



Photoelectrical properties of the system ITO/poly(4,4''-dipenthoxy-3'-dodecyl-2,2':5',2''-terthiophene)/Al: Effect of electrosynthesis conditions

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Abstract

The photoelectrical properties of the system ITO/poly(4,4''-dipenthoxy-3'-dodecyl-2,2':5',2''-terthiophene)/aluminum are strongly dependent on the electrochemical preparation parameters of the polymer. In particular the polymerization temperature has a significant influence on the photoelectronic characteristics of polymer. The best properties were attained with polymers prepared at higher temperatures (32–40 °C).

1. Introduction

Morphology is of utmost importance for the electronic and photoelectronic properties of conducting polymers [1–3]. Regioregular alkyl-substituted polymers are prepared by chemical methods [4]. They are quite soluble in organic solvents and polymer films are generally obtained by spinning or casting. The structure of the electrosynthesized conducting polymers was found to be less regular than that of the same materials prepared by chemical methods [5]; this is why the former have received less attention for electronic applications. Consequently, insufficient information is available on the dependence of the electronic properties of these materials on the parameters of the electrochemical polymerization [6, 7]. A number of papers deal with the effect of the morphological and electrical characteristics of conducting polymers, prepared by means of the electrochemical technique, on the polymerization temperature and film thickness. A more regular morphology and an improvement of the related properties can be generally achieved by decreasing the polymerization temperature [8–14]. However, this cannot be considered a general rule. The trend of the morphology against polymerization temperature may depend on the coupling rate of the radical cations and therefore on the size and kind of the monomer. A slow reaction rate could also lead, other than to a more selective coupling, to the formation of oligomers.

The electrical characteristics of polymer films are improved by decreasing the thickness [3, 4], mainly in the case of films synthesized by the electrochemical technique [15, 16]. In a previous paper [17] we put forward the hypothesis that, during the first cycles of the preparative cyclic voltammetry, the electrode covering occurs by oligomer precipitation and then, during the later cycles, the film grows by a different mechanism. The visible spectra of very thin polymer films (< 80–100 nm) showed a maximum absorbance blue-shifted with respect to thicker films, revealing a high percentage of oligomers.

The purpose of this work was to highlight how the optoelectronic properties of a Schottky-type junction based on a conducting polymer prepared by electrochemical technique can be improved by changing the electrosynthesis conditions. Poly(4,4''-dipenthoxy-3'-dodecyl-2,2':5',2''-terthiophene) (pDDTT) was considered with the aim of understanding the effect of two different substituent groups in the same thiophene chain (both electron donors but with different electron affinities) on the photoelectronic properties of the material. The presence of two substituent groups with different electron affinities could favour the exciton dissociation. Long hydrocarbon chains and alkoxy groups in the 4,4'' position assure a reasonable solubility of the polymer, provide a certain degree of structural order and allow the electrochemical polymerization, as reported by other authors [18] who, previously, performed the electrochemical polymerization of this kind of thiophenes.

2. Experimental details

Films of pDDTT were deposited on ITO substrate (Balzers, $23 \Omega/\square$) by cyclic voltammetry (CV) of 0.5×10^{-3} M DDTT in 1:1 v/v acetonitrile (AN)/dichloromethane (DM) + 0.1 M tetrabutylammonium perchlorate (TBAP) at different temperatures (thermobath Haake Q-F3). Films with different thicknesses were obtained by varying the number of cycles. A Pt wire was used as counter-electrode, separated from the electro-synthesis solution by a glassy septum, and the reference was a saturated calomel electrode (SCE). The CVs of the films were carried out in pure AN + 0.1 M TBAP. The monomer was synthesised and purified as described in [19]. AN (UVASOL Merck product), was stored under argon pressure and manipulated under a flow of the same gas; DM, (Merck product *pro analysi*), was dehydrated with CaCl_2 for 12 h, successively distilled in the presence of P_2O_5 under argon flux, and then stored in the dark under argon pressure. TBAP (Fluka AG 'purum') was crystallized from methanol. The electro-synthesis and electrochemical characterisations were carried out with an AMEL 5000 multifunction apparatus. The thickness of the films were measured by using a Tencor profilometer, model Alpha Step 200. The top electrode was made by vacuum evaporating a semi-transparent aluminium layer (11 nm thick) onto the polymer films. The photocurrent was measured with a Keithley 486 picoammeter. The junctions were illuminated through the aluminium side with a 1000 W Xe arc lamp. The incident light intensity was varied by using neutral density filters. The optical bench was equipped with a water filter to cut off infrared radiation and a glass filter to cut-off the wavelengths shorter than 350 nm. The incident light intensity was measured with an Oriel thermopile and corrected for the Al layer absorption. No correction was made for light reflection. The experiments were done under controlled conditions (22 ± 2 °C and under dry argon flow).

