

Electro and Spectrochemical Behavior of Poly Carbazol-9-Yl-Methanol

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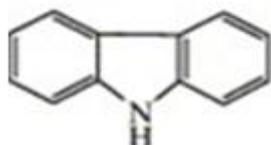
Abstract: Electroactive polycarbazol-9-yl-methanol (PCz-CH₂OH), film was formed on Pt electrode surface by oxidative electropolymerization of a new carbazole derivative. Electrochemical polymerization was carried out in a reaction medium containing monomer and 0.1M tetrabutylammonium tetrafluoroborate (TBABF₄) mixture in acetonitrile (ACN) using repetitive cycling at a scan rate of 100 mV. Electrochemical polymerization of carbazole (Cz) and carbazol-9-yl-methanol(25mM) were studied with cyclic voltammetry on both platinum (Pt) and indium tin oxide (ITO) electrodes. The polymers were characterized using FTIR, Raman spectroscopy, UV VIS, ¹H NMR, and ¹³C NMR spectroscopy.

I. Introduction

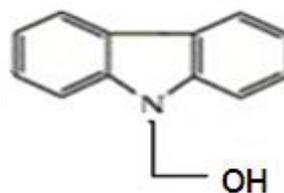
Polymers such as polypyrrole, polyaniline, polythiophene, and polycarbazoles that have been extensively studied for their synthesis, characterization and applications. The electrochemical and spectroscopic techniques have been employed in elucidation of anodic oxidation pathway of carbazole and N-substituted derivatives. However, lately other classes of polymers like polycarbazole are gaining considerable attention due potential applications in light emitting diodes (OLED); as green and blue light emission was achieved using carbazole (Cz) derivatives. Sensors and rechargeable batteries (Anodic oxidation) of carbazole and its N-substituted derivatives were, extensively studied by Ambrose et al. They investigated the reactivity of cation radicals formed from benzene ring substituted carbazole using electrochemical and spectroscopic techniques [1].

Poly(N-substituted carbazoles) show interesting optical and electronic properties that have been used in field effect transistors, electroluminescent diodes and batteries. Previous work has shown that poly(N-substituted carbazoles) are colorless when neutral, green at an applied potential of 0.7V versus saturated calomel electrode (SCE), and blue at 1.0V. [2]. Many heterocyclic nitrogen compounds, like carbazole, attracted attention as conducting polymers because of their electrical and photoelectrical properties, for this reason carbazole and its derivatives of poly(N-alkyl-3,6-carbazolene) were the first reported π -conjugated polymer containing carbazole [3,4]. The conductivity of carbazole containing polymers such as poly N-vinyl carbazole was reported by H.Hoegl [5]. Their photoconductive [6], electrochromic behavior [7] promised a wide range of applications[8,9,10]

The most widely studied conducting polymers are polyaniline, polypyrrole, and poly thiophenes. Relatively, little attention has been paid to chemical polymerization of the above conducting polymers. Chemical polymerization is of particular importance since this synthesis is the most feasible route to large scale production. Moreover, it was shown that synthesis yield polymers of high molecular weights[11].



Carbazole



carbazol-9-yl-methanol or N-methanol carbazole

II. Materials And Methods

2.1 Materials: All chemicals the of Analar grade obtained from Aldrich and BDH .

2.2.Methods: Normal cyclic voltammograms were carried out using CH1700B,CH1400, EG&G, model-273 potentiostat-galvanostat [12]

FT IR spectra was obtained using Thermo model-NICOLET-İS 10 FTIR [12].

NMR spectra wAS using 400MHz AV NMR spectrometer[12].

The UV-VIS-NIR spectra were taken using Lambda 75 spectrophotometer of Perkin Elmer Raman spectroscopy using Surface enhancement Raman spectroscopy DeltaNu (SERS). The morphology after electropolymerization on the ITO electrode, the obtained film was coated with silver (Ag) and characterized by SEM.[12]. Measure Conductivity was measured using four-probe techniques[13].

III. Results And Discussion

Polymethanol carbazole was formed in acetonitrile on disk electrode. When few cycles are applied a thin film, of a green colour, was deposited but partially dissolves in blank solution. After successive cycles a dark green polymeric film was obtained. However, CVs of poly N-methanol carbazole were not observed due to polymer high solubility in blank solution.

Figure 3.1 shows the Cyclic voltammograms (CVs) of PCz thin films electrochemically deposited on Pt disc electrode recorded in 0.1 M TBABF₄ as supporting electrolytes in acetonitrile. The onset potentials of carbazole oxidation with TBABF₄/ACN were obtained at 0.96 and 1.05V respectively. Figure 3.2 shows the multisweep scans and clearly shows the gradual growth of polycarbazole. CVs are the same in acidic and neutral media but solubility is decreased in acidic media.

