

A comparative study of two different media on the electropolymerization of 2-(9-ethylcarbazol-3-yliminomethyl)phenol: Cyclic voltammetry, impedance spectroscopy, XPS and UV-visible measurements.

Abstract

Carbazole-based monomer, 2-(9-ethylcarbazol-3-yliminomethyl)phenol denoted SIC, was synthesized, characterized and then polymerized by potentiostatic methods. Oxidative polymerization carried out in two media, *i.e.* Bu₄NBF₄ (0.1M)/MeCN and LiClO₄/MeCN + (35 mM) HClO₄, led to two polymers, poly(2-(9-ethylcarbazol-3-yliminomethyl)phenol) denoted PSIC and poly(2-(9-ethylcarbazol-3-yliminomethyl)cyclohexa-2,5-diene-1,4-dione) denoted PDIC, structurally different. The formation of PDIC in acidic medium was explained by the hydroxyl function oxidation of SIC followed, after its hydrolysis, with the formation of two quinones units, ortho and para. Ortho and para quinones were given in evidence by macroscale electrolysis of the monomer at their oxidation potential. The obtained polymers were characterized by cyclic voltammetry, electrochemical impedance spectroscopy, XPS, IR and UV-Vis spectroscopy and their electrochemical band gap values were calculated.

Keywords: *Conducted polymer; Electropolymerization; Cyclic voltametry; Polyimine; Bandgap*

1. Introduction

Electronic polymers are the subject of much research due to their ability to reversible change from an insulating state to a conducting one; this allows their uses in several applications, from energy storage materials to electronic devices. Among the organic polymers, polycarbazoles exhibit an interesting electro-optical and photochemical properties [1,2] due to the high electron-donating character of the carbazole ring. When synthesized in protic medium, polycarbazole films present a fair conductivity and stable redox properties [3], the proton doping playing an important role in the observed electrical behavior [4].

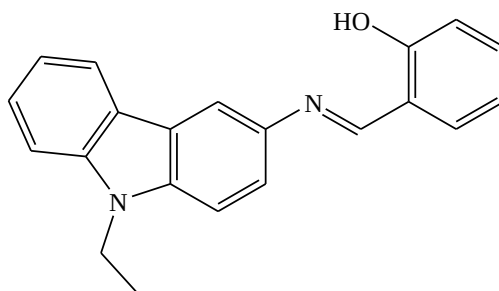
In this present work, we investigated the study of electrosynthesis of a polyimine with carbazole unit. The potential advantage of imine-based polymers is the easiness to prepare their monomers by simple condensation between an amine and an aldehyde. We reported the electrochemical behavior and the anodic electropolymerization of 2-(9-ethylcarbazol-3-yliminomethyl)phenol (SIC) in two electrolytic solutions, in Bu₄NBF₄ and LiClO₄ / HClO₄ in MeCN solvent respectively.

32 2. Experimental

33 2.1. Materials

34 3-amino-9-ethylcarbazole and salicylaldehyde were obtained from *Aldrich*, and used without
 35 further purification. Tetrabutylammonium tetrafluoroborate was obtained from *FLUKA* and
 36 recrystallized in a mixture of water/methanol and dried at 100°C for 24h. Aluminium oxide was dried
 37 at 300°C under vacuum for at least 24h prior to use.

38 The monomer was prepared by condensation between 3-amino-9-ethylcarbazole and salicylaldehyde in
 39 ethanolic medium. A yellow product was obtained with a yield of 65 % (m.p. 114°C).



40 2-(9-ethylcarbazol-3-yliminomethyl)phenol

41 2.2. Electrochemical measurements

42 All electrochemical experiments were carried out using a computer-controlled VoltaLab PGZ
 43 301 potentiostat/galvanostat. All data were collected and analyzed using Voltamaster software. A
 44 three-electrode cell consisting of glassy carbon disk (GCE) as working electrode (1 cm²), an Ag/AgCl
 45 electrode as reference and a platinum wire as counter electrode were used. A 0.1 M solution of
 46 tetrabutylammonium tetrafluoroborate (Bu₄NBF₄) in acetonitrile was used as supporting electrolyte.
 47 Anhydrous Al₂O₃ was added for drying into the electrolytic solution. All solutions were deaerated by
 48 bubbling N₂ gas for a few minutes prior to electrochemical measurements. The potential of
 49 ferrocene/ferrocinium redox couple in the supporting electrolyte-solvent system was measured and
 50 found to be 0.435 V vs. Ag/AgCl. Square wave parameters were pulse half-peak-to-peak $\Delta E_{SW} = 25$
 51 mV, staircase step height $\Delta E_S = 5$ mV and scan rate $v = 100$ mV/sec. The electrochemical impedance
 52 measurements on the modified electrode were done over the frequency range from 0.1 Hz to 100 KHz
 53 with 10 mV as amplitude. For large-scale electrolyses, the working potential was controlled by a
 54 Taccussel potentiostat PRT 20-2X and the charge consumption was measured with a Tacussel IG 6-N
 55 integrator.

56 2.3. Optical measurements

57 UV-Vis measurements were performed on a Jasco V-660 spectrophotometer. The absorption
 58 spectra of the compounds were recorded on ITO glass transparent film (solid phase). *Ex situ*

spectroscopy coupled to electrochemical experiments was used to follow the optical properties of the polymers in neutral and oxidated redox states. The infrared absorption spectra were recorded on a Jasco FT/IR-6300 spectrometer. The XPS analyses were performed with photoelectron spectrometer ESCALAB 250 (Thermo VG).

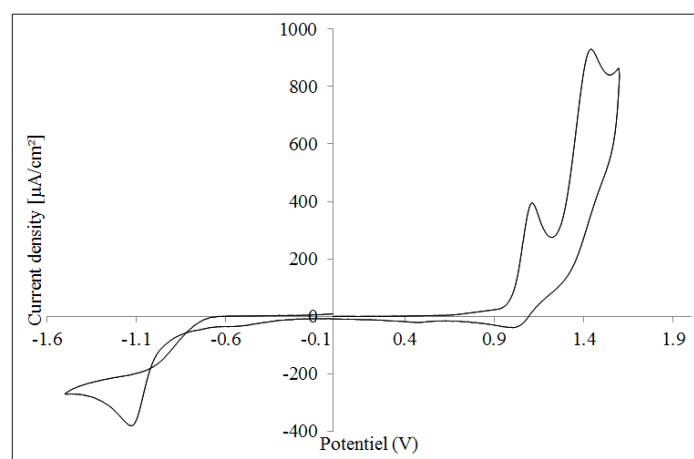
2.4. Theoretical calculations

Theoretical calculations were performed to estimate the theoretical values of the HOMO and LUMO of ortho and para quinones. The geometry optimization is performed by the DFT method using the program Gaussian 09. The used functional is B3LYP (Becke 3-parameter-Lee Yang-Parre). The figures were generated with GaussView 5.0.

