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Electro-oxidation of 2,2′-dithienylketone

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The anodic electropolymerization process of 2,2′ dithienyl ketone in acetonitrile or dichloromethane electrolytic solutions on Pt, Au or SnO_2 electrodes, has been studied by means of cyclic voltammetry and potential step methods. The electrochemical response indicates that the electro-oxidation process is slightly solvent dependant, but the electrode substrate determines the film quality. Nucleation and growth mechanisms were established and give rise of the film morphology and in thin layers. FTIR, EPMA and XPS analysis indicates that during the electro-oxidation process oligomerization is produced through the thiophene rings, while the carbonyl groups remain intact. Electrodeposit conductivity values allows one to suggest their use in the preparation of electroluminescent diodes. *© 2003 Kluwer Academic Publishers*

1. Introduction

There is a great interest in the new applications of conjugated polythiophenes (PTh): electrochromic devices, nonlinear optics, electroluminiscent diodes, etc. [1]. The use of these polymeric materials requires properties such as conductivity, mechanical resistance, and processing. In this sense, many efforts are being made, specially oriented to the modification of the precursory monomer and to the conditions used during the synthesis. Thus, the design of new structures has been mainly focussed on the introduction of π system in the α position of thiophene ring [2], condensations with benzene rings (benzothiophenes) [3], introduction of electron donor groups in sp^2 carbons [4, 5] or dioxolane groups in sp^3 carbons [6].

The introduction of electron-wihtdrawing groups, such as carbonyl [4], 1,3-dioxolane [5] or dicyanomethylene [7] to bridge the 4,4′ position of a bithienyl precursor allowed the preparation of polymers having a significantly reduced band gap related to PTh. For cyclopenta (2,1-b:3′,4′-b′) dithiophene 4-one, such reduction results from the strong stabilization of the *LUMO*, while the carbonyl group seems to have only a moderate effect on the energy level of the monomer and polymer *HOMO* levels [8, 9].

In any case, the majority of structural modifications of precursory monomers have been performed in positions 4 and 4′. However, little effort has been devoted to position 2, mainly because of its participation in the polymerization mechanism [4, 10, 11] although the synthesized polymers starting from 2,5′ vinylthienilenes have been successfully prepared, with a reasonable conductivity [6, 12–14]. The chemical synthesis of poly (3-alkylthienylketones) has recently been reported, and the possibility that they could give use to n-doped conducting polymers [8] nevertheless, the voltammetric reduction was irreversible [15].

In this work, the electro-oxidation of 2,2′-dithienyl ketone in different experimental conditions has been studied, with the aim of analyzing the effect of 2,2′-thiophene substitution in the products obtained associated to PTh. The effect of variables which govern the electropolymerization process, such as solvent or electrodic substrate, was also determined. The electrodeposits were also characterized by FTIR, EPMA and XPS together with conductivity measurements. Finally, their potential as organic diodes materials was established.

2. Experimental

2.1. Monomer synthesis and characterization

2,2′-dithienylketone (DTK) was synthesized from 2-thiophene carboxylic acid. The product was prepared and characterized by reported methods [16–19]. The monomer was purified dissolving it in 10% KOH aqueous solution, and extracting with $CHCl_3$.

Elemental analysis of brown crystals m.p. 90°C. Found: C, 54.65; H, 3.02; S, 30.54. Calculated: C, 55.64; H, 3.11; S, 30.00. ^{1}H-NMR Bruker 200 MHz ($CDCl_3$) [ppm]: 7.17 (dd, 1H, 3.78, 1.17 Hz), 7.68 (dd, 1H, 1.08, 3.86 Hz), 7.88(dd, 1H, 1.16, 2.68 Hz). ^{13}C-NMR Bruker 50 MHz ($CDCl_3$) [ppm]: 178.7 (C=O), 142.9 (C_2), 133.5 (C_3), 133.1 (C_5), 128.0 (C_4). FTIR pellets KBr [cm^{-1}] νC=O 1613, δCH_{oop} (2-sust) 860, 780, 727.

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2.2. Monomer electro-oxidation and electrodeposits characterization

The setup for cyclic voltammetry (CV) and potential step (PS) experiments have been previously described [20]. Polycrystalline non-annealed Pt or Au discs (geometrical area 0.07 cm^2) and Ag/AgCl in tetramethylammoniun chloride (Me_4NCl) were used as working and reference electrodes, respectively. Potentials with respect to the latter were corrected to that of the saturated calomel electrode (SCE) [21]. Before each experiment, the working metal electrodes were polished with alumina slurry (particle size 0.3 μm) on soft leather, and afterwards, washed with deionized water and anhydrous acetonitrile or dichloromethane. A Pt gauze, separated from the working electrode compartment, was used as counter electrode.

The transparent electrodes used were commercial SnO_2 Solems (geometrical area 0.4 cm^2). The whole glass substrate was covered, therefore, some SnO_2 had to be removed. After masking a 2 mm line broad, the SnO_2 was etched using Zn + HCl [22]. Then the substrate was cleaned using H_2O_2 treatment following a process described by Osada *et al.* [23], which corresponds to the first solution (SC1) of the RCA process first described by Kern and Puotinen [24]. The substrates were treated with 80°C H_2O-H_2O_2 (30%)-NH_4OH 25% solution (5:1:1 volume parts) during 20 min. Later, it was washed with boiling water for 5 min, sonicated in acetone/water solution, and dried during 24 h. It has been proven that the use of boiling water is helpful to obtaining impurity-free surfaces [25].

