

# Electrical and spectroelectrochemical investigation of thiophene-based donor-acceptor copolymers with 3,4-ethylenedioxythiophene

Marcus Henrique de Araujo<sup>1</sup>, Tulio Matencio<sup>1</sup>, Claudio Luis Donnici<sup>1</sup> and Hállen Daniel Rezende Calado<sup>1,2\*</sup> 

<sup>1</sup>*Departamento de Química, Universidade Federal de Minas Gerais – UFMG, Belo Horizonte, MG, Brasil*

<sup>2</sup>*Centro de Tecnologia de Nanomateriais e Grafeno – CTNano, Belo Horizonte, MG, Brasil*

\*hallendaniel@ufmg.br

## Abstract

This work reports the spectroelectrochemical and electrical behavior of electropolymerized donor-acceptor like (D-A) copolymer films, based on 3,4-ethylenedioxythiophene (EDOT) and beta-substituted electron-acceptor thiophenes. Initially, the copolymer films were deposited on indium tin oxide substrates, which spectroelectrochemistry measurements were carried out with an UV-Vis spectrophotometer. Hence, it was possible to observe the electrochromic properties of these materials, visualizing the color changing towards different potentials applied. The experiments have shown that these D-A like copolymers presented good electrochromic properties, such as optical contrast, coloration efficiency, and switching times. Additionally, films prepared on a platinum working electrode were investigated by electrochemical impedance spectroscopy, which has shown the electrical behavior of those copolymers and their potential as candidates to capacitive devices building. Therefore, the combination of electron-donor EDOT with those electron-acceptor monomers is indeed a useful strategy to tailoring and fine-tuning the physicochemical properties of polythiophenes with innovative applications.

**Keywords:** *donor-acceptor copolymers, electrical behavior, polythiophenes, spectroelectrochemistry.*

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## 1. Introduction

The polythiophene semiconductor materials have been massively studied for applications as active layer in organic-electronic devices<sup>[1,2]</sup>, and their derivatives have booth environmental and thermic stability, as well good optoelectronic properties, allowing the uses in electrochromic devices<sup>[3-6]</sup>, organic photovoltaic devices<sup>[7-9]</sup>, solar cells<sup>[10-12]</sup>, organic light-emitting diodes<sup>[13-15]</sup>, rechargeable batteries<sup>[16-19]</sup>, among several others. Recently, conducting polymers have also been applied on the design of soft actuators and bioelectronic interfaces<sup>[20,21]</sup>, e.g., the work of Lu et al.<sup>[22]</sup> who have developed a pure PEDOT:PSS hydrogel with high electrical conductivity, high stretchability, and superior stability as a promising electrical interface with biological tissues for sensing and stimulation.

Although, it should be noted that among all those possible applications, we can highlight the organic light-emitting diodes (OLED) and non-emissive electrochromic devices (ECD), which require a fine-tuning of colors in terms of its tonality, saturation, intensity, and brightness<sup>[4]</sup>. Different strategies in synthesis have been described to reach new materials with the largest planarity as possible, increasing the chain length and alternating between donating and accepting electron groups, systems named D-A, for increase conjugation<sup>[4]</sup>.

The correlation and influence of the monomer structure under the material electrochromic properties can be verified, particularly on the work of Dyer et al.<sup>[23]</sup>. Such investigation showed that for D-A based polymers, it might be possible to build multicolored electrochromic devices with high efficiency, whose color change follows the composition and photoelectrochemical properties of the material. Nowadays, it can be found a considerable number of publications concerning the D-A-like copolymers with different substituted thiophenes<sup>[9,24]</sup>, which makes it very interesting to put efforts on this research line.

From the 80's, the use of spectroelectrochemical techniques (coupling spectroscopic and electrochemical techniques) emerged in several research lines, e.g., on the conducting polymers field, where the UV-Vis spectroscopy is widely used to determine electrochromic parameters as well to investigate the electrochemical kinetic<sup>[6,25-27]</sup>. Worldwide, we can find plenty of works reporting the synthesis of thiophene-based copolymers and their spectroelectrochemical behavior. In this way, Vogel and Holze<sup>[28]</sup> have published a work presenting the electrosynthesis of aniline-thiophene copolymers with a new spectroelectrochemical behavior with a slight prevailing of aniline in such properties.

In another example, Zagorska et al.<sup>[29]</sup> have synthesized copolymers based on 3-alkylthiophenes and thiophene functionalized with an azo chromophore leading to a mix of electrochromic properties. Alakhras has also published a work presenting new copolymers obtained potentiostatically from selenophene and thiophene units, which provided changes on the electro-optical properties<sup>[30]</sup>. Another work mentions the preparation of a copolymer of 2,5-di(thiophen-2-yl)-1-p-tolyl-1H-pyrrole (DTTP) with 3,4-ethylenedioxythiophene (EDOT)<sup>[31]</sup>. Through the spectroelectrochemical characterization, the electrochromic parameters of such copolymer have shown to be better than the homopolymer, such a lower energy band gap, optical contrast of 20% and a switching time less than 1 s<sup>[31]</sup>.

