



INVESTIGATION OF THE ELECTROCHEMICAL AGING OF POLY(3-HEXYLTIOPHENE) USING IMPEDANCE SPECTROSCOPY



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ABSTRACT

In this paper, the electrochemical ageing of poly(3-hexylthiophene) was studied using two different films electrodeposited under different experimental conditions. The first one has been prepared in acetonitrile with 0.1 mol L^{-1} of monomer + 0.1 mol L^{-1} of LiClO_4 (Film I). The second one has been synthesized in the same solvent with 0.2 mol L^{-1} of monomer + 0.2 mol L^{-1} of LiClO_4 , plus the addition of 10 mmol L^{-1} of pure water (Film II). The electrochemical ageing has been carried out by the application of an overoxidation potential. At every 20 minutes, a cyclic voltammogram and electrochemical impedance experiments were measured. Each film has exhibited different pathway for the ageing process. Film II showed a smooth degradation of the electrochemical properties, mainly at the interface polymer chains and solution in the pores. The other one, Film I, has presented a two steps degradation process, been the first, up to 120 min, characterized by smooth changes in all the electrochemical parameters necessary to describe the polymer. After 120 min, the second degradation process occurs characterized by an abrupt change in all the parameters, indicating an important change not only in the electrochemical degradation of the polymer but also in its morphology, measured by SEM micrographs. Furthermore, two electrode impedance electronic experiments confirmed an important degradation of the bulk polymer for Film I.

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1. Introduction

Poly(3-hexylthiophene), P3HT is the most exploited Pth derivative [1–3] given its range of absorption, low bandgap, and high hole mobility being widely used in bulk heterojunction solar cells. The durability of such organic devices is very limited compared with inorganic and hybrid ones. It is especially the case in those ones where the polymers are the active material and are submitted to successive oxidation/reduction cycles. One possibility to explain these results is the ion transport “in” and “out” of the polymer, which is necessary to compensate the generated charges in the polymer chains during the redox process. This intercalation can cause a mechanical stress in the material [4,5], which leads to premature ageing.

Despite its importance, only a small number of papers investigate the impact of the ageing in the electrochemical properties of the polymers. Tourillon [6], for example, studied poly(3-alkylthiophenes) (P3ATs) films under different experimental conditions in both absence or presence of water and at different

pH values. The authors observed a strong effect of the solution pH on the electrochemical degradation, which they proposed to be related to a nucleophilic effect. In 1991, Harada et al [7], using cyclic voltammetry up to the superoxidation region, demonstrated that this process is irreversible, i.e., once the film degrades, it can no longer be recovered. A very important observation was made by Wang [8], who has described a relationship between the deactivation process of P3AT and the solvent pKa value. Pud, in 1994 [9], studied the stability and the anodic degradation of many conducting polymers. In that paper, the authors observed that the superoxidation does not disable all of the polymer properties. For example, the charge storage of polypyrrole does not decrease after the process. Besides, the author observed that a morphological change occurs in the film due to the gas formation as byproduct of polymer superoxidation. In a previous work of our group, it was discussed the aging effect itself, focusing on the changes occurred on properties of polypyrrole [10] and PANI/PSS self-assembled films [11]. In those works, it was used impedance spectroscopy and data were analyzed using transmission line models. The choice of the electrochemical impedance technique occurred because, with a single measurement, it is possible to separate the different processes that occur at the interface polymer/solution, the polymer chains and solution in the pores. It was observed an

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important increase in the charge transfer resistance at the interface polymer solution in the pores. Such change alone, in that case, was not followed by an important degradation of the electrochemical polymer chain properties themselves.

To analyze impedance data, the most used approach is the use of equivalent circuits. But, for porous electrodes, many authors have proposed that this approach is not valid [12–16]. One alternative proposition to describe impedance results for porous electrodes is the use of transmission line models (TL) [14,17]. Differently from rough electrodes, in a porous one, the hollows are of such magnitude that they can be considered as channels existing around the material and then, a transmission line model is adequate to describe the system. Scheme 1 represents a generalized transmission line model. In such description, two phases are being considered, the electrolyte inside the pore (χ_1) and the material itself (χ_2).

The elements χ_1 and χ_2 describe the ohmic drop at each point along each of the channels, and ζ describes the connection of the interface with these two media [18]. Then, the total impedance in this type of system is given by (Eq. 1) [19]:

$$Z = \frac{\chi_1 \chi_2}{\chi_1 + \chi_2} \left(L + \frac{2\lambda}{\sinh(L/\lambda)} \right) + \lambda \frac{\chi_1^2 + \chi_2^2}{\chi_1 + \chi_2} \coth\left(\frac{L}{\lambda}\right) \quad (1)$$

where, $\lambda = \left(\frac{\zeta}{\chi_1 + \chi_2} \right)^{\frac{1}{2}}$. Thus, the elements χ_1 , χ_2 e ζ should be designed such that the adjustment of impedance spectra can consistently describe the physical of the electrochemical phenomena. This can be done using the equivalent circuit elements that are similar processes that may be occurring. In this paper, the choice of the elements that are inserted in the TL model was based on literature data of different authors who studied the impedance of conductive polymers.