Prior to all experiments, solutions were purged with high purity argon, and an argon atmosphere was maintained over the solutions during the measurements.

Acetonitrile and dichloromethane (Aldrich, anhidrous) were stored in a dry argon atmosphere and over molecular sieves (4 Å). To ensure minimum water content, the solvents were manipulated by syringes. Supporting electrolytes was tetrabutylammonium hexafluorophosphate ($TBAPF_6$), supplied by Aldrich, and vacuum dried at 60°C. DTK electrochemical study was carried out with solutions containing 0.025 M–0.1 M monomer and 0.1 M supporting electrolyte. In PS experiments, the electrode was first switched from 0.2 to 1.2 V during 60 s. Electrodeposition was achieved by a further step to potentials between 2.05–2.09 V. The purpose of this potential-time program was reported elsewhere [26]. In CV experiments, the potential was successively scanned between -0.5–2.2 V at 100 mVs^{-1}. Chronopotential step and potentiodynamic experiments were obtained at BAS CV-50W interfaced to IBM-PC computer.

Light-emitting diodes (LEDs) have been prepared by Al deposition under vacuum on top of the film deposited onto a tin oxide (ITO) coated glass substrate. The I–V and electroluminiscent curves were measured with a Keithley 617 programmable electrometer, a Keithley 2000 multimeter, and a Lambda IEEE-488 programmable power supply model LLS6060-GPIB interfaced to an IBM-PC computer.

Electron spectroscopy for chemical analysis (ESCA) was performed with a Leybold spectrometer at the University of Nantes. ESCA was used for XPS measurements. The X-ray source was a magnesium cathode (1253.5 eV) operating at 10 kV and 10 mA. The energy resolution was 1 eV at an energy pass of 50 eV. High resolution scans with a good signal/noise ratio were obtained in the C1s, S2p, O1s region of the spectrum. The quantitative analysis was based on the determination of the C1s, S2p, O1s and N1s peak areas with 0.2, 0.44, 0.36 and 0.60, respectively, as sensitive factors. The sensitive factors were given by the manufacturer. The vacuum in the analysis chamber was of about 10^{-6} Pa. All spectra were recorded under identical conditions.

The decomposition of XPS peaks into different components and the quantitative interpretation were made after the subtraction on the background using the Shirley method [27]. The developed curve fitting programs allow the variation of parameters such as the Gauss/Lorentz ratio, the full width at half a maximum (FWHM), the position and the intensity of the contribution. These parameters were optimized by a curve-fitting program to obtain the best decomposition. To check the surface contamination, some etching was done: sputtering with argon was accomplished at pressures of $<5 \times 10^4$ Pa, a 10-mA emission current, and a 3-kV beam energy using an ion gun. With these experimental conditions, all the surfaces of the sample were sputtered.

Elemental analysis was performed in an Elemental Analyzer C, H, N, S, O, Mod. EA 1108. FTIR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer by the KBr pellet method. Conductivity measurements were carried out on pellets, using the four probe method in an Elchema CM-508 conductimeter.

3. Results and discussion

By means of cyclic voltammetry (CV) the electrochemical response of 2,2′-dithienylketone was studied under different conditions, thus checking the effect of the potential, the electrodic substrate, solvent, and supporting electrolyte. In Fig. 1 voltammetric responses for different electrodic substrates are shown. As it may be observed, in just one phase it is possible to see a nucleation loop during the first anodic hemicycle (Fig. 1a), attributable to monomer electropolymerization, like it was seen in the electrochemical synthesis of other polymers [20, 28, 29]. When the number of voltammetric cycles increases, there is a decrease in the anodic current, which may be interpreted as a decrease in conductivity of the electrodic modified surface. Apart from that, in these conditions, the anodic response is irreversible.

The electrodic substrate change, from Pt to Au (Fig. 1b), brings about significant differences in the voltammetric response, just as in many other cases, because the substrate change leads to differences in the nucleation process [28]. In the voltammogram, it is also possible to see that the difference between the anodic and the cathodic charge is quite large. Besides, at the potential used for the ketone polymerization, Au normally undergoes dissolution without observing any

