

# Synthesis of 3',4'-Disubstituted Terthiophenes. Characterization and Electropolymerization. I. 3',4'-Dibromo-2,2':5',2''-terthiophene in Photovoltaic Display

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**ABSTRACT:** Recent studies on conducting polymers have demonstrated that polymers of 3-substituted thiophene produce very stable compounds. Although this kind of substitution improves the regularity, structural defects still exist. To overcome this drawback, the polymerization of 3,4-disubstituted thiophene is proposed as a convenient way of synthesizing regular, highly conjugated conductive polymers. Our interest is thus focused on the synthesis of tetra-substituted thiophene derivatives, their polymerization, electrochemical properties, spectral characteristics, oxidizing potential, and the feasibility of photocells development. In this article, we report the synthesis and characterization of 3',4'-dibromo-2,2':5',2''-terthiophene which, as such or modified, may be a good starting product for obtaining new monomers of 3',4'-disubstituted terthiophenes, that would

allow the effect of the substituents on the properties of the respective polymers to be studied. In addition, the monomer was electropolymerized and the resulting deposit was electrochemically and morphologically characterized. Two conclusions were drawn: first, more uniform and homogeneous layers than those of polythiophene are obtained; second, the thin layers of the polymer, electron acceptors, absorb in the visible. Finally, photocells were assembled to investigate their photovoltaic effect. Although the so prepared solar cells showed some photovoltaic effect, the yield was low. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5314–5321, 2006

**Key words:** conjugated polymers; heteroatom-containing polymers; electrochemistry; conducting polymer

## INTRODUCTION

In recent years, many studies have been conducted to develop processable conductive polymers. In this context, polythiophenes have attracted great attention because of their potential applications as organic materials for the preparation of a variety of electric or electronic devices.<sup>1,2</sup> To obtain materials with improved properties, the study of polymers generated by the modification of these molecules has received considerable attention too. It has been demonstrated recently that the polymerization of 3-substituted thiophenes, carried out by chemical or electrochemical oxidation, gives very stable conducting polymers, with interesting electrical conductivity and electroluminescent properties.<sup>3–5</sup> The presence of a substituent in the third position provides polythiophenes with adequate physical and electrochemical properties,<sup>2</sup> leading to deposits

with improved structural characteristics. However, although the 3-substitution enhances the regularity, the polymer still shows some structural defects due to irregular coupling, ramifications, crosslinking, etc.<sup>6</sup> The polymerization of 3,4-disubstituted thiophenes for obtaining a regular, highly conjugated conductive polymers may be a good starting approach. Consequently, our interest has been focused on the synthesis of tetra-substituted derivatives of thiophene. Electrochemical properties, spectral characteristics, oxidization potential, polymerization, and the potential utilization of the prepared products as photocells, will be assessed. In this article, we report the synthesis and electropolymerization of 3',4'-dibromo-2,2':5',2''-terthiophene, modified or not, could be utilized to generate new monomers of 3',4'-disubstituted terthiophenes. These products will allow evaluating the effect of the substituents on properties such as morphology, regularity, conductivity, etc. of the resulting polymer.

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## 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<sub>2</sub> before use) containing a 2-bromothiophene solution in diethyl ether and magnesium granules, under nitrogen.

FTIR spectra were measured on a PerkinElmer 1710 FT Spectrophotometer for solid dispersion with KBr pellets. <sup>1</sup>H and <sup>13</sup>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<sup>2</sup> 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.<sup>7</sup> 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).

#### Synthesis of 3',4'-dibromo-2,2':5',2''-terthiophene

Grignard's reagent was slowly injected through a septum into a three-neck round-bottom flask containing 30 mg (0.075 mmol) of Pd(tpp)Cl<sub>2</sub>, 1.0000 g (2.5 mmol) of 2,3,4,5-tetrabromothiophene, and 20 mL of diethyl ether. The mixture was refluxed for 24 h under N<sub>2</sub>. 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<sub>4</sub>). 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.

#### Polymerization of 3',4'-dibromo-2,2':5',2''-terthiophene and solar cells assembly

Poly(3',4'-dibromo-2,2':5',2''-terthiophene) was prepared by electropolymerization of 3',4'-dibromo-

2,2':5',2''-terthiophene, using 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. The preparation of solar cells, or photocells, was accomplished following the amply bibliography available,<sup>8</sup> and will be discussed further on.