Considering the issues discussed, the present work aims at to study the electrochemical ageing of poly(3-hexylthiophene) films by electrochemical impedance spectroscopy, and analyze the data using transmission line model. Additionally the present work aims to study the mechanism of aging for polymers prepared under different conditions following the proposition of Kabasakaloglu et al., 1999 [21]. about the importance of the preparation variables on the material's properties. Thus, it was investigated films prepared using two different conditions.

2. Materials and methods

Analytical grade reagents (Sigma–Aldrich) were used in this work. The monomer, 3-hexylthiophene, was used without pretreatment. Two samples P3HT films were electrochemically prepared. The first one (Film I) was electropolymerized from a

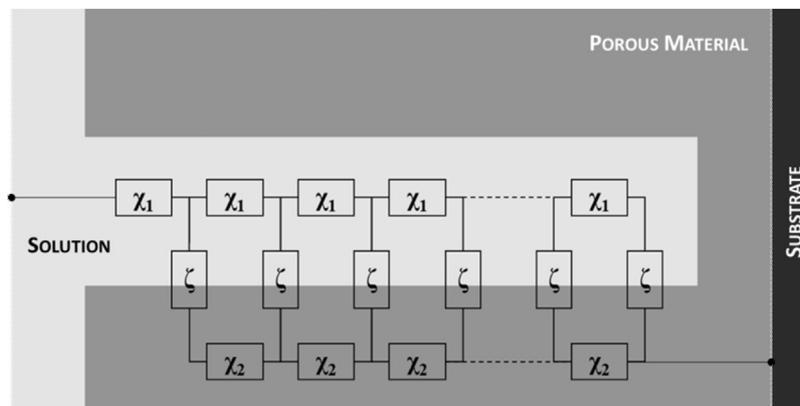
solution with 0.1 mol L⁻¹ monomer and, as a supporting electrolyte, LiClO₄ 0.1 mol L⁻¹ in acetonitrile (ACN). The second (Film II) has been synthesized electrochemically in a solution with a concentration of monomer and electrolyte 0.2 mol L⁻¹, plus 200 ppm (10 mmol L⁻¹) of ultra-pure water. After synthesis, the film was removed from the solution, washed with ACN, and placed in a solution containing only the supporting electrolyte at the concentration of 0.1 mol L⁻¹, wherein the electrochemical characterization was performed. All experiments were carried out at 298 K in a dry chamber with N₂. The electrosynthesis and electrochemical characterizations were carried using a potentiostat AUTOLAB® model PGSTAT302 N with FRA module.

The electropolymerization has been carried out potentiostatically (1.5 V vs Ag) on a platinum electrode (Area=0.2 cm²) to a growing charge of 1.0C cm⁻² per mole of monomer. As auxiliary electrode a platinum net was used. The cyclic voltammograms (CV) were recorded in the potential range 0.0 and 1.0 V versus Ag in ACN/0.1 mol L⁻¹ at 10 mV s⁻¹ sweep rate. The impedance spectra were obtained at a dc potential of 0.9 V (versus Ag) before each degradation step. The investigated frequency window was between 10 kHz up and 10 mHz, being collected 10 points per decade with 10 mv of alternating voltage amplitude.

A second type of impedance experiment were carried out using two identical microelectrodes (Fig. 1a) with A=0.25 m² and is separated by 70 μm (Fig. 1b), to measure only the electronic transport in the polymer. The polymer was deposited completely covering the gap between on the electrodes (Fig. 1c). In this case, we are only measuring the electronic properties of the polymer to split the degradation process in its electrochemical and electronic parts. These impedance spectra were obtained at OPC potential also before each degradation step. The investigated frequency range were the same with ac voltage of 10 mV too.

In order inhibit the drying of the polymer, we carry out these measurements inside the same solution used in different experiments describe before. It is important to point out the the electrochemical ageing process has been investigated using the three electrode configuration and, then, the electronic properties of the polymer, after each step of ageing is studied using the electrode describe in Fig. 1. During the electronic measurement, the counter electrode and the reference electrode were disconnected from the potentiostat and the microelectrodes have been measured using a two electrodes configuration. which is common for semiconductor experiments. Therefore, this new set of data will be called electronic measurements. A detailed schematic representation of the experimental setup are present in supplementary information

The accelerated degradation of the films was performed by polarizing the electrode at a potential 1.11 V (vs Ag) during 20 min,



Scheme 1. Representation of a generic transmission line model.

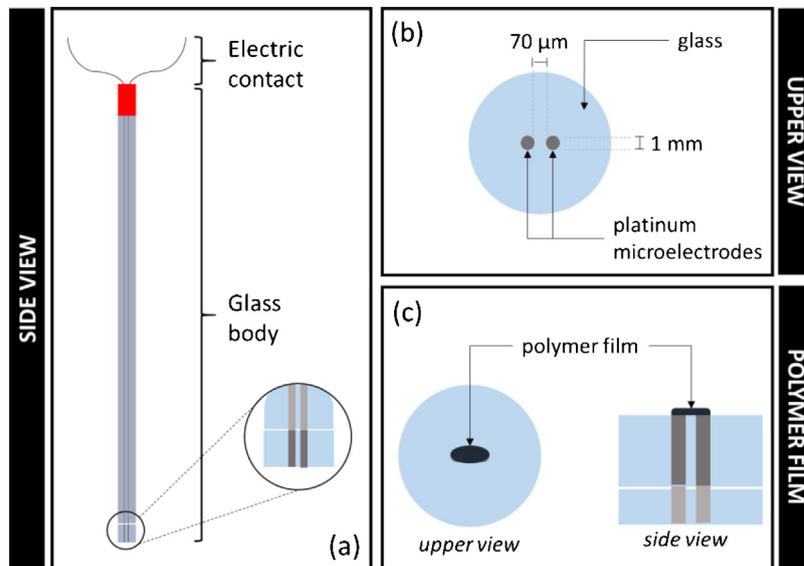


Fig. 1. Schematic representation of the electrode used to carry out the electrochemical impedance spectroscopy.