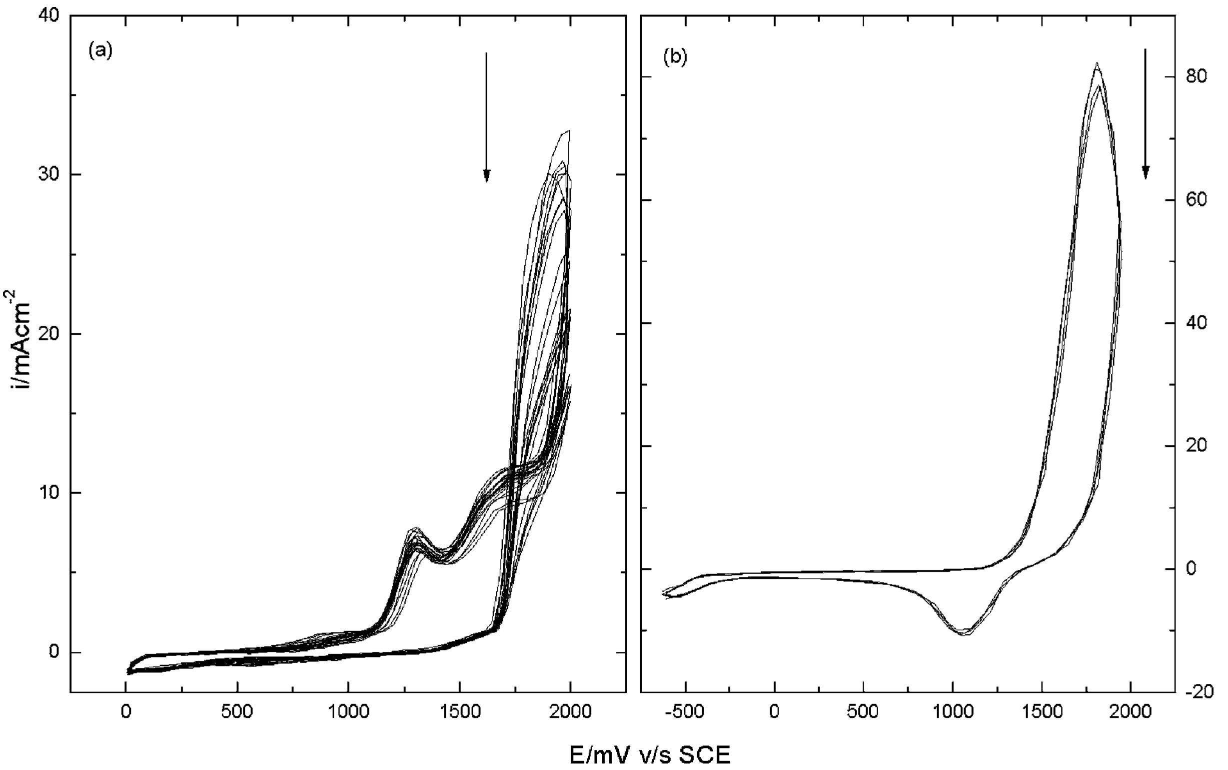


Figure 1 CV profiles of DTK in CH_3CN at 100 mV · s^{-1}. Interfaces: (a) Pt/0.1M DTK + 0.1 M $TBAPF_6$ and (b) Au/0.1 M DTK + 0.1 M $TBAPF_6$.

polymerization. On account of this, Pt was mainly used as a working electrode in this study.

It is possible to observe in Fig. 2 that the voltammetric profile is slightly sensitive to the solvent nature, there finding a similar response in the two media studied. Nevertheless, it is possible to see that the use of acetonitrile allows a better resolution of anodic and cathodic peaks, decreasing the potential at which they appear. It is known that the solvent effect on the electropolymerization mechanism includes the improvement of the physical properties of the deposit, there originating a polymer with a more compact structure, finer morphology, and mechanical stability [30]. It is also known that the presence of water in the electrolytic medium, modifies and, in some cases, prevents thiophene polymerization, there obtaining deposits having poor mechanical properties [31]. In this case, it was thought more appropriate to use acetonitrile than dichloromethane, and to increase the precautions in order to eliminate water from the electrolytic media.