Figure 3.3 shows that the direct electropolymerization of the monomer occurred in the first cycle at oxidation and reduction potentials of 1.45volts and 0.95volts respectively (Table 3.1).

Table 3.1 oxidation and reduction potential of carbazole and its derivatives.

	E _{pa} (oxidation of monomer(V))	E _{pc} (reduction of poly carbazole)
Carbazole	1.37	0.90
N-methanol carbazole	1.45	0.95.

Figure 3.4 shows the polymerization of N-methanol carbazole in acidic media(25Mm HBF₄). Homogenous and stable polymer was obtained after adding acid, also the polymer solubility was decreased which showed in blank solution in (figure 3.5), but the film was not homogenous.

The dry conductivity of poly carbazol-9-yl-methanol was measured as 6.7x 10⁻³ S/cm using four probe point dry conductivity measurement technique.

Figure 3.6 shows The FTIR of polycarbazol-9-yl-methanol. The strong band at 3401cm⁻¹ in monomer is assigned to O-H group. The absorption was strong and broad. All the peaks are broader after electrochemical oxidation, as we shown for N-H group was shifted to 3547cm⁻¹ and all peaks are broader after electrochemical oxidation this result has agreement with literature [14,15]. After electropolymerization O-H band disappeared. The band at 1620 cm⁻¹ may be attributed to C=O group which produced in replacement of O-H group. The band at 1215 cm⁻¹ attributed due to C-O group. The band at 1215cm⁻¹ due to C-H bending vibration. The band at 1400-1600 spectral range assigned to the ring in acidic media after electrolysis holding potential at 1.4V.

Figure 3.7 shows the UV-vis spectrum of poly N-methanol carbazole in the region of 350-800nm. Two main absorption peaks could be observed, the peak around 350nm is due to conjugated double bond of benzene ring of poly N-methanol carbazole for (π-π*) transition. The broad band around 600 nm was the characteristic of conductive species due to (n-π*) which is in agreement with literature [16].

Figure 3.8,3.9 shows ¹H NMR(aromatic range) for polycarbazole and poly N-methanol carbazole respectively obtaining using aBurker 400 MHz AV NMR. using concentration of 80mg/ml for sample.

¹H NMR of monomer: (from literature)
8.12 (H,d), 7.8 (2H,s),7.7(H,s),7.1(H,m).

The above spectrum showed the value of NMR of monomer polymer of carbazole, which is in agreement to literature. [17,18].

¹H NMR of monomer (h2), at 8.15(CH,d),7.55 (CH,d), 7.4 (CH,t), 7.2 (CH,t).

¹H NMR of polycarbazole(h1), at 8.6 (CH,s)8.25 (CH,d), 7.7 (CH,d), 7.6(CH,d), 7.5(CH,d), 7.4(CH,t), 7.2(CH,t).¹H NMR of polycarbazole(h3), at 8.6 (CH,S)8.25 (CH,d), 7.7 (CH,d), 7.6(CH,d), 7.5(CH,d), 7.4(CH,t), 7.2(CH,t).

The ¹H NMR of carbazol-9-yl-methanol (Cz-CH₂OH) exhibits the peaks in aromatic range. ¹H NMR of monomer of Cz-CHOH (h5). The doublet peak at 8.16 due to 1H at 4, 5 position, the doublet (CH, d) at 7.70 ppm due to 1H at 1,8 position, the triplet at 7.45 (CH, t) due to 1H at 2, 7 position, the other triplet peak at 7.25 ppm due to 1H(CH, t), at 3, 6 position. The triplet peak which was appeared at 6.45 ppm (CH₂,t) due to OH group and the doublet at 5.8 due to aliphatic CH₂ bounded to OH (CH₂,d) (Figure 3.9). As mentioned above, the polymerization mainly proceeds by C-C and C-N couplings but in our derivatives C-N couplings does not appear because the N atom closed by substituted.

Figure 3.10 and 3.11 show ¹³C NMR spectrum (aromatic range) for polycarbazole and poly Carbazol-9-yl -methanol¹³C NMR δ (ppm) (DMSO-d₆) of monomer (h2), 140 (quaterner a),126(C₂), 123(quaterner

b),121(C₄),119(C₃),111(C₁). ¹³C NMR δ (ppm) (DMDO-d₆) of PCz (h1),139 ,131,136 124,,121,122,118,117, ,110 ¹³C NMR δ (ppm) (DMDO-d₆) of PCz (h3),139 ,,131,136,124,,121,122,118,117, ,110

¹³C NMR spectra of these polymers showed six main peaks assigned to the carbons of the two carbazole rings. ¹³C NMR δ (ppm) (DMDO-d₆) aromatic range of monomer (h5),139.68 (quaterner a), 125.90 (C₂), 122.50 (quaterner b),120,12(C₄),119.31(C₃),109.73 (C1).

