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# The electropolymerization of several poly(3-methylthiophene) films in the same used solution and its consequence in their properties

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**ABSTRACT:** The effect of the electropolymerization of seven poly(3-methylthiophene) (P3MT) films in the same used monomer solution have been investigated. Cyclic voltammetry, UV-visible, scanning electron microscopy, and electrochemical impedance measurements were carried out to understand the effect of the solution reusing on the polymer electrochemical properties. The obtained results show that, as the solution is reused, the polymerization rate increase and the charge in of the cyclic voltammetry decrease. Besides, there are important changes in the sample's morphologies, with the increase of the synthesis number, the amount of fibers increase and this leads to lower the conductivity of the polymer film. In agreement to this, the impedance data analysis shown important changes in the interfacial electronic parameters, i.e., changer transfer resistance and double-layer capacitance, used to describe the films. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2017**, *134*, 44368.

**KEYWORDS:** conducting polymers; electrochemistry; properties and characterization

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## INTRODUCTION

Conducting polymers comprises one of the most attractive fields in chemistry regards to the development of new organic materials, which can be synthesized by chemical or electrochemical procedures. It is important to note that, although the chemical synthesis easily be scaled to industrial level, the electrochemical synthesis offers several advantages, including rapidity, simplicity, and generation of the material directly on the electrode, in which often is used. However, the electropolymerization process has its own complexities and is dependent on many experimental variables: concentration of monomer, temperature, supporting electrolyte and solvent, substrate material and the type of electrical signal applied to the working electrode.[1–3] In the literature, it is possible to find many articles about the nucleation and growth mechanism of these materials,[4–9] as well as the effect of the experimental variables on their properties.[10–16] Otero[17] wrote as important work on the electrogeneration of the conducting polymers and explained that the polymerization mechanism is complex[4] (Figure 1) and could occur with parallel reactions.

Thus, the polymerization has been described as a radical reaction with the formation of a cation-radical monomer at the anode surface. Then the coupling of two radicals occurs and the polymerization continues with successive coupling of cation-radicals to form the polymer chain.[4]

It is common sense, in the case of polythiophene derivatives, to prepare just one polymer film per solution and then replace it by a fresh one to polymerize a second sample, and in this way, a few articles discuss the presence of oligomers in the solution. Zhang *et al.*[18] prepared poly(3-methylthiophene), P3MT, in fresh-made monomer solutions and in used ones. Comparing the results, the authors observed a difference in the threshold potential of the polymerization and decided to use newly prepared monomer solutions.

Roncali *et al.*[19] studied the effect of oligomer size on the polythiophene properties, by synthesizing films starting from oligomers with several sizes. The authors have found a decrease in the polymer conjugation length as increasing oligomer length. Wei and Tian[20] have investigated the addition of oligomers as additives to the electrosynthesis of poly(3-alkylthiophenes), and observed an increase in the regularity of the polymer chains with a bathochromic shift in their electronic spectra. It was also noticed that even the average molecular weight of the polymers is decreased as concentration oligomers increased during the synthesis. Del Valle *et al.*[21] also investigated the effect of different starting oligomer sizes in the process of nucleation and growth of polythiophene. They observed that as the starting chain length increases, the voltammetry profile decreases regarding to the higher aromatic character of the longer units.

However, to the best of our knowledge, there is no published article on the consequences to reuse the polymerization solution