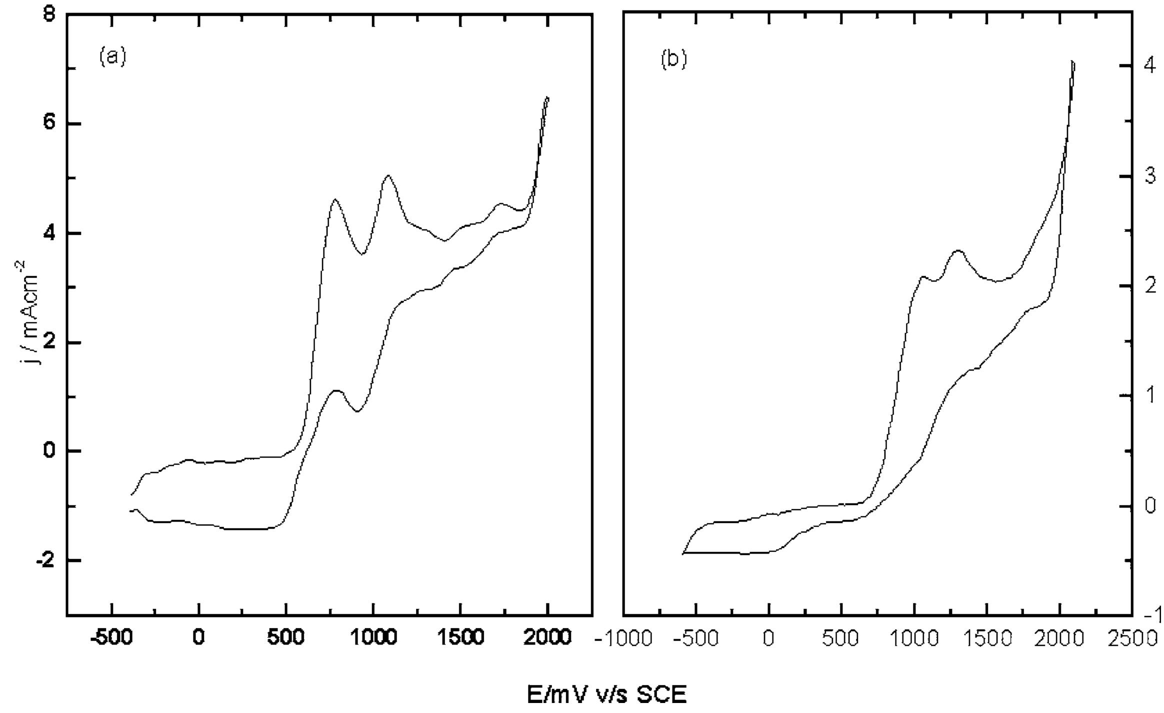


Figure 2 CV profiles of DTK at 100 mV · s^{-1}. Interfaces: Pt/0.1 M DTK + 0.1 M $TBAPF_6$ in: (a)CH_3CN and (b) CH_2Cl_2.

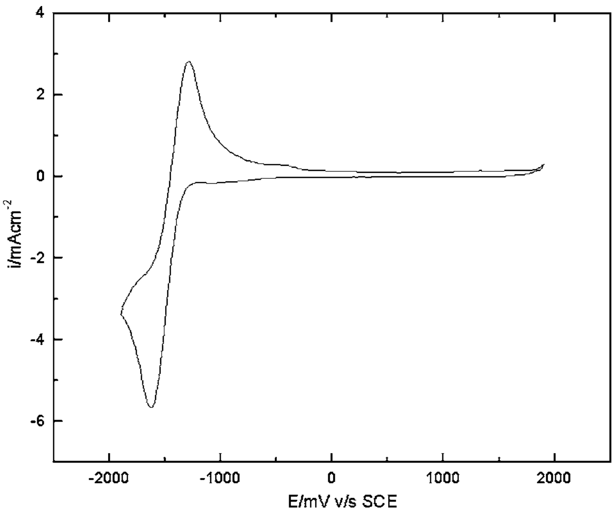
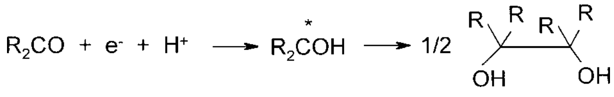


Figure 3 CV profile of DTK at 100 mV·s^{-1}. Interface: Pt/0.1 M DTK + 0.1 M TBAPF$_6$ in CH$_3$CN.

Notwithstanding the fact that the anodic electropolymerization generates more adequate deposits, the cathodic process was also studied with the aim of comparing the behaviour of this monomer in front of oxidation and reduction. The cathodic profile (Fig. 3) shows a reversible process, which may be assigned to CO reduction to COH, via a free carbinolate radical, just as suggested when THF is used as solvent [32]. Nevertheless, the behavior shown by the dimer in THF is different, because in this case, a deposit having an acceptable conductivity is obtained [8]. However, the cathodic polymerization of this monomer is not feasible, because the free carbinolate radical may only dimerize, through the process suggested in the literature, showed in Equation 1 [32]:

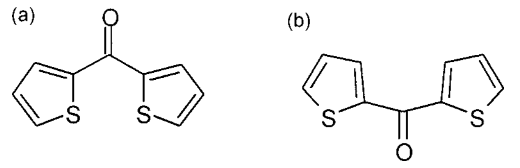


$$R_2CO + e^- + H^+ \longrightarrow R_2\overset{*}{C}OH \longrightarrow 1/2\ R_2C(OH){-}C(OH)R_2$$

(1)

The mechanism of Equation 1 has also been suggested when Au is used as electrodic substrate [33]. In this case, the cathodic CV patterns from various 2-dithienyl ketone derivatives show the presence of a monoelectronic reversible process ($E_{cp} = -1.58$ V *vs* SCE). In general, aldehyde and ketone reduction in aprotic medium, proceeds through the formation of a radical anion which gives rise to a dianion by further reduction.

The corresponding radical anion has been detected by EPR [33]. When the amount of rings present in the monomer increases, the voltammograms show one or two cathodic waves related to the reversible monoelectronic process. The values of this potential decrease with the increase in the oligomer long chain. This effect facilitates the dianion formation along the oligomer series. An extensive study of the radical anions formed by electrochemical reduction in different solvents, like dimethylformamide, acetonitrile, and dimethylsulphoxide, clearly indicates the presence of two species, as two interconventing conformers, mainly trans-trans and cis-cis (Scheme 1) [34].



Scheme 1 Intercoventing conformers of DTK: (a) *trans-trans*; (b) *cis-cis*.

Therefore, the difference between the cathodic and anodic behaviour of DTK becomes evident because, while in the former only a dimer is obtained, in the latter the formation of, at least, oligomers seems possible. Visually in this case, a film formed on the electrodic substrate is observed. However, the current decrease during the anodic polymerization process requires a more detailed analysis.