and then carried out for three voltammetric cycles at the same potential window described above at a sweep rate of 50 mV s^{-1} . Here is important to describe that is common use a narrow potential window during the electrochemical characterization of a

conducting polymer compared to the potential value used during the electropolymerization under potentiostatic condition. The applied potential necessary to oxidize a monomer molecule is higher than those necessary to oxidize a dimer, and continuously

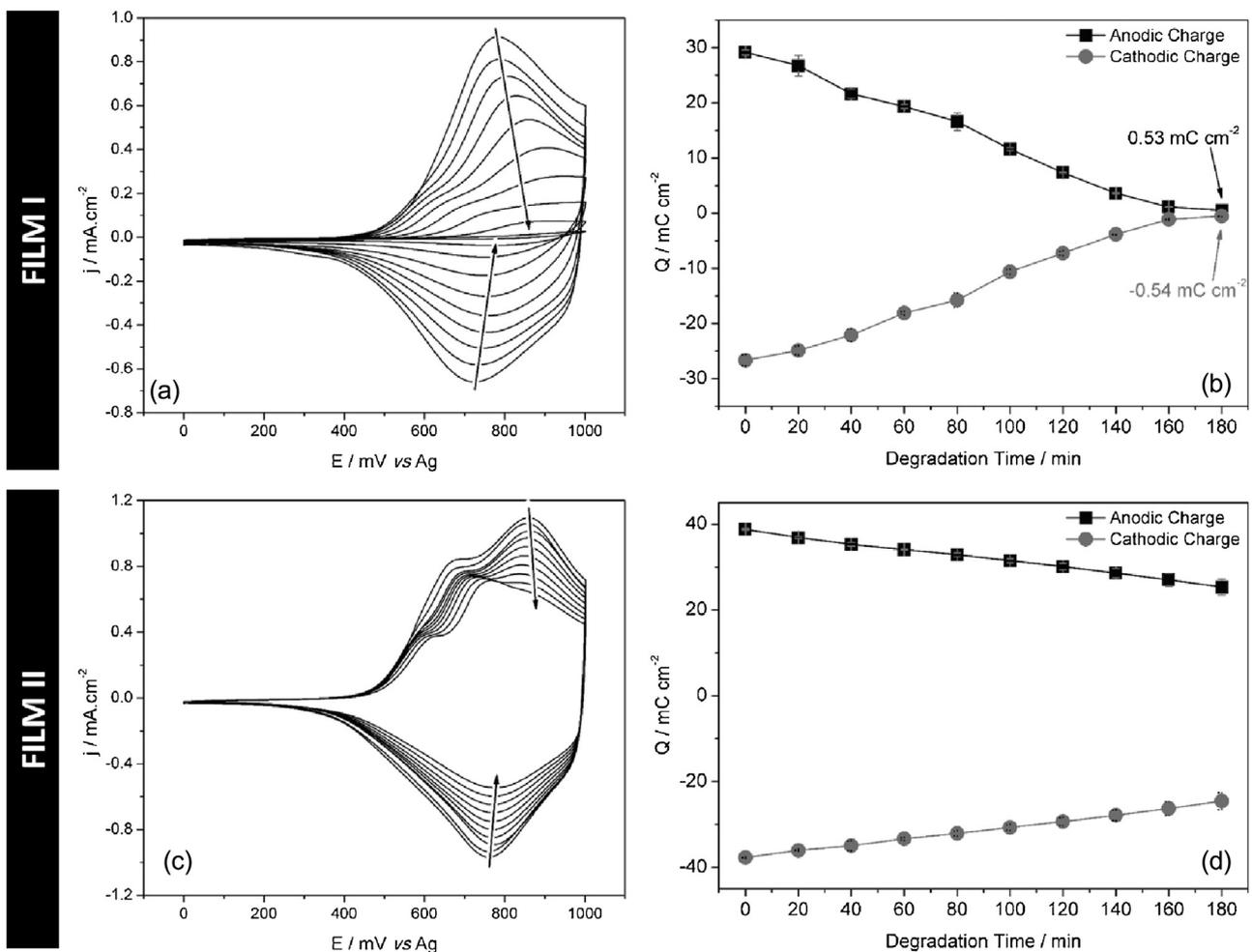


Fig. 2. Cyclic voltammetry for the P3HT Film I (a) and Film II (c) after each degradation step and (b) comparing the newly synthesized film and film degraded after 180 min, ACN/LiClO_4 0.1 mol L^{-1} , $\nu = 10 \text{ mV s}^{-1}$.

decrease as the polymeric chain increase. Indeed, to investigate the electrochemical properties of the polymer in a blank (i.e., in the absence of monomer) is the polymerization potential is used as an anodic vertex value in cyclic voltammetry, the material is complete degradation in only one cycle. Then, we choose to aging the polymer using a potential value that lead to slow enough degradation to be followed using an adequate number of experiments.