The X-ray diffraction patterns of the polymer put on a low background quartz plate, were recorded by a Philips powder diffractometer (PW1050/81-PW1710), equipped with a graphite monochromator in the diffracted beam. CuK_α X-radiation was employed and the step-scanning recording was performed in the $3\text{--}50^\circ 2\theta$ range, at $0.01^\circ 2\theta$ steps and with a fixed counting time 10 s.

3. Results and discussion

Figure 1 compares the second cycle of the CVs inherent to DDTT polymerization at -14 and $+32$ °C. The peaks of the growing polymer, followed by long capacitive tails, are sharper for films deposited at the higher temperature. The anodic peak potential is shifted towards negative values by increasing the temperature of synthesis and displays a sharper form. The CVs of the films obtained are in agreement with those inherent to the film synthesis (Figure 1(b)).

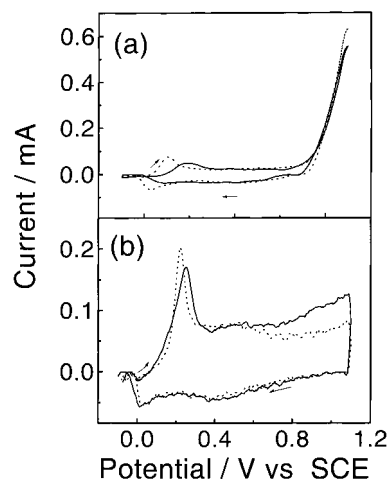


Fig. 1. (a) Electrosynthesis of pDDTT: CVs (second cycle) of 5×10^{-3} M DDTT in 1:1 AN/DM mixed solvent + 0.1 M TBAP at -14 °C (full line) and $+32$ °C (dotted line). (b) CV (second cycle) in ACN 0.1 M + 0.1 M TBAP of the polymer films prepared at -14 °C (full line) and $+32$ °C (dotted line). Scan rate 20 mV s^{-1} .

The films show a structured absorption band (Figure 2). The location of the vibronic peaks was determined by using smoothed numerical second derivatives of the absorption curves and assuming that their energy corresponds to the minima [20–22]. The values found were 661 nm (0–0 transition), 603 nm and 548–563 nm. The energy difference between the first two was $h\nu_{\text{ph}}$ 0.18 eV (1455 cm^{-1}) and fits very well with the C=C stretch mode in Raman spectroscopy. For the shoulder at lower wavelength the fitting is not so good and two very close minima were detected suggesting the possible coexisting presence of chains with shorter conjugation lengths, especially in low temperature prepared films. Comparing the spectra of the films electropolymerised at different temperatures, from -14 to $+32$, an enhancement of the zero-phonon vibronic transition, a sharper absorption edge and a shift of the absorption maxima could be observed. All these elements gave an indication of a higher structural order in the films prepared at higher temperature.

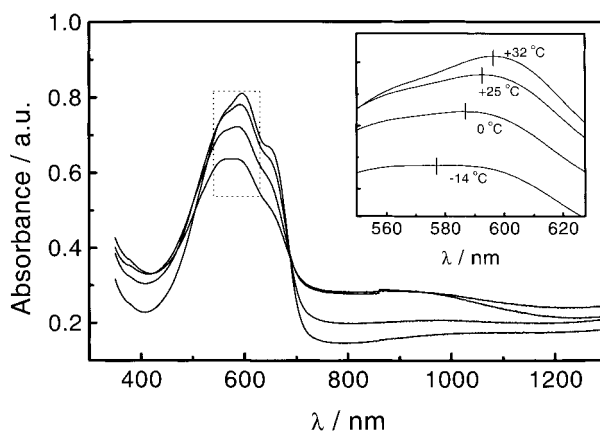


Fig. 2. Spectra of pDDTT films (thickness 100–150 nm) synthesized at different temperatures.