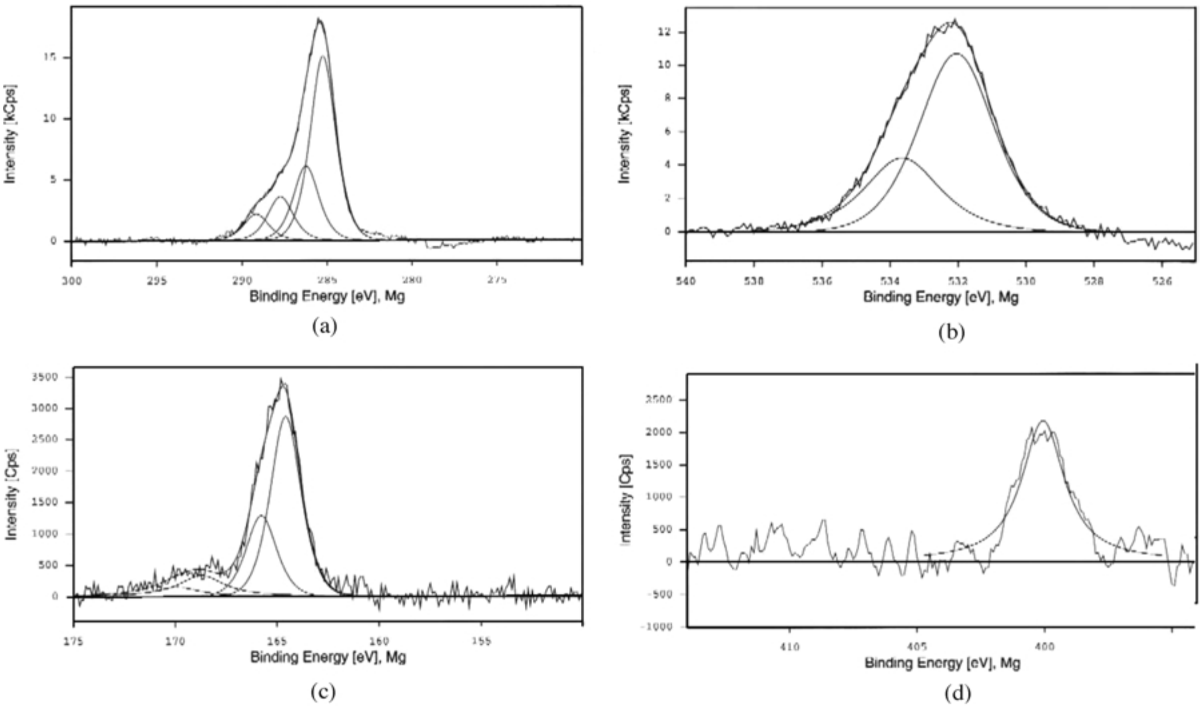
It is known that during this process different chemical reactions may occur, among them, the molecule fragmentation which would lead to a homolytic rupture between the carbonyl carbon and the ring, there originating two radical fragments. Besides, during thiophene oxidation radicals are produced and, the coupling between each other, or with a neutral molecule, leads to oligomerization [35, 36]. It is in this point that the chain growth begins. However, no massive deposit is originated on the electrodic surface, due to the coupling among thiophene radicals; so, it is possible to think that the homolytic rupture is not produced in a large degree, that is to say, the carbonyl group would be stabilized between these two rings.

Composition of the electrodeposits obtained in the same conditions of Fig. 1a was determined through electron probe microanalysis, EPMA (Table I). In each case, there is some oxygen contamination, and there also is some nitrogen present. These extra atoms may be related to air, electrolyte salt and/or solvent contamination. This has been checked by XPS measurements. The XPS quantitative analysis confirms the oxygen contamination while some nitrogen has also been found. XPS being a surface analysis, the contamination measured concerns mainly to the surface contamination. However, the strong oxygen excess measured is a good match with the EPMA study. Besides, there is some relative sulphur deficiency which confirms film contamination.

In some samples, some dopant (fluorine) is present. Frequently, however, the relative concentrations of the atomic dopant are small and the doping process may be considered reversible. It should be noted that the etching speed of nitrogen and oxygen is far higher than that of carbon. Therefore, during the etching, the C—N and C—O bonds are preferentially broken and no real information on the polymer may be obtained after such process.

TABLE I Electrodeposits quantitative analysis

Atomic%	C	O	S	N
Theoretical	75	8.3	16.7	0
EPMA	70	14.3	13.7	2
XPS	60	31.0	8.0	1



(a) (b) (c) (d)

Figure 4 Decomposed XPS spectrum of poly(DTK): (a) C1s, (b) O1s, (c) S2p and (d) N1s.

Then, the decomposition of XPS peaks was performed (Fig. 4). It should be noted that in this polymer there is some nitrogen superficial contamination, while there is sulphur deficiency and oxygen excess (Table I). XPS has detected no dopant.

The decomposition of C1s peak (Fig. 4a) shows that four contributions are present. The first contribution situated at 285 eV may be attributed to the C—C bond. This C—C binding energy has been taken as reference, because it is the most common case [37]. The second one, at 286 eV, is more difficult to be attributed. Its binding energy is a little too high to be attributed to C—S, but it is a little too small to be attributed to C—OH. In fact, it corresponds to C—N. However, the relative atomic value of the contribution (23 atomic %) may not be attributed to only a C—N contamination, it should be attributed to a mixture of C—S, C—N, C—OH. The third contribution situated at 287.5 eV corresponds to the expected C=O bond, there may also be a surface contamination contribution. The fourth peak may be assigned to a COOH surface contamination.