3. Results and discussion

3.1. Electrochemical polymerization of SIC in Bu_4NBF_4 (0.1M)/MeCN

The electrochemical behavior of SIC was investigated at GCE electrode by cyclic voltammetry (CV) and square wave voltammetry (SWV). Using CV, the voltammogram obtained during electrooxidation of 5×10^{-3} M SIC in Bu_4NBF_4 (0.1M) / MeCN (Fig.1) showed two peaks, at 1.12 and 1.45 V vs. Ag/AgCl reference electrode respectively. Those two peaks also appeared in SWV's voltammograms (Fig.2), but at slightly lower potentials, at 1V and 1,3 V. This difference may be due to the high sensitivity of SWV technics, compared to cyclic voltammetry [5].



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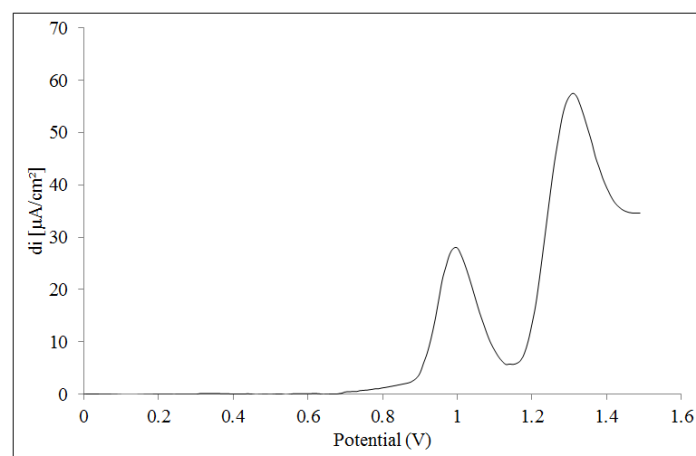
Figure 1. Cyclic voltammogram of **SIC** (5×10^{-3} M) in Bu_4NBF_4 (0.1 M)/MeCN; first cycle, $v = 100$ mV/s; working electrode: GCE; reference electrode: Ag/AgCl

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The first peak probably corresponds to the oxidation of hydroxyl moiety which reacts easily due to the presence of n electrons into the oxygen atom [6] and at this potential, no polymerization of

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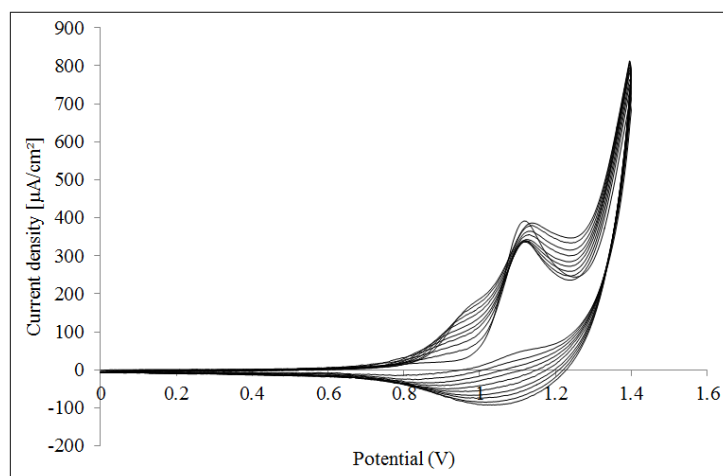
SIC was possible. The second peak corresponds to the formation of the radical cation of the monomer obviously. In the cathodic scan region, SIC showed only one irreversible reduction peak related to the reduction of imine moiety [7].



85

86 **Figure 2.** Square wave voltammogram of **SIC** (5×10^{-3} M) in Bu_4NBF_4 (0.1 M)/MeCN; $v = 100$ mV/s;
87 working electrode: GCE; reference electrode: Ag/AgCl

88 Performed with CV, the electrochemical polymerisation of SIC by recurrent potential scans in
89 the range from 0 V and 1.4 V in Bu_4NBF_4 (0.1M)/MeCN (Fig.3) led to the gradual development of a
90 new redox system centred at lower potential than the monomer, around 1.1 V. The current densities of
91 the new system increased during the successive cycles, indicating that the formed polymer film had a
92 good adherence on the electrode [8].



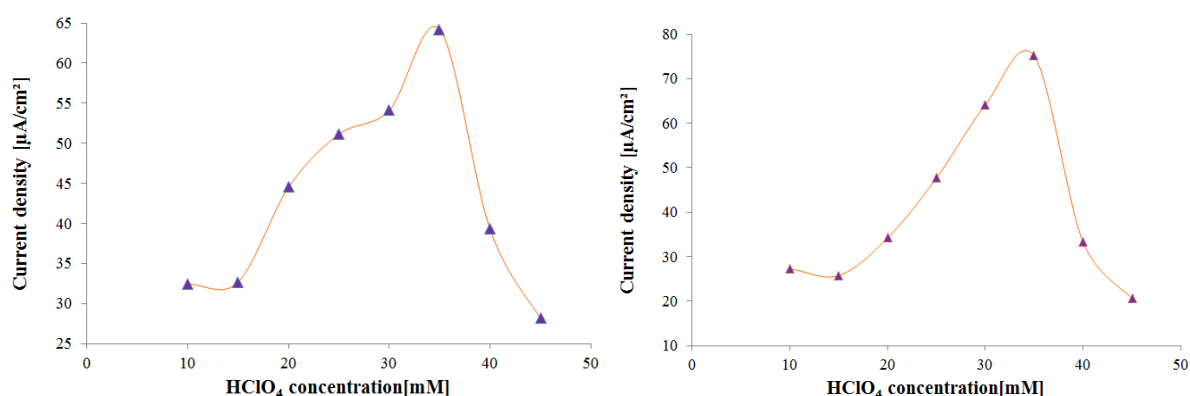
93

94 **Figure 3.** Electropolymerization of of **SIC** (5×10^{-3} M) in Bu_4NBF_4 (0.1 M)/MeCN; 10 sweeps between
95 0 and 1.4 V; $v = 100$ mV/s; working electrode: GCE; reference electrode: Ag/AgCl

96

97 *3.2. Electrochemical polymerization of SIC in LiClO_4 (0.1M)/MeCN in the presence of HClO_4*

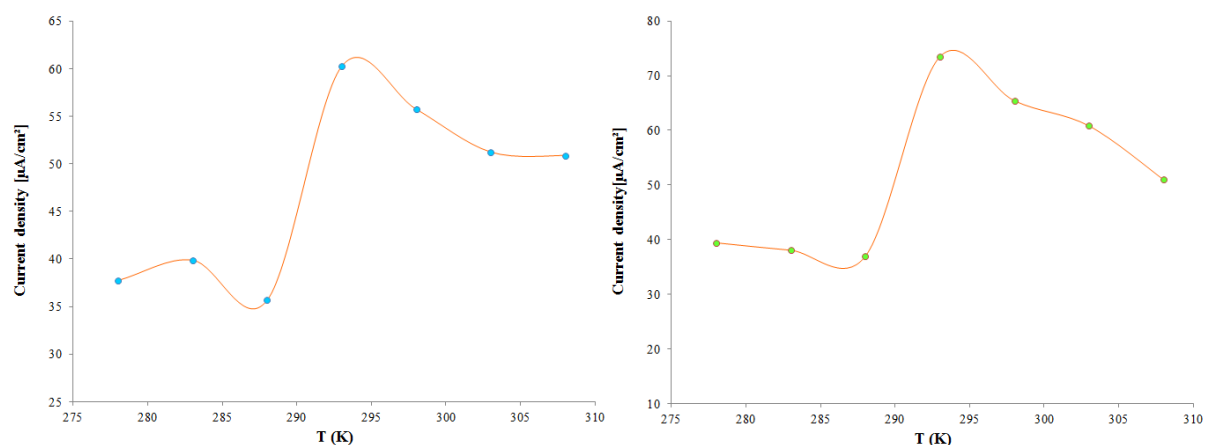
98 In an acidic medium, the imine bond undergoes a protonation which increases commonly the
 99 planarity of the polymeric material and subsequently, improves its electrical properties. A preliminary
 100 study of the SIC electropolymerisation was carried out to specify the appropriate concentration of
 101 HClO_4 to add in the electrolytic solution. Changing the acid concentration from 10 to 50 mM, the
 102 current densities values at p-doping/undoping potential of the PDIC polymer ($E_{1/2} = 1.02\text{V}$) versus
 103 HClO_4 concentration (Fig.4) showed a maximum at 35 mM. Beyond, this value decreased, denoting
 104 that a stronger acid concentration would limit the growth of the PDIC polymer [9].



