

Electrochemical Synthesis of Poly(3,4-ethylenedioxythiophene) on Steel Electrodes: Properties and Characterization

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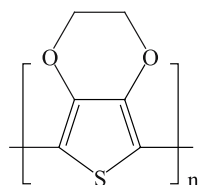
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Abstract

Electrodeposition of poly(3,4-ethylenedioxythiophene) by electrochemical polymerization of 3,4-ethylenedioxythiophene has been performed on steel electrodes rather than on the typically used inert electrodes (Pt, Au, graphite carbon). The polymer was generated by cyclic voltammetry, chronopotentiometry and chronoamperometry from a 10 mM monomer solution in acetonitrile with 0.1 M LiClO₄. Elemental analysis of the generated polymer indicated that the monomeric units support 0.54 positive charges balanced with ClO₄¹⁴⁻ counterions. Electrochemical, electrical and structural properties of the prepared material have been characterized. The good adherence of films combined with its excellent properties indicate that poly(3,4-ethylenedioxythiophene) can be a suitable material for anticorrosion applications.

Introduction

π -conjugated polymers, especially those based on polyanilines, polypyrroles, polythiophenes and polyphenylenes, have received significant attention throughout the course of the past 2 decades owing to a wide range of promising electronic, electrochemical and optical applications [1–8]. Among the many materials that have been developed during this period, poly(3,4-ethylenedioxythiophene) (PEDOT; Structure 1) is one of the most successful polythiophene derivatives because of its interesting properties [9–15].



PEDOT

PEDOT exhibits not only a high conductivity but also an unusual stability in the oxidized state, being considered as the stablest conducting polymer currently available [9–13]. Furthermore, the oxidative polymerization of PEDOT monomer using poly(styrene sulfonic acid) (PSS) polyelectrolyte as the charge-balancing dopant promotes the formation of a water-soluble polyelectrolyte system

PEDOT/PSS with good film-forming properties, high conductivity and excellent stability [9, 14, 15]. On the basis of these properties, PEDOT derivatives have been used as antistatic coatings for photographic film, electrode material in inorganic electroluminescent lamps, material for through-hole plating of printed circuit boards, etc. [9, 13].

A very promising technological application of π -conjugated polymers involves their use as protective coatings on steel, an environmentally friendly approach to corrosion prevention. Since the pioneering studies of DeBerry [16, 17], where the corrosion inhibition of stainless steel by polyaniline was demonstrated, there has been significant progress in the anticorrosion applications of electroactive coatings [18–25]. Thus, polyaniline coatings are now commercially available as anticorrosive coatings [18–20]. Furthermore, corrosion retarding has also been achieved using polypyrrole coatings [21–23] and, more recently, polythiophene coatings [24, 25]. Electrodeposition of conducting polymers by electrochemical polymerization of the corresponding monomers is usually performed on chemically inert electrodes (Pt, Au, graphite carbon). However, direct electrodeposition of polymer films on steel surfaces by in situ electropolymerization is highly desirable since it is expected to be a new method to prevent corrosion.

In this work and within a wide project devoted to developing anticorrosive coatings based on polythiophene

derivatives, we have studied the electrochemical, electrical and structural properties of PEDOT doped with ClO_4^- anions when it is anodically synthesized on steel electrodes. The polymer was generated by cyclic voltammetry (CV), chronopotentiometry (CP) and chronoamperometry (CA). The kinetics for the electrogeneration of oxidized PEDOT at several low oxidation potentials was followed by ex situ ultragravimetry. The density and electrical conductivity of the resulting oxidized forms were determined. The composition and molecular structure of the material synthesized were characterized by elemental analysis, IR spectroscopy and X-ray diffraction. The results were compared with those reported in the literature for PEDOT produced using different conditions and/or substrates [10, 14, 15, 26–29].

Methods

3,4-Ethylenedioxythiophene (EDOT) and acetonitrile of analytical reagent grade from Aldrich Chemical were used as monomer and solvent, respectively, without further purification. Anhydrous lithium perchlorate from Aldrich, analytical reagent grade, was stored in an oven at 80 °C before its use in the electrochemical trials.

Anodic polymerization of EDOT was studied by CV, CP and CA using a PAR 273A potentiostat–galvanostat connected to a PC and controlled through a PAR M270 program. Electrochemical experiments were conducted in a three-electrode two-compartment cell under nitrogen atmosphere (99.995% in purity) at 25 °C. The anodic compartment was filled with 40 ml of a 10 mM monomer solution in acetonitrile containing 0.1 M LiClO_4 as supporting electrolyte. A volume of 10 ml of electrolyte solution was placed in the cathodic compartment. Steel AISI 316 sheets of 4-cm² area were employed as working electrodes. The counter electrode was a steel sheet of 2-cm² area. In order to avoid interferences during the electrochemical analyses, the working and counter electrodes were cleaned with acetone before each trial. The reference electrode was a $\text{Ag} | \text{AgCl}$ electrode containing a KCl saturated aqueous solution ($E^\circ = 0.222$ V at 25°C), which was connected to the working compartment through a salt bridge containing the electrolyte solution.