The O1s peak (Fig. 4b) may be decomposed in two contributions. The first one, situated at about 533 eV, corresponds to C=O bonds in the polymer, the second one, at 533.4 eV may be assigned to contamination. It may correspond to some C—OH contaminant but also to some absorbed water [38].

It should be noted that the S2p line corresponds to a doublet. However, in Fig. 4c, it is possible to see that more than a doublet is needed to obtain good peak decomposition. The main contribution situated at 164.3 eV corresponds to C—S bonds of the polymer. The small contribution situated at 168.5 eV corresponds to oxidized sulphur, which means that, on the surface of the film there is some sulphur oxidation. The small nitrogen contribution (Fig. 4d) corresponds to covalent nitrogen, which may be attributed to air contamination but also to some solvent contribution, since some nitrogen is also present in the bulk of the films as shown by EPMA.

It should be noted that after etching during 1 min, in the case of sulphur, only the contribution corresponding to C—S bonds is still present, which shows that S oxidation is a surface phenomenon.

On the other hand, it was found that the reactivity of this molecule is lower than that of thiophene, because experiments made in identical conditions, but in the presence of thiophene, reveal the incorporation of a carbonyl group in the deposit (FTIR 1634 cm^{-1}), which may be attributed to the homo or copolymer. Conductivity measurements (Table II) show a direct relation with thiophene ratio in the solution, although the conductivities are lower than those of PTh prepared in analogue conditions. This would indicates that the incorporation of carbonyl units in the polymeric matrix modifies PTh electronic conductivity. Probably, this phenomenon may be attributed to the following factors: if there are thiophene blocks, in each end of which carbonyl groups are located, the electronic de-localization would be limited to just some rings. If the number of rings is larger, the effect of this group may be the loss of chain planarity, and, if the incorporation of carbonyl group is at random, the loss of planarity would be even more pronounced.

TABLE II Conductivity of electrodeposits prepared from DTK/thiophene

DTK (M)	Thiophene (M)	Conductivity ($\text{S} \cdot \text{cm}^{-1}$)	Dopin (g)
$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$3 \cdot 10^{-4}$	Yes
$5 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$	$11 \cdot 10^{-4}$	Yes
$5 \cdot 10^{-2}$	$1.25 \cdot 10^{-2}$	$1 \cdot 10^{-4}$	Yes
$5 \cdot 10^{-2}$	$5 \cdot 10^{-2}$	$9 \cdot 10^{-8}$	No
$5 \cdot 10^{-2}$	$2.5 \cdot 10^{-2}$	$16 \cdot 10^{-8}$	No

One way of verifying this hypothesis is by means of theoretical calculations, using small molecules as models, so as to obtain a generalization about the polymer. Calculation performed on several oligo 2-thienyl derivatives has shown the localization properties of the *HOMO* and *LUMO* of DTK dimer [39]. *HOMO* shows the interruption of conjugation at every carbonyl carbon atom, where an extra electron in the *LUMO* is delocalized along all the chain. This means that the corresponding poly (2-thienyl ketone) electrical conductivity along the chain is not favoured by the quinoid structure formation upon doping [40]. Having this fact present, a low conductivity might be expected, which would explain the current decrease during polymerization.

Together with the electronic interactions, conductivity decrease may also be influenced by diverse conformations the rings may adopt. A model describing the internal rotation of neighbouring bi-thiophene rings show that there are two stable isomers, from coplanar formation to perpendicular one [41]. Conformation studies [42–44] indicate that the sulphur atom is always in the same place as the carbonyl group, implying that the thienyl ring is coplanar, that is to say, the cis-cis formation is mostly privileged. The resulting *LUMO* energy indicates that stabilization is larger than the expected from electron-withdrawing inductive effect of carbonyl group, in other words, the electron affinity of these compounds is much higher than that of the oligothiophenes containing the same fragments number. Extrapolated cathodic peak potential (E_{cp}) values for the polymer are much higher than that of PTh. The high electron affinity of polyDTK counteracts the high ionization energy (IE) values, so that the *HOMO-LUMO* energy gap is close to that of PTh [45].

With the aim of determining the electrodeposition nucleation and growth mechanism (NGM), j/t transients were drawn from similar solutions to the previous ones, working in the potential range in which this process is observed. Different equations containing one to four terms were considered to fit the correct transient. Each one of these terms represents a different classical NGM [46, 47]. The best equation to fit all the experimental curves of this work, with an error smaller than 2%, was as follows:

$$j = at[\exp(-bt^2)] + ct^{-0.5}[1 - \exp(-dt)] \quad (2)$$

In this equation, the first term corresponds to an instantaneous nucleation mechanism under charge transfer control, with bi-dimensional growth (IN2D). The second term corresponds to an instantaneous nucleation with 3D growth mechanism under diffusion control (IN3D). Constants a, b, c, and d, are described through the following equations:

$$a = \left(2\pi n M h F N_{2\mathrm{D}} k_2^2\right)/\rho \quad (3)$$

$$b = \left(\pi N_{2D} M^2 k_2^2\right)/\rho^2 \quad (4)$$

$$c = (nFD^{0.5}C_\infty)/(\pi^{0.5}) \quad (5)$$

$$d = N_0 \pi k D(6) \quad (6)$$

TABLE III Effect of the experimental parameters assayed on the numerical constant of Equation 2 for DTK electro-oxidation on Pt disc electrode from DTK + 0.1 M TBAPF$_6$ in CH$_3$CN