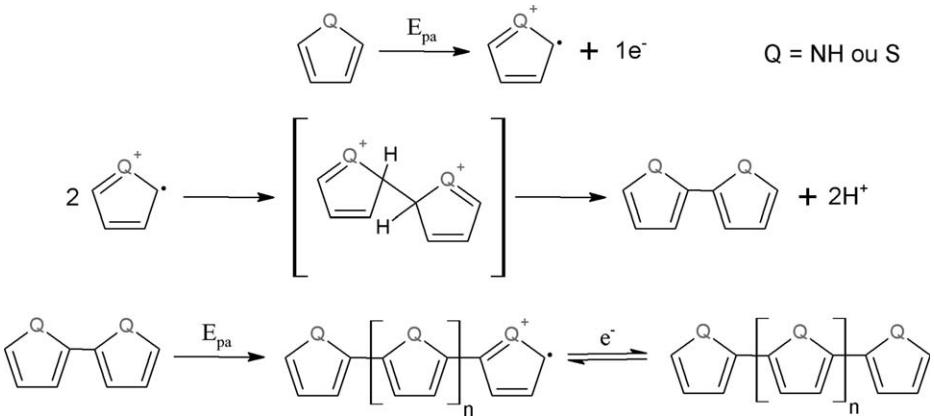


**Figure 1.** Electrodeposition mechanism for five-member heterocyclic monomers.

of the formed polymers. Then, the objective of this work is to investigate the effect of the solution reused on the properties of P3MT films. In order to understand this effect, seven polymerizations in the same solution and their electrochemical properties were analyzed.

The use of the same solution to prepare several films showed the samples are different because of the oligomers produced on each synthesis. The amount of the soluble oligomers formed is linear, as noticed by using UV-vis data and the morphology of the films change from compact to more fibrous, after several films prepared in the same solution.

## EXPERIMENTAL

3-methylthiophene was supplied by Aldrich and was used without further purification. Analytical grade lithium perchlorate and acetonitrile from Sigma-Aldrich were used.

A three electrodes one-compartment cell was used. The working electrode was a platinum disc ($A = 0.2$ cm$^2$). A silver wire and platinum sheet were used as pseudo reference and auxiliary electrodes, respectively. Before each deposition, the platinum working electrode was cleaned using polishing cloth with diamond paste (0.1 μm) and rinsed with acetone.

Poly(3-methylthiophene) were prepared at constant potential of 1.5 V, in acetonitrile with 0.1 mol L$^{-1}$ 3-methylthiophene (3MT) and 10 mL of 0.1 mol L$^{-1}$ $LiClO_4$. Seven different samples were prepared using the same solution, maintained the formation charge fixed at 600 mC cm$^{-2}$ in each of them. After each polymerization, the auxiliary electrode was flame-cleaned, and the pseudo reference was polished and rinsed with acetonitrile to guarantee the reproducible conditions.

After each synthesis, the polymer film was rinsed with acetonitrile and placed in a second cell containing only the supporting electrolyte, 0.1 mol L$^{-1}$ $LiClO_4$ in acetonitrile. Then, the redox characteristics of the samples were investigated using cyclic voltammograms in the potential range between −0.2 V and 0.85 V at 50 mV s$^{-1}$. Besides, each film was also studied using electrochemical impedance measurements. The data were obtained at a *dc* potential of 0.75 V, in the frequency window 10 kHz down to 10 mHz, collecting 10 points per decade at 10 mV of alternating voltage amplitude. The electrosynthesis and electrochemical characterizations were carried using a potentiostat AUTOLAB© model PGSTAT30 with FRA module.

The measurements of UV-visible spectra of the solution after each polymerization were carried out using a spectrophotometer Cary model 5G UV-VIS-NIR. Finally, to follow the morphological changes it was used Field Emission Gun Scanning Electron Microscopy (FEG-SEM) a Phillips LX-30 equipment.

## RESULTS AND DISCUSSION

Figure 2 exhibits the current density as function of the polymerization time during the synthesis of films prepared using the same solution. Expanding the initial period of anodization it is possible to observe the nucleation process of the samples. After that, there is an increase in the current density associated to the increase in the polymer film area. Several articles[5–7] proposed that the oligomers formed precipitate instantaneously on the electrode surface followed by a three-dimensional growth of the islands until the complete coverage of the surface.

Although there are discrepancies and inversions in the behavior of the growth curves generally, as the solution is used more than one time to prepare a polymer, it is possible to observe an