105

106 **Figure 4.** Influence of HClO_4 concentration on current density measured at p-doping/undoping
 107 potential of PDIC. a) Anodic current density, b) Cathodic current density.

108 The ion mobility is another factor which can influence a potentiodynamic polymerization. This
 109 mobility increases when the temperature increases; however, this is not always a significant option and
 110 can influence the electropolymerization process, providing short, no-structured and less conductive
 111 chains.



112

113 **Figure 5.** Influence of temperature on current density values measured at p-doping/dedoping
 114 potential of PDIC. a) Anodic current density, b) Cathodic current density.

115 The influence of temperature between 5° to 30°C on the polymer electroactivity is shown in
 116 figure 5, which represents the current densities values recorded at doping-undoping potential ($E_{1/2} =$

1.02V) versus the temperature. The anodic and cathodic currents intensities gave a rise simultaneously when the temperature increased from 5°C to 20 °C and then decreased. So, we worked at room temperature, at 20°C, the temperature providing the best electroactivity. The figure 6 presents the cyclic voltammogram obtained during SIC 5×10^{-3} M electrooxidation in LiClO₄ (0.1M)/MeCN + 35 mM HClO₄. The voltammogram exhibited two peaks with unequal intensities, the first at 0.98 V is reversible and we shall show later in the text that it was assigned to the oxidation of hydroxyl function, and the second at 1.32 V is irreversible. However, SWV's voltammogram (Fig.7) shows three oxidation peaks at 0.93, 1.24 and 1.44V. The first peak, as on CV's voltammogram, was assigned to the oxidation of the hydroxyl function, while the second and third peaks, blended in one peak at 1.32 V in CV, were related to the oxidation of imine and carbazole moieties.

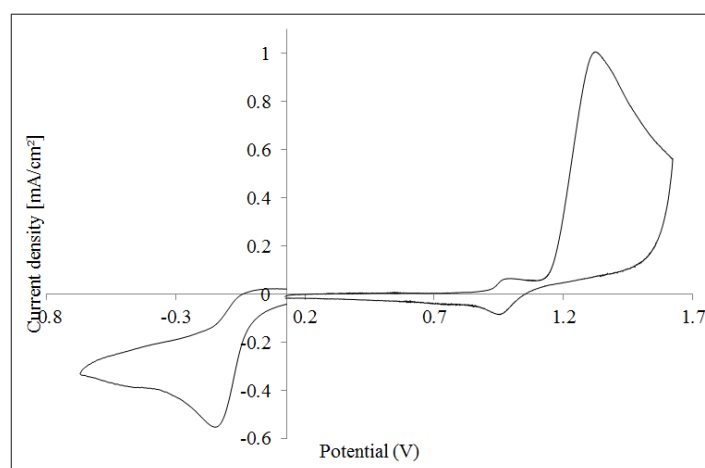


Figure 6. Cyclic voltammogram of **SIC** 5×10^{-3} M in LiClO₄ (0.1 M)/MeCN + 35 mM HClO₄; $v = 100$ mV/s; working electrode: GCE; reference electrode: Ag/AgCl

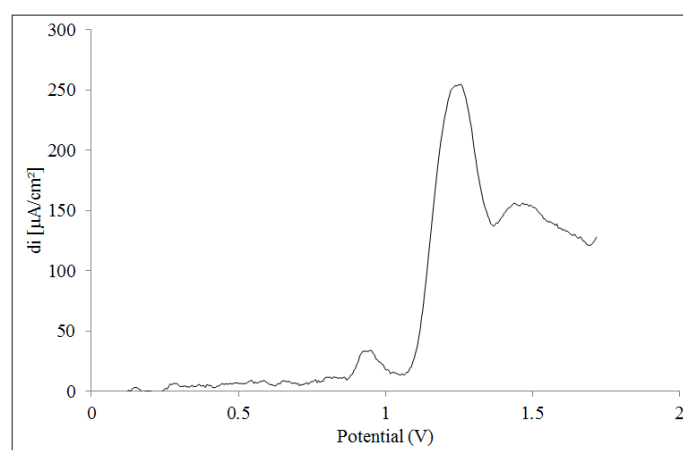


Figure 7. Square wave voltammogram of **SIC** 5×10^{-3} M in LiClO₄ (0.1 M)/MeCN + 35 mM HClO₄; $v = 100$ mV/s; working electrode: GCE; reference electrode: Ag/AgCl

The electrochemical polymerisation of SIC performed in protic medium (Fig.8a) led to the growth of a new redox system centred at lower potentials than the monomer (around 1.02 V) and showed a different electrochemical behavior from which was recorded in aprotic solvent. Thus,

according to Enache T.A. and *al.*, the oxidation of differently substituted phenols in acidic medium on glassy carbon occurs at 1V, before oxidation of the conjugated system of the monomer in this study, and leads to a fast hydrolysis of the phenol resulting in the formation of two products, ortho-quinone and para-quinone (schemes 2 and 3). The both compounds showed a reversible electrochemical behavior with the transfer of two electrons and two protons [6]. In this study, on the negative-going of the first scan (Fig.8b), the two very weak reduction peaks recorded at 0.39 and 0.67 V were attributed to the reduction of the two 2-substituted phenol oxidation products, the peak at 0.85 V corresponding to the OH oxidation. E_{Red2} corresponds to the reduction of ortho-(2-substituted)quinone in ortho-(2-substituted)catechol, and E_{Red1} corresponds to the reduction of para-(2-substituted)quinone in para-(2-substituted)hydroquinone. On the second positive scan (Fig.8b), two anodic peaks were recorded at $E_{Ox1} = 0.5$ V and $E_{Ox2} = 0.72$ V, showing the reversibility of the two reductive peaks of quinones.

