**Original Research Article**

# Electrochemical Synthesis, and Electrochromic properties of Poly(2-(9H-Carbazol-9-yl)acetic acid) film.


## Abstract

A poly(2-(9H-carbazol-9-yl) acetic acid) thin-film was formed on the surface of a platinum (Pt) electrode by oxidative electropolymerization of a new carbazole derivative. Electrochemical polymerization was performed in reaction medium containing monomer and 0.1 M TBABF4 mixture in acetonitrile (ACN) using repeated cycling at a scanning rate of 250 mV. The electrochemical polymerization of 2-(9H-carbazol-9-yl) acetic acid (25mM) was studied using cyclic voltammetry on both Pt and ITO electrodes. The structure of the soluble polymer was elucidated by nuclear magnetic resonance ($^{1}$H and $^{13}$CNMR) and Fourier transform infrared (FTIR) spectroscopy. The weight average molecular weight of poly(2-(9H-carbazol-9-yl) acetic acid) was determined using gel permeation chromatography (GPC) and found to be 130900 g/mol. Characterizations of the resulting polymer were performed by cyclic voltammetry, dry conductivity measurement and scanning electron microscopy (SEM), while the UV-Visible spectroscopy and electrochemical spectroscopic studies indicated that the poly(2-(9H-carbazol-9-yl) acetic acid) film showed a green color in the oxidized state, and high transmittance in the neutral state. Moreover, the poly(2-(9H-carbazol-9-yl) acetic acid) film is soluble in common organic solvents, such as DMSO, THF, NMP, and DMAC. The conductivities of poly(2-(9H-carbazol-9-yl) acetic acid) is about 4.3x $10^{-2}$ S/cm.



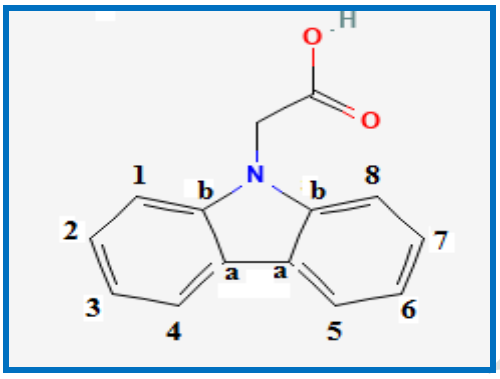
key words: Carbazole; Electrochemical, poly(2-(9H-carbazol-9-yl) acetic acid; Electropolymerization; voltammetry


## 1.Introduction

Conducting polymers such as polypyrrole, polyaniline, polythiophene, and polycarbazoles 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 several- N-substituted derivatives. Carbazole was intensively studied by chemists. 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 by using carbazole (Cz) derivatives sensors and rechargeable batteries. In the 1990s, Nishio and co-workers were able to synthesize several conductive polymers such as

(polyimine dibenzyl, polyphenothiaxine, polyacetylene, polythiophene , polycarboxylate, polyfuran, polypyrrole) by the Shirakawa method [1], where they were found to be suitable as positive electrode materials for lithium secondary batteries [2]. 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 76 ring substituted carbazole using electrochemical and spectroscopic techniques[3]. The author 2015 reported that an electrically conductive thin-film of poly(9H-carbazol-9-yl) methanol, could be synthesized in its conductive doped from their monomer in the electrolytic medium by an anodic electropolymerization reaction in platinum electrode, and ITO substrate by repetitive cyclic voltammetry without any catalyst, so this method could be considered as a clean method, and it does not requires passage through a halogenated substrate [4]. In practice, the cathodic electropolymerization used less than the anodic oxidation method, because its requires more material as a catalyst such as nickel, this substance deposited on the electrode is obtained in the neutral state, therefore it is non-conductive, which can be inhibit the reaction and requires to regenerate the active surface by doping the polymer [5]. Poly (N-substituted carbazole) shows interesting optical and electronic properties have been used in field effect transistors, electroluminescent diodes and batteries. Previous work has shown that poly(N-substituted carbazole) compounds are colorless when neutral, green at an applied potential of 0.7V versus saturated calomel electrode (SCE), and blue at 1.0V. Attemps to anodically been realized in aprotic solvents and lead to short electropolymerized N-ethylcarbazoles (ETCZ) have oligomers [6]. Many poly heterocyclic nitrogen compounds attracted attention as conducting polymers because their electrical and photoelectrical properties, for this reasons carbazole and its derivative such as poly(N-alkyl-3,6-carbazolene) compound was the first reported π-conjugated polymer containing carbazole [7]. Electrostatic imaging techniques have been applied to study the chemical aspects of the photoconductivity of poly-N-vinylcarbazole and a variety of other polymers with aromatic or heterocyclic chain units exhibit photo-induced discharge by Helmut Hoegl [8], while Lange et al. 1998 studied the effects of side chain position on the luminescence properties of poly(p-phenylene vinyiene) and their derivatives[9]. Electrochemical current response and optical transmittance of an electrochromic cell fabricated using polycarbazole films electrochemically deposited on indium-tin oxide (ITO) glass as a positive electrode and a platinum cathode were measured by Verghese and co-workers [10]. Recently, the author 2021 revealed the possibility of preparing of 3-(9H-carbazol-9-yl) propannitrile monomers, and then this polymer was electrochemical polymerzied to give a new soluble polymer in some organic solvent , with green color in oxidation state and and a transparent color in reducing state with the backbone of carbazole[11]. This study aims to synthesize conductive