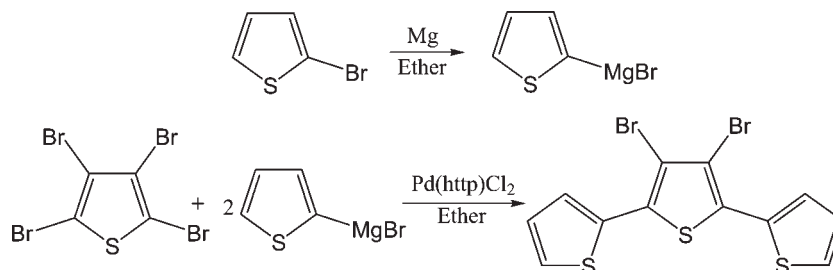
## RESULTS AND DISCUSSION

The monomer was synthesized according to methods described in the literature,<sup>9,10</sup> using a metal-catalyzed transition, coupled with the Grignard's reagent (Scheme 1). The tetrabromothiophene was condensed with four equivalents of 2-thienyl Grignard's reagent, in the presence of palladium(I) dichlorotriphenylphosphin (Pd(tpp)Cl<sub>2</sub>), as catalyst, which favors the substitution in positions 2 and 5 of the thiophene ring. It is noteworthy that the key of this synthesis lies in the use of palladium as catalyst, in a 2 : 1 relationship that leads, firstly, to condensation in position 2, followed by condensation in position 5 giving the desired product. This product, on the other hand, is used to generate a variety of 3',4'-disubstituted compounds of terthiophene, of great interest in the field of conductive polymers and, especially, to study the effect of the substituents in this type of molecules.

The product, 43% yield and m.p. 91–93°C, was characterized by microanalysis, FTIR (Table I), and NMR (Fig. 1), which corroborated the proposed structure.

The NMR analysis (Fig. 1) showed the following: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.51 ppm (2H, dd), 7.44 ppm (2H, dd) 7.15 ppm (2H, dd). <sup>13</sup>C NMR (200 MHz, CDCl<sub>3</sub>): δ = 134.05 (C 5', 5''), 131.08 (C 3', 3''), 112.45 (C 4', 4''), and only three quaternary signals at δ = 127.41, 127.14, and 126.83 ppm, respectively.

The electropolymerization of 3',4'-dibromo-2,2':5',2''-terthiophene was performed from solutions containing 1.2 × 10<sup>-2</sup>M monomer and 0.05M supporting electrolyte. Characterization of the product was then accomplished by cyclic voltammetry. The limiting cathodic and anodic potentials were -0.20 and 1.40 V, respectively. The cathodic limiting potential was selected



Scheme 1 Synthesis of 3',4'-dibromo-2,2':5',2''-terthiophene.

**TABLE I**  
**Elemental Analysis and IR Bands of the**  
**Monomer Vibration Modes of Terthiophene**  
**Dispersed in KBr Pellets**

Element	% Theor.	% Exp.	vFTIR (cm <sup>-1</sup> )	Assignment <sup>6,7</sup>
C	35.38	35.41	3097, 3080	vCβ—H <sub>heterocycle</sub>
H	1.25	1.29	1513, 1414	vCα=Cβ <sub>ring</sub>
S	23.67	23.68	1349	vCα—Cβ <sub>ring</sub>
			1287	vC—S <sub>ring</sub>
			1079, 1047	δ vC—H <sub>ring</sub>
			818	γ Cβ—H <sub>out of plane</sub>
			690	C—Br

v, stretching vibration; δ, in-plane deformation vibration; γ, out-of-plane deformation vibration.

because it represents the lowest overpotential needed to produce the oxidization of the monomer and its subsequent polymerization and, at the same time, without altering the voltammetric profile.

As for the anodic limiting potential, values lower than 1.40 V produce no deposit at all on the electrode surface, whereas potentials above that value bring about erratic results, probably due to overoxidization of the polymeric coating.