¹³C NMR δ (ppm) (DMDO-d₆), PC-CH₂-OH (h4) 140.5, 139.31 , 133.31, 126.22, 125.44, 123.67, 120.81, 122,119.85, 118.61, 110.25, 110.18.

The polymer was not formed in acidic media or degradation may be occurs in situ (Figure 3.11).

Figure 3.12 and 3.13 show the Raman spectra of polycarbazol-9-yl-methanol and its polymer respectively carried out using Surface enhancement Raman spectroscopy(SERS) of polycarbazol-9-yl-methanol. The monomer's spectrum the absorption of group C-O str. at 1016 nm, absorption at 1378 attributed to arom.C-H bend,1520 due to C=C str., and 1605 C=O str. This values differ when compared with values of poly carbazol-9-yl methanol. (figure 3.12).

Figure 3.14 show the Raman spectra of (ITO+Ag as base line.) As shown there are some differences between Raman and FTIR and spectrums are very complicated due to the fact that some substances are IR inactive but Raman active or vice versa. Raman line intensities are greatly enhanced by excitation with wavelength which are closer to the electronic peak of substance and due to photochemical reaction that may occurs. However, filters are used in Raman instrument, as the photo decomposition or fluorescence is very high [19]. The intensity of Raman peaks depend on intensity of the source, active groups and polarizability

Figure 3.15,3.16 show show the SEM micrographs of oxidized polycarbazole and polycarbazol-9-yl-methanol respectively

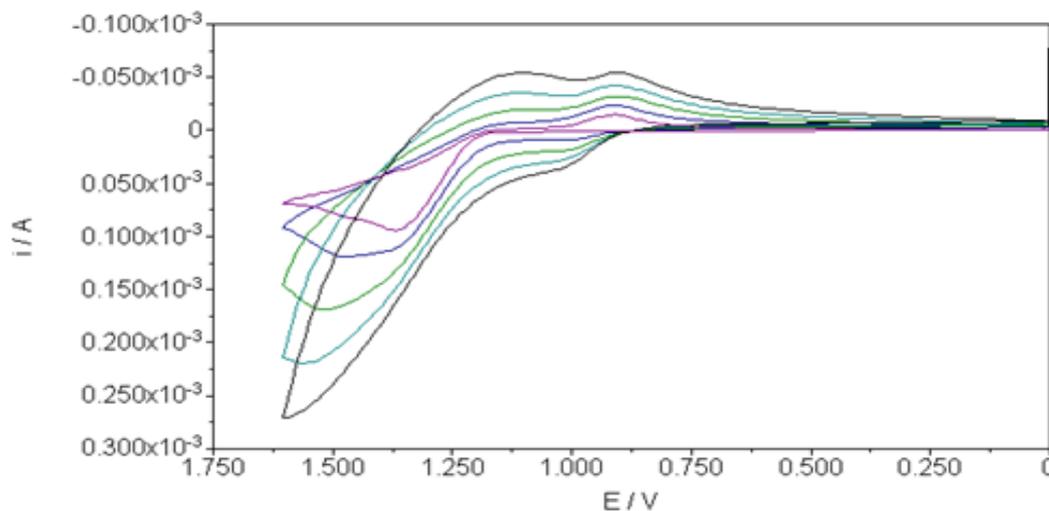


Figure 3.1 CVs (20 cycle) of carbazole (25mM), multicycle in TBABF₄ (0.1M) /ACN, scan. rate 100mv/s, Ag/AgCl as ref.electrode, Pt wire as counter electrode, Pt disc as working electrode.

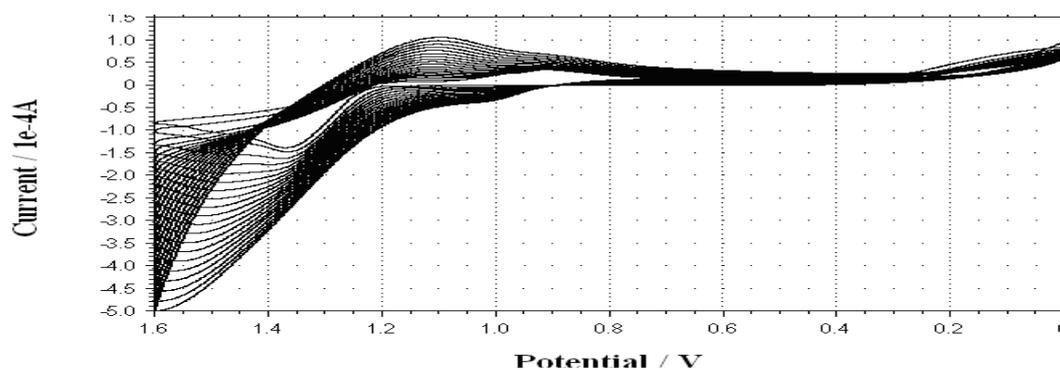


Figure 3.2 CVs (20 cycle) of polycarbazole (25mM) in TBABF₄ (0.1M) /ACN in 50 mM HBF₄, scan rate 100mv/s, Ag/AgCl as reference electrode, Pt wire as counter electrode, Pt disc as working electrode.)