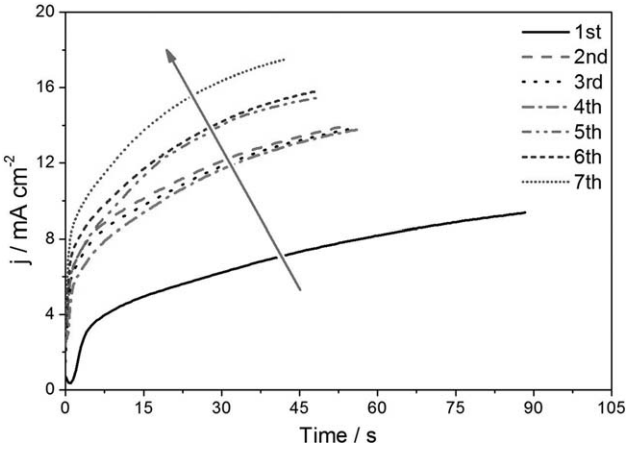


**Figure 2.** Synthesis chronoamperograms of seven P3MT films in the same solution. Each sample was prepared at constant potential of 1.5 V, in ACN/$LiClO_4$ 0.1 mol L$^{-1}$ + 3MT 0.1 mol L$^{-1}$ until a fixed charge of 600 mC cm$^{-2}$.

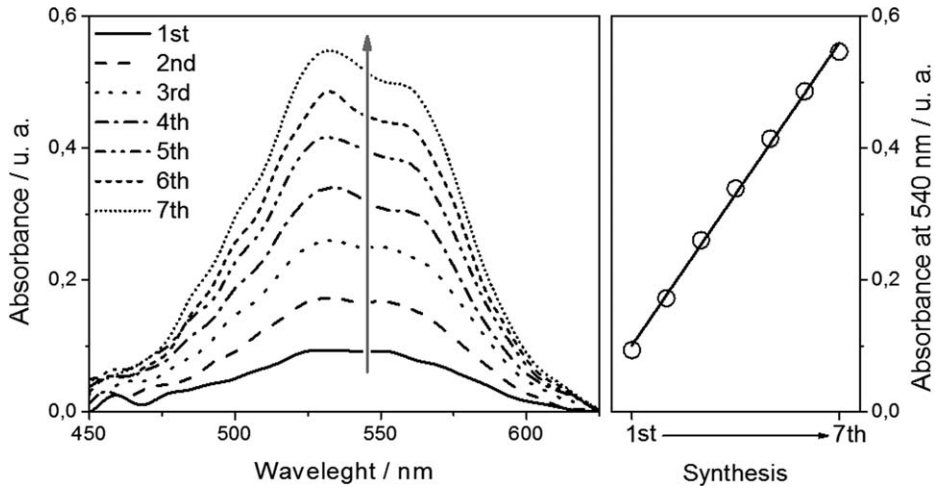


**Figure 3.** UV-vis experiments after each electropolymerization of 1.5 V, in ACN/$LiClO_4$ 0.1 mol $L^{-1}$ + 3MT 0.1 mol $L^{-1}$ until a fixed charge of 600 mC $cm^{-2}$. (a) UV-vis spectra and (b) absorbance at 540 nm.

nonlinear increase in the polymer growth rate. We stress out here that a deepest discussion about it will be carried out forward with the support of more results. Besides, at the same time, it is observed light purple coloration in the solution, the associated amount of soluble products, i.e., oligomers. Increased staining was followed by UV-vis of the solution, Figure 3.

In Figure 3(a), a strong absorption peak at 540 nm characterizes the oligomers in the solution. It is readily apparent a linear increase in absorbance as a function of the number of consecutive syntheses in solution [Figure 3(b)]. Furthermore, there is no displacement in the peak position. This last fact could mean that soluble products produced during the syntheses have an approximately constant chain length, once it is well established a decrease in HOMO-LUMO energy difference as the oligomer chain length increases.[22] Besides, there is a direct correlation among the presence of oligomers in the solution and the increase in the polymer growth rate, once the needed charge to extend the chain length decreases as the amount of oligomers in the solution increases.

Another important observation from Figures 2 and Figure 3, is the polymerization efficiency, i.e., the percentage of solid polymer formation, slightly raised once the amount of oligomers increased linearly. It is assumed that if only two parallel reactions occur, the film deposition and the soluble oligomer formation. The amount of soluble oligomers growth has a constant rate, because the absorbance evolution is linear. However, both current density and synthesis time changes are not linear, it means that the efficiency during each electropolymerization process is not constant, as well as not present a linear change. It is sure that, if more than two reactions occur, this conclusion could be not true.