Regarding the electrical behavior of copolymers, Chen et al.<sup>[32]</sup> have synthesized a copolymer based on 3,4-ethylenedioxythiophene (EDOT) and 3-thienyl ethoxybutanesulfonate (TEBS) showing conductivity almost 6 times higher than compared with pure homopolymer (PEDOT). In the same way, Ates and Ekmen prepared an EDOT-pyrrole (Py) copolymer with a slight gain on the capacitance when compared with both homopolymers that could be a promising electrode material for high-performance electrical energy storage devices<sup>[33]</sup>. In a different approach, Kulandaivalu et al.<sup>[34]</sup> prepared a copolymer of EDOT and aniline by electrodeposition and performed electrochemical impedance spectroscopy experiments to understand its electrical behavior and proposed a path to analyze the results, which explained that the incorporation of the EDOT in aniline makes the interfacial resistance of the copolymer to be lower than neat polyaniline.

Yijie et al.<sup>[35]</sup> have proposed the electrosynthesis of D-A-like copolymers containing a benzothiadiazole unit as the acceptor monomer and different thiophene derivatives as the donating units. In this way, they were able to manage the fine-tuning colors of the materials in booth neutral and oxidized state by varying the electron-rich character of the incorporated thiophene moieties.

We have published a previous work about the synthesis and structural characterization of thiophene monomers: 3-thiophene phenylacetate – PhTAc-2a, 3-thiophene(4-nitrophenyl)acetate – PhTAc-2b, and 3-thiophenephenylcarboxylate – PhTCb, as well as the synthesis and electrochemical characterization of their copolymers with EDOT. In this work, we have given sequence on the characterization of these materials by performing spectroelectrochemical experiments, in order to figure out the electrochromic properties of these donor-acceptor copolymers. Besides, we have run chronoabsorptometry experiments, which allowed us to calculate important electrochromic parameters, such as optical contrast, coloration efficiency, and switching times. Finally, we have studied the electrical profile of those materials by the EIS technique. These experiments and properties for PEDOT film are well known. Therefore, it is essential to mention that we have performed the experiments for PEDOT film just in order to compare its results with the copolymers ones.

## 2. Materials and Methods

### 2.1 Materials

The electron-acceptor monomers: 3-thiophene phenylacetate (PhTAc-2a), 3-thiophene(4-nitrophenyl)acetate (PhTAc-2b), and 3-thiophenephenylcarboxylate (PhTCb) were synthesized and characterized on previous work. More detailed information about the electropolymerization and characterization of these copolymers can be found in previous work<sup>[36]</sup>. 3,4-ethylenedioxythiophene (EDOT, 97%) and sodium perchlorate ( $\text{NaClO}_4$ , 98%) were purchased from Aldrich. Acetonitrile (ACS) was purchased from Synth. The indium tin oxide (ITO) coated glasses ( $8\text{--}12\ \Omega$ ;  $7.0 \times 50.0 \times 0.7\ \text{mm}$ ) were purchased from Delta Technologies.

### 2.2 Preparation of the D-A copolymers

After testing the oxidizing potential for the electron-acceptor monomers<sup>[36]</sup>, solutions of these monomers with EDOT have been prepared in acetonitrile containing 0.1 M of  $\text{NaClO}_4$  and using a content of 4:1 (moles/moles) of EDOT:monomer. The films for the spectroelectrochemical characterization were electrodeposited onto ITO coated glass by cyclic voltammetry (20 cycles at a scanning rate of  $50\ \text{mV s}^{-1}$ ) through a PalmSens potentiostat. For the electrochemical impedance spectroscopy measurements, freshly films have been prepared onto a platinum working-electrode ( $0.01\ \text{cm}^2$ ) also by cyclic voltammetry under the same conditions cited before.

### 2.3 Spectroelectrochemical characterization

After washed with acetonitrile, each thin film substrate was transferred to a quartz cuvette (1.0 cm) filled with a 0.1 M  $\text{NaClO}_4$ /acetonitrile solution. On the cuvette, it was attached a platinum wire as counter-electrode and a silver wire as pseudo-reference. This system was put into a spectrophotometer (Varian – Cary 100 Bio) to measure the spectra for different potentials applied. Before the readings, it was applied the conditioning potential during 50 s through a PalmSens potentiostat. The steps of potential were 0.3 V, contemplating the electroactivity window of each copolymer.