The X-ray diffraction patterns of the films (Figure 3) show a sharper peak at lower diffraction angle and a second one, superimposed on the amorphous scattering, at higher angle. In polythiophene-type polymers, the first peak is generally assigned to the distance between the chains lying in the same plane and the second one to the distance between the planes having interfaced aromatic rings [23, 24]. The parameters of the diffractometric peaks are the following:

- (a) first peak: $2\theta = 3.63$ (distance = 24.4 Å) for the polymer prepared at 32 °C, $2\theta = 3.75$ (distance = 23.6 Å) for that prepared at -14 °C.
 (b) second peak: $2\theta = 24.9$ (distance = ~3.6 Å) for polymers prepared at both temperatures.

The sharpness of the signals is related to the degree of crystal structure. The first halo is very sharp and its wideness is comparable with that conventionally assigned to quasi-crystal structures ($\delta(2\Theta) < 2.1^\circ$, where Θ is the diffraction angle [23]). The inset of Figure 3 displays a sharper low-angle halo for the polymer prepared at +32 °C than that for the polymer prepared at -14 °C. The ratio between the wideness of the low-angle peaks of the polymers prepared at different temperatures is very similar to the same ratio of the oxidation peaks (compare Figure 1(b) and Figure 3 inset). This suggests a minor number of different structures, and therefore a more regular morphology for the polymers prepared at higher temperatures. Also the high angle peak is sharper for the polymer prepared at higher temperatures.

Generally, a decrease of temperature improves the selectivity of the cation radical on the coupling site, but decreases the coupling rate reaction. In the case of DDTT the coupling reaction occurs in 4,4'' positions because of the orienting effect of the electron donor -OR groups. However, DDTT is a molecule with high molecular weight; consequently, at the higher temperatures the electrolyses led to a polymer with higher molecular weight and with a wider π -electron conjugation. The results reported here support this hypothesis.

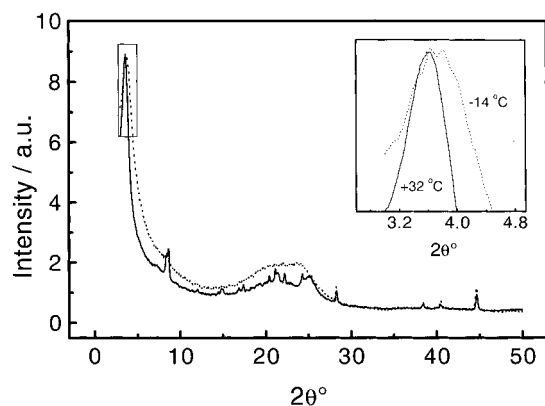


Fig. 3. X-ray diffraction patterns for the films prepared at -14 °C (dotted line) and 32 °C (straight line). Inset magnifies region of halos connected to distance between polymer chains laying in one plane. The higher order degree of the film synthesized at the higher temperature is evident.

The higher temperatures could also make the self-assembling of the polymer chains during the electrodeposition easier and increase the solubility of the oligomers.

To study the effect of film thickness, the samples were prepared by cyclic voltammetry with different cycle numbers. The voltammetry of films prepared with different number of cycles shows substantial differences regarding the cyclable charge. During the first cycles the cathodic charge is much lower than the anodic one but the ratio (ρ) of the cathodic to anodic charge increases by increasing the number of the preparative cycles. At a scan rate of 20 mV s⁻¹ the values of ρ are, respectively: 0.13 (1 cycle), 0.5 (2 cycles), 0.65 (3 cycles), 0.74 (4 cycles), 0.88 (6 cycles). In a previous paper dealing with the polymerization of dihexadecyl-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene [17] it was suggested that this behaviour was due to the inclusion of oligomers into the polymer electrode films.

