

SYSTEMATIC STUDY OF THE ELECTROPOLYMERIZATION OF 2,5-DI(-2-THIENYL)-PYRROLE

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Abstract

Electropolymerization of 2,5-di(-2-thienyl)-pyrrole was carried out in dichloromethane and acetonitrile on platinum. Acetonitrile was found to be the most suitable solvent for film formation. The effect of supporting electrolyte and the monomer concentration on the electropolymerization process is discussed. The surface morphology of the polymer was investigated by scanning electronic microscopy (SEM). Stable and adherent films were synthesized evidencing the

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critical importance of water presence during the synthesis of this kind of systems, and the relevance of controlling experimental variables affecting hardly the morphology of the film, hence, the macroscopic properties of the polymeric deposit like conductivity and doping level.

1. Introduction

The significant and versatile properties of conducting polymers [4-6, 9, 14] in the present technological progress are unquestionable and it has been the subject of thousands of investigations. However, there are two main limiting features of conducting polymers that restrict their technological expectations: low stability and processability. In order to overcome the low solubility or unmeltability of conducting polymers, the synthesis of block copolymers has been tried [11]. Among this studies, it is worth mentioning that dealing with chemical generation of trimers possessing two or more heteroatom rings derived from furan, pyrrole, and thiophene [3, 7]. 2,5-di(-2-thienyl)-pyrrole, TP (Figure 1), is one of such compounds, which is capable of forming a soluble conducting polymer when is anodically synthesized [8].

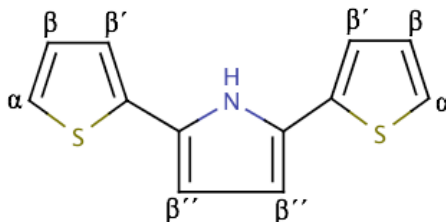


Figure 1. 2,5-di(-2-thienyl)-pyrrole.

Electropolymerization processes present many advantages over traditional chemical synthesis, although there are still several topics deserving urgent systematic and fundamental studies to achieve a total control and understanding of the process. In this work, we propose a systematic study aimed at the optimization of the variables governing the process (solvent, supporting electrolyte, monomer concentration), utilizing conventional electrochemical methods.

To compare the results with those previously reported, we will work under fully anhydrous conditions. It was demonstrated that in some cases, the presence of water gives rise to passivation of the working electrode, inhibiting the polymer growth or leading to non-conducting films [1].

2. Experimental

All chemicals and solvents were purchased from Aldrich and were utilized as received. This study was performed by using a conventional three-compartment, three-electrode cell. A polycrystalline platinum disk (0.07cm^2 geometrical area) or a glass coated with a thin transparent film of SnO_2 (1cm^2 geometrical area) was used as working electrode. A coiled Pt wire of large area, separated from the electrolytic solution by a sintered glass, was employed as counter electrode. All potentials quoted in this paper are referred to Ag/AgCl electrode in tetramethylammonium chloride that matches the potential of an SCE at room temperature [2]. Prior to each experiment, the Pt electrode was polished to a mirror finishing with alumina slurry (particle size 0.3 μm), rinsed with water, and anhydrous acetonitrile, respectively. The electropolymerization of 2,5-di(-2-thienyl)-pyrrole was carried out by using a 0.001, 0.005, and $0.01\text{mol}\cdot\text{L}^{-1}$ solution of the monomer in anhydrous acetonitrile, CH_3CN and $0.01\text{mol}\cdot\text{L}^{-1}$ tetrabutylammonium hexafluorophosphate TBAPF_6 or tetrabutylammonium trifluoromethylsulphonate $\text{TBASO}_3\text{CF}_3$ (dried at 110°C and kept into a desiccator until use) as supporting electrolyte. The same conditions were employed in the electropolymerization of 2,2':5',2''-terthiophene (TT). High purity argon was flushed through the solution for 15-20min prior to each experiment and over the solution during the measurement. Glassware was kept into an oven at 60°C . All measurements were performed at room temperature. Dry syringes were employed for the manipulation of anhydrous acetonitrile maintained under inert atmosphere and over molecular sieves. The electrochemical work was performed on a radiometer model PGZ 100 Voltalab

potenciostat/galvanostat. Data were recorded by means of a compatible computational program (Voltmaster). Working conditions for cyclic voltammetry will be specified along the text. SEM was accomplished on an analyzer Model Leo 1420 VP, Leo Microscopy Ltd.

3. Results and Discussion

3.1. Electropolymerization by cyclic voltammetry

Figure 2 shows typical cyclic voltammograms recorded for the oxidation of a 0.001, 0.005, and 0.01 mol·L⁻¹ TP and 0.1 mol·L⁻¹ TBAPF₆ in acetonitrile solution on platinum.