On the sequence, new copolymer films were prepared, also on ITO coated glass, to run the chronoabsorptometry experiments using the same spectrophotometer and a PGSTAT204 potentiostat to record the chronoamperometry curves. In this case, it was also used a quartz cuvette containing 0.1 M  $\text{NaClO}_4$ /acetonitrile and the same electrodes as described before. Through the potentiostat, the potential was switched starting from the lowest (neutral) to the highest (oxidized). Each potential was applied during 10 s and, simultaneously, the transmittance variation and chronoamperometry curves have been recorded.

The transmittance variation curves allow determining the response times to the bleaching/coloring processes by measuring the time taken when the transmittance changing reaches 95%. In addition, it is possible to calculate other electrochromic parameters from the transmittance and amperograms curves, such as the optical contrast ( $\Delta T$ ) – the difference between colored and bleached states transmittance, and the coloration efficiency ( $\eta$ ) – calculated from the equation<sup>[37]</sup>:

$$\eta = \frac{\Delta OD}{\Delta Q} \quad (1)$$

where  $\Delta OD$  is the optical density variation in a fixed wavelength; and  $\Delta Q$  is the sum of injected/ejected charges per surface unit. We can use the following equation to determine the  $\Delta OD$  value:

$$\Delta OD = \log(T_{\text{red}} / T_{\text{ox}}) \quad (2)$$

where  $T_{\text{red}}$  is the bleached state transmittance; and  $T_{\text{ox}}$  is the colored state transmittance.

## 2.4 Electrochemical Impedance Spectroscopy (EIS) characterization

The EIS curves (Nyquist diagrams), were measured with a PGSTAT potentiostat in a three-electrode system (WE = CE = Pt, and RE = Ag/Ag<sup>+</sup>) using a 0.1 M NaClO<sub>4</sub>/acetonitrile as electrolytic solution. To scheduling the experiments, two potentials ( $E_{\text{dc}}$ ) were used: -0.5 V (reduced polymer) and 1.5 V (oxidized polymer), excitation amplitude of 10 mV and frequency range from 100 kHz to 10 mHz. The thickness of PEDOT and its copolymers studied by EIS were estimated from the film polymerization charges, assuming 2.25 electrons per monomer and a film density of 1 g cm<sup>-3</sup>[38].

The representation of the electric behavior of our cell can be assimilated to a Randle circuit, which circuit is usual in electrochemistry[39]. In this equivalent circuit based on the simple process, we have the electrolyte resistance,  $R_s$ , the double-layer capacitance,  $C_{\text{dl}}$ , and the faradaic impedance  $Z_f$ . This last one translates the faradic processes that depend on the frequency and consequently cannot be represented by simple linear circuit elements. A typical representation of  $Z_f$  is a charge transfer resistance in series with a pseudo-capacitance or the same resistor in series with a Warburg impedance which is a type of resistance to mass transfer. This equivalent circuit illustrates the usual behavior of the conductive polymers and corresponds to either the simple diffusion-kinetic model or the distributed transmission line model or the more complex model that describes the mixed electron and ionic conduction taking into account the percolation of charge by electromigration[40].

The determination of the parameters of the circuit was not performed from the simulation of the equivalent circuit. We calculate these values directly from the impedance diagrams using boundary conditions.  $R_s$  is determined through the diagram's intersections with the  $Z'$  axis at high frequencies,  $R_{\text{ct}}$  is determined to estimate the semicircle diameter and  $C_{\text{dl}}$  is calculated from the following relation:

$$C_{\text{dl}} = \frac{1}{2\pi R_{\text{ct}} f} \quad (3)$$

where  $f$  is the frequency that corresponds to the maximum of the half-circle.

The low-frequency capacitance,  $C_{\text{lf}}$  is calculated from the following relation:

$$C_{\text{lf}} = \frac{1}{2\pi f |Z''|} \quad (4)$$

where  $Z''$  is the imaginary part of the EIS spectra.

## 3. Results and Discussions

### 3.1 Spectroelectrochemistry

In order to know the electroactivity window suitable for each copolymer, the films have been characterized by cyclic voltammetry (25 mV s<sup>-1</sup>) in a monomer-free solution containing 0.1 M of NaClO<sub>4</sub>/acetonitrile. The voltammograms and the respective chemical structure of these copolymers are presented on Figure 1. Figure 2 shows the spectroelectrochemical results, whose inset graph presents the absorbance variation curves in function of the potential applied, for each corresponding maximum absorbance wavelength.