Still discussing about on the efficiency of polymerization, it depends on many parameters, such as concentration of current on the working electrode surface as well as the size, shape, and number of nucleation sites. Therefore, there is a clear tendency, the first film to the last, there is an increase in current density and hence decreasing the electrodeposition time is not constant or linear these changes, then there is reversal in behavior, as is the case of the second to fourth curves.

Nevertheless, it is noteworthy that in the present case, there is no any evidence of a third parallel reaction, since no new band absorption appeared in the UV-vis spectra nor differences in the profile of the chronoamperometric curves was observed. From a different point of view, it is observed important changes in the sample's morphologies (Figure 4).

The main difference observed in Figure 4 is the increase in the number of fibrils as the films were prepared in a reused solution. Basicaly, the first film is mainly a compact one. Correia and Abrantes,[23] studying poly(3-methylthiophene), observed that a dense ordered layer is obtained as the time to transform the oligomer in polymeric chains increases. Considering this idea, it means that the polymeric chains, for the first films prepared, are longer than for the others prepared in the same solution. Indeed, it is expected that for fibrous structure an increase in the current density during the polymerization at constant potential occurred due to an increase in the surface area as observed in Figure 4.

However, also is expected that for high polymerization rates, the chain lengths decrease, once the probability of termination reaction increases under this condition[24] leading to a negative effect on electrochemical properties of the materials. Indeed, in Figure 5(a) it is observed a continuous decrease of the current density peak, and consequently, in the charge, as the number of films prepared increases. Considering that the formation charge was maintained constant and that the same amount of oligomers is generated in each electropolymerization coupled with the consideration that there are only two reactions occurring, the same amount of polymer is deposited on the electrode in each polymerization. As consequence, the changes observed in the cyclic voltammetry, could be explained only by changes in the polymer electrochemical properties.

Until now, the experimental evidences showed that reusing of the solution leads to different films with each time less