Schottky-type junctions between pDDTT and aluminium were realised in order to study the effect of both the polymer thickness and temperature of synthesis on the photoelectrical device performance. By illuminating the junctions with white light through the semitransparent aluminium electrode, a photovoltaic effect was observed. In Figure 4 the short-circuit photocurrent (j_{sc}) is shown as a function of the polymer thickness, for an incident irradiation power (P_{in}) of 20 mW cm⁻² and with pDDTT synthesized at 25 °C. The cells based on the thinnest polymer (synthesized with only one voltammetric cycle, about 75 nm thick) exhibited very poor performance. This could be due to a high concentration of oligomers in the polymer film. Alternatively, incomplete light absorption could be hypothesised for the thinner films. In previous papers dealing with photovoltaic cells based on poly(3-methylthiophene) films [25, 26], it was reported that incomplete light absorption occurred for layers as thick as about 80 nm, corresponding to the depletion layer calculated for the dedoped polymers. In our devices, the best results were obtained with the polymer synthesised with

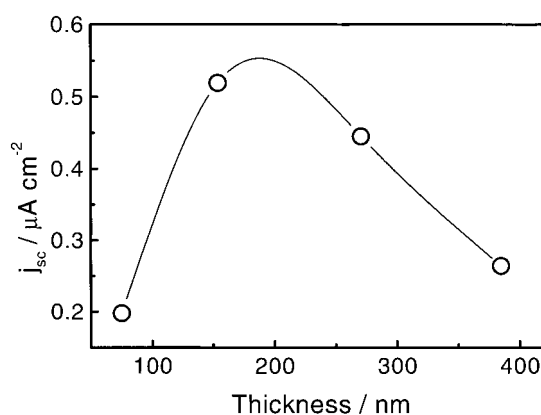


Fig. 4. Short-circuit photocurrent as a function of the polymer film thickness of the system ITO/pDDTT/Al. pDDTT synthesized at +25 °C. Incident irradiation power 20 mW cm⁻². Junction area 0.2 cm².

two voltammetric cycles (~ 160 nm thick). By further increasing the polymer thickness, the photocurrent decreased, the series resistance being a limiting factor of the device performance.

pDDTT films prepared with two voltammetric cycles were used for the investigation on the effect of the temperature of synthesis. The characterization of the junctions based on pDDTT synthesised at various temperatures demonstrated considerable differences in the photoelectrical properties of the devices. Whereas no meaningful differences were observed for the open-circuit photovoltage, notable effects were observed on the photocurrent values. The short-circuit photocurrent for an incident irradiation power of $2 \times 10^{-2} \text{ W cm}^{-2}$ is reported as a function of the temperature of synthesis in Figure 5. j_{sc} is a power function of P_{in} over the considered illumination range (Figure 6, inset), but with a power factor (α) that increases by increasing the temperature of synthesis (Figure 6). Values of α ranging between 0.5 and 1 are very common in imperfect materials and are expected by assuming an exponential trap distribution [27]. Better values of α , obtained for higher temperatures, indicate a lower density of trapping centers and, therefore, a more regular structure of the semiconductor.

The junctions were also tested in photoconductive mode, that is, under reverse polarization. As already demonstrated [28–30], conjugated polymers should be very attractive candidates for photodiode applications, with sensitivities comparable with that of photodiodes made with inorganic semiconductors, even at relatively low reverse voltages of operation. Figure 7 compares the photosensitivity (PS) at a reverse bias of 0.8 V for three different values of the temperature of synthesis. PS is a decreasing function of P_{in} , the photocurrent being a sublinear function of the incident irradiation power. As expected, PS is small if compared to the typical photosensitivity (10^{-1} A W^{-1}) of the best polymer photodiodes based on donor/acceptor heterojunctions (e.g., [28–30]). However, the main value of the results reported in this paper is in the advancement of the understanding of the basic material science. The oper-