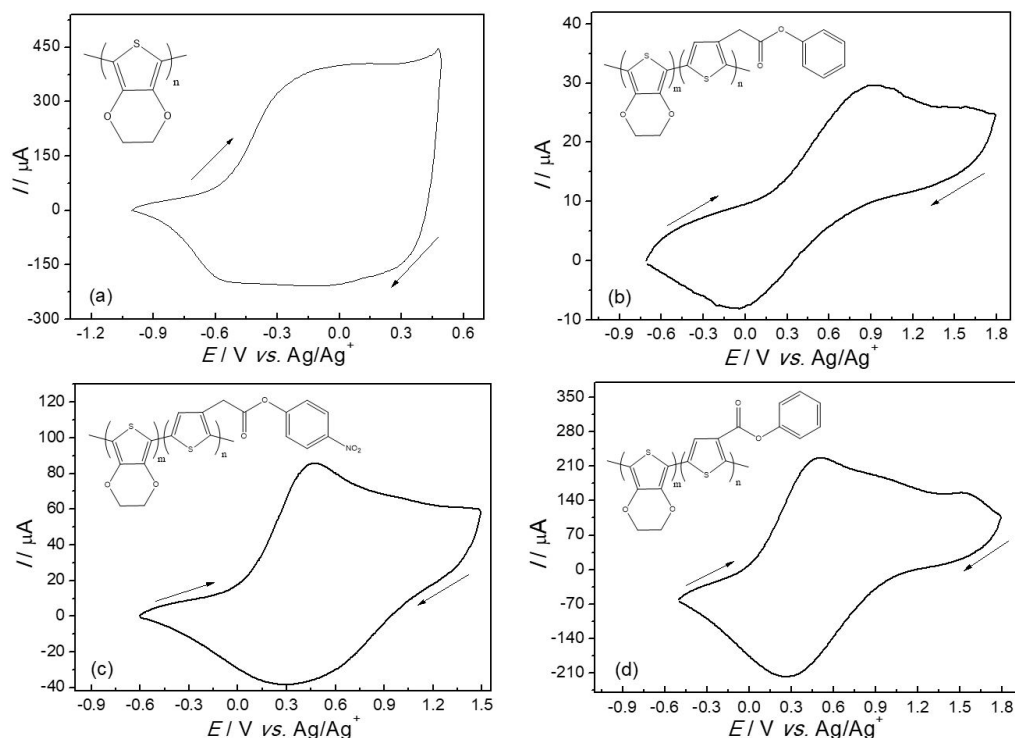
After the analysis of the spectroelectrochemical curves, it can be observed that PEDOT and copolymers films presented an absorption band in the high-energy side of the spectrum when in their reduced state. As we apply the shifts of potential, the energetic states of the polymer change that is corroborated by the quenching of the transition between the valence band (VB) and conducting band (CB), also to the appearance of a band near to the infrared region. This band appearance is linked to the generation of new energy levels inside the band gap during the doping process, which leads to polaron and bipolaron states generation[41].

Also, all the films presented color changing in function of the conditioning potential, going from a colored neutral state to a colored oxidized state. Indeed, PEDOT-co- PhTAc-2a film presented a brownish neutral state and a grayish oxidized state, PEDOT-co-PPhTAc-2b changed from dark-purple to light-blue, and PEDOT-co-PPhTCb changed from purple to grayish-green.

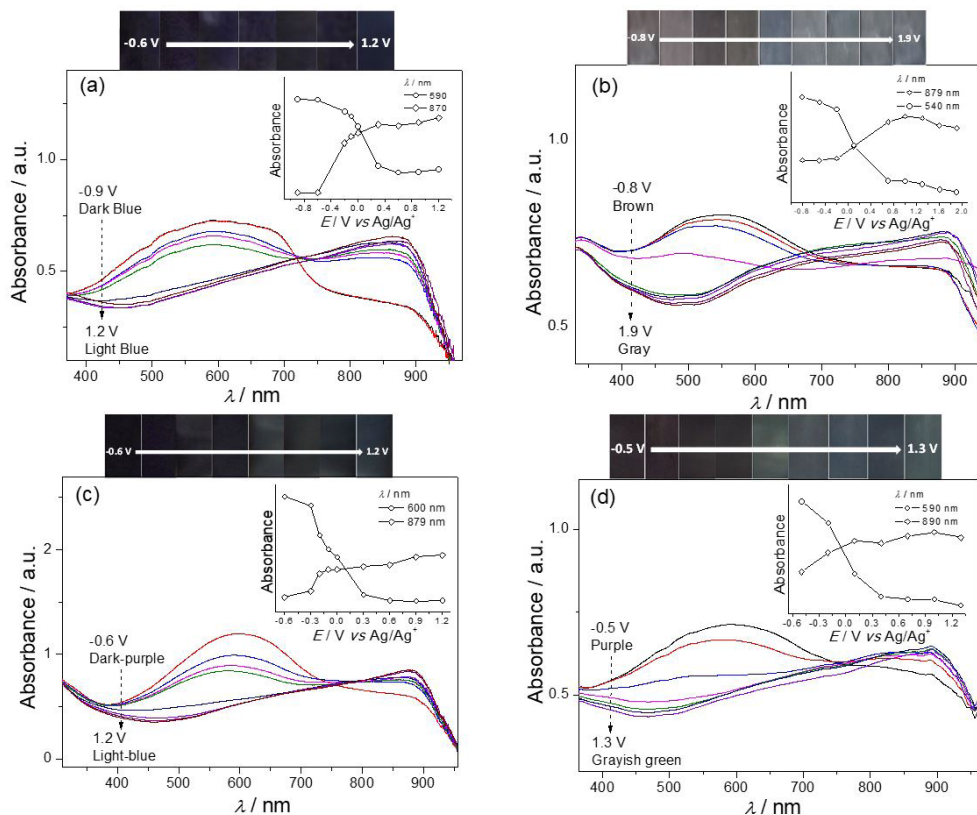
In general, all the spectroelectrochemical curves from the copolymers seemed to be similar to PEDOT curves, and this may be explained by the higher amount of EDOT monomer in the copolymer backbone so that it could be expected a more significant influence of EDOT over the spectroelectrochemistry.