Films of oxidized PEDOT were electrogenerated by CA considering different polymerization times. The weight W_{ox} of insoluble polymer was determined as the difference between the masses of the coated and uncoated electrodes using a COBOS analytical balance with a precision of 10^{-4} g. Samples for analysis were obtained by scratching their deposits from the working steel electrode. The resulting powders were placed in a filter, rinsed with bidistilled water and ethanol and, subsequently, dried under vacuum for 24 h [30, 31]. The percentage of doping ClO_4^- in each collected polymer was obtained from reduction of approximately 2 mg of sample with carbon, followed by determination of the amount of chloride ions released by standard ion chromatography. This analysis was performed with a Kontron 600 HPLC liquid

chromatograph fitted with a Waters IC-Pak anion column at 30 °C and equipped with a Wescan conductimetric detector.

The density of the oxidized polymers was determined by the flotation method from $\text{CCl}_4 + \text{C}_2\text{H}_5\text{I}$ mixtures. The electrical conductivity was measured by the sheet-resistance method from films synthesized on steel electrodes of 4-cm² area, following a procedure described previously [30].

A Bomem Michelson MB100 FTIR spectrophotometer, with a resolution of 4 cm⁻¹ in the absorbance mode, was employed for the characterization of the polymer films. The samples were placed in an attenuated total reflection accessory with thermal control and a diamond crystal (Golden Gate Heated Single Reflection Diamond ATR, Specac-Teknokroma).

X-ray diagrams were recorded in a vacuum at room temperature, with calcite as a calibration standard. A modified Statton camera (Warhus, Wilmington, DE, USA) with Ni–Cu radiation of wavelength 0.1542 nm was used.

Identification of low molecular mass oligomers was performed by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry. Spectra were recorded using a Fisons VG Quattro triple quadrupole mass spectrometer equipped with a cesium gun operating with a potential energy of 10 V. Samples were prepared using the procedure previously reported [31].

Results and discussion

Electrochemical behavior

Figure 1 presents the cyclic voltammogram of 10 mM EDOT in acetonitrile with 0.1 M LiClO_4 on a steel electrode. The CV was registered at a scan rate of 100 mV·s⁻¹ in the potential range –0.50 to 2.00 V. Two anodic peaks, O_1 and O_2 , were detected. The anodic peak potential of the first peak, $E_p^a(O_1) = 1.53$ V, is higher than those obtained on a Pt electrode for 10 mM EDOT solution with 0.1 M LiClO_4 in propylene carbonate and water [$E_p^a(O_1) = 1.45$ and 1.34 V, respectively, at a scan rate of 100 mV·s⁻¹] and in acetonitrile and water mixed with a soluble substituted β -cyclodextrin [$E_p^a(O_1) = 1.38$ and 1.26 V, respectively, at a scan rate of 50 mV·s⁻¹] [26, 27]. The anodic peak potential of the second peak O_2 overlaps the oxidation of the medium at a potential higher than 3.00 V. No reduction peak is seen in Figure 1 because the oxidation of EDOT is an irreversible process up to 2.00 V. Onset of polymerization occurred at 1.20 V, this value being very similar to that reported for 50 mM EDOT in acetonitrile with 0.05 M Et_4NClO_4 on a Pt electrode (1.25 V) [10].

Uniform, adherent, insoluble and dark-blue polymeric films grew on the working steel anode when the monomer began to be oxidized from potentials higher than 1.20 V. Potentials higher than 1.70 V produced films of lower adherence owing to the release of large amounts of generated polymer into the medium. This behavior may be attributed

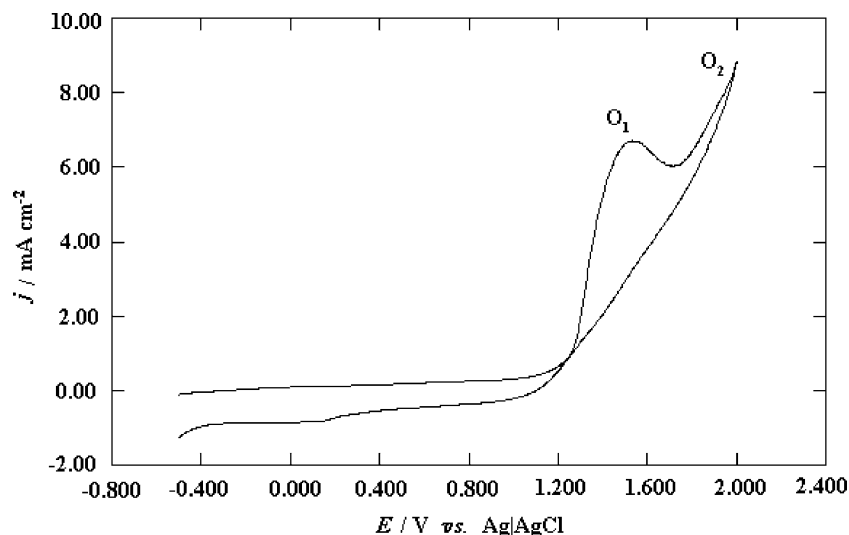


Figure 1. Cyclic voltammogram for the oxidation of a 10 mM 3,4-ethylenedioxythiophene (EDOT) solution in acetonitrile with 0.1 M LiClO₄ on a 4-cm² steel electrode. Initial and final potentials -0.50 V; reversal potential 2.00 V. Scan rate 100 mV s^{-1} . Temperature $25 \text{ }^\circ\text{C}$.

to the occurrence of degradative cross-linking reactions at higher potentials.