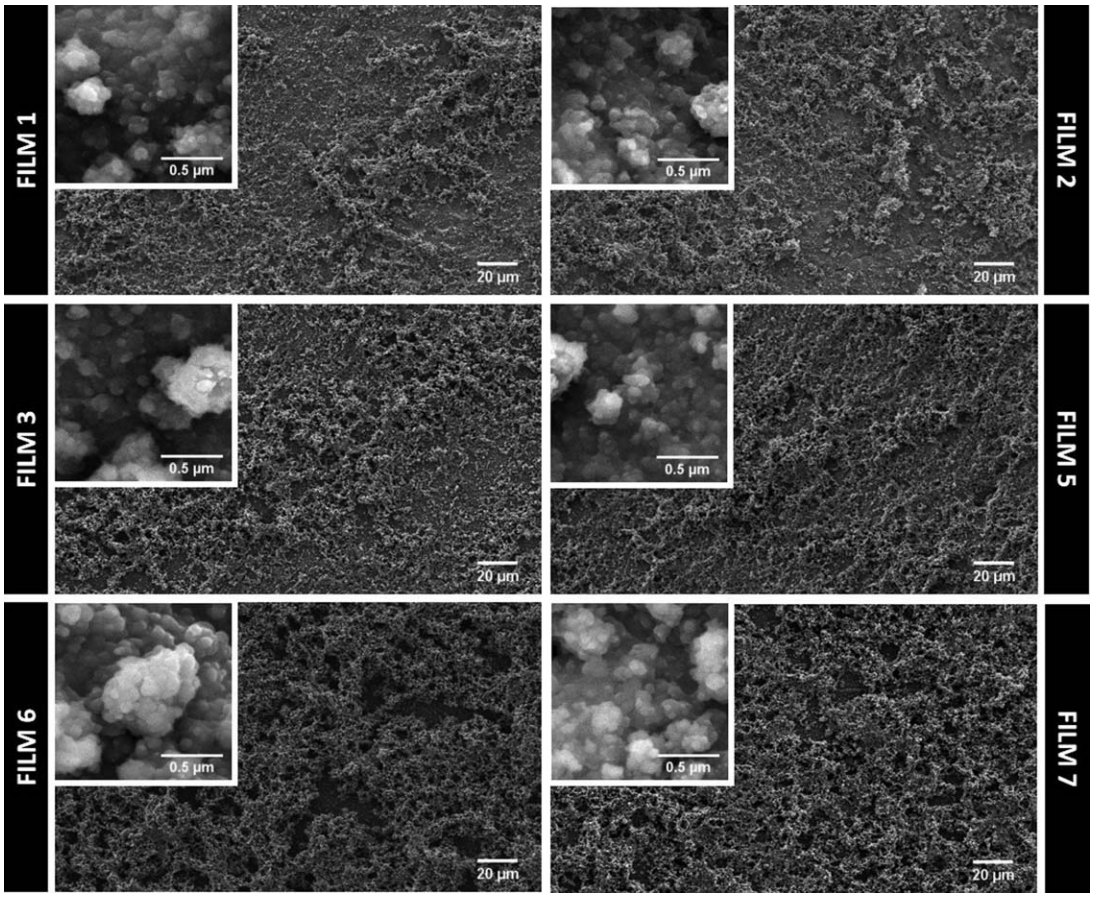


**Figure 4.** SEM Micrographs for the seven poly(3-methylthiophene) prepared using the same solution. Electropolymerization of 1.5 V, in ACN/$LiClO_4$ 0.1 mol $L^{-1}$ + 3MT 0.1 mol $L^{-1}$ until a fixed charge of 600 mC $cm^{-2}$.

electrochemical activity. To investigate the mechanism of the change in the polymer's properties, impedance measurements were carried out and the data were analyzed using transmission line model.[25] This approach, transmission line models, is adequate to describe soft porous materials. In this sense, it is important to stress out that any intercalation compound can be described, from an electrochemical point of view, as a porous material, meaning the existence of a potential drop inside the material related to ionic transport, and/or electronic transport and through the interface between the polymeric chains and the solution in the pores. It is also important to notice that the intercalation of solvated counter ions can lead to polymer volume change during the redox reactions, an intrinsic process that leads to premature aging of the material.[26]

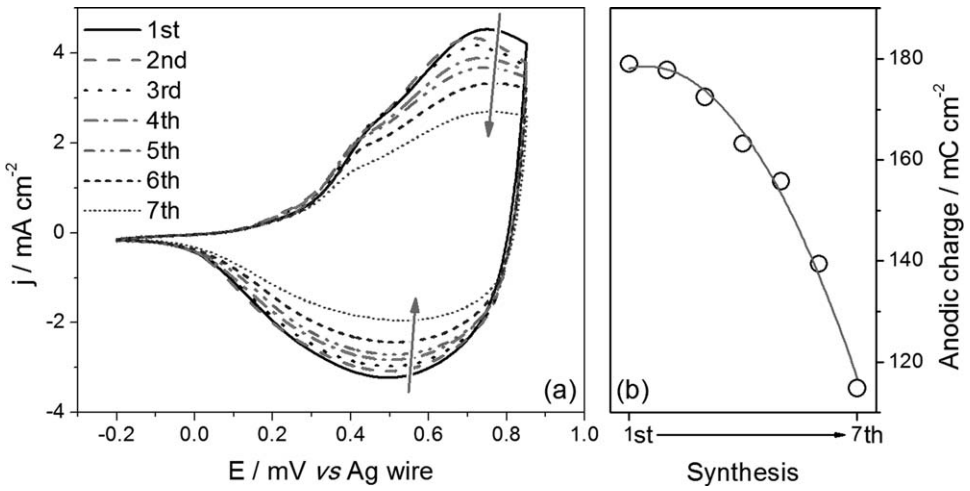


**Figure 5.** (a) Cyclic voltammetry profiles and (b) anodic charge for each film, ACN/$LiClO_4$ 0.1 mol $L^{-1}$, $v = 50$ mV $s^{-1}$.