The maximum absorption value to the films at reduced state, as well as the onset energy and the molecular orbital energies for each polymer, are presented in Table 1 below. The onset energy was extracted from the Tauc curves (Figure S1 at the Supplementary Material section) and the HOMO energy was calculated through the onset of the anodic peak potential (extracted from the voltammogram).

The band gap and the molecular orbital levels (HOMO and LUMO) for PEDOT film are corroborated with the literature[42]. This table shows that the copolymers presented a shift towards the high-energy side of the spectrum (hypsochromic shift) in comparison to PEDOT, which may be explained by the presence of substituted groups on the polymeric structure, rising the possible electronic transitions. This shift was lower for PEDOT-co-PPhTCb since there is more electron delocalization due to the resonance effect of the group -COOPh, directly attached to the thiophene ring[36]. On the other hand, PEDOT-co-PPhTAc-2b presented the opposite effect: the band shifting to the low-energy spectrum region (bathochromic shift), which corroborates the influence of the electron-withdrawing effect of the nitro group[36]. When we observe the band gap values ( $E_g$ ), it is evident a bathochromic shift found to copolymer films, referring to a decrease on the transition energy value, which may be linked,



**Figure 1.** Cyclic voltammograms and chemical structure for PEDOT (a), PEDOT-co-PPhTAc-2a (b), PEDOT-co-PPhTAc-2b (c) and PEDOT-co-PPhTCb (d);  $E/V$ = potential/volts,  $Ag$  = silver,  $\mu A$  = microampere.



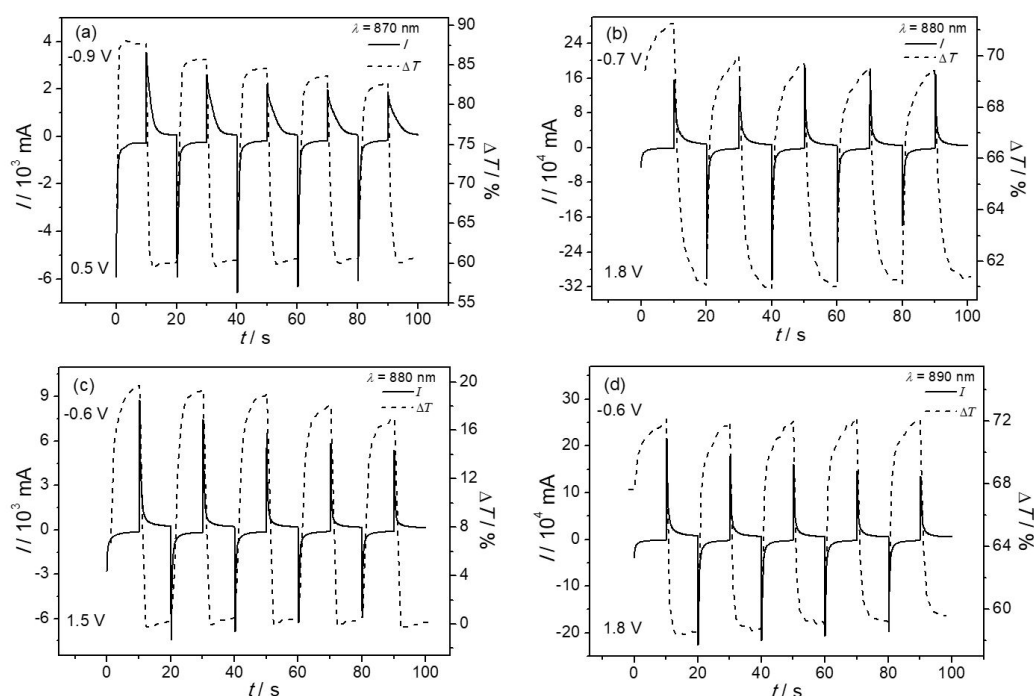
**Figure 2.** Spectroelectrochemical curves and digital photographs to the films of PEDOT (a), PEDOT-co-PPhTAc-2a (b), PEDOT-co-PPhTAc-2b (c) and PEDOT-co-PPhTCb (d);  $E/V$ = potential/volts,  $Ag$  = silver,  $\lambda/nm$  = wavelength/nanometers.