Whenever the optimal limiting potentials are used, a loop of current is observed at 1.2 V, even for the first sweep [inset as shown in Fig. 2(a)], as a result of a modification on the electrode surface due to deposit formation. The increase in the oxidization current observed on successive sweeps has been attributed to doping, occurring simultaneously with film growth. Figure 2 also shows that after each voltammetric scan an anodic shift of potential takes place. This shift has been attributed to a lengthening of the oligomer chains that decreases its oxidizing potential due to an increase in conjugation. Figure 2(b) shows the voltammetric response of the deposit generated under conditions of Figure 2(a), obtained from a solution containing just the supporting electrolyte, i.e., corresponding to a doping–undoping process of the film. A very stable profile is readily attained, which shows that the electro-activity of the deposit goes up to about 1.30 V. This value is significantly higher than the one obtained for polythiophene under the same working conditions. In addition, the process proved to be quite reversible, since the oxidization and reduction charges are nearly the same. Although it is not the aim of this work, we may suggest the use of this kind of modified electrode as a material for the development of batteries.

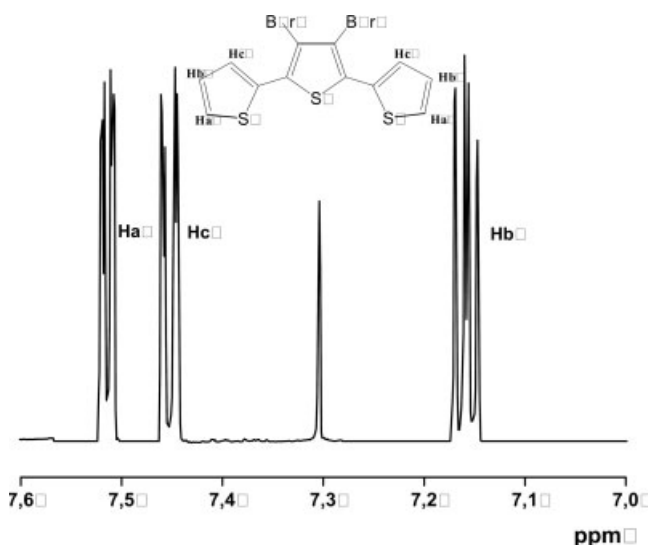
It must be emphasized that polymerization of this monomer has to be conducted in strictly water-free conditions. Traces of water prevent deposit formation or lead to erratic results. Electropolymerization being a radical process, oxidization of water prior to

oxidization of the monomer with production of radical intermediates, triggers a series of chemical reactions that lean against the selectivity of the polymerization process.

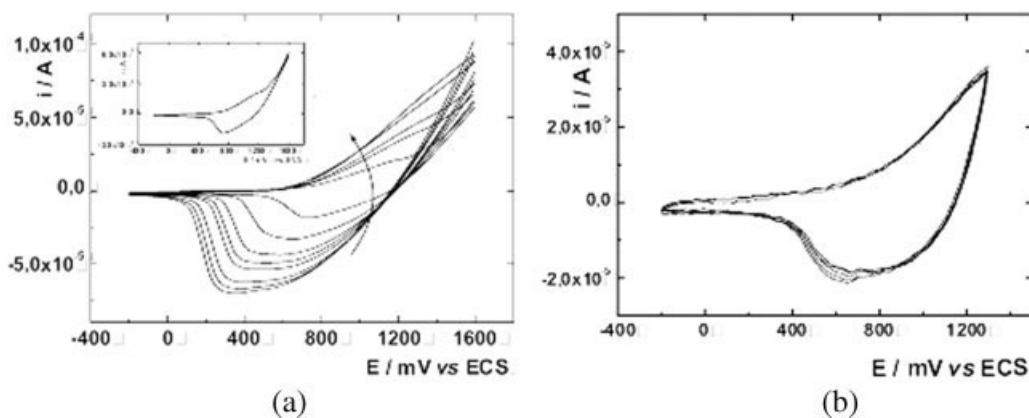
Following the characterization by cyclic voltammetry, electropolymerization at constant potential was conducted, applying potentials close to those corresponding to the nucleation-and-growth loop observed for the oxidization of the monomer. Figure 3(a) lists the more relevant transients obtained in this case. As can be seen, the more appropriate potential lies precisely, not more than 1.5 V. At lower potentials, deposition still occurs, but much longer times of polymerization are needed. On the other hand, potentials above 1.5 V produce overoxidization of the polymeric film. From these potentiostatic transients, the global nucleation-and-growth mechanisms (NGM) of polymerization can be established. The NGM of electropolymeric deposits are made of different contributions that may occur simultaneously or successively, and are a function of the electrolysis time.<sup>11–13</sup> In the present case, deconvolution of the obtained transients indicates that the NGM can be given by the following equation:

$$J = at[\exp(-bt^2)] + c[1 - \exp(-dt)] + et - 0.5[1 - \exp(-ft^2)] \quad (1)$$

where the first term corresponds to an instantaneous nucleation mechanism with bidimensional growth,  $NI_{2D}$ ; the second to a diffusion-controlled instantaneous nucleation with tridimensional growth,  $NI_{3Dif}$ ; and the latter, to a charge-transfer controlled nucleation