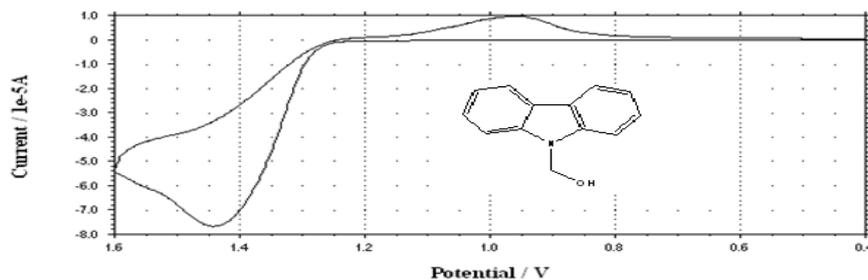


Figure 3.3 CV (one cycle) of carbazol-9-yl-methanol (25mM) in TBABF₄ (0.1M) / ACN, scan rate 100mv/s, Ag/AgCl as reference electrode, Pt wire as counter electrode, Pt disc as working electrode.

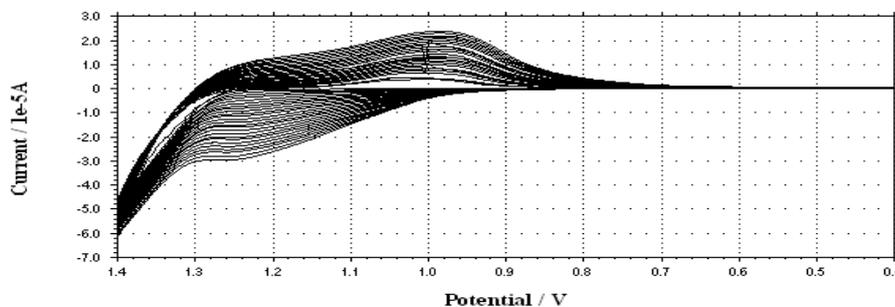


Figure 3.4. CVs (20 cycle) of Polycarbazol-9-yl-methanol (25mM) in TBABF₄ (0.1M) / ACN, scan rate 100mv/s., Ag/AgCl as ref. electrode, Pt wire as counter electrode, Pt disc as working.

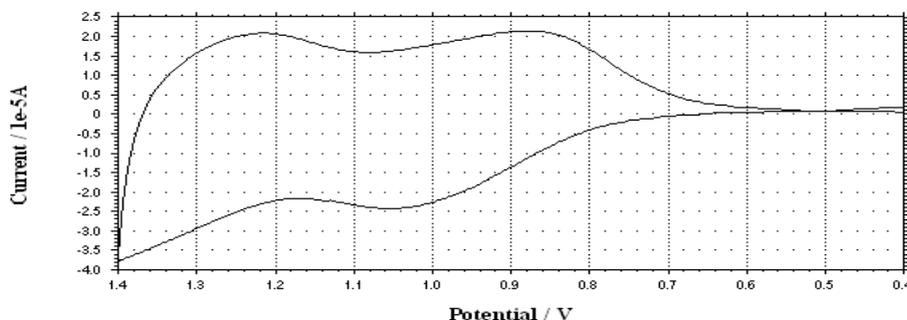


Figure 3.5 CVs (one cycle) of Poly carbazol-9-yl-methanol (25mM) in blank solution (TBABF₄ / Acetonitrile), scan rate 100mv/s.