**Table 1.** Data of maximum of absorption ( $\lambda_{\max}$ ), transition onset energy ( $E_g$ ), highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for PEDOT and the D-A copolymers; determined under reduction potential ( $E$ ).

	$E/V$	Absorption	Onset	Molecular Orbitals	
		$\lambda_{\max}/\text{nm}$	$E_g/\text{eV}$	HOMO/eV	LUMO/eV
PEDOT	-0.9	596	1.53	-3.67	-2.14
P(EDOT-co-PhTAc-2a)	-0.8	544	1.45	-4.51	-3.06
P(EDOT-co-PhTAc-2b)	-0.6	602	1.61	-4.41	-2.80
P(EDOT-co-PhTCb)	-0.5	591	1.40	-4.34	-2.94

**Table 2.** Data of optical contrast ( $\Delta T$ ), coloration efficiency ( $\eta$ ), oxidation switching time ( $\tau_{\text{ox}}$ ), and reduction switching time ( $\tau_{\text{red}}$ ) for PEDOT and copolymer films.

	Thickness/nm	$\Delta T$	$\eta/\text{cm}^2 \text{C}^{-1}$	$\tau_{\text{ox}}/\text{s}$	$\tau_{\text{red}}/\text{s}$
PEDOT	24.9	27.63	40.55	1.10	1.97
P(EDOT-co-PhTAc-2a)	10.5	10.18	43.79	1.38	1.54
P(EDOT-co-PhTAc-2b)	15.5	19.01	304.7	1.81	2.58
P(EDOT-co-PhTCb)	65.5	12.70	37.61	1.15	1.21

**Figure 3.** Transmittance spectra (dashed line) and chronoamperograms (solid line) to the films of PEDOT (a), PEDOT-co-PPhTAc-2a (b), PEDOT-co-PPhTAc-2b (c) and PEDOT-co-PPhTCb (d);  $t/\text{s}$  = time/seconds.

again, to the D-A groups effect, meaning a larger electronic density conjugation, and in turn, decreasing the transition energy value<sup>[36]</sup>. On the contrary, it was observed a slight increase in the band gap energy for PEDOT-co-PPhTAc-2b, which may probably be linked to the electron-withdrawing effect of the nitro group.

The chronoabsorptometry curves (Figure 3) show the transmittance spectra on the UV-Vis region versus time and the chronoamperograms. Then, it was possible to measure the switching times for coloration and bleaching processes beyond calculating the electrochromic parameters using Equations 1 and 2. These results are presented in Table 2.

By taking a look into Table 2, PEDOT-co-PPhTAc-2b film has presented coloration efficiency almost 7.5 times higher than neat PEDOT. This behavior may be related to the

nitro group presence, acting as a strong electron-withdrawing group, fortifying the electron-acceptor effect of the PhTAc-2b block<sup>[36]</sup>. All copolymer films have presented moderately fast switching times located on the scale of a few seconds, as observed in other works<sup>[43–46]</sup>. Besides, we have noticed that the copolymers, based on electron-acceptor monomers that possess a methylene group (PhTAc-2a and PhTAc-2b), presented the highest switching times. On the contrary, PEDOT-co-PPhTCb film, which does not have this methylene group, has presented faster switching times, which might be associated with a direct conjugation path among the D-A blocks, increasing the conjugation length and, therefore, decreasing the response times.

It is well-known from the literature that the thickness of the film directly interferes in the electrochromic properties,

where the higher thickness is supposed to lead to greater performances<sup>[4]</sup>. The thickness found for the copolymers reported on Table 2, even neat PEDOT, was much lower when compared with other D-A copolymers and, therefore, the values of optical contrast and coloration efficiency were quite lower<sup>[47-49]</sup>. Nevertheless, with thickness, almost twice lower than PEDOT, P(EDOT-co-PhTAc-2a) and P(EDOT-co-PhTAc-2b) films have presented electrochromic properties similar or even higher than neat PEDOT, which is an improvement after all.

Another fact that may influence over the electrochromic properties of the polymer is the methodology used during the electropolymerization process. Gu et al.<sup>[50]</sup> have employed chronoamperometry method to prepare an isoindigo-based donor-acceptor polymer with EDOT and exhibiting an outstanding electrochromic performance with coloration efficiency around  $360 \text{ cm}^2 \text{ C}^{-1}$ , fast switching time of 0.5 s, and high optical contrast of almost 60%. Indeed, the chronoamperometry is a faster technique to grow thicker polymeric films when compared to the cyclic voltammetry. Once the polymers of this work have been electropolymerized through cyclic voltammetry, this explains the lower thickness and, consequently, the apparent poor values of electrochromic parameters.