**Figure 1** <sup>1</sup>H-NMR spectrum of 3',4'-dibromo-2,2':5',2''-terthiophene.



**Figure 2** (a) Potentiodynamic response of 3',4'-dibromo-2,2':5',2''-terthiophene; (b) voltammetric response of the deposit obtained in 2(a).

with tridimensional growth,  $NI_{3Dct}$ . Consequently, the variables in eq. (1) are defined as follows:

$$a = \frac{2\pi\eta MhFN_{2D}k_2^2}{\rho}; \quad b = \frac{\pi N_{2D}M^2k_2^2}{\rho^2}; \quad c = N_{3D}Fk_3;$$

$$d = \frac{\pi M^2k_3^2N_{3D}}{\rho^2}$$

$$e = \frac{\pi FD^{1/2}C_\infty}{\rho^{1/2}}; \quad f = \frac{A'k\pi D}{2}; \quad A' = AN_{Dif};$$

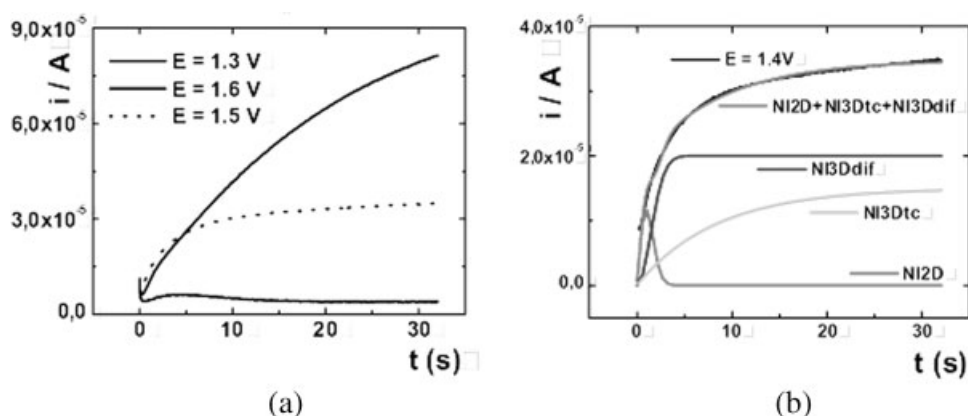
$$k = \frac{4}{3} \left( \frac{8\pi C_\infty M}{\rho} \right)^{1/2}$$

where  $\eta$ ,  $F$ ,  $M$ , and  $\rho$  have their usual meaning;  $h$ ,  $N_{2D}$ , and  $k_2$  are the height, the number of nuclei formed at  $t = 0$ , and the growth rate constant of the 2D nucleus, respectively;  $N_{3D}$  is the number of 3D nuclei formed at  $t = 0$ ;  $k_3$  and  $k_3'$  are the rate constants for the growth parallel and perpendicular to the surface of the 3D nucleus;  $D$  is the diffusion coefficient;  $C_\infty$  is the bulk concentration of the monomer;

$A$  is the rate constant of nucleus formation, and  $N_{Dif}$  is the number of nuclei formed at  $t = 0$  under diffusion control. So far, the value of each of these variables is not accessible from the NGM; thus, on deconvolving the curves just the global value is established, represented by  $a$ ,  $b$ ,  $c$ ,  $f$ , etc.<sup>11-17</sup>

Figure 3(b) shows, as an example, a deconvoluted transient, where, on the one hand, we can appreciate that the addition of the three contributions correspond exactly to the experimental transient, and on the other hand, that for very short times, a noticeable predominance of instantaneous nucleation with bidimensional growth, lasting about 3 s is observed for this particular working potential, and the other two contributions become important just after this time, prevailing at longer times only the diffusional contribution. By this time, the deposited film has reached such a thickness that the growth is restricted only by diffusion of the monomer, which must reach the electrode/solution interphase from the bulk of the solution, to be oxidized, and thus, to lengthen the polymeric chains.