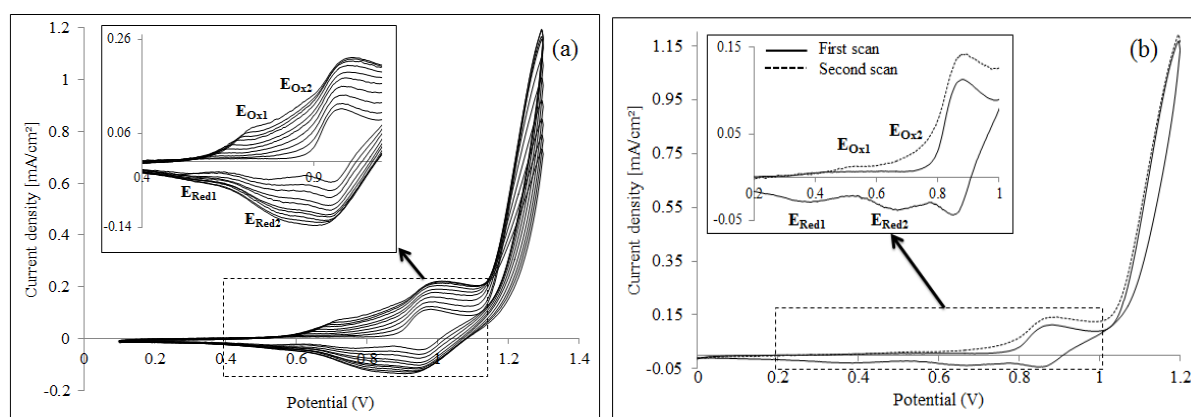


Figure 8. Electropolymerization of SIC (5×10^{-3} M) in LiClO_4 (0.1 M)/MeCN + 35mM HClO_4 ; $v = 100$ mV/s; between 0 and 1.29 V; working electrode: GCE; reference electrode: Ag/AgCl a) 10 sweeps; b) First and second sweep.

So, in the protic medium, the protoned monomer (SIC) undergoes hydrolysis around 1V, which modifies its structure before its polymerization. This reaction which is very fast, lead to the formation of two isomers, *para*-quinone and *ortho*-quinone which oxidizes at the same potential. Therefore, the theoretical calculations showed that the two isomers para- and ortho- quinones, have practically the same HOMO value (-5.46 eV and -5.4 eV, respectively), and a very near LUMO value (-3.41 eV and -3.53 eV, respectively) (Fig.9).

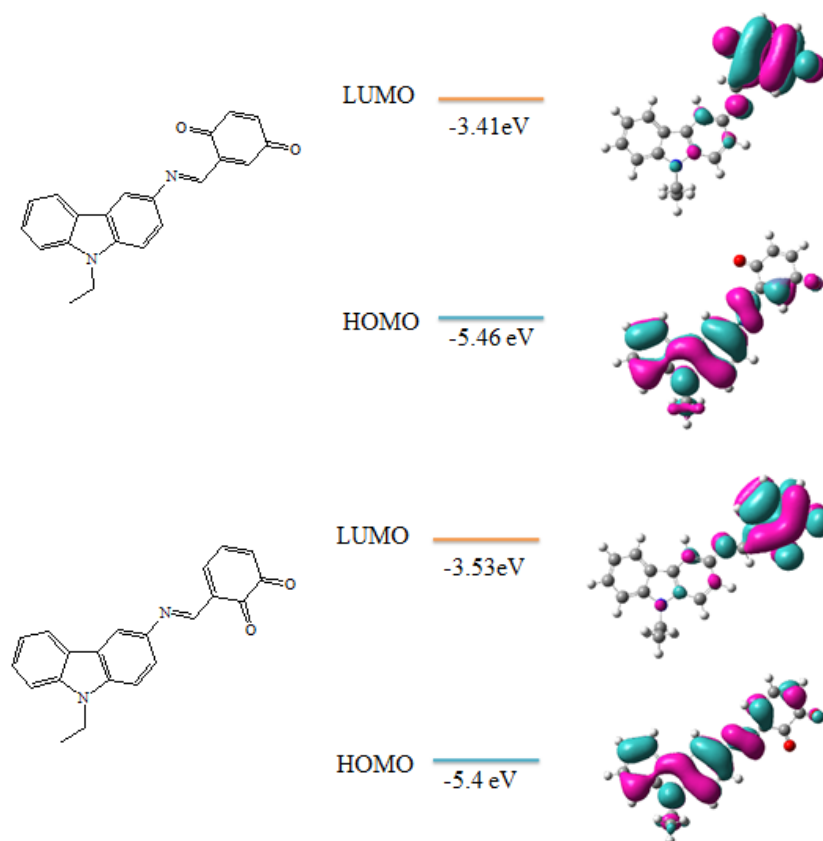


Figure 9. The contour plots and energy values of HOMO and LUMO orbitals of *para*- and *ortho*-quinone compounds.

The variation of the potential of the first oxidation peak of SIC as a function of the logarithm of sweep rate $E_{pa}=f(\log v)$ was a straight line (Fig.10) with zero slope value, confirming that the oxidation of hydroxyl function occurred rapidly [10] and was in a good agreement with the literature.

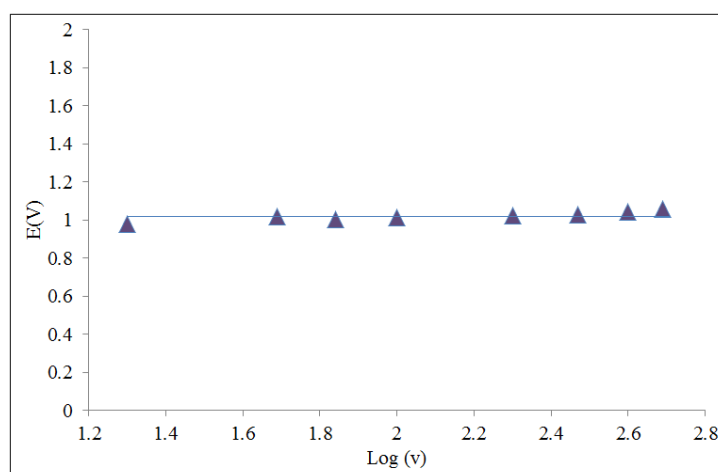


Figure 10. Variation of the potential of the first oxidation peak of **SIC** as a function of the logarithm of sweep rate $E_{pa}=f(\log v)$ on GCE in LiClO_4 (0.1 M)/MeCN + 35mM HClO_4 . Scan rates from 20 to 500 mV/s.

To confirm that the nature of the compounds formed was due to the hydrolysis of hydroxyl function, a large-scale electrolysis of SIC at controlled potential value of 0.96 V was carried out. A nacre white product was formed immediately, which once again confirmed the velocity of the reaction. The ^1H NMR spectrum (Fig.11) of the obtained precipitate, denoted DIC, is in accordance with the disappearance of the OH function after oxidation; moreover, the two peaks of phenolic ring protons recorded between 6.98 and 7.37 ppm before oxidation, have moved to smaller values namely 6.3 to 6.5 ppm, reflecting therefore the change in the environment of the corresponding protons.