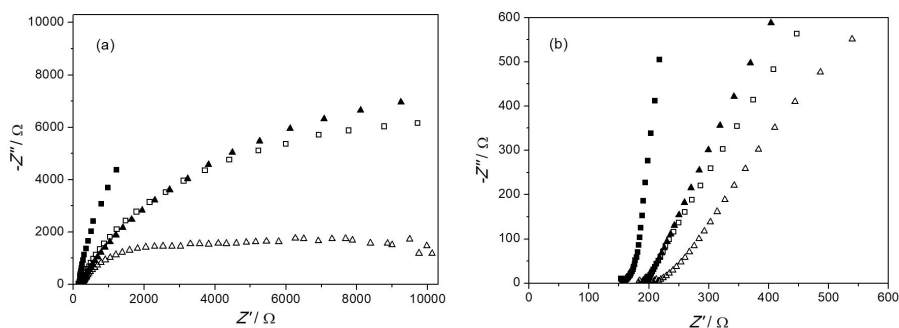
### 3.2 Electrochemical Impedance Spectroscopy (EIS)

The impedance experiments took place by applying two potentials:  $E_{\text{dc}} = -0.5 \text{ V}$  – reduced polymer and  $E_{\text{dc}} = 1.5 \text{ V}$  – oxidized polymer. Figure 4a below shows, on the shape of the Nyquist diagram, the impedance results, at low frequencies, obtained for PEDOT and its several

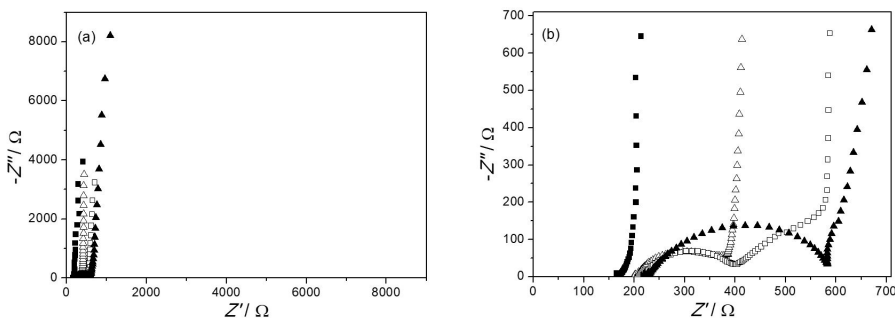
copolymers at the oxidized state ( $E_{\text{dc}} = 1.5 \text{ V}$ ). On the other hand, Figure 4b shows the impedance results at high frequencies.

As it can be observed, at higher frequencies, the PEDOT behavior is in agreement with the literature results<sup>[38]</sup>, pointing the presence of an almost vertical line, Figure 3b, typical of a capacitive behavior, and indicating a fast electrical charge transfer at the interface metal | PEDOT | electrolyte. However, to the copolymers, this electronic transference appears to be slower and it is translated by line with a slope  $< 90^\circ$ . The profile observed at low frequencies, Figure 3a, it was also observed by Bobacka et al.<sup>[38]</sup>, and it is assigned to a reaction that happens in parallel to the electrode doping that might be related to the presence of oxygen traces in the electrolyte solution. This behavior fits with the model proposed by Vorotyntsev et al.<sup>[51]</sup>, which counts a charge transfer involving the ionic and electronic shape between the polymer and the solution. The intersection at high frequencies of the Nyquist diagrams with  $Z'$  axis is mainly related to the electrolyte resistance, amount near to  $150 \Omega$  for PEDOT and  $200 \Omega$  for copolymers. This variation might be since this resistance would also exist a resistive contribution due to the polymer | platinum interface. We have neglected effects due to the ohmic resistance (electronic) of the oxidized films since we will see in the following part that in the reduced state, the behavior of this high-frequency resistance is the same.

The Nyquist diagrams recorded at reduced state ( $E_{\text{dc}} = -0.5 \text{ V}$ ) are presented in Figure 5. At lower frequencies (Figure 5a), the behaviors are similar and show a vertical



**Figure 4.** Nyquist diagrams to ■ PEDOT, Δ PEDOT-co-PPhTAc-2a, □ PEDOT-co-PPhTAc-2b, and ▲ PEDOT-co-PPhTCb films;  $E_{\text{dc}} = 1.5 \text{ V}$ ; (a) low frequencies; (b) high frequencies;  $Z = \text{impedance}$ .