Figure 4 depicts micrographs of potentiostatic and potentiodynamic electrodeposits. As usual, deposits



**Figure 3** Experimental potentiostatic transients of 3',4'-dibromo-2,2':5',2''-terthiophene in  $CH_2Cl_2$ , at Pt disk: (a) experimental  $i/E$  curves at various electrolysis potentials; (b) experimental potentiostatic transient and global NGM contributions, for  $E = 1.5$  V.

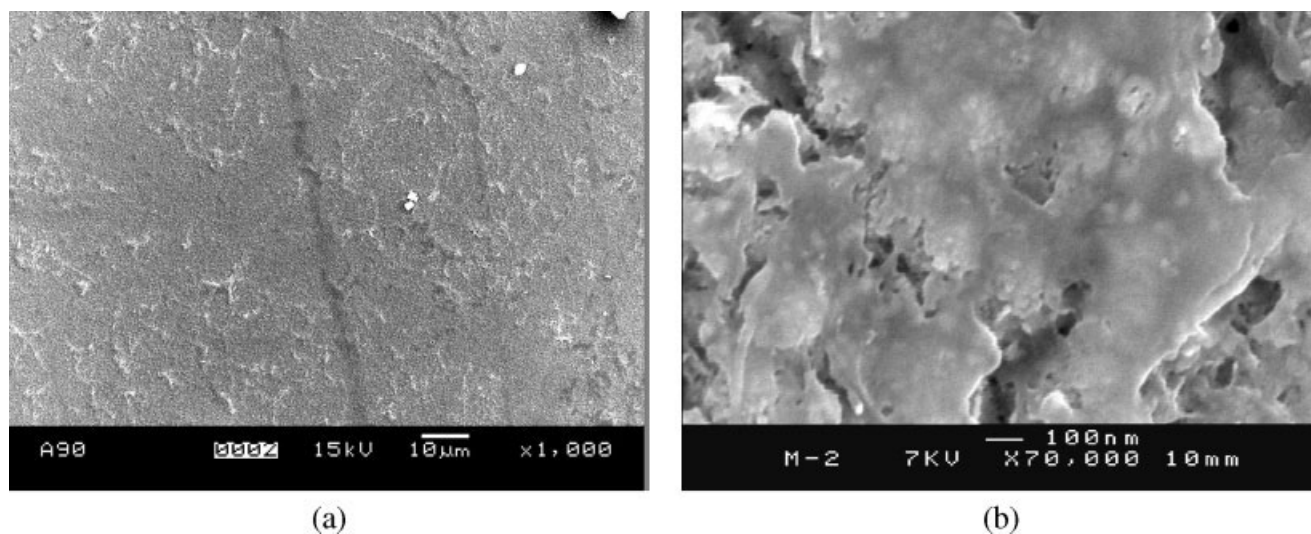


Figure 4 SEM micrographs of electrodeposits obtained by: (a) CP; (b) CV.

obtained by cyclic voltammetry (CV), give more uniform surfaces because during the potential sweep, ordering of the deposit is favored. However, it is surprising that in all the cases, the surface appears quite homogeneous, made of granules of identical size. This is consistent with that predicted by the NGM, as only instantaneous nucleation was found, i.e., at the outset, a determined number of nuclei that grow as a function of the electrolysis time is formed, but no nuclei are obtained thereafter which, in other cases, would mean heterogeneous sizes. In other words, an excellent agreement has been obtained between the predicted NGM morphology and what is observed in the SEM micrographs, which proves the validity of the correlation established herein. Thus, the method proves very useful for predicting the morphology by means of data obtained *in situ*, during the electropolymerization.<sup>11–17</sup>

These results are also consistent with those previously reported for the electropolymerization of thiophene in a variety of working conditions.<sup>11–15</sup> Furthermore, they allow, under determined experimental conditions (solvent, monomer concentration, and/or supporting electrolyte, etc.), to favor one or another contribution as a function of the electrolysis time and working potential, and thus to exert a certain degree of control on the morphology of the deposit to be obtained. In this particular case, for instance, it is possible to grow very thin layers of a highly ordered deposit by applying successive potential pulses of 1 s duration, since only the bidimensional growth contributes. In contrast, for thiophene, even when the working conditions are changed, the same cauliflower-like morphology is always attained, which is a characteristic of these