Electropolymerization was also studied using multiple scan CV. The electrodeposition of PEDOT on the electrode by CV at a scan rate of $100 \text{ mV} \cdot \text{s}^{-1}$ between -0.50 and 1.60 V is shown in Figure 2. The irreversible oxidation of the monomer appears on the first cycle followed by a nucleation loop. On subsequent cycles, monomer oxidation occurs at slightly lower potentials as a result of the modification undergone by the electrode surface after the first cycle, i.e., the electrode was covered by electro-deposited PEDOT. A new peak of oxidation, O'_1 , appears at $E_p^a(O'_1) = 0.685$ V. This peak corresponds to an oxidation process that occurs at a potential lower than that of O_1 . The growth of the polymer films on the steel electrode was regular and continuous. The current density increases with the number of cycles, a value of $11.35 \text{ mA} \cdot \text{cm}^{-2}$ being reached after 12 cycles. This value is higher than that derived using the same scan rate with Pt electrodes [26],

suggesting that the polymer deposition is faster when we use steel electrodes.

The chronopotentiometric study for the electrogeneration of polymer films was performed at different current densities over 120 s. Figure 3 shows the chronopotentiograms obtained at current densities of $5.0 \text{ mA} \cdot \text{cm}^{-2}$ (curve a), $4.0 \text{ mA} \cdot \text{cm}^{-2}$ (curve b), $3.0 \text{ mA} \cdot \text{cm}^{-2}$ (curve c), $2.0 \text{ mA} \cdot \text{cm}^{-2}$ (curve d) and $1.0 \text{ mA} \cdot \text{cm}^{-2}$ (curve e). For 1.0 , 2.0 and $3.0 \text{ mA} \cdot \text{cm}^{-2}$ the potential stabilizes very rapidly at approximately 1.2 V, which corresponds to the O_1 peak in CV (Figure 1), leading to the formation and subsequent growth of uniform, adherent, insoluble and black films on the steel electrode. This significant behavior indicates that the molecular diffusion of the monomer is very high, allowing the polymerization to continue at such high current densities. Conversely, low adherent films were generated at $4 \text{ mA} \cdot \text{cm}^{-2}$, since the potential stabilizes at about 1.6 V, which is associated with the overoxidation of the polymer (O_2), after passing a maximum below the

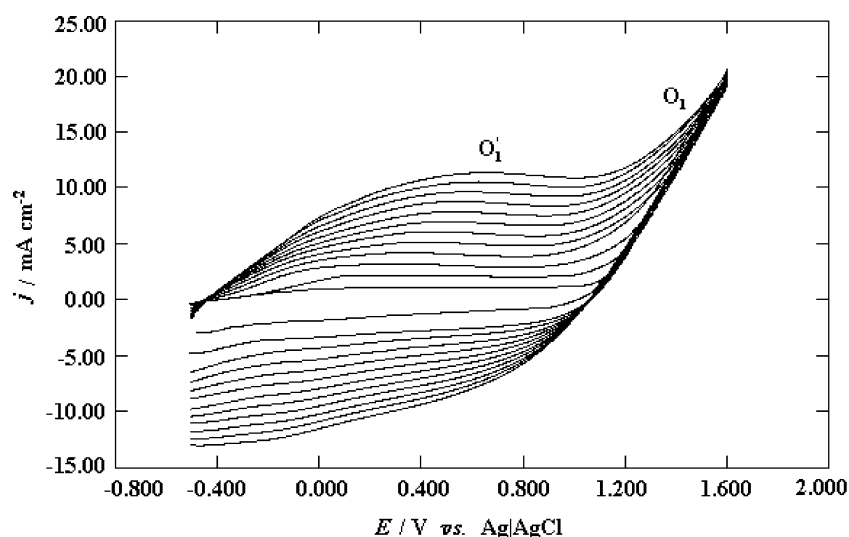


Figure 2. Electrodeposition of poly(3,4-ethylenedioxythiophene) (PEDOT) by multiple potential scanning from a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on a 4-cm² steel electrode. Scan rate 100 mV s^{-1} . Temperature $25 \text{ }^\circ\text{C}$.