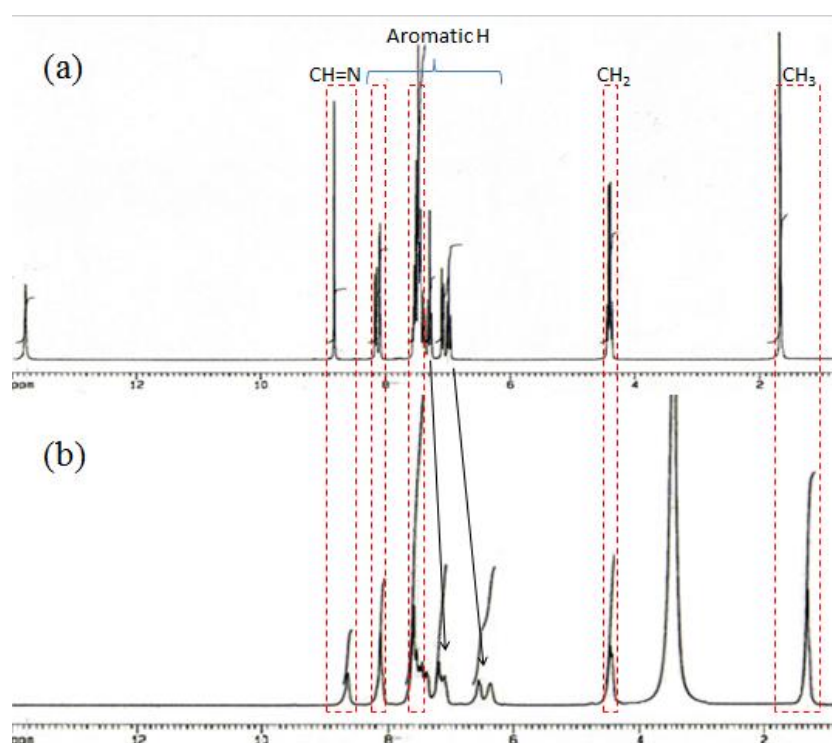
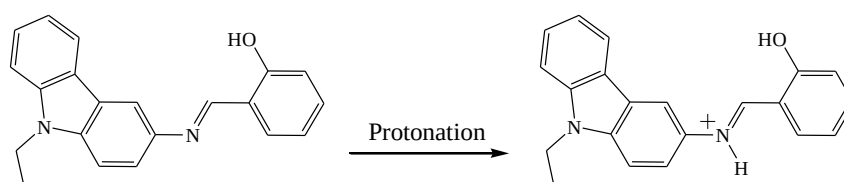


Figure 11. ^1H NMR spectrum of a) SIC, b) DIC.

Furthermore, the color change that occurred when we dissolved SIC in MeCN with $\text{LiClO}_4(0.1\text{M})/35\text{ mM HClO}_4$ led us to think that SIC underwent a chemical protonation. Treated with a solution of HClO_4 (35 mM) in MeCN, SIC changed color from yellow to orange and its infrared analysis showed the appearance of new bands (Fig.12) of which the signal recorded at 1229 cm^{-1} was assigned to the vibration of the group C-N^+ [10]. So, we can presume that SIC underwent a protonation before its electropolymerization (Scheme.1).



Scheme.1 Protonation of SIC

From these data, we can say that the electropolymerized monomer in the protic medium is different from that electropolymerized in organic medium. DIC is composed of two isomers, ortho and para-quinone (Scheme.2) that exhibited a redox behavior with a transfer of two electrons and two protons (Scheme.3).

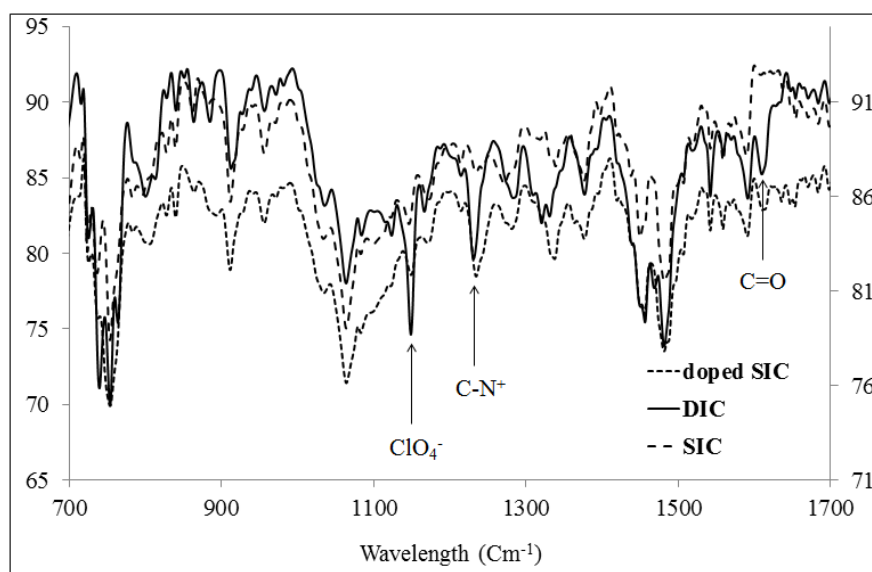
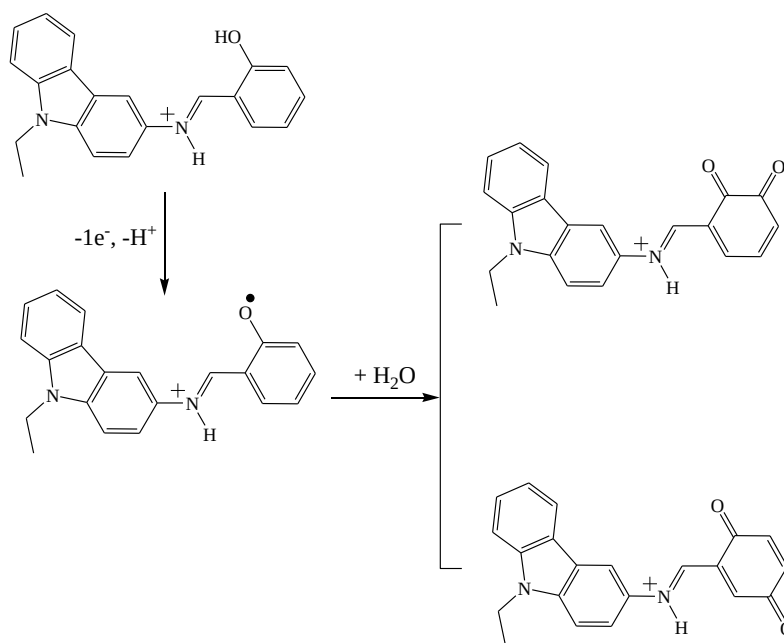
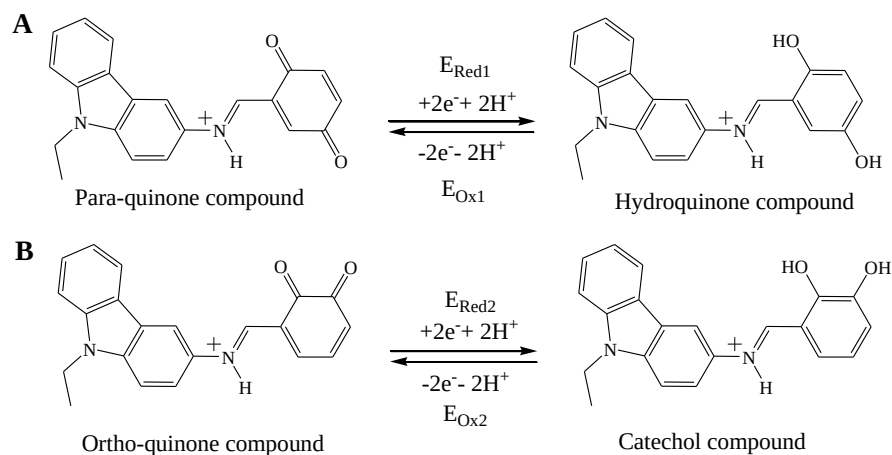


Figure 12. IR spectra of SIC (---), DIC (—) and protoned SIC (·····).