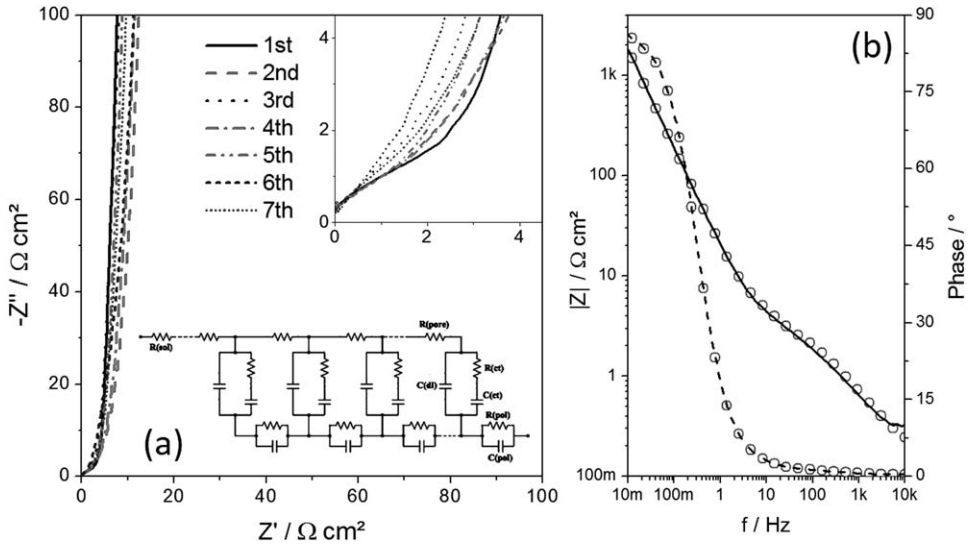


**Figure 6.** (a) Nyquist plots of each film normalized by solution resistance and (b) bode plots presenting the experimental and calculated data first film prepared. Frequency range from 10 kHz down to 10 mHz, *dc* potential of 0.75 V and *ac* perturbation of 10 mV.

Figure 6(a) presents the Nyquist plots for those seven films prepared in the same solution and it is observed a continuous change in the curves. To analyze the data, it was used the transmission line model presented in the inset of Figure 6(a).[27,28] The model describes the material as composed of two branches, where the first one is the cavity of the pore and the solution inside it and the second one is the polymeric chains. Connecting them is proposed a modified interface, compared to an