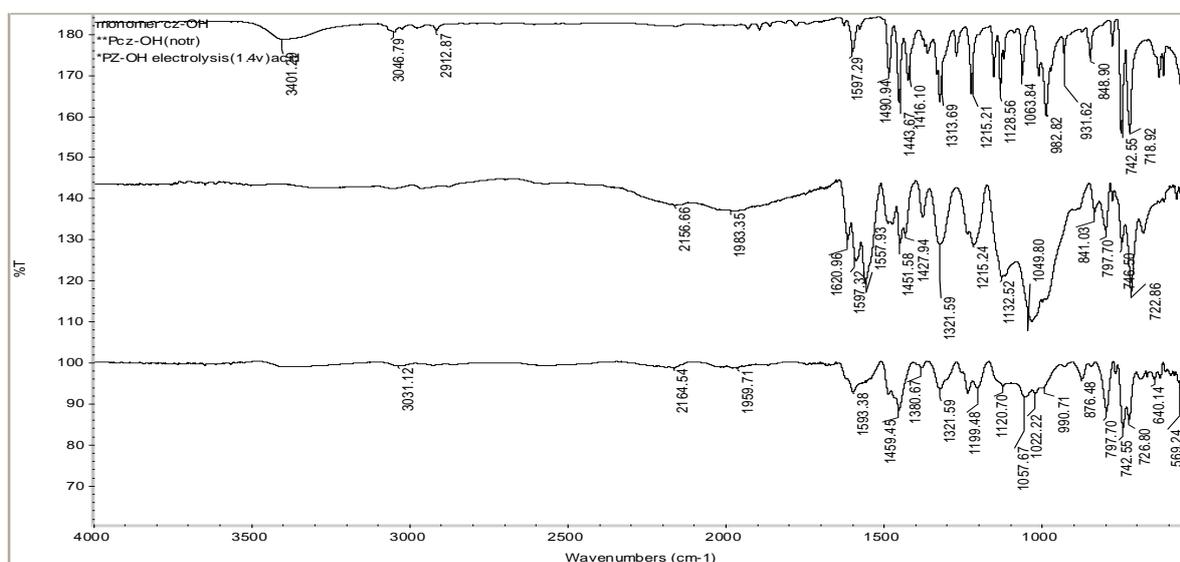


Figure 3.6 FTIR spectra of monomer of N- methanol carbazole, poly N- methanol carbazole, (25mM) and poly N- methanol in acid media film which was electrodeposited from acetonitrile solution containing 50mM TBABF₄.

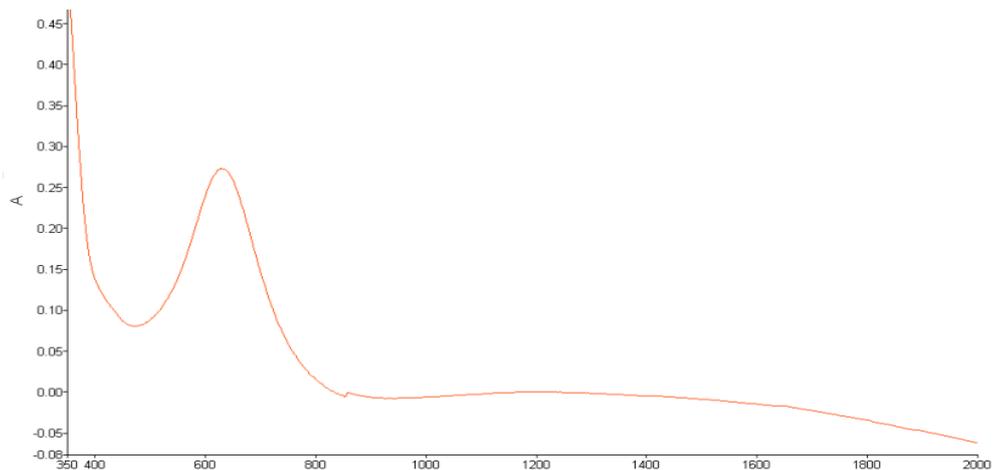


Figure 3.7 UV/vis spectrum of poly carbazol-9-yl-methanol(25mM).

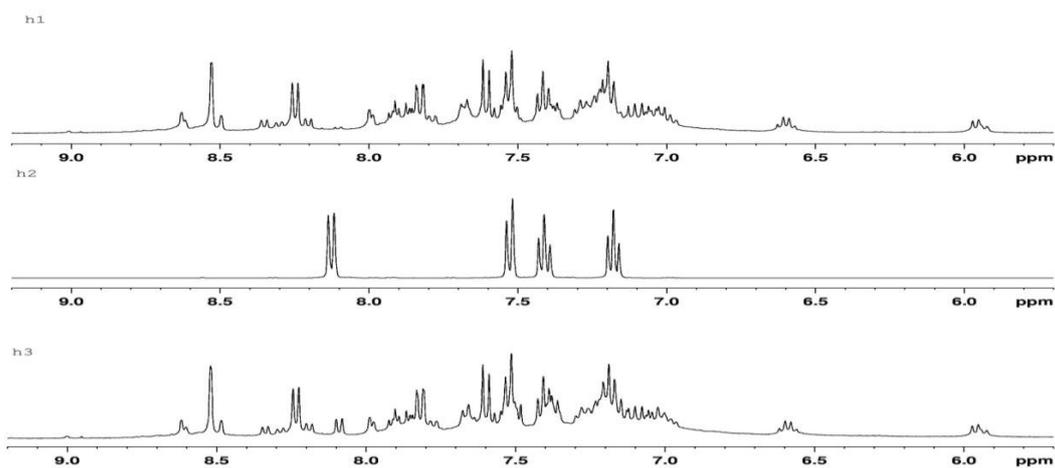


Figure 3.8 H^1 NMR (aromatic range) of monomer(80mg/ml (h2), polycarbazole) in neutral (h1).