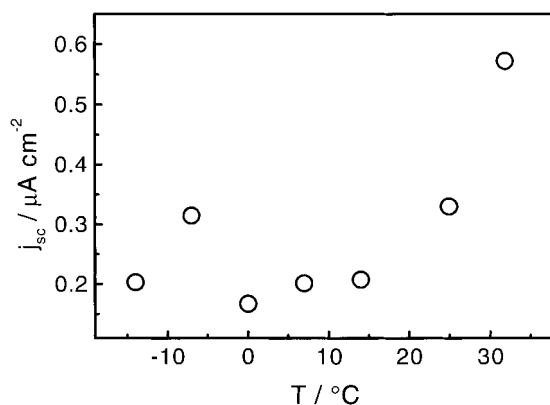


Fig. 5. Short-circuit photocurrent as a function of synthesis temperature for system ITO/pDDTT/Al. pDDTT film thickness: 160 nm. Incident irradiation power 20 mW cm^{-2} . Junction area 0.2 cm^2 .

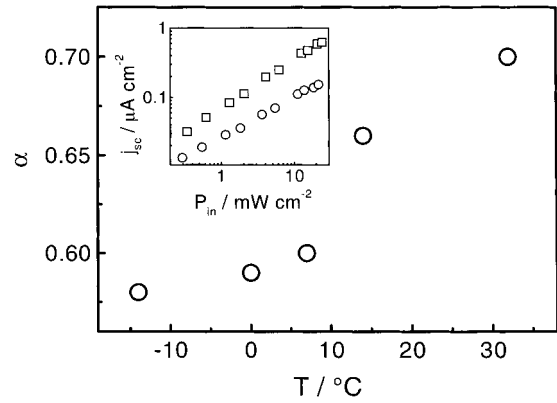


Fig. 6. Variation of α with the synthesis temperature of the polymer for the system ITO/pDDTT/Al. Inset: short-circuit photocurrent as a function of incident irradiation power of system ITO/pDDTT/Al with polymer synthesized at -14°C (\circ) and $+32^\circ\text{C}$ (\square). pDDTT film thickness: 160 nm.

ation of a photodetector is basically controlled by photogeneration and transport. Higher photocurrents may be partly ascribed to better transport properties of the polymer prepared at higher temperatures, in agreement with their higher structural order.

4. Conclusions

The morphology of pDDTT prepared by cyclic voltammetry depends considerably on the synthesis parameters. Contrasting with the most investigated polymers, the order degree was improved by increasing the polymerization temperature from -14°C to 32°C . Consequently, the short-circuit photocurrent of the junctions based on the same polymer increased in the same way. An explanation of this can be found by taking into account that the monomer molecule is big and a high temperature can increase the rate of the radical cation coupling and the weight of the polymer chains. Probably, as the monomer structure favours

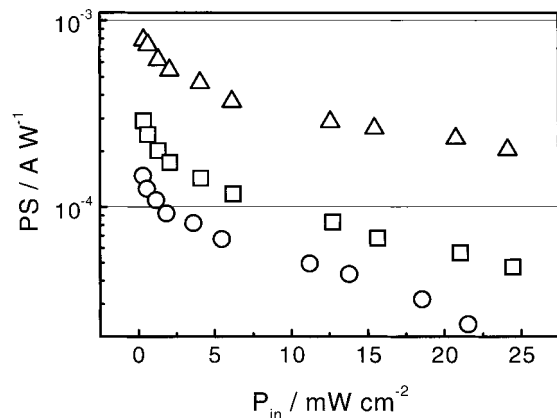


Fig. 7. Photosensitivity as a function of the incident irradiation power for the systems: ITO/pDDTT/Al with the polymer synthesized at: -14°C (\circ), $+7^\circ\text{C}$ (\square), $+32^\circ\text{C}$ (\triangle). pDDTT film thickness: 160 nm. Reverse bias applied 0.8 V. Junction area 0.2 cm^2 .

anyway the selectivity of the coupling site, the increase of the temperature leads to a polymer with wider regions of conjugate double bonds and more regular structure. Consequently, better photoelectrical properties of the related photoreceptor devices are obtained. Another possibility to be considered is easier self assembling of the polymer chains during the polymerization process and a higher solubility of the oligomers at the higher temperatures. The best results were obtained with thin films (100–150 nm) and high synthesis temperatures (32–40 °C).

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