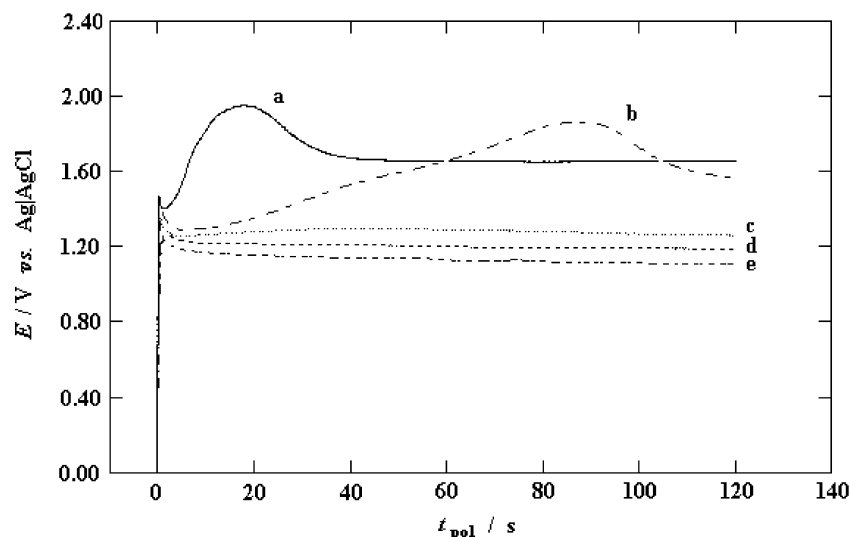


Figure 3. Chronopotentiograms recorded for the oxidation of a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on a 4-cm² steel electrode. Applied current density (a) 5.0, (b) 4.0, (c) 3.0, (d) 2.0 and (e) 1.0 mA·cm⁻². Temperature 25 °C.

oxidation potential of the medium (3.0 V). The same behavior was identified for a current density of 5.0 mA·cm⁻², although the stabilization is faster than for 4.0 mA·cm⁻², i.e., 42 and 115 s, respectively.

In order to prevent the overoxidation of the polymer, we decided to synthesize films of PEDOT by CA, fixing the polymerization potential (E_{pol}) to 1.40 V, this value being slightly lower than $E_{\text{p}}^{\text{a}}(O_1)$. This condition is expected to ensure the polymerization of the monomer but avoid the degradative cross-linking reactions that typically take place at higher potentials. Figure 4 shows the resulting chronoamperogram. Uniform, adherent, insoluble and dark-blue polymer films grew on the steel electrode. The current density stabilizes at 1.82 mA·cm⁻², 2, this value being notably higher than those reported in the literature for other thiophene derivatives [31–33].

The graphical representation of the anodic intensity (I_{anod}) against $t_{\text{pol}}^{1/2}$ using the data shown in the chronoamperogram of Figure 4 provides a linear fitting $y = c, x$ with $c = 7.141 \times 10^{-3} \text{ A}\cdot\text{s}^{-1/2}$ for values of t_{pol} ranging from

3.6 to 41.2 s. The diffusion coefficient (D) of EDOT can be deduced by applying the Cottrell equation to this interval:

$$I = n_{\text{av}}FAC^* \left(\frac{D}{\pi t} \right)^{1/2} + I_c, \quad (1)$$

where I_c cancels over 1 ms, C^* is the molar concentration (10 mM), F is the Faraday constant, A is the area of the electrode and n_{av} is average number of electrons transferred by each monomer that is incorporated into the polymer chain (1.78, see later). It should be noted that the fulfillment of the Cottrell equation implies that the process is controlled by diffusion. The diffusion coefficient obtained for EDOT monomers during generation is $5.43 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$. This value, which is within the range typically expected for substances in solution, reflects the good mobility of EDOT molecules in acetonitrile. Furthermore, it indicates that the diffusion of the monomer towards the surface of the electrode is the limiting step in the electrogeneration process.

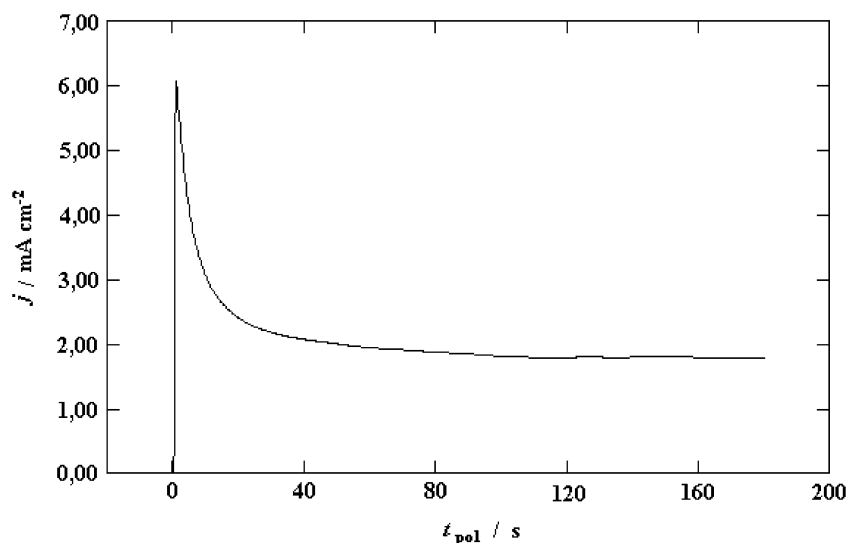


Figure 4. Chronoamperogram obtained for the oxidation of a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on a 4-cm² steel electrode by applying a constant potential of 1.40 V. Temperature 25 °C.