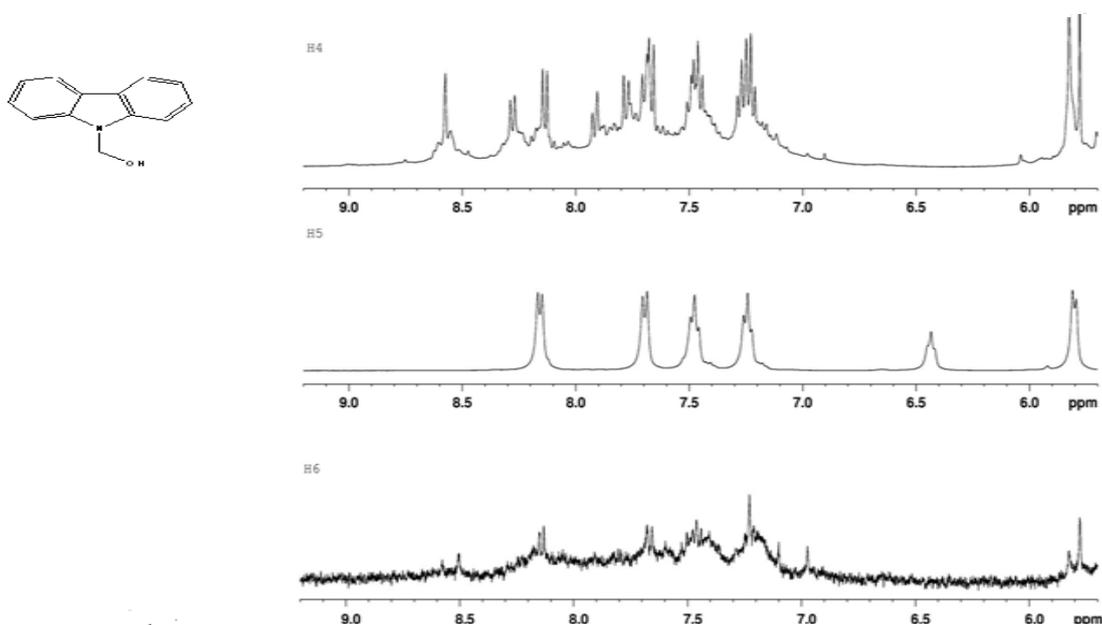


Figure 3.9 H^1 NMR (aromatic range) of monomer of carbazol-9-yl-methanol (h5), electrochemically deposited polycarbazol-9-yl-methanol) in acetonitrile neutral media (h4) and in acetonitrile presence of HBF_4) (h6).