DTK (M)	E (mV)	a (mAcm^{-2} s^{-1})	b (s^{-2})	c (mAcm^{-2}s^{-2})	d (s^{-1})
$2.5 \cdot 10^{-2}$	2070	0.06101	0.1930	0.22060	0.0595
	2080	0.12677	0.6475	0.22060	0.2042
	2090	0.27651	2.1158	0.22060	0.5644
$5 \cdot 10^{-2}$	2050	0.009216	0.0488	0.76936	1.2287
	2060	0.07096	0.0488	0.76936	1.8656
	2070	0.09276	0.0674	0.76936	2.0496
	2080	0.20899	0.0711	0.76936	2.8811
	2090	0.30586	0.0929	0.76936	3.2090
$1 \cdot 10^{-1}$	2050	0.009881	0.0274	0.43023	2.8837
	2060	0.04071	0.0774	0.43023	3.2273
	2070	0.13314	0.1487	0.43023	4.2930
	2080	0.25046	0.2846	0.43023	5.3259
	2090	0.37443	0.3069	0.43023	5.8510

where n, F, M and ρ have their usual meaning, h and k_2 are the height and growth rate of the 2D nucleus, $N_{2\mathrm{D}}$ and N_0 are the instantaneous nuclei number formed at $t = 0$ in 2D or 3D form, D and C_∞ are the diffusion coefficient and the bulk monomer concentration. Table III summarizes the values of a, b, c and d obtained under the different experimental conditions used in this work. From these values the current transients were deconvoluted, and the different current contributions were revealed.

There is a large number of nucleation and growth mechanisms in literature, which have been suggested for the electropolymerization of thiophene and its derivatives [26, 28, 48, 49]. However, in this study, the fact that more than one mechanism is operating, simultaneously or successively, has been considered, just as Schrebler *et al.* described it [50]. Fig. 5 shows the corrected current transient at different potentials, which has been fitted according to Equation 2; the two contributions, IN2D and IN3D, are also ploted. The analysis of such curves shows that these contributions are time dependent, as explained next:

i. When $t < 2$ s, the NGM process take place simultaneously with two contributions.

ii. From $t > 2$ s, the second contibution (IN3D mechanism under diffusional control) became more important. It may also be seen that from $t = 4$ s, the IN2D contribution decreases up to the point that the only important process is the IN3D contribution because the 2D nuclei begin to coalesce. In this way, the IN3D contribution practically dominates the region over 5–7 s.

In the IN2D mechanism, short chain oligomers are involved in the electropolymerization of thiophene and 3-methyl thiophene [49, 51]. This effect was explained by strong monomer (or short oligomers) interaction with platinum surface which favour the formation of 2D layer [52]. The results described herein suggest that the behaviour of DTK is analogous to the reported one for thiophene and 3-methyl thiophene.

Through theoretical calculations [39, 45], it has been suggested that the monomer *HOMO* level presents a