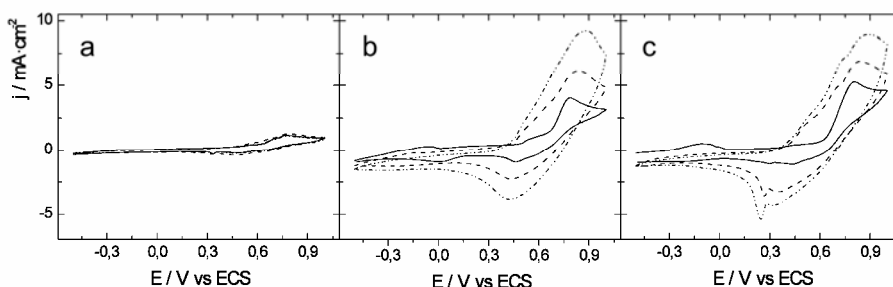


Figure 2. Voltammetric profiles between -0.5V to 1.0V in acetonitrile. Interface $\text{Pt}|\text{TBAPF}_6$ $0.1\text{mol}\cdot\text{L}^{-1}$ + (a) TP $0.001\text{mol}\cdot\text{L}^{-1}$, (b) TP $0.005\text{mol}\cdot\text{L}^{-1}$, (c) TP $0.01\text{mol}\cdot\text{L}^{-1}$. Scan rate $100\text{mV}\cdot\text{s}^{-1}$. Cycle 1(—), cycle 10 (---), cycle 20 (-·-).

Oxidation of the monomer was observed at *ca.* 0.75V during the anodic scan. Film behaviour appeared between 0.3V and 0.6V .

All films exhibited high adherence showing a dark violet colour during the positive sweep, changing to a yellow-green deposit through the negative scan. This represents an important difference with previous studies [10], which reported dissolution of the polymer during the cathodic sweep forming a cloud around the electrode. This difference was attributed to the anhydrous conditions employed that give rise to a stable and adherent film.

For the sake of comparison, the voltammetric profile of the thiophene analogous 2,2':5',2''-terthiophene (TT) was obtained for the monomer under the same experimental conditions mentioned above (Figure 3).

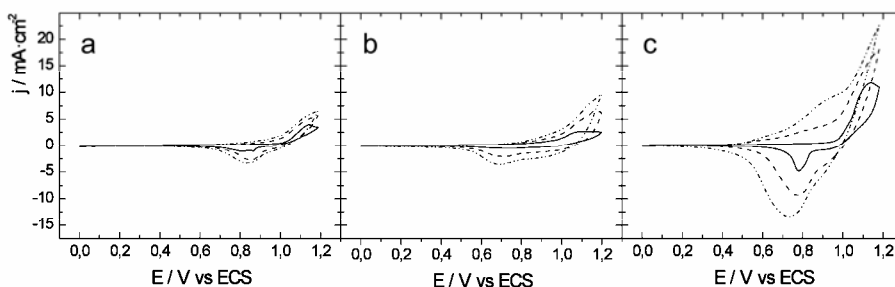


Figure 3. Voltammetric profiles between -0.5V to 1.0V in acetonitrile. Interface $\text{Pt}|\text{TBAPF}_6$ $0.1\text{mol}\cdot\text{L}^{-1}$ + (a) TT $0.001\text{mol}\cdot\text{L}^{-1}$, (b) TT $0.005\text{mol}\cdot\text{L}^{-1}$, (c) TT $0.01\text{mol}\cdot\text{L}^{-1}$. Scan rate $100\text{mV}\cdot\text{s}^{-1}$. Cycle 1(—), cycle 10 (---), cycle 20 (-·-).

The oxidation potential of the TT monomer is about 1.1V (Figure 3), i.e., 0.35V higher than the value associated to TP. The lower value for TP is ascribed to the pyrrole unit present in the monomer, which has lower oxidation potential [15]. This contributes to the stability of the system, evidenced by a smaller amount of energy needed to overcome the oxidation process.

On the other hand, as depicted in Figures 2 and 3, there is a shift of the monomer oxidation peak to more cathodic potentials as the number of sweep increases. This fact is indisputable experimental evidence indicating that the length of the oligomer chain is growing up, generating more conjugated species having lower oxidation potentials [13]. Furthermore, it demonstrates the existence of a high density oligomeric region HDOR [16], the main step of the polymerization process.

3.2. Concentration effect

Table 1 summarizes the charge related to the anodic scans showed in Figure 2. The monomer concentration in solution is proportional to the current density and the recorded charge.