Scheme 2. First oxydation mechanism of SIC



Scheme 3. Redox behavior of: A) Para-quinone compound, B) Ortho-quinone compound.

3.3. Polymers electroactivity

The study of electrodeposited films of PSIC and PDIC polymers in both electrolytic media was done in another cell containing only the electrolytic solutions, without monomer. During the positive scans, in the two media (Fig.13), voltammograms showed the redox behavior corresponded to the positive doping/undoping process, due to the participative accumulation of anionic charges, BF_4^- and ClO_4^- respectively in the polymeric matrices, pointing out the electroactive nature of the formed materials [11]. On the other hand, in the protic medium, the redox peaks appearing at $E_{1/2} = 0.61V$ was related to the redox moiety para-quinone / hydroquinone [6] in the polymer matrices. However, the redox system corresponding to ortho-quinone/catechol moiety was overlapped with the one of PDIC. The electrochemical behavior of PSIC and PDIC affirms the difference existing between the structures of the both polymers.

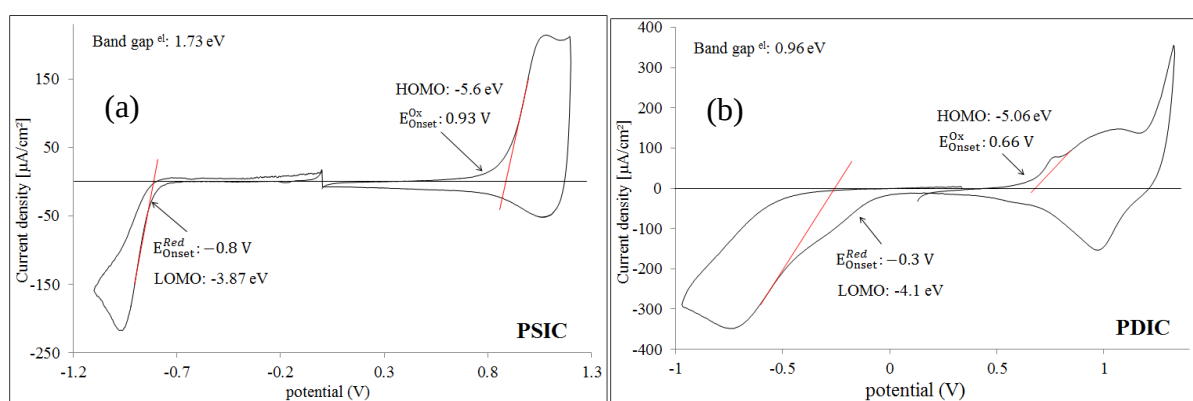


Figure 13. Cyclic voltammograms for oxidation of: a) **PSIC** coated GCE in Bu_4NBF_4 (0.1 M)/MeCN; b) **PDIC** coated GCE in $LiClO_4$ (0.1 M)/MeCN + 35mM $HClO_4$. $v = 100mV/s$.

The thin layer film of both polymers was analyzed by XPS as this measurement is much more sensitive than IR. The XPS spectra of PSIC and PDIC films deposited on ITO are represented on figure 14. Either for PSIC or PDIC, the band at 399.9 eV corresponds to the N_{1s} signal, whereas the one at 532.5 eV to the signal of O_{1s} [12]. In the spectrum of PSIC, there are two bands in the C region (Fig.15), corresponding to C-C (284.7eV) and C-OH (286.5 eV) [13]. However, in the spectrum of PDIC, we have the band of the C-C (284.7eV) accompanied by another one at 288.2 eV (Fig.16) corresponding to C=O energy [14].

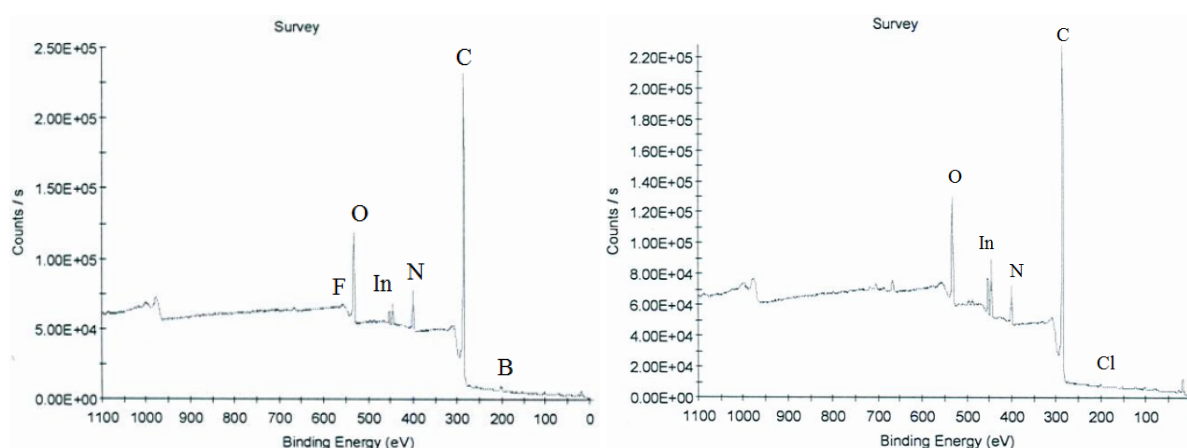


Figure 14.Survey spectra of ITO coated with a) PSIC, b) PDIC

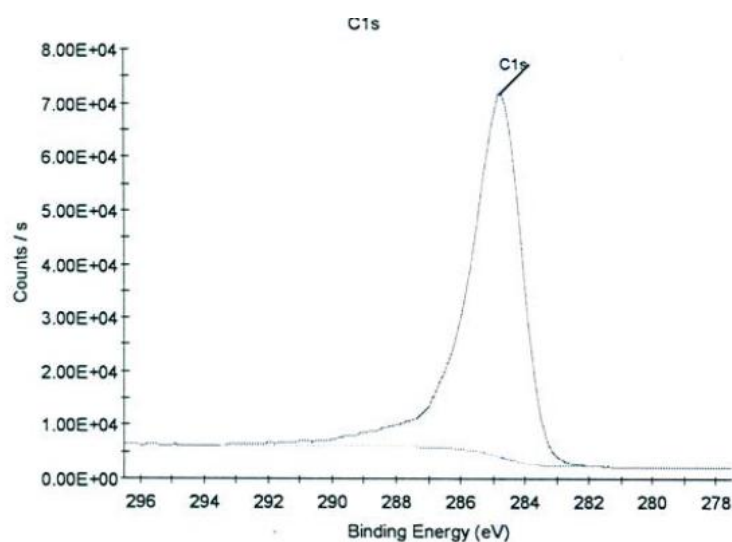


Figure 15.Survey spectra of ITO coated with PSIC.