To follow any possible morphological change in the samples, Scanning Electron Microscopy (SEM) images measuring using a FEI model Inspect F50 were obtained after synthesis of both films, at 100 min and at 180 min of degradation for both films.

3. Results and discussion

Fig. 2a and 2c illustrate typical voltammograms obtained during the electrochemical aging of the both P3HT samples. Initially, a reversible redox process was observed, which, as the number of voltammetric cycles increases, shows an important decrease in the current associated with both anodic and cathodic processes. For aging times lower than 100 min, the cathodic

current peak was still well defined, whereas, for longer experimental times, this characteristic is lost. Finally, for Film I and aging time of 180 min, all the electrochemical fingerprints of the voltammogram disappear, indicating that the rate or even the mechanism of aging in both films could be different.

For Film I, the decrease of the current peak and consequently the overall charge (Fig. 2b) during the experiments occur linearly, and, after 180 min, it is 3% of its original value. It is interesting that, although a decrease in the electrochemical charges is observed, there is no change in the ratio between the anodic and cathodic charges. Film II did not show a drastic change between the voltammetric profiles, and the decrease in the total anodic charge is 38.5% (Fig. 2d) of its original value. However, a large displacement of the redox processes in the polymer was observed with the second peak, which shifted about 80 mV to the positive direction at 180 min of degradation. The appearance of a third anodic peak was also noted at around 620 mV and a drastic reduction in the peak at 860 mV.

From a different point of view, the impedance data of Film I, in the Nyquist and Bode diagrams (Fig. 3), show a strong change in the material during its electrochemical aging. It is possible to observe

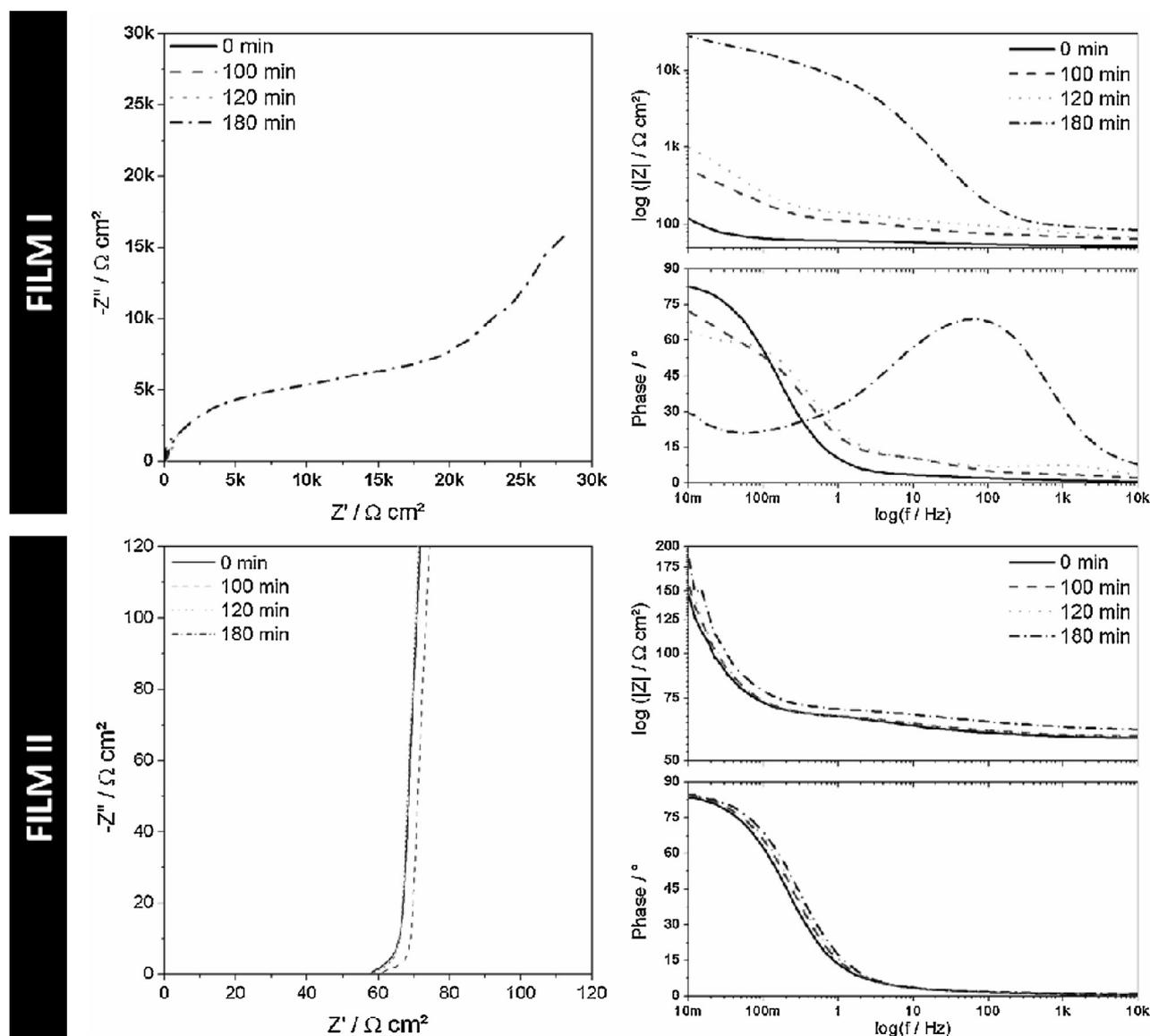


Fig. 3. Nyquist plots (left) Bode Diagrams (right) of the P3HT Film I and Film II in the degradations steps of 0 min (—), 100 min (---), 120 min (···) and 180 min (· · ·).