Table 1

Cycle	TP = 0.001mol·L ⁻¹ Q (mC·cm ⁻²)	TP = 0.005mol·L ⁻¹ Q (mC·cm ⁻²)	TP = 0.01mol·L ⁻¹ Q (mC·cm ⁻²)
1	3.43	8.32	9.54
10	3.57	16.40	18.20
20	3.97	26.20	27.40

Charge related to anodic hemicycles of TP electropolymerization in TBAPF₆ 0.1mol·L⁻¹ + acetonitrile. All values were obtained from Figure 2.

As the monomer concentration increases, so does the number of oligomer units at the HDOR, provoking a greater oligomer precipitation upon the electrode. Thus, the charge increase is a consequence of the growth of the polymer film and the inclusion of anions to counterweigh the charge. As for the lower concentration experiment, the difference in charge between the first and last cycle is approximately 13%, indicating that the monomer concentration is not enough to produce a saturation of the HDOR. For a 0.005mol·L⁻¹ solution, the difference in charge considerably increased and the corresponding value for each cycle remained almost constant as compared with the higher concentration case. In conclusion, intermediate concentrations are the most appropriate ones to obtain films under the established experimental conditions.

3.3. Solvent effect

Voltammetric profiles were recorded by using the same experimental conditions mentioned in previous sections, but now using dichloromethane as solvent (Figure 4).

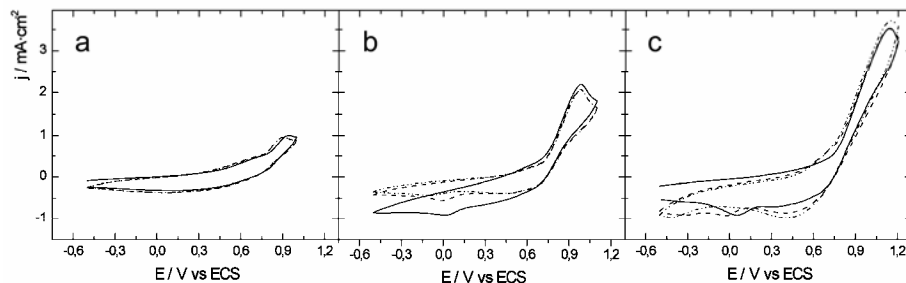


Figure 4. Voltammetric profiles between -0.5V to 1.18V in dichloromethane. Interface $\text{Pt}|\text{TBAPF}_6\ 0.1\text{mol}\cdot\text{L}^{-1}$ + (a) $\text{TP}\ 0.001\text{mol}\cdot\text{L}^{-1}$, (b) $\text{TP}\ 0.005\text{mol}\cdot\text{L}^{-1}$, (c) $\text{TP}\ 0.01\text{mol}\cdot\text{L}^{-1}$. Scan rate $100\text{mV}\cdot\text{s}^{-1}$. Cycle 1(—), cycle 10 (---), cycle 20 (—·—).

Comparison of Figures 2 and 4 allows distinguishing the decrease in current density and charge (Tables 1 and 2) due to the larger solubility of TP oligomers in this medium. Consequently, the HDOR needs longer times to be formed here than in acetonitrile, which in a potentiodynamic context means a larger number of potential sweeps to form the polymer film.

As far as the oxidation potential of the monomer is concerned, this is higher than the value recorded in acetonitrile (approximately 0.95V). This is related to the larger stability of the species in this solvent, requiring higher amounts of energy to begin the oxidation process.

Table 2

Cycle	$\text{TP} = 0.001\text{mol}\cdot\text{L}^{-1}$	$\text{TP} = 0.005\text{mol}\cdot\text{L}^{-1}$	$\text{TP} = 0.01\text{mol}\cdot\text{L}^{-1}$
	$Q\ (\text{mC}\cdot\text{cm}^{-2})$	$Q\ (\text{mC}\cdot\text{cm}^{-2})$	$Q\ (\text{mC}\cdot\text{cm}^{-2})$
1	2.08	3.13	4.30
10	2.28	2.92	5.09
20	2.20	2.90	4.97

Charge related to anodic hemicycles of TP electropolymerization in $\text{TBAPF}_6\ 0.1\text{mol}\cdot\text{L}^{-1}$ + dichloromethane. All values were obtained from Figure 4.

3.4. Effect of supporting electrolyte

Figure 5 shows voltammetric profiles for the oxidation of a 0.001, 0.005, and 0.01M TP solution in 0.1M TBASO₃CF₃ acetonitrile solution on platinum and 100mV·s⁻¹ scan rate, between -0.5V and 0.9V.