Electrochemical control of oxidized PEDOT.

After generation of polymer films by CA (see earlier), each coated electrode was rinsed several times with water, dried in a nitrogen flow and immersed in the electrolyte solution of the control cell for CV analysis. Figure 5 shows typical control voltammograms in the potential range from -0.50 to 1.60 V. Two consecutive oxidation peaks, O'_1 and O'_2 , appear: the first one with $E_p^a(O'_1) = 0.245$ V, while $E_p^a(O'_2)$ overlaps with the oxidation potential of the medium. In addition, two reduction peaks with $E_p^c(R'_1) = -0.145$ V and $E_p^c(R'_2) = 0.730$ V are detected in the cathodic scanning, indicating the presence of redox pairs in the recorded potential range. This should be interpreted as the formation of polarons in the polymer chains. The total reduction charge is more than 80% of the total oxidation charge as determined from the integration of the cathodic and anodic areas. This corresponds to a quasireversible redox pair, i.e., anodic and cathodic charges are equal in ideally reversible processes. Furthermore, the redox properties of the material are almost unaltered after six consecutive oxidation-reduction cycles. This notable electrochemical stability combined with the successful electrogeneration on steel surfaces favor the applicability of PEDOT as a potential corrosion protector.

Electropolymerization kinetics and polymer composition

The kinetics for the oxidation-polymerization of EDOT was studied by generating films under a constant potential of 1.40 V and considering different t_{pol} values on steel anodes. Reproducible film weights, W_{ox} (in milligrams per square centimeter), were always obtained until a t_{pol} of 720 s. The polymerization charge, Q_{pol} (in millicoulombs per square centimeter), consumed in each process was directly calculated on each chronoamperogram. The variation of W_{ox} against Q_{pol} , which is plotted in Figure 6, provides a linear correlation with an excellent regression coefficient

($r \geq 0.997$). This is consistent with a faradic process. The slope of this plot corresponds to the current productivity, which is expressed as milligrams of PEDOT electrogenerated per coulomb of charge consumed during electropolymerization. Thus, the resulting productivity, $0.875 \text{ mg} \cdot \text{C}^{-1}$, is independent of the electrode area.

On the other hand, elemental analysis of electrogenerated material revealed that oxidized polymer contains 27.42% in weight of ClO_4^- counterions, confirming its salt structure. Accordingly, each monomeric unit incorporated into the polymer during electrogeneration contains 0.539 ClO_4^- ions. Thus, the formula for a molecule of oxidized PEDOT formed by n chemical repeating units can be written as $[(\text{EDOT}^{0.539+})_n(\text{ClO}_4^-)_{0.539 n}]_{\text{solid}}$. From these data, the number of electrons, n_{ox} , consumed to incorporate a monomer into the polymer and to oxidize the resulting chain can be calculated using the following expression:

$$n_{\text{ox}} = \frac{MQ_{\text{pol}}}{FW_{\text{org}}}, \quad (2)$$

where M is the molar mass of EDOT (142 g mol^{-1}), F is the Faraday constant and W_{org} is the mass of the organic components in each film, which is determined as follows:

$$W_{\text{org}} = W_{\text{ox}}(1 - W_{\text{dop}}), \quad (3)$$

where W_{dop} is the mass of ClO_4^- per polymer unit of mass. Calculation of W_{dop} led to $W_{\text{org}} = 0.7258 W_{\text{ox}}$. The average n_{ox} value derived from Equation 2, taking $Q_{\text{pol}}/W_{\text{ox}}$ as the inverse of the productivity, is 2.32. After discounting the oxidation charge used to compensate the charge of the dopant ion, the average number of electrons per monomer incorporated into the polymer chain is 1.78. This value is close to that predicted for the formation of an infinite linear molecule from a typical condensation mechanism (2.00), which involves two protons and two electrons in the formation of the $\alpha - \alpha$ bond between the terminal

