimized to produce a film of the required thickness and morphology.

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