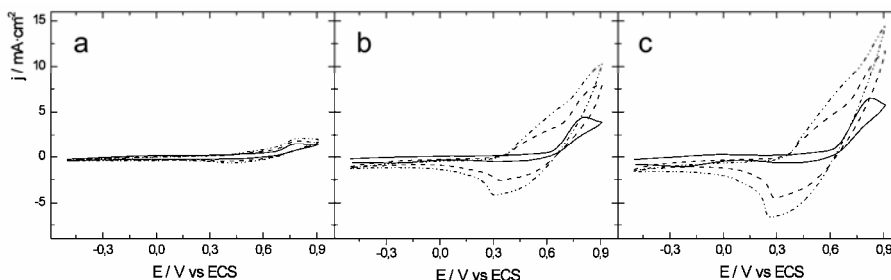


Figure 5. Voltammetric profiles between -0.5V to 0.9V in acetonitrile. Interface Pt|TBASO₃CF₃ 0.1mol·L⁻¹ + (a) TP 0.001mol·L⁻¹, (b) TP 0.005mol·L⁻¹, (c) TP 0.01mol·L⁻¹. Scan rate 100mV·s⁻¹. Cycle 1(—), cycle 10 (---), cycle 20 (-·-).

Comparison of Figures 5 and 2 (wherein TBAPF₆ was employed), the profile remained almost equal except for the monomer oxidation peak that presents a poorer definition. The last fact is due to the change in the alkaline character of the supporting electrolyte, which allows electrical conduction, but also plays an important role in the mechanism of growth of the polymer net [12]. As for the oxidation mechanism propose here, anions with a stronger basic character are more efficient taking apart protons from the oligomer cationic structure. PF₆⁻ ion is able to form larger amounts of stable oligomer species in comparison to SO₃CF₃⁻, clearly illustrated in Tables 1 and 3, where all values for the anodic charge were higher in the first case.

Table 3

Cycle	TP = 0.001mol·L ⁻¹	TP = 0.005mol·L ⁻¹	TP = 0.01mol·L ⁻¹
	Q (mC·cm ⁻²)	Q (mC·cm ⁻²)	Q (mC·cm ⁻²)
1	3.11	4.65	7.12
10	3.53	12.60	16.70
20	4.01	16.30	20.80

Charge related to anodic hemicycles of TP electropolymerization in TBASO₃CF₃ 0.1mol·L⁻¹ + acetonitrile. All values were obtained from Figure 5.

Another effect related to the basic character and size of the anion PF₆⁻, is the possibility of extracting alpha or beta protons from the oligomer structure (Figure 1). According to this, it can be expected the formation of films with some degree of polymerization by coupling of β - H atoms of internal pyrrole and thiophene rings. Such type of cross-linked polymers will coat lesser electrode surface, as depicted in Figure 6: SEM micrographs using both supporting electrolytes and solvents.

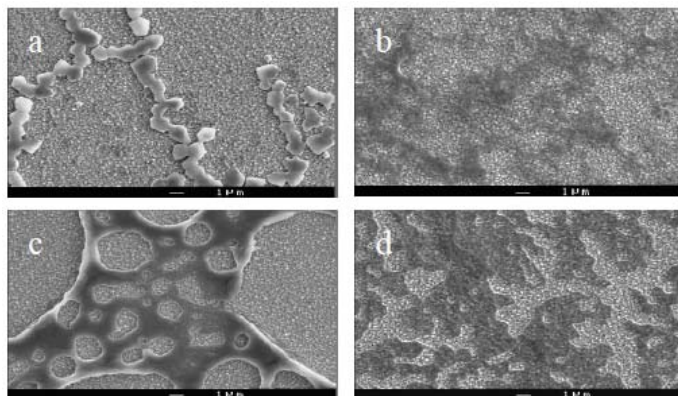


Figure 6. SEM micrographs of polyTP deposits on conducting glass (SnO₂). Interface SnO₂ | TP 0.005mol·L⁻¹ (a) TBAPF₆ 0.1mol·L⁻¹ + CH₃CN, (b) TBASO₃CF₃ 0.1mol·L⁻¹ + CH₃CN, (c) TBAPF₆ 0.1mol·L⁻¹ + CH₂Cl₂, (d) TBASO₃CF₃ 0.1mol·L⁻¹ + CH₂Cl₂. Scan rate 100mV·s⁻¹.

4. Conclusion

The 2,5-di(-2-thienyl)-pyrrole monomer is able to form solid, adherent, and stable films by anodic polymerization under anhydrous conditions. The choice of solvent and supporting electrolyte has a great influence on the electropolymerization behaviour, being acetonitrile the best solvent under the above mentioned experimental conditions and the polymerization rate being faster in TBAPF₆ than in TBASO₃CF₃, but with the formation of a higher level of cross-linked chains. SEM analysis confirmed that the coating on the platinum electrode can be modified simply by changing experimental variables such as supporting electrolyte and solvent, which change macroscopic properties such as conductivity and doping level.

Chronoamperometric measurements are required to analyze in detail the nucleation and growth mechanism of the polymer and its use as *p*-layer in photocells.

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