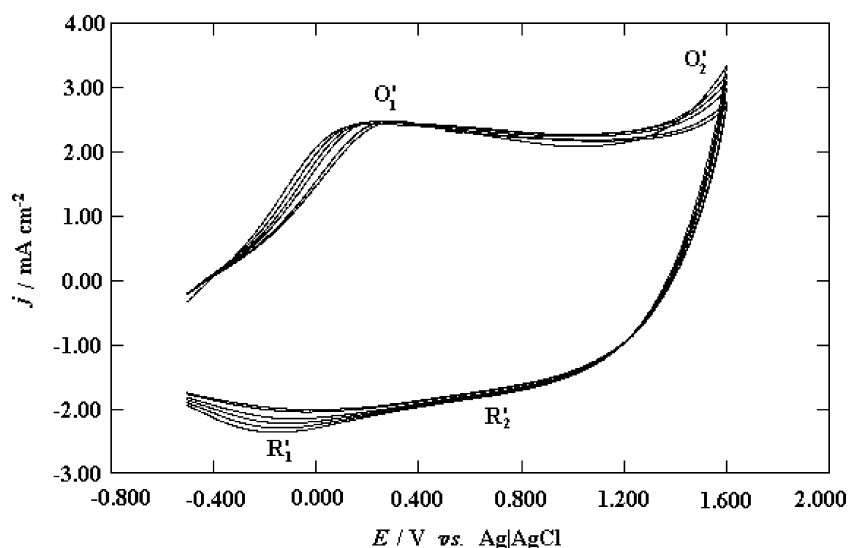


Figure 5. Control voltammograms for the oxidation of PEDOT films on 4-cm^2 steel in acetonitrile with 0.1 M LiClO_4 , at $100 \text{ mV}\cdot\text{s}^{-1}$ and at 25°C . Initial and final potentials -0.50 V; reversal potential 1.60 V. The films were generated for 300 s under the conditions given in Figure 4.

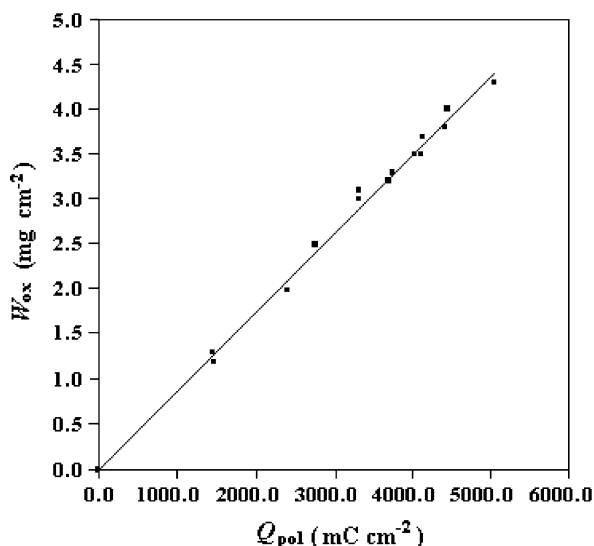


Figure 6. Variation of the weight per area unit of PEDOT films deposited on steel from a 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ at a constant potential of 1.40 V with polymerization charge consumed. Temperature 25 °C.

monomeric unit of the chain and the incorporated monomer [34, 35]. The fact that the number of electrons consumed to produce linkages between monomeric units is less than 2.00 can be explained by the existence of parallel processes, i.e., chemical polymerization reactions, during the electropolymerization.

Electrical and structural properties of PEDOT

The samples of PEDOT generated are insoluble in common organic solvents, which is explained by both the formation of very long chains during electropolymerization and their rigid conjugated structure. The density determined for this material is 1.650 g · cm⁻³, this value being higher than that measured for polythiophene prepared by polymerization of α -tetrathiophene (1.551–1.562 g · cm⁻³ depending on the polymerization potential) [31]. Indeed, the high density of PEDOT should be attributed to the length of the polymer chains and absence of cross-links, i.e., the material generated is mainly composed of long linear chains. This is agreement not only with n_{ox}^m but also with MALDI-TOF mass spectrometry studies, which indicated the absence of oligomers in films of PEDOT.