that the main part of the change occurs for aging times higher than 120 min for Film I. In a different manner, Film II did not show such a sudden change.

The observation of two steps of degradation can be clearly seen in the evolution of impedance parameters obtained from the fitting of the spectra using the transmission line model proposed by Garcia-Belmonte et al. [20] and Bisquert et al. [16]. The model (Fig. 4), which was also used in previous work of our research group [10], is a model of two channels of a polarizable electrode and the interface of the media; in this case, the polymer and the electrolyte in the pores characterize a porous material.

In this model, Branch I describes the processes occurring in the pore solution, and Branch II describes those ones occurring in the polymer chains themselves, the interface of the polymer chains, and the electrolytes in the pores. Then, $R(\text{pore})$ is related to the charge transport of ions within the pores of the material, which could be different from that found in the bulk of the solution, $R(\text{sol})$. $R(\text{pol})$ and $C(\text{pol})$ are related to the charge transport and storage in the polymer chains, respectively. $C(\text{ct})$ and $R(\text{ct})$ represent the charge transfer process (ion intercalation) at the interface polymer chain/pore. $C(\text{ct})$ is necessary to describe the delay that occurs at the entrance of the ions within the polymer and its transport to an active site [21]. Finally, $C(\text{dl})$ is the capacitance of the double layer between the polymer chain and the solution in the pores.

Unlike other materials, the transferred charge at the polymer electrolyte interface are ions, so in the present case, both the resistance and capacitance of charge transfer, $R(\text{ct})$, and $C(\text{ct})$ are parameters that are associated with ionic charge transference or storage, respectively, at this interface. After the intercalation within the polymer, these ions must move to an appropriate trap site. As a consequence, there is a delay between entry of the ions into the material and its effective interaction with the active site leading to a charge separation, which could be understood as an additional pseudocapacitance in the model used, $C(\text{ct})$.

Fig. 4 presents the behavior of $R(\text{pol})$ as a function of the aging process for two different polymers prepared as described in the experimental section. The behavior of this parameter is quite different for the two materials studied. For Film I, it is possible to observe an increase of about 400% in $R(\text{pol})$ for a degradation time up to 120 min. Then, a clear increase in the slope of the curve occurs, meaning that between 120 to 180 min of aging, $R(\text{pol})$ changes almost 3 orders of magnitude, i.e., an increase of 780%. Differently, Film II showed no change in the slope and only an 180% increase during the electrochemical degradation procedure using the same conditions as those for Film I. This is a very important observation because it means that polymers prepared using different experimental conditions can have different electrochemical degradation behavior.

In the present case, Film II has been synthesized using 0.2 mol L^{-1} of monomer, $0.2 \text{ mol L}^{-1} \text{ LiClO}_4$ and 200 ppm (10 mmol L^{-1}) of water

added to acetonitrile, and Film I was prepared using 0.1 mol L^{-1} of monomer, $0.1 \text{ mol L}^{-1} \text{ LiClO}_4$ and in the absence of water. In the literature, it is described that poly(3-methylthiophene) electrochemically prepared using 0.2 mol L^{-1} of monomer presents a higher conductivity compared to those prepared using 0.1 mol L^{-1} of the compound [22,23]. Indeed, this fact also occurs in the present case, as can be observed in Fig. 6. In this sense, the initial values of the $R(\text{pol})$ is $16 \Omega \text{ cm}^{-1}$ for Film I and $6.7 \Omega \text{ cm}^{-1}$ for Film II.

In addition, the presence of a small amount of water leads to an increase in the reproducibility as well as in the conductivity of the material. In summary, in comparing both films, Film II presents a smooth degradation, whereas Film I presents a two-step degradation in which the first step, until 120 min, is characterized by a stronger degradation compared to Film II, and then an overwhelmingly increase in the polymer resistance after 120 min. To further analyze the mechanism of the observed changes, two different plots are presented in Figs. 6 and 7.

Fig. 6 presents the change in $R(\text{ct})$ as a function of the degradation time. For Film I, Fig. 5a, a logarithm increase of $R(\text{ct})$ is observed as the aging process occurs with a subtle change in the slope at 120 min. Film II, in different form, presents a small increase of $R(\text{ct})$ followed by a stabilization of this parameter. In a previous paper [10], we discussed the process associated with $R(\text{ct})$ to be related to the ion transport through polymer chains. Then, from those results, which are in agreement with those presented here, it is possible to propose that the intercalation process needs a higher amount of energy compared with the pristine material. Of course, this is not an explanation itself but the observation of an effect.