polymer from 2-(9H-Carbazol-9-yl) ethanoic acid monomer by electrochemical polymerization of the monomer. The study also aims to study the solubility, average molecular weight, conductivity, and functional properties of Poly(2-(9H-Carbazol-9-yl) ethanoic acid). The chemical synthesis of carbazol-9-yl-carboxylic acid has been previously described[12]




**Scheme 1 The structure of the 2-(9H-Carbazol-9-yl)acetic acid monomer.**

## 2. Materials and Methods

All chemicals and reagents were used without further purification such carbazole obatined from BDH laboratory, sodium hydroxide 98% pellets (anhydrous ). The analytical grad of 99 % DMSO reagent, bromacetic acid, and tetrabutylammonium tetrafluoroborate (TBABF4) were obtained from Sigma-Aldrich, while acetonitrile (Merck, HPLC grade) was used as received.

### 2.1 Synthesis of 2-(9H-carbazol-9-yl) acetic acid

Exactly 8.35 g carbazole and 6.0 g sodium hydroxide were dissolved in 20 mL DMSO and heated to 85 °C for 30 min. Then, 8.35 g of bromacetic acid was added slowly and in batches. The solution was stirred overnight and then poured into 200 ml cold water. Then the solution was filterated and the product was precipitated by adjusting the filtrate at pH 4. The precipitate was washed and air dried. Electropolymerized 2-(9H-carbazol-9-yl) acetic acid monomer on Pt electrode were dissolved by immersion in dimethyl sulfoxide (DMSO) and this process was repeated several times to concentrate the solution. Electrochemical and electrochemical spectroscopic studies were carried out in ITO as work electrode, Pt wire as indicator electrode, and Ag wire adjusted versus the Fc/Fc+ redox couple (+0.3 V) as Pseudo-reference Electrode.

### 2.2 Spectroscopic Measurements

The infrared spectra of 2-(9H-carbazol-9-yl) acetic acid monomer, poly(2-(9H-carbazol-9-yl) acetic acid), and poly(2-(9H-carbazol-9-yl) acetic acid) + HBF4 (25mM) films were attained at ±25 oC from 400 to 4000 cm-1 using diffuse reflectance, thermo model-Nicolet- IS 10 FTIR. Raman spectroscopy profiles were obtained using surface enhancement Raman spectroscopy Delta Nu

(SERS). The NMR data were determined using a NMR spectrometer (Bruker 400 MHz AV NMR). UV-Vis/ NIR spectra with a scan rate of 2000 nm/min, of both 2-(9H-carbazol-9-yl) acetic acid monomer, and poly(2-(9H-carbazol-9-yl) acetic acid) polymer in neutral and acid media were measured at room temperature using Lambda 75 UV–Vis/ NIR spectrophotometer of Perkin Elmer.

**2.3 SEM analysis**

The shape of synthesized oxidized poly(2-(9H-carbazol-9-yl) acetic acid) was obtained by the scanning electron microscope (JEOL, Japan JSM 6390A) using diffrent magnification (2000, 20,000 50,000x) with diffrent picture width (µm).

**2.4 Measurement of conductivity**

The conductivity of the poly(2-(9H-carbazol-9-yl) acetic acid) film was measured by an a.c. 4-probe (Pt tips; d=0.50mm placed on linearly 5mm PTFE head) method. poly(2-(9H-carbazol-9-yl) acetic acid) film coated on Pt macro electrode was stripped and cut to 2×5mm dimensions and placed under 4-probe tips. Electrical conductivity measurement is carried out drive current from the two external tips of the 4-probe and measuring the voltage drop over the two internal tips. The ENTEK conductivity meter automatically calculated the conductivity of the poly(2-(9H-carbazol-9-yl) acetic acid) film using the drive current, voltage drop and film thickness.