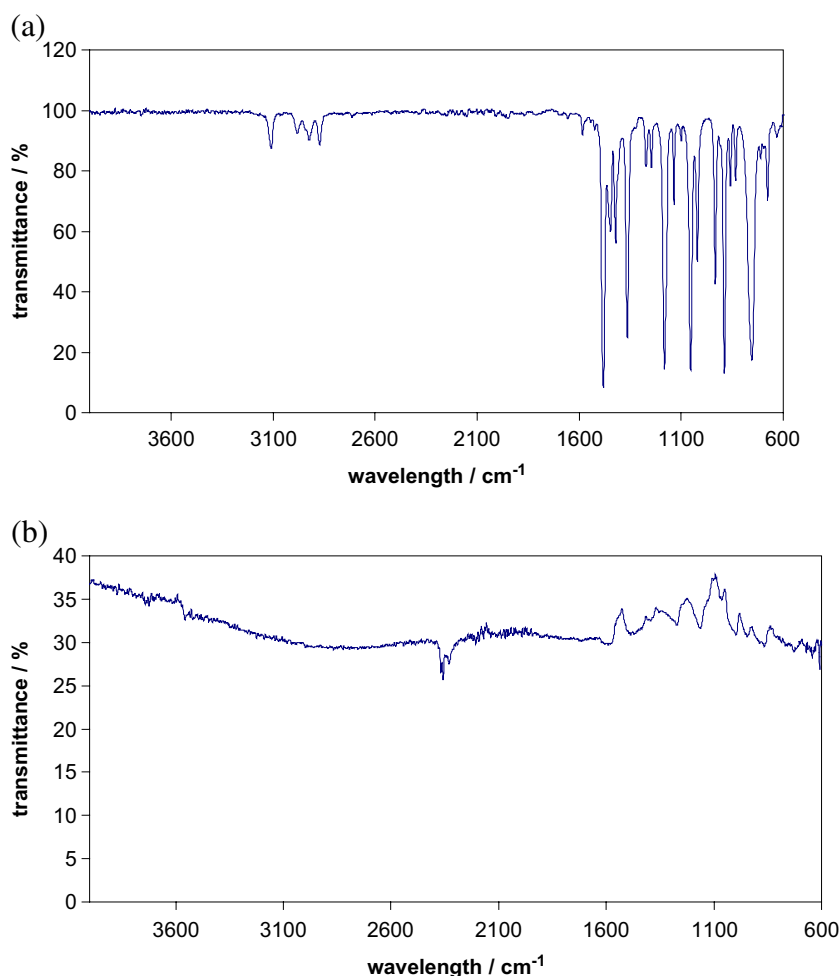


Figure 7. Fourier transform IR spectra obtained for (a) pure EDOT and (b) PEDOT.

The electrical conductivity measured for the polymer obtained on a 4-cm² steel electrode is 315 S·cm⁻¹. This high value is in good agreement with that reported by Pei et al. [10] for perchlorate-doped PEDOT films formed on Pt electrode surfaces (210 S·cm⁻¹). These authors suggested that higher conductivities could be obtained by optimizing the experimental conditions, as has been achieved in the present study. The film conductivity measured for polystyrene sulfonate doped PEDOT is small (1–2 S·cm⁻¹) with respect to that reported in this work [15]. However, it increases 2 orders of magnitude (100–200 S·cm⁻¹) when the interaction between the two polymers is improved by the addition of polyols such as sorbitol or glycerol to the dispersion from which the film is cast [14, 15, 29].

In addition, the degree of order of this electrochemically polymerized material was examined by X-ray diffraction analysis. The results indicated that perchlorate-doped PEDOT is completely amorphous. This is in agreement with X-ray diffraction studies on PEDOT samples with polystyrene sulfonate acting as a counteranion [10, 28]. Although this was attributed to the polymeric nature of polystyrene sulfonate [28], our results indicate that amorphous character of PEDOT samples does not depend on the counterion.

A comparative IR analysis of the electrogenerated polymer within the wavelength region 1,200–600 cm⁻¹ was carried out to investigate its structure in terms of linkages. The IR spectrum of pure EDOT (Figure 7a) shows remarkable bands centered at 1,182 and 756 cm⁻¹ with relative intensities of 1:1, which correspond to the absorption of the C–O–C bending mode of the ethylenedioxy moiety and the C^α–H out-of-plane bending mode, respectively. As expected, the bands are much weaker in the IR spectrum of PEDOT (Figure 7b) owing to the strong interactions with the ClO₄⁻ counterion. In spite of this inconvenience, the bands associated with the C–O–C bending and C^α–H out-of-plane bending modes discussed earlier can be identified at 1,175 and 750 cm⁻¹, respectively, with relative intensities of 4.2:1. Accordingly, it is apparent that the relative intensity of the C^α–H out-of-plane bending mode is lower in the polymer chain than in the monomer, indicating that anodic electropolymerization of EDOT predominantly provides linear molecules through the formation of α,α-linkages.

Conclusions

Cyclic voltammograms of 10 mM EDOT solution in acetonitrile with 0.1 M LiClO₄ on steel AISI 316 electrodes exhibit two consecutive oxidation processes. The first process, with $E_p^a(O_1) = 1.53$ V, corresponds to the primary oxidation–polymerization of monomer, whereas the second process is due to the overoxidation of the material, the peak being overlapped with the that of the oxidation potential of the medium. Multiple-scan CV revealed the irreversible oxidation of the monomer in the first cycle followed by a nucleation loop, the monomer oxidation occurring at

slightly lower potentials owing to the modification undergone by the electrode surface. The CP study confirmed the generation of uniform and adherent films up to 3.0 mA·cm⁻², the first oxidation being the only process occurring. Uniform and adherent oxidized PEDOT films can also be synthesized from this solution by CA. Control voltammograms of these deposits reflect the presence of a large number of electroactive polarons in the range of potential from –0.50 to 1.60 V, the total reduction charge being more than 80% of the total oxidation charge. Furthermore, the material preserves almost unaltered its redox capacity after six consecutive cycles of oxidation–reduction.

The polymer doped with ClO₄⁻ presents a salt structure as determined by elemental analysis. The monomeric units support average positive charges close to 0.54, balanced with ClO₄⁻ counterions. Furthermore, the n_{ox}^m value and the IR spectra indicate that the most frequent linkages are the α,α ones. Overall these results are consistent with the high conductivity measured for the PEDOT generated in this work.

The good adherence of films together with its excellent physical, electrical and electrochemical properties indicate that PEDOT can be a suitable material for anticorrosion applications.