**Figure 5.** Nyquist diagrams to ■ PEDOT, Δ PEDOT-co-PPhTAc-2a, □ PEDOT-co-PPhTAc-2b, and ▲ PEDOT-co-PPhTCb films;  $E_{\text{dc}} = -0.5 \text{ V}$ ; (a) low frequencies; (b) high frequencies;  $Z = \text{impedance}$ .

**Table 3.** Data of resistance ( $R_s$ ), charge transfer resistance ( $R_{ct}$ ), double-layer capacitance ( $C_{dl}$ ), and low-frequency capacitance ( $C_{lf}$ ) to PEDOT and copolymers films.

	$R_s/(\Omega \text{ cm}^{-2})$	$R_{ct}/(\Omega \text{ cm}^{-2})$	$C_{dl}/(\mu\text{F cm}^{-2})$	$C_{lf}/(\text{F g}^{-1} \text{ cm}^{-2})$
PEDOT	16,900	-	-	488,400
PEDOT-co-PPhTAc-2a	20,000	20,000	190	1,355,800
PEDOT-co-PPhTAc-2b	21,900	19,600	86	920,300
PEDOT-co-PPhTCb	22,200	36,000	110	87,300

line with a slope near to  $90^\circ$  (capacitive profile). Figure 5b illustrates the behavior at higher frequencies.

The four copolymers have shown similar diagrams, which allows seeing at higher frequencies, in the diagrams intersection with the  $Z'$  axis, a resistance near to  $200 \Omega$  and, as in the oxidized state, which can be assigned to the electrolyte resistance associated in series with the polymer | platinum interface resistance. At intermediate frequencies, it is observed a characteristic semicircle of the double-layer resistance in parallel with the charge transfer resistance. Furthermore, at lower frequencies, the behavior seems to be purely capacitive, with an almost vertical line crossing over the  $Z'$  axis. Peculiarly, PEDOT-co-PPhTAc-2b shows, at intermediate frequencies, a Warburg behavior, translated by a line with a slope near to  $45^\circ$  – related to the observation of the diffusive process during the polymer redox reactions. At the PEDOT diagram, it is only observed the capacitive process and it was no possible to see the semicircle presented in the copolymers diagrams. In Table 3, the impedance values are presented for each process seen in Figure 4a and Figure 4b diagrams.

Differently from PEDOT, the copolymers have presented a  $R_{ct}$  value quite high, indicating a greater difficulty for charge transfer. The electron-acceptor effect of the substituent influences at position 3 on the thiophene ring over the data of resistance obtained is also notable. In the same way, as presented out in the switching times analysis, the PhTCb copolymer has shown a more significant variation of  $R_{ct}$  value, perhaps also due to the direct conjugation between the thiophene ring and the carboxylic substituent, which may worsen even more the charge transfer.

On the other hand, the  $C_{dl}$  values are compatible with the double-layer capacitance values usually expected for platinum in contact with the electrolyte<sup>[52,53]</sup>, confirming the porosity of the films.

It is noteworthy that the  $C_{lf}$  values were quite high, indicating such materials as promising candidates for supercapacitors devices building, and this might be due to the efficient electron conjugation between the electron-donor monomer (EDOT) and electron-acceptor monomers (PhTAc-2a, PhTAc-2b, and PhTCb) from the D-A system, proposed in this work.

If we make a comparison between spectroelectrochemical and impedance results, it is possible to observe that when the polymer remains reduced or neutral, it presents a higher resistance. Instead, when the polymer is oxidized, it is noticed the arising of new energetic states within the band gap, and the resistance became lowest.

## 4. Conclusions

In this work, the spectroelectrochemical experiments have shown that D-A-like copolymers prepared by electropolymerization of EDOT and electron-acceptor thiophene derivatives have presented electrochromism. Such color changing was visually noticed, beyond observing the arising of new bands at the absorption spectrum as the potential changes.

Additionally, through the experiments of chronoabsorptometry, it was possible to determine some electrochromic parameters indispensable to study the device building viability, like the optical contrast and the coloration efficiency, beyond the switching times to electrochemical stimulation, in which those D-A-like copolymers have demonstrated a potential application on electrochromic devices building.

The impedance results show that in the oxidized state, there is a fast electrical charge transfer at the interface metal | polymer | electrolyte and in the reduced state, the charge transfer is much slower and there is a purely capacitive behavior at low frequencies. Finally, the  $C_{dl}$  values have confirmed the film porosity and capacitive profile at low frequencies indicating that those materials also have potential applicability to supercapacitors building.

## 5. Acknowledgements

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## 6. References

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## **Supplementary Material**

Supplementary material accompanies this paper.

**Figure S1.** Tauc curves for PEDOT (a), PEDOT-co-PPhTAc-2a (b), PEDOT-co-PPhTAc-2b (c), and PEDOT-co-PPhTCb (d).

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