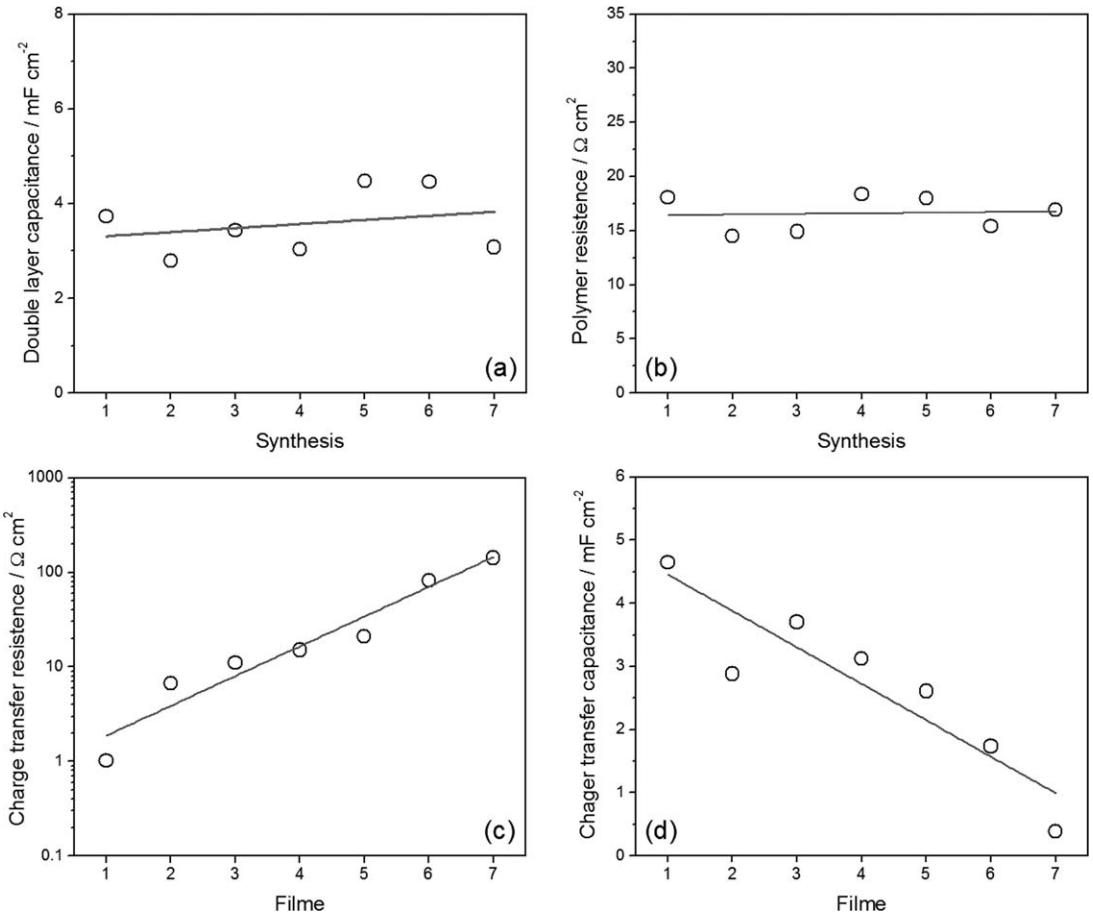


**Figure 7.** Impedance spectra parameters, fitted by transmission line model, in function of number of synthesis: double layer capacitance (a), polymer resistance (b), charge transfer resistance (c), and capacitance (d).

interface of a flat electrode. In this model, there is a nonideal double layer capacitance, $C_{dl}$, which is described by a constant phase element. It should be emphasized so therefore that the discussion about the nonideality of the capacitances is beyond the purpose of this work. In parallel with $C_{dl}$ is the charge transfer resistance, $R_{ct}$. In the present case, this parameter is associated to the intercalation of the counter ions necessary to neutralize the electronic defect generated in the polymer during the redox reaction. It was demonstrated in the literature[28–30] that the description of the interface polymer/pores using only these two equivalent circuit elements is not complete. It is also necessary another nonideal capacitance, called charge transfer capacitance, $C_{ct}$. This last element is used to describe the time delay between the ion transport thought the interface and the time necessary to stabilize the trap-site in the polymeric chain.[26,31] In Figure 6(b), using Bode plot, it is presented the calculated and experimental data for one sample to show the fit accuracy of the model used. Similar fit precision have been obtained for all the samples investigated.

Figure 7, present the parameters described in the model [Figure 6(a), inset]. The first interesting point is that there is no important difference in the polymer resistance, Figure 7(b), it could mean that the polymeric chains have the same length. Moreover, no significant change seen for the double layer capacitance, Figure 7(a), could mean that there is no any important change in the surface area of the polymer solution interface. From a different point of view, there is a decrease in the charge transfer capacitance that could be related to a decrease in the number of ionic species stored in the polymer chains as counter ions. Finally, from Figure 7(c), there is a very important increase in the charge transfer resistance, which means that the counter ions transfer through the polymer interface needs more energy as the number of polymers prepared in the same solution increases. It is important to stress out that this information agrees with those presented in Figure 7(d).

In summary, the electroactivity of the films synthesized in the same solution tends to decline as more films are produced and this is due to the fact that the process of intercalating is increasingly hampered. This fact is quite sharp, even, an electronic point of view, the material itself has no changes in properties, i.e., its resistance is practically the same between the first and seventh film. Although there are changes in the morphology of the interface, as seen in Figure 4, electrochemically the electroactive area also remains constant. This may mean that the oligomers in solution are possibly incorporated into the film, this leading to less compact structure, but which, however, these oligomers have no electrochemical activity due to their chain length.

## CONCLUSIONS

The reuse of a polymerization solution to prepare seven films carried out here show that the samples are different. After each synthesis, there are oligomers in the solution, which are residue from the previous synthesis. Thus, from all the data using different techniques, it is possible to propose that the changes the polymers prepared in the same solution could be related to alteration in the charge transfer processes thorough the polymer solution in the pores interface. Such changes come from the increase in the polymerization rate leading also to change in the morphological structure of the material. Further, as have been described in the literature, the presence of oligomers leads to rapid formation of a continuous film, which causes a more open and less compact morphology with different electrochemical properties.The electrochemical properties, measured using CV, present an important decrease. Finally, using impedance spectroscopy it was detect an increase in the charge transfer resistance and a consequent decrease in the ions concentration in the polymer.

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