Fig. 7 using the definition of $C(\text{dl})$, which is a linear function of the area, shows the decrease in their values is a clear indication of a volume change in the material. Consequently, a smaller amount of available ions inside the pores, a reduction in the intercalation process, and a lower value of capacitance will be also observed. Then, for Film I, the values of $C(\text{dl})$ until 120 min has a change in the same form as Film II, indicating a decrease in the folding of the material. Then, correlating the data presented in Fig. 6 and Fig. 7, one possible explanation could be an irreversible change in the polymer morphology following Harada et al. [7]. Fig. 8, which presents the micrographs changes for both films supports this proposition.

Before the first degradation step, both films exhibited important morphologic differences. Film I presented an interconnected network microstructure comprised of globules and small pores throughout the surface, while the microstructure formed in Film II was possibly a result of the coalescence of smaller globules. The second set of images was acquired at 120 min of degradation, which proved to be the limit to smooth degradation for the Film I. In Film II, the globules increased in size while that for the Film I part of the globules in the network gave rise to agglomerates, which grew greatly in size after the degradation process, decreasing the porosity. Therefore, the disappearance of the

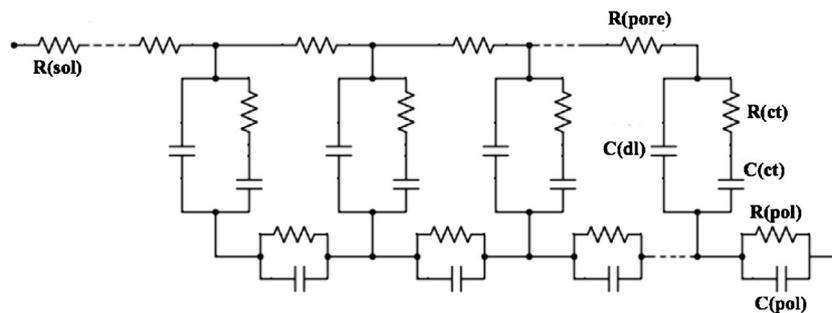


Fig. 4. Transmission Line model utilized for fitting of impedance spectra.

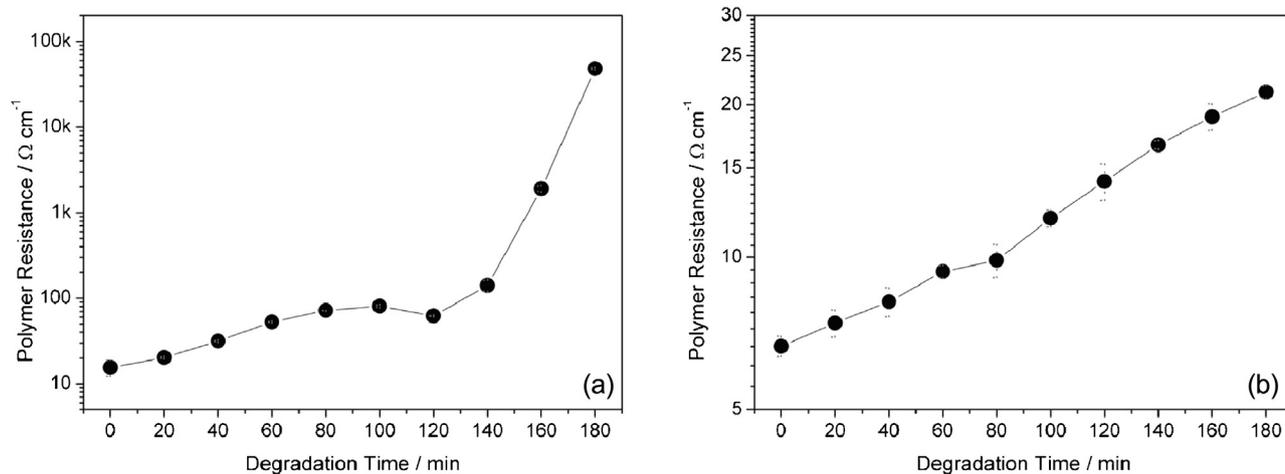


Fig. 5. Resistance of polymers for Film I (a) and Film II (b) versus degradation time.