Acknowledgements

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References

1. T. A. Skotheim, R. L. Elsenbaumer and J. R. Reynolds, Eds., *Handbook of Conducting Polymers*, 2nd edn., Marcel Dekker, New York, 1998.
2. J. Roncali, *Chem. Rev.*, **97**, 173 (1997).
3. J. D. Stenger-Smith, *Prog. Polym. Sci.*, **23**, 57 (1998).
4. W. J. Feast, J. Tsibouklis, K. L. Pouwer, L. Groenendaal and E. W. Meijer, *Polymer*, **37**, 5017 (1996).
5. D. Fichou, Ed., *Handbook of Oligo and Polythiophenes*, Wiley-VCH, Weinheim, 1999.
6. J. Roncali, *J. Mater. Chem.*, **9**, 1875 (1999).
7. A. J. Heeger, *Synth. Met.*, **55–57**, 3471 (1993).
8. A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed. Engl.*, **37**, 402 (1998).
9. B. L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, *Adv. Mater.*, **12**, 481 (2000).
10. Q. Pei, G. Zuccarello, M. Ahlskog and O. Inganäs, *Polymer*, **35**, 1347 (1994).
11. G. Heywang and F. Jonas, *Adv. Mater.*, **4**, 116 (1992).
12. M. Dietrich, J. Heinze, G. Heywang and F. Jonas, *J. Electroanal. Chem.*, **369**, 87 (1994).
13. F. Jonas, E. Krafft and B. Muys, *Macromol. Symp.*, **100**, 169 (1995).
14. X. Crispin, S. Marciniak, W. Osikowicz, G. Zotti, A. W. D. van Der Gon, F. Louwt, M. Fahlman, L. Groenendaal, F. De Schryver and W. R. Salaneck, *J. Polym. Sci., B, Polym. Phys.*, **41**, 2561 (2003).
15. S. Timparano, M. Kemerink, F. J. Touwslager, M. M. De Kok and S. Schrader, *Chem. Phys. Lett.*, **394**, 339 (2004).
16. D. W. DeBerry, *J. Electrochem. Soc.*, **131**, 302 (1984).

17. D. W. DeBerry, *J. Electrochem. Soc.*, **132**, 1022 (1985).
18. Y. Wei, J. Wang, X. Jia and J. M. Yeh, *Polymer*, **36**, 4535 (1995).
19. B. Wessling, W.-K. Llu and R. L. Elsenbaumer, *Synth. Met.*, **71**, 2163 (1995).
20. B. Wessling, *Adv. Mater.*, **6**, 226 (1994).
21. F. Beck, R. Michaelis, F. Schluten and B. Zinger, *Electrochim. Acta*, **39**, 229 (1994).
22. C. A. Ferreira, S. Eiyach, J. J. Aarón and P. C. Lacaze, *Electrochim. Acta*, **41**, 1801 (1996).
23. B. N. Grgur, N. V. Krstajic, M. V. Vojnovic, C. Lacnjevac and L. J. Gajic-Krstajic, *Prog. Org. Coat.*, **33**, 1 (1998).
24. Z. Deng and W. H. Smyrl, *J. Electrochem. Soc.*, **138**, 1911 (1991).
25. G. Kousik, S. Pitchumani and N. G. Renganathan, *Prog. Org. Coat.*, **43**, 286 (2001).
26. A. S. Saraç, G. Sönmez and F. Ç. Cebeci, *J. Appl. Electrochem.*, **33**, 295 (2003).
27. V. S. Vasantha and K. L. N. Phani, *J. Electroanal. Chem.*, **520**, 79 (2002).
28. D. W. Breiby, E. J. Samuelsen, L. B. Groenendaal and B. Struth, *J. Polym. Sci., Part B, Polym. Phys.*, **41**, 945 (2003).
29. S. K. M. Jönsson, J. Birgersson, X. Crispin, G. Grezynsky, W. Osikowicz, A. W. D. van der Gon, W. R. Salaneck and M. Fahlman, *Synth. Met.*, **139**, 1 (2003).
30. J. Carrasco, E. Brillas, V. Fernández, P. L. Cabot, J. A. Garrido, F. Centellas and R. M. Rodríguez, *J. Electrochem. Soc.*, **148**, E19 (2001).
31. E. Brillas, J. Carrasco, R. Oliver, F. Estrany, J. Vilar and J. M. Morlans, *Electrochim. Acta*, **45**, 4049 (2000).
32. E. Brillas, R. Oliver, F. Estrany, E. Rodríguez and S. Tejero, *Electrochim. Acta*, **47**, 1623 (2002).
33. F. Estrany, R. Oliver, E. García, E. Gualba, P. L. Cabot and E. Brillas, *Collec. Czech. Chem. Commun.*, **68**, 1326 (2003).
34. E. M. Geniè, G. Bidan and A. F. Diaz, *J. Electroanal. Chem.*, **149**, 101 (1983).
35. V. S. Vashanta and K. L. N. Phani, *J. Electroanal. Chem.*, **520**, 79 (2002).