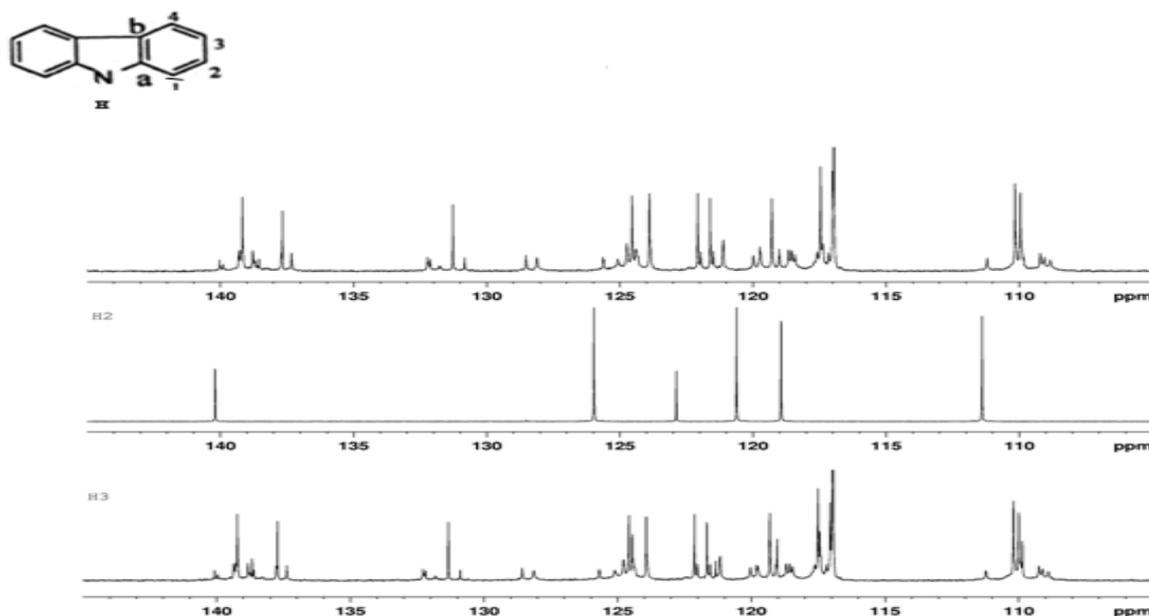


Figure 3.10. ^{13}C NMR of (aromatic range) of monomer (h2), polycarbazole) in neutral (h1) and with HBF_4 (25m M)(h3).

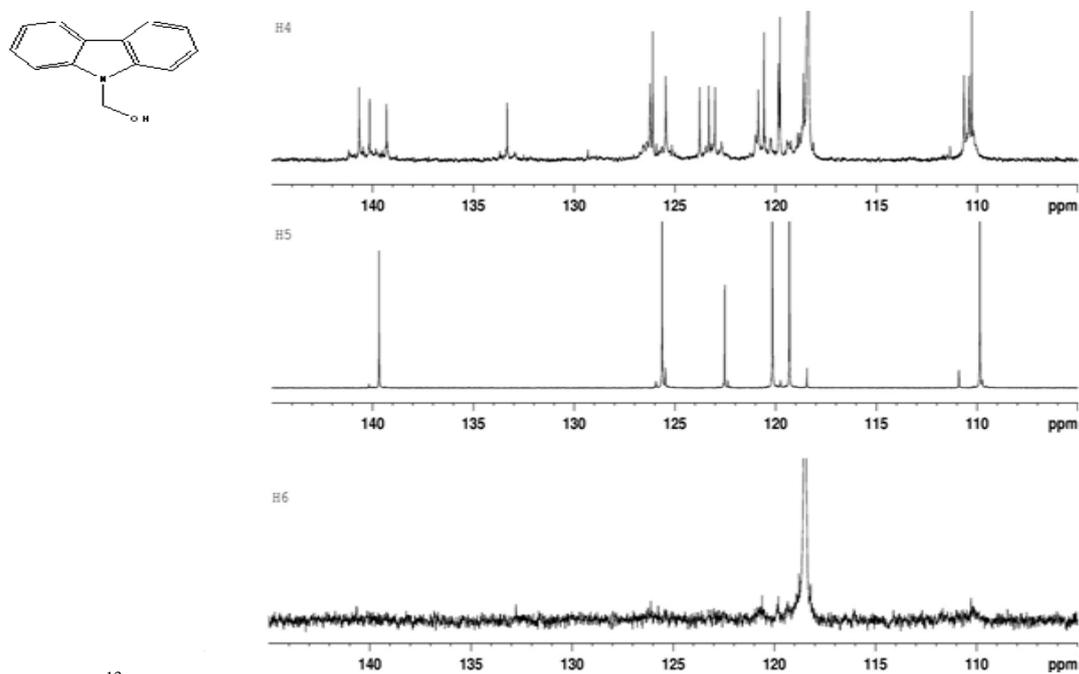


Figure 3.11. ^{13}C NMR of (aromatic range) of monomer of carbazol-9-yl-methanol (h5), electrochemically deposited polycarbazol-9-yl-methanol) in acetonitrile neutral media (h4) and in acetonitrile presence of (HBF_4) (h6).

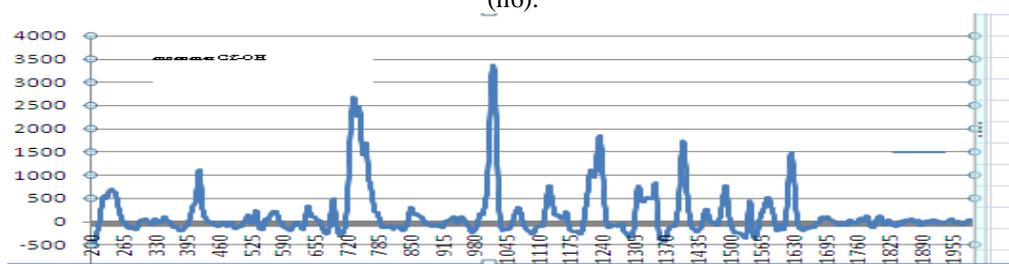


Figure 3.12. Raman spectrum of monomer of carbazol-9-yl-methanol (cm^{-1})