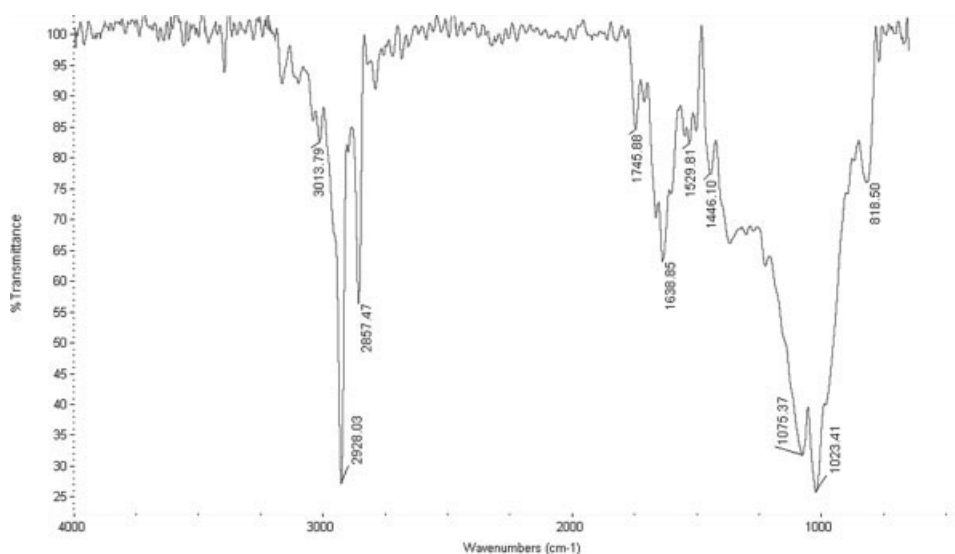


Figure 5 FTIR spectrum of the deposit obtained in the conditions of Figure 2(a).

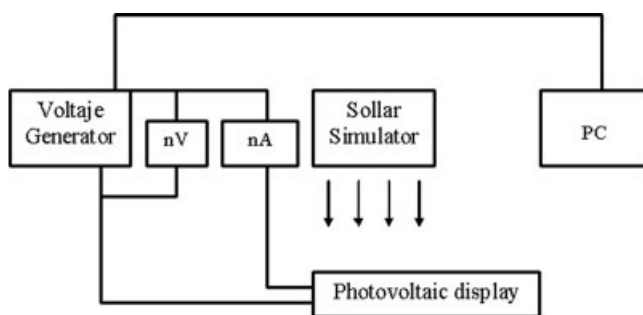


Figure 6 Device utilized for electrical characterization.

systems and is also consistent with the progressive nucleation that always accompany these processes.

As far as the control of the morphology is concerned, the substitution proposed herein seems to be promising in the attainment of the sought goal, i.e., to get orderly deposits, whose structural 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. Regardless of the electrodeposition conditions, a spectrum such as that of Figure 5 is obtained. The FTIR spectrum of thiophene ring exhibits specific peaks at 818, 1023, 1075, and 1446  $\text{cm}^{-1}$ . Broadening of these peaks in this spectrum indicates the formation of a polymeric bulk material, and suggests  $\alpha$ - $\alpha_0$  couplings of the thiophene rings. The intensity of the bands due to a  $-\text{CH}$  stretching of thiophene ring is reduced in the spectrum of the polymer. The decrease in intensity can be attributed to the  $\alpha$ -hydrogens of the terminal thiophene rings of the chains and can also be indicative of  $\alpha$ - $\alpha_0$  couplings. The strongest band arises around 786–790  $\text{cm}^{-1}$  was assigned to a 2,5-disubstituted thiophene rings. Finally, the lack of new bands permitted to confirm that the polymer was completely undoped at the moment of the optical and electronic measurements.

With the aim of evaluating the behavior of the deposits, a device was developed. The results obtained for solar cells, or photocells, are presented and discussed below.