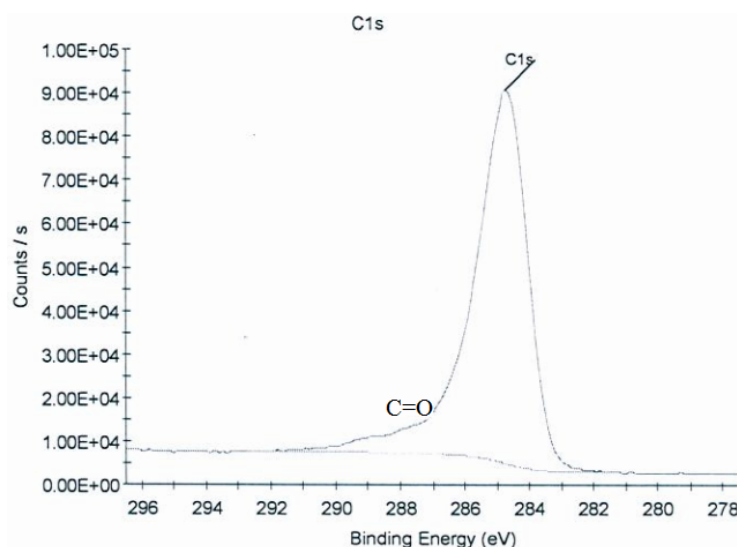


Figure 16. Survey spectra of ITO coated with PDIC.

3.4. Calcul of the electrochemical bandgap

The properties of conjugated polymers depend on their structures and the delocalization of π electrons that is related to the planarity of the chain. Thus, due to its protonated state, the PDIC would be more planar than the PSIC and then, its electrical properties would be better, which resulted in a reversible electrochemical response (Fig.13b).

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels could be estimated by cyclic voltammetry from the onset of oxidation and onset of reduction potentials according to the equations [15]:

$$E_{\text{HOMO}} (\text{eV}) = - [E_{\text{onset}}^{\text{ox}} + 4.4]$$

$$E_{\text{LUMO}} (\text{eV}) = - [(E_{\text{onset}}^{\text{red}} + 4.4)]$$

The obtained results of the difference in energy E_g between HOMO and LUMO were presented in Fig.13a and 13b and summarized in Table.1.

Table 1. Electrochemical band gaps.

	$E_{\text{onset}}^{\text{ox}}$ (vs.Ag/AgCl) ^a	$E_{\text{onset}}^{\text{red}}$ (vs.Ag/AgCl) ^a	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g^{el} (eV) ^b
SIC	1.20	-0.96	-5.87	-3.71	2.16
PSIC	0.93	-0.80	-5.60	-3.87	1.73
DIC	1.14	-0.01	-5.54	-4.39	1.15
PDIC	0.66	-0.30	-5.06	-4.10	0.96

^a The onset potentials are determined from the intersection of the two tangents drawn at the rising current and baseline charging current of the CV courb . ^b Energy of the band-gap calculated from the difference between the energies of the HOMO and the LUMO band [15].

The electrochemical bandgap recorded for the PDIC is very smaller than that recorded for the PSIC and is an indication reflecting the conductivity of the material, which is related to the doping level. Indeed, when a polymer is oxidized, by analogy of the admitted results, an electron is removed from the HOMO and a positive polaron or radical cation is created. The energy level associated with that positive polaron, partially relocated on monomer units of the polymer chain, is represented by a destabilized bonding orbital of which the energy is higher than the energy of the HOMO. Furthermore, the protonation of imine moiety, which was preferably compared with that of the amine sites [16], increases planarity of polyazometines [17], which induced a reduction of the LUMO and an increase in the HOMO, and subsequently a decrease of the bandgap. So, it was clear that in the medium containing LiClO_4 (0.1M) / MeCN + 35 mM HClO_4 , the PDIC underwent protonation and electrochemical doping, which explained a low energy bandgap.

3.5. Electrochemical impedance measurements

The electrochemical impedance spectroscopy helped us to understand the charge transport mechanism of the electrolyte ions during the redox reaction. A lot of work has been focused on the mass transport in conducting polymers. However, due to the complexity of these phenomena, their complete understanding is not achieved yet. The impedance measurements were performed at a potential corresponding to the oxidation state of polymers, around 1 V.

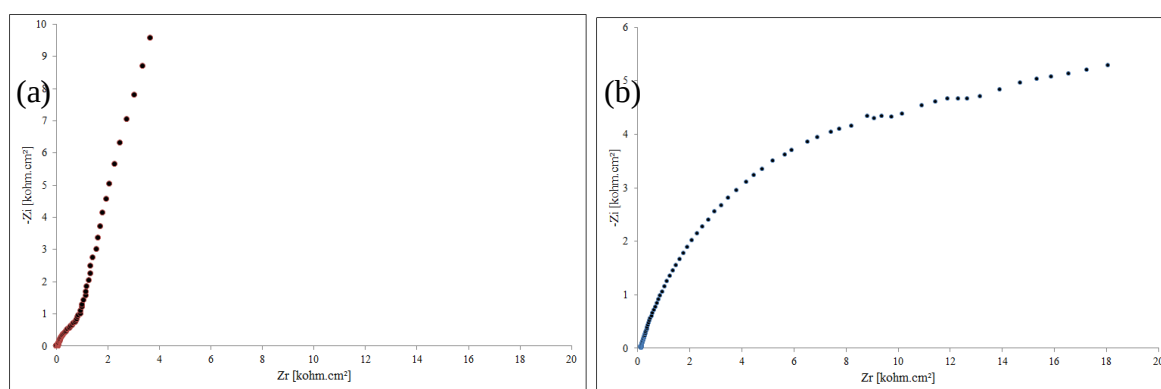


Figure 17. Nyquist diagrams of: a) PDIC, b) PSIC.

The figure 17 shows the nyquist diagrams of the CCE coated with PSIC in Bu_4NBF_4 (0.1 M)/MeCN and PDIC in LiClO_4 (0.1 M)/MeCN + 35mM HClO_4 . The diagram corresponding to the PDIC (Fig.17a) is characterized by a beginning of arc in high frequency region which is assigned to the charge transfer at the contact interface between the coated electrode and the electrolyte solution. For low frequency region, on one hand, the nyquist plot of PDIC presented a straight line with slope of 45° which was typically assigned to diffusion in film. On the other hand, the low-frequency region was assigned to diffusion process of the counter-ions of the electrolyte in the polymer film. Nyquist

diagram of PSIC (Fig.17b) showed also a beginning of arc in high frequency. However, there was a difference between the diameters of the semicircles. The charge resistance of PDIC film was much lower than that of PSIC film, and consequently, the PDIC is more conductive than the PSIC [18].

3.6. Electrochromic properties

Optical properties of the polymer films on ITO glass were observed by recording the changes in the absorption spectra under voltage at 0V and 1V. The electronic absorption of neutral films exhibited an absorption band around 355 nm and 305 nm for PSIC and PDIC, respectively. These bands which were due to $\pi \rightarrow \pi^*$ transition lose intensity during oxidation.