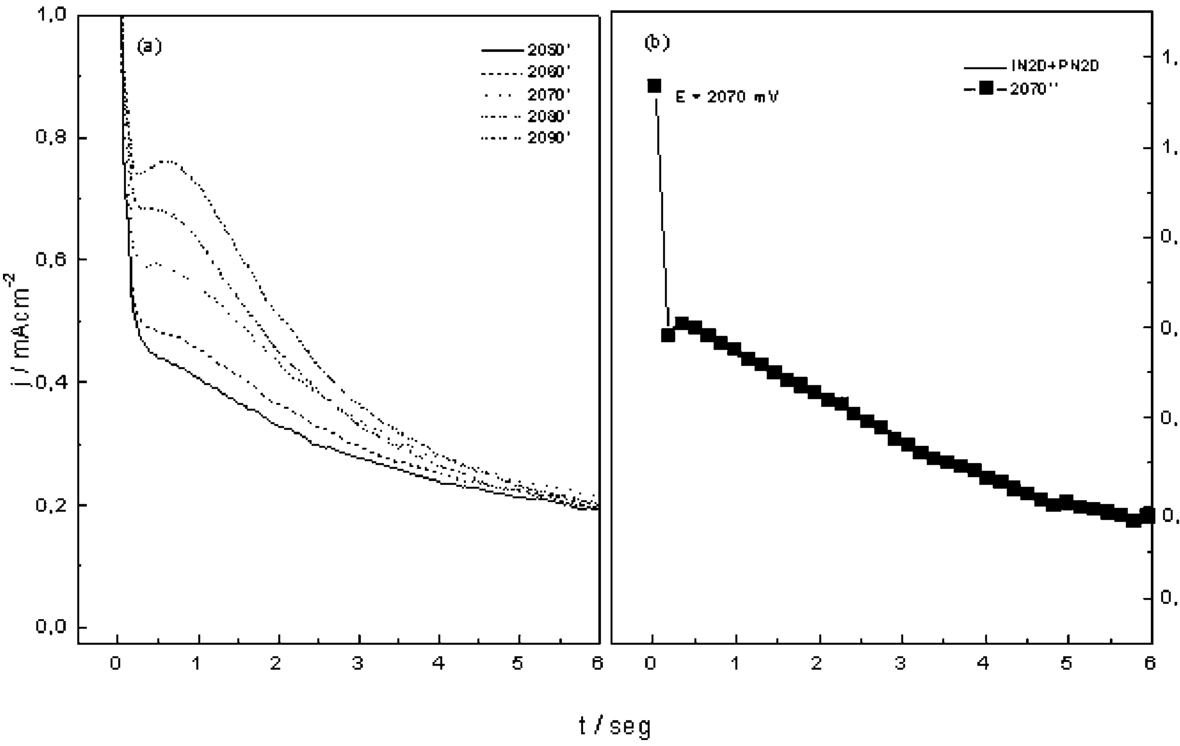


Figure 5 (a) Current-time transients for DTK electro-oxidation at different potentials. Interface: Pt/0.1 M DTK + 0.1 M TBAPF$_6$ in CH$_3$CN. (b) Corrected current-time transients fitted by means of Equation 2, $E_{(\mathrm{pol})} = 2070$ mV. IN2D and IN3D contributions were calculated from the respective terms of the same equation.

conjugation interruption at each carbonyl group, consequently, the electronic de-localization when forming a radical cation, is restricted to one ring, there limiting the monolayer growth, and decreasing the polymer conductivity.

At longer periods of time, the main contribution is the diffusional one, confirming in this way the formation of an oligomeric high density region (OHDR), just as it has been proposed in the thiophene electropolymerization mechanism [50]. When this region is generated, the process begins to be controlled by diffusion, because the monomer must "go through" in order to continue oxidizing and lengthening the nucleus chains which have already been deposited on the electrode.

Thus, the results given by the NMG indicate that the nucleation of this type of deposit is instantaneous, and it occurs in very short periods of time. This indicates that the carbonyl group has a strong deactivating effect, there restricting the deposit growth, which explains the formation of thin films with a compact and uniform morphology.

Summing up, the results found for DTK NGM indicate that in this type of electrodeposit, the growth is attributable to short chain oligomer formation, which explains the thin films and the low conductivities. Anyway, the XPS results confirm that the oligomerization is produced through the thiophene rings, while the carbonyl groups remain intact.

Although the previous results may be considered not too supportive in relation to the most common applications of conducting polymers, which require very high conductivities, the behaviour of these deposits suggests their use in the preparation of electroluminiscent diodes [39, 53]. Therefore, studies were made in order to determine their properties to be used in such preparation.

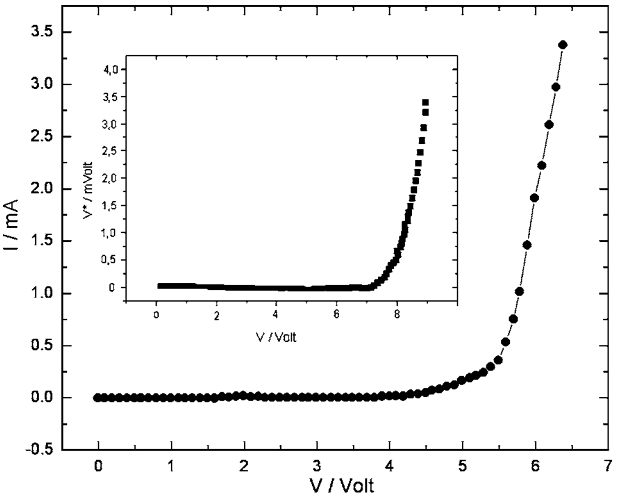


Figure 6 Characteristic curves of ITO/poly(DTK)/Al device at room temperature: current-voltage and (inside) photodiode tension curve.

Fig. 6 shows I–V and electroluminescent characteristics obtained from a device with the ITO/polyDTK/Al configuration. Current and light intensity increase rapidly with a bias of over 2 V and 5 V, respectively, which are typically rectifying characteristics. As it may be seen from the I–V curve, the threshold voltage is considerably low if compared to that of PPV-based polymer [54]. The two curves have the same shape, but it can be seen that the electroluminescence appears after the current increase in the forward direction.

These responses, as a preliminary study, confirms that the electrodeposits here obtained can be assayed in diode devices. A complete investigation about this is actually in course.

4. Conclusions

By means of cyclic voltammetry, it has been possible to establish the feasibility of electropolymerisation of 2,2′ dithienylketone, although the theoretical calculations, and the experimental results show that, on account of structural reasons, doping in this kind of materials is not favoured.

In all employed conditions, the voltammetric response is irreversible, though cathodically, there is a reversible system which corresponds to the carbonyl group reduction.

Optimal electrochemical conditions for the electro-oxidation of DTK were the use of Pt as working electrode and acetonitrile as electrolytic media. The nucleation and growth mechanism of these deposits show two contributions, one controlled by the charge transfer, and the other, with diffusional control. This mechanism explains the obtention of thin films.

The electrodeposit properties (thin films with low conductivity) allows to suggest electro-oxidized DTK for the development of electroluminiscent organic diodes (OLED).

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