The introduction of organic layers in the construction of solar cells was carried out by two techniques: blend (a coating, some 10 nm thick is deposited utilizing the spin-coating technique, from a solution containing *p*- and *n*-type polymers) and the bilayer (thin layers of organic semiconductors of both kind of doping are deposited).<sup>18</sup> The efficiency of these devices is related to, among other factors, the thickness of the constituent layers of the solar cell. Except for type-p polymers, all the deposits that make up the photocell can be controlled by thermal evaporation techniques. In the case of the polymer, this control is accomplished either by the time of electrolysis (CP method) or by the number of voltammetric

cycles (CV method).<sup>19</sup> In the present work, a glass substrate coated with a ZnO layer was used for the preparation of solar cells. A layer of poly(3',4'-dibromo-2,2':5',2''-terthiophene), an electron donor, was then coated onto the surface using electrochemical techniques. The following layers were also deposited: perilene 3,4-9,10-tetracarboxylic dianhydride (PTCDA), as acceptor, LiF, and Al using special equipment and high vacuum. Control of the thickness was performed by means of a quartz balance coupled to those instruments. Consequently, the configuration of the devices is as follows: glass/ZnO (180 nm)/poly(3',4'-dibromo-2,2':5',2''-terthiophene)/PTCDA (200 nm)/LiF (<15 nm)/Al (100 nm).

The efficiency of the devices was evaluated with the aim of developing photovoltaic cells. To this purpose, a simulator was employed, as depicted in Figure 6.

Illuminated characteristics were measured under the global AM1.5 spectrum using a standard ORIEL solar simulator calibrated at 100  $\text{mW} \cdot \text{cm}^{-2}$  with the help of adapted ORIEL filters.

Cyclic voltammetry which provides the most homogeneous deposits (Fig. 4), helps in obtaining polymeric coatings with the best photovoltaic performance indicators, which agrees well with other authors results. They found that the deposit grown by CV affords the best photoelectrochemical cell devices, better than those obtained with polymers grown by potentiostatic methods.<sup>20,21</sup> The thickness of the deposit, as mentioned above, is a function of the number of cycles. Nevertheless, no photovoltaic effect was observed in solar cells made of polymers prepared by the use of a small number of voltammetric cycles. In contrast, on increasing the number of cycles up to 20, the cell exhibited the expected photovoltaic effect as shown in Figure 7.

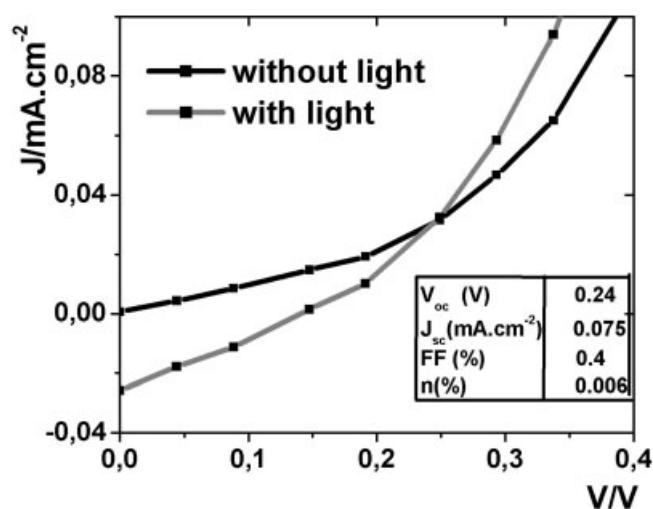
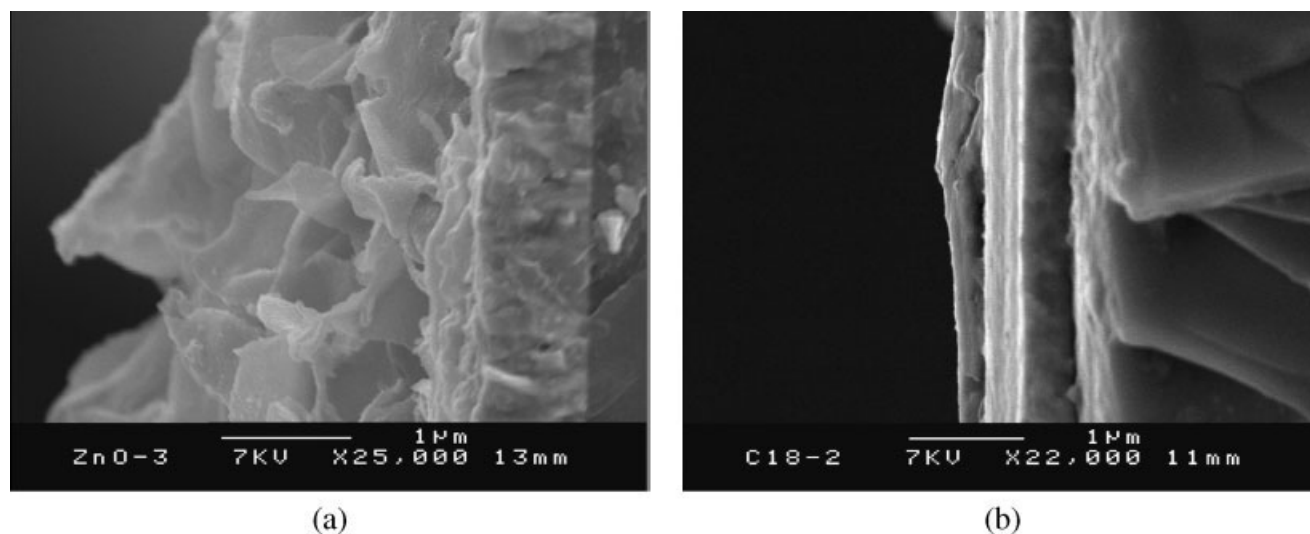