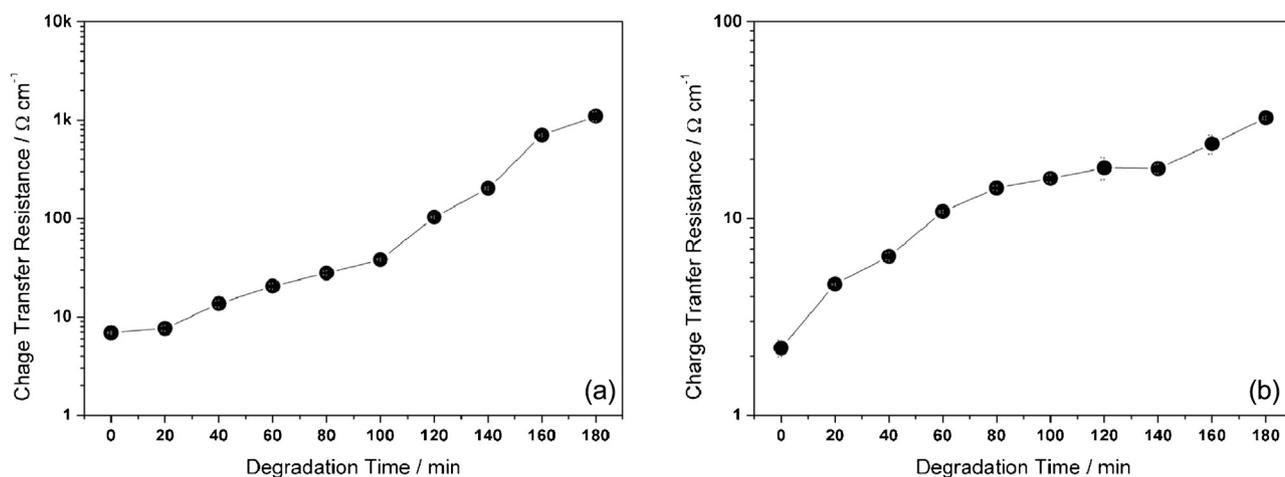


Fig. 6. Charge transfer Resistance for Film I (a) and Film II (b) versus degradation time.

network could be responsible for the change in the material behavior for degradation times higher than 120 min.

Then, considering only Film I the consumption of the network part of the polymer could be related to the change, which is observed at 120 min of degradation. Besides, such transformation

leads to important variation in $R(\text{pol})$, $R(\text{ct})$ as well as in $C(\text{dl})$. For Film II, where only globules are observed changes in the electrochemical behavior upon degradation are also observed and could be explained by the increase of the globules size and density.

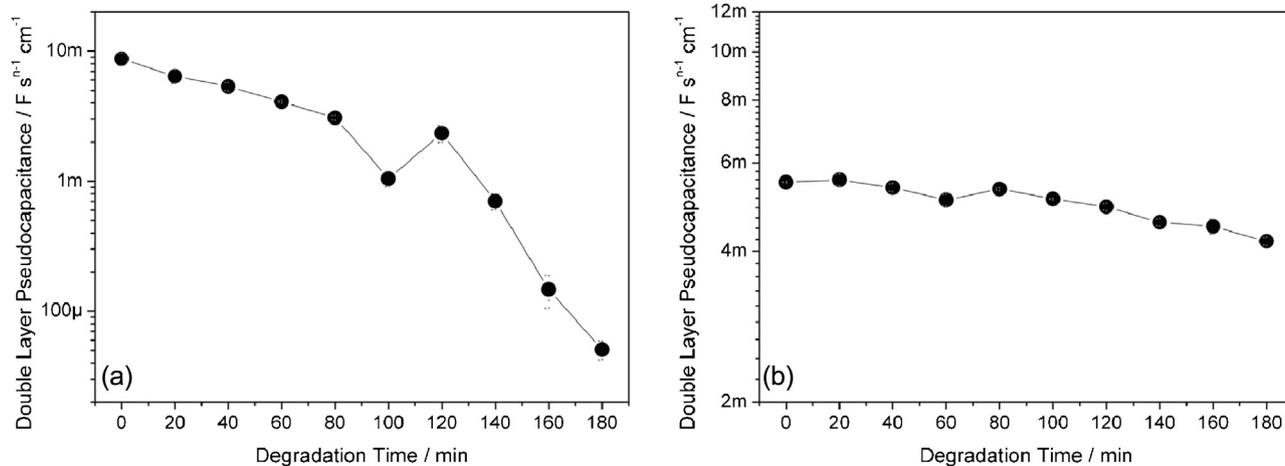


Fig. 7. Double Layer capacitance for Film I (a) and Film II (b) versus degradation time.