Prepared in LiClO_4 (0.1M)/MeCN/ HClO_4 (35 mM) electrolytic solution, the PDIC thin layers presented a slightly yellow color at 0.0 V potential. This color became green when the film was polarised at 1.0 V. This color change was accompanied by a modification in the optical spectrum (a broad band around 560 nm) (Fig.18). Prepared in Bu_4NBF_4 (0.1M)/MeCN electrolytic solution at 1.0 V, the PSIC thin layers presented a light brown color and showed no change in color when it was polarized in the same medium. However, polarised at 1.0 V in the LiClO_4 (0.1M)/MeCN/ HClO_4 (35 mM) electrolytic solution, the film of PSIC turned red brick. This color change was accompanied by the appearance of an absorption band at 477 nm (Fig.19). So this spectral consequence of oxidative doping, the change in color, was supposed to be due to protic medium.

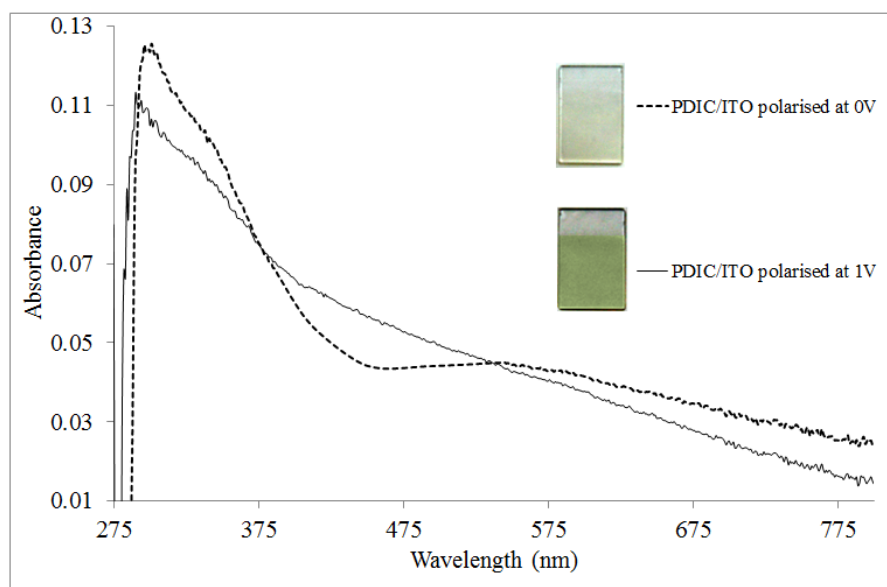


Figure 18. The absorbance versus the wavelength registered with PDIC / ITO polarized in the LiClO_4 (0.1M) / MeCN + (35mM) HClO_4 , at: 0V (-----) and 1V (---). SIC/ITO (—).

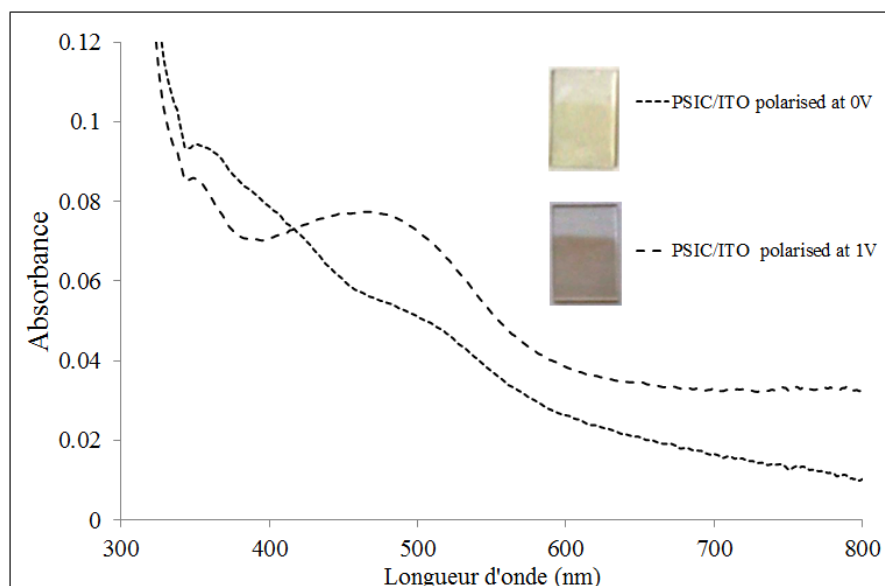


Figure 19. The absorbance versus the wavelength registered with PSIC / ITO polarized in the LiClO_4 (0.1M) / MeCN + (35mM) HClO_4 at: 0V (-----) and 1V (---). SIC/ITO (—).

The difference in surface topography was observed by the atomic force microscopy working in the contact mode (Figure 20). The 3D view shows that there are numerous smaller surface undulations with a precipitation of different shapes [19]. However, we notice that precipitations in PDIC are not as numerous as in the PSIC thin film.

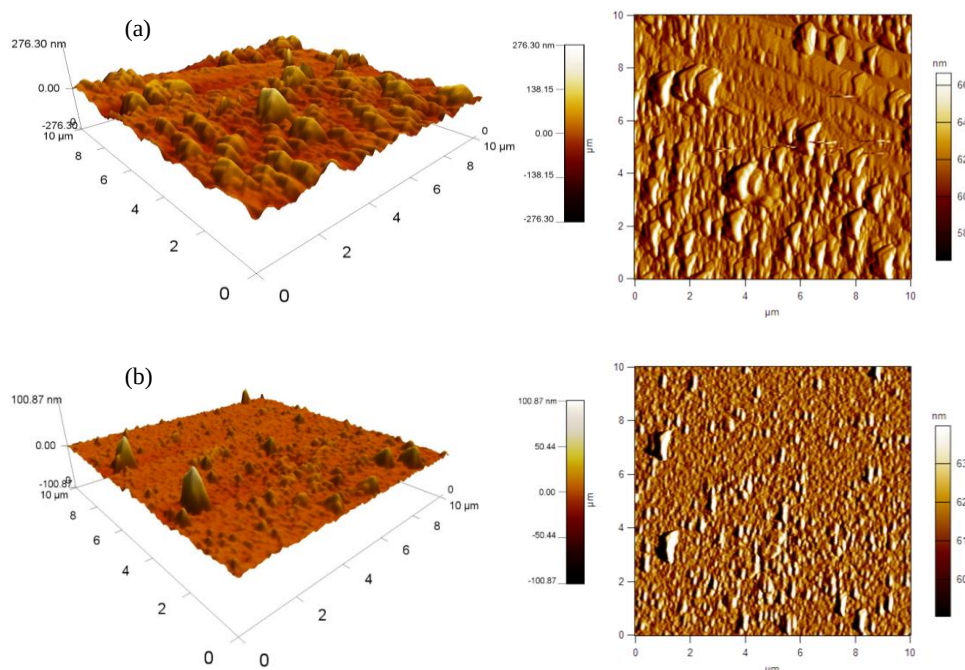


Figure 20. AFM image of: a) PSIC thin layer, b) PDIC thin layer.

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317 **References**

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