Figure 7 Response of a device Glass/ZnO/PTCDA/poly(3',4'-dibromo-2,2':5',2''-terthiophene)/LiF/Al. Characteristic  $J = F(V)$ .



**Figure 8** Micrograph (MEB) of electrodeposits obtained by CV: (a) 40 cycles; (b) 20 cycles.

The measured open circuit voltage is 0.24 V while the short circuit current is  $7.5 \times 10^{-2} \text{ mA cm}^{-2}$ . The fill factor is 0.4, which gives an efficiency of 0.006%.

The deposit in this case is much thicker than that usually recommended and the low efficiency obtained may be ascribed to this fact. However, as micrographs in Figure 8 show, the deposit is still quite uniform and homogeneous. It also shows that the maximum thickness for obtaining a really uniform film and photovoltaic effect, is a deposit of about 200 nm thick generated by 20 voltammetric cycles. A deposit of about 500 nm thick is obtained when 40 voltammetric cycles are used. Furthermore, it can be clearly appreciated that, owing to the diffusional control, the kind of nuclei obtained correspond to a disordered growth.

To improve the yield, we propose the optimization of the electrodeposition of the polymer with the purpose of obtaining more uniform coatings, but still having a maximum thickness of about 100 nm. We hope that in this way, an improvement in the performance of the device will be possible.

Recently, Tsekouras et al.<sup>20</sup> reported the highest efficiency ever for a photoelectrochemical cell using a conducting polymer, 0.101% under halogen light (solar simulated) intensity of  $500 \text{ W m}^{-2}$ . The photoelectrochemical cell was constructed using a liquid electrolyte, such as  $\text{I}_3^-/\text{I}^-$ , which was sandwiched between a polyterthiophene-coated ITO coated glass working electrode and a Pt-coated ITO coated glass counter electrode. However, this important result has been possible, precisely, after optimizing the electropolymerization conditions, in a way analogous to that realized in the present contribution. They also concluded that to improve the results, tailoring the polymer architecture using optimized polymer growth conditions must be accomplished. Thus, the

proposed route is the same and corroborates the study carried out in the present work. On using solid polymer electrolytes, regardless of the type of polymeric material, the yield is not satisfactory too.<sup>22-24</sup>

## CONCLUSIONS

The proposed method is appropriate for the synthesis of 3',4'-dibromo-2,2':5',2''-terthiophene and can be tried for the preparation of other 3',4'-disubstituted monomers of terthiophene, with the purpose of improving the properties of the resulting polymers. Exclusion of water from the electrolytic medium permits deposits of poly(3',4'-dibromo-2,2':5',2''-terthiophene), to be obtained either by potentiostatic or by potentiodynamic techniques and, in addition, to regulate the thickness and the morphology of the coating as a function of the number of cycles or the time of electrolysis, respectively. This procedure makes possible for obtaining a polymer that, when used as *p*-layer in a solar cell, displays a photovoltaic effect, although the yield is low. This shortcoming may be overcome by optimization of the electrodeposition conditions or by modifying the structure of the monomer by the introduction of other moieties.

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