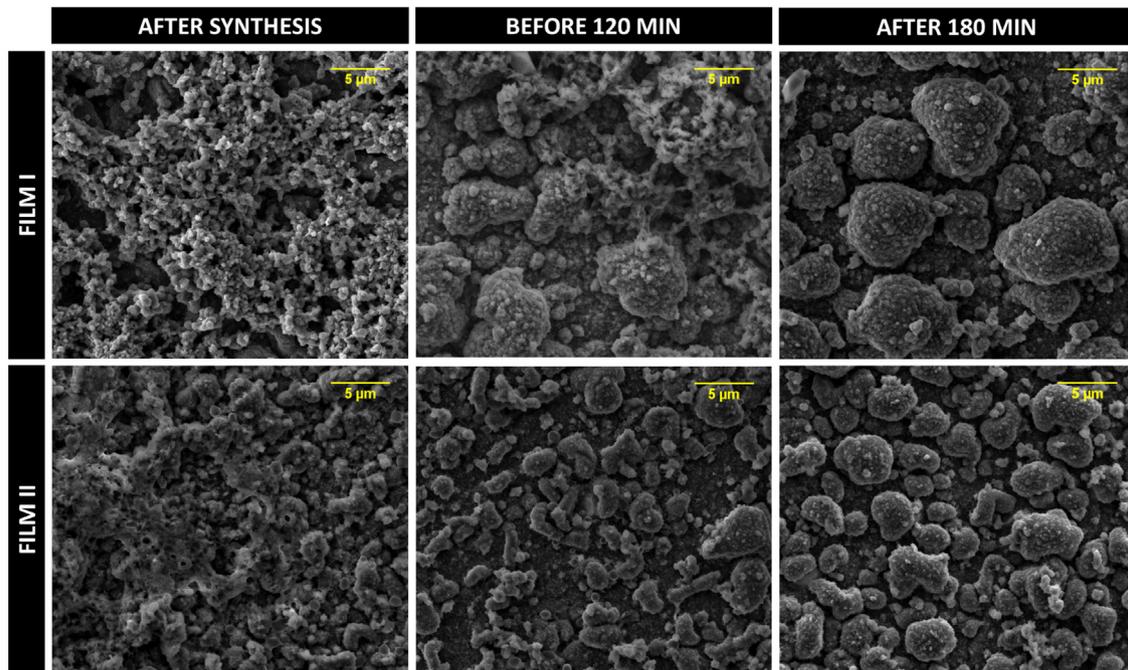


Fig. 8. Scanning Electron Microscopy images of the Films I and II after synthesized, before 120 min and after 180 min of degradation time.

To fit the electronic impedance data it was used an equivalent circuit model. In this configuration setup, there is no ionic intercalation process, then it is not necessary to use a transmission line model. The model consists of a resistor parallel with a capacitor to describe the electronic charge transport, $R(\text{cf})$ and $C(\text{cf})$, respectively. A second resistor in parallel to a second capacitor is necessary to describe the energy barrier between the electrical contact and the polymer, thus $R(\text{co})$ and $C(\text{co})$. Both sub circuits are connect in series, which is a conventional model to interpret semiconductor materials. The Nyquist and Bode diagrams as well as the model used, are present in the supplementary information. Considering the purpose of this work, in Fig. 9, is presented the time variation of polymer resistance for both films, Film I and Film II, as a function of aging time. Film I resistance present an important increase, more than 1000 times, whereas Film II, present a subtle one. These data corroborate that the Film I electrochemical

ageing process is associated also to a polymer chains electronic degradation.

Considering the data above, it is important to point out that the electrochemical aging is complex process which involves morphological changes, changes in ionic transport in the interface, as well as involve electronic charge transport.

4. Conclusions

In this work, by applying an overpotential to superoxidize the polymer, we have studied the effects of electrochemical aging of two films of poly(3-hexylthiophene) obtained at two different experimental conditions. The two selected syntheses have different initial properties as well as proceed by different rates of aging, each of them reaching distinct degrees of degradation. These

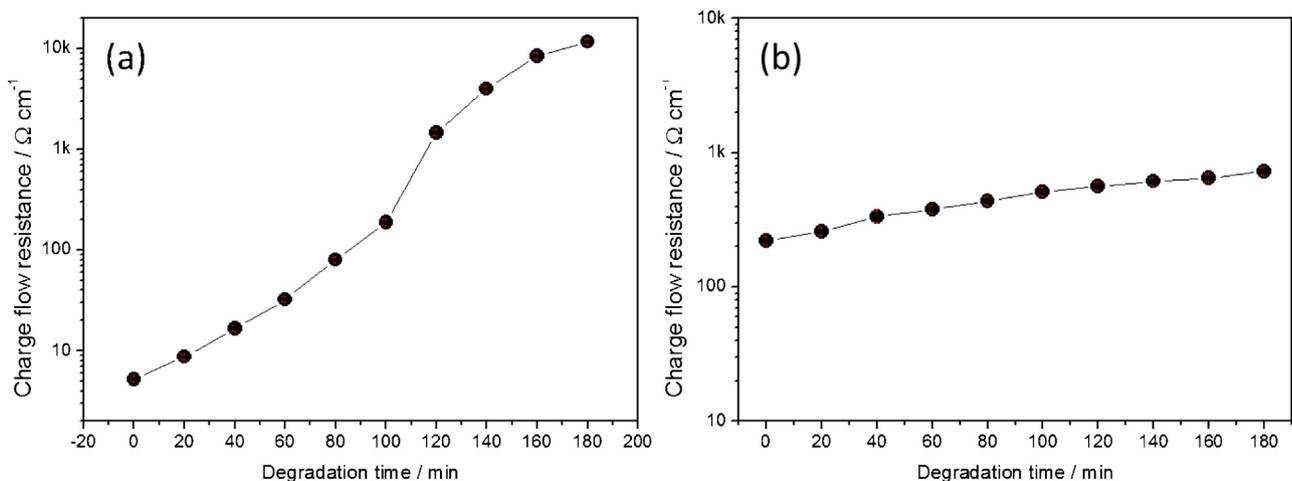


Fig. 9. Charge flow resistance versus degradation time to Film I (a) and Filme II (b).

observations indicate that the synthesis affects the durability of the polymer during the electrochemical aging process.

One of the polymers has shown a smooth degradation preserving most of its properties at the end of the aging process. The other one presents a two-stage aging mechanism. In the first step, up to 120 min, a severe degradation is observed as shown by the changes in all the electrochemical parameters that described the polymer obtained by both cyclic voltammetry and impedance. Then, for this last sample, after 120 min, a second step of degradation is characterized by an overwhelming increase in the polymer resistance and charge transfer resistance. In addition, there is a strong decrease in the capacitance of the double layer that could be related to a change in the polymer wilting decreasing the polymer volume. This last proposition concerning the change in the polymer morphology is in agreement with different works in the literature that emphasize the irreversibility of the aging process.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2015.12.198>.

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