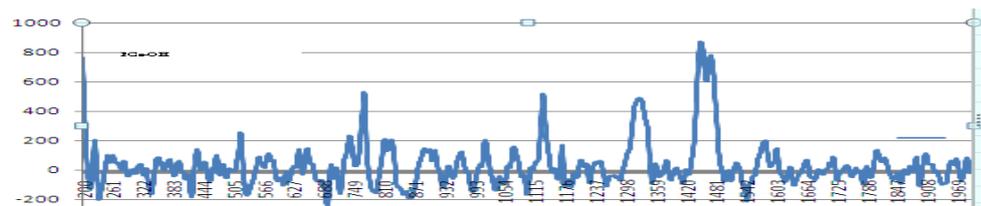


Figure 3.13. Raman spectrum poly carbazol-9-yl-methanol (cm⁻¹)

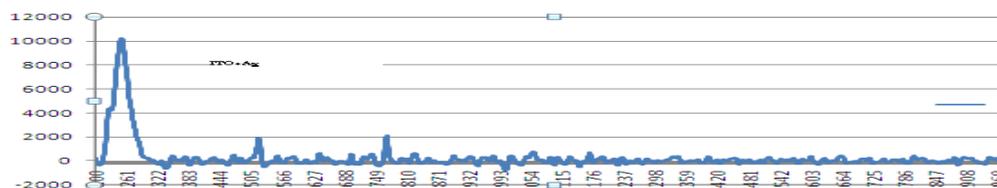


Figure 3.14. Raman spectrum of ITO+Ag (as baseline).

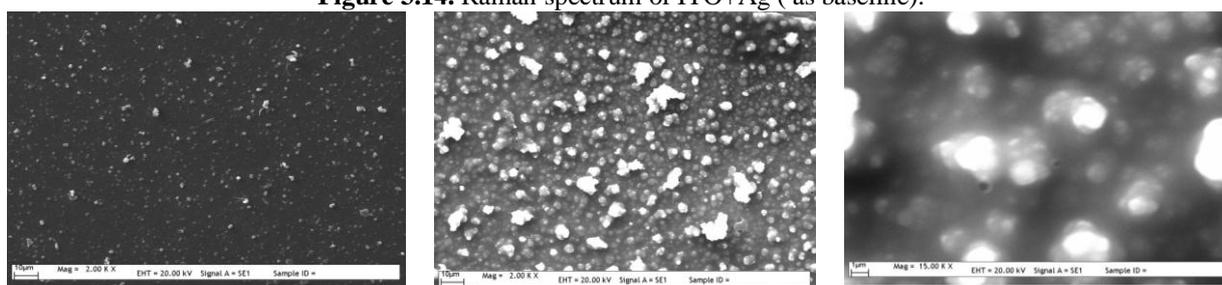


Figure3.15. Scanning electron micrograph of oxidized polycarbazole.

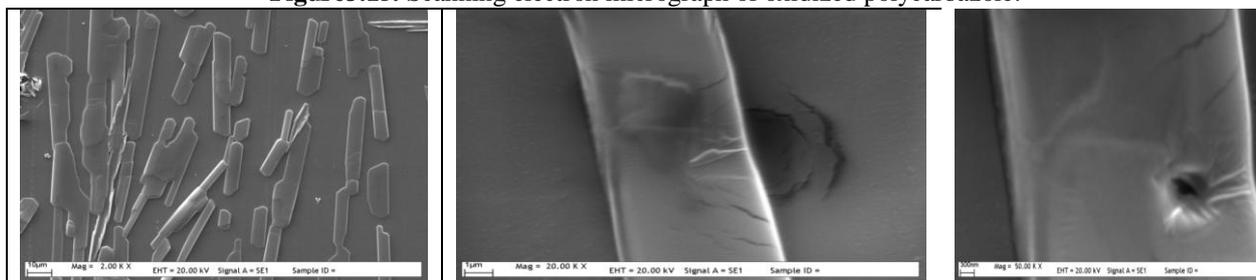


Figure 3.16. Scanning electron micrograph of oxidized polycarbazol-9-yl-methanol+HBF₄).

The surface morphology of the films deposited from electrochemical deposition were obtained using SEM images(Figure3.16). We can see important surface roughness is observed, ever if, electrodeposited films are homogeneous in naked eyes.

IV. Conclusions

- Carbazole monomers are , electrochemically, polymerized to give polymers that consist of carbazol back bone
- The polymers show electrical characterizations.
- The electrochromic systems formed exhibit strong green colour on oxidation and transparent on reduction
- Spectroscopic data give strong evidence of the formation of polymer material.

Acknowledgment

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