**3. Results and discussion**

Electropolymerization of carbazole on Pt disc electrode by cyclic voltammetry Cyclic voltammograms of PCz thin films electrochemically deposited on Pt disc electrode recorded in 0.1 M TBABF4 as supporting electrolytes in acetonitrile as shown in Fig. 1. The onset potentials of carbazole oxidation with TBABF4/ACN were obtained at 0.96 and 1.05 V respectively as shown in Fig. 1. After the first cycle, the first peak intensity increased and potentials shifted toward higher values. Gradual increase in the intensity of the cathodic wave with repeated scans indicate that the product is gradually deposited on the surface of the Pt disc electrode ( Fig.1).

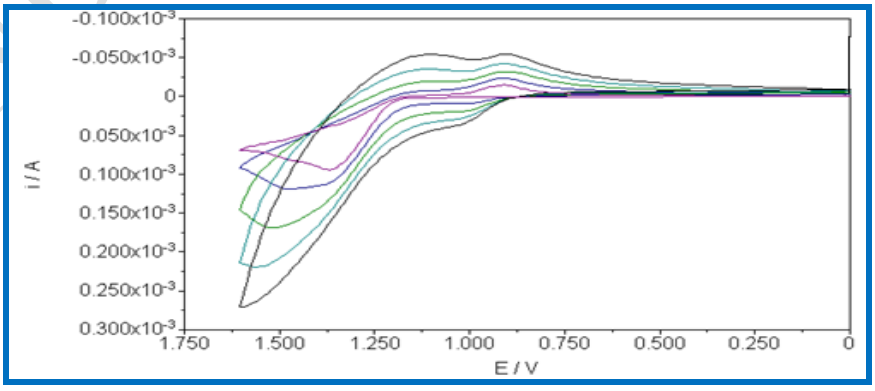



**Fig1. Cyclic voltammograms of carbazole ( 25mM ), multicycle (20 cycle) in supportıng electrolyte (0.1M) TBABF4 + ACN, scan rate 100 mv/s. Ag/AgCl as reference electrode, Pt wire as auxiliary electrode, Pt disc as**

**working electrode. CVs were recorded each every 5 cycle, first cyle and last cycles are showed purple and black line respectively.**

Fig. 2 shows that the direct electropolymerization of 2-(9H-carbazol-9-yl) acetic acid monomer was occurred when we scaned first cycle. the oxidation potential ($E_{pa}$ 1.38V) and reduction potential($E_{pc}$ 1.00V) as we showed $E_{peak}$ for all carbazole derivatives below in (table 1). As we mentioned above the poly carboxylic carbazole was formed in acetonitrile on disc electrode, when we applied few cycle thin film immediately deposed on disc (green colour) but film is partially dissolved in blank solution. After successive cycles, we obtained dark green polymeric film in monomer containing electrolysis solution. However we can not taken CV of poly carboxylic carbazole due to the high solubility in blank solution.

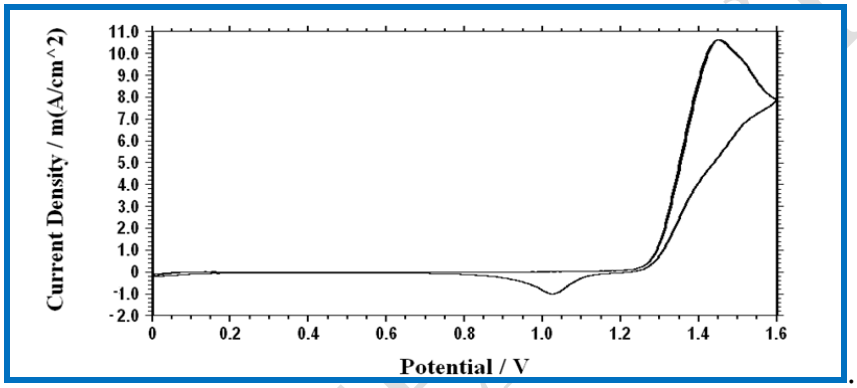



**Fig 2. Cyclic voltammograms of 2-(9H-carbazol-9-yl) acetic acid (25mM ) (one cycle) in supportıng electrolyte $TBABF_4$ (0.1M)+ACN, scan rate 100 mv/s, Ag/AgCl as reference electrode, Pt wire as auxiliary electrode, Pt disc as working electrode.**

Fig. 3 shows that in acidic media ($HBF_4$ 25mM in acetonitrile) obtained polymer more better formed and be doped partially soluble conducting polymer. When we increased the concentration of acid (50mM) the result is the nearly same, but especially solubility more less conforming polymer. For this reason we carried out polymerization using constant potential electrolysis as well as scanning CV. Homogenous and doped films were obtained using constant potential at 1.6 V. In blank solution is partially dissolved so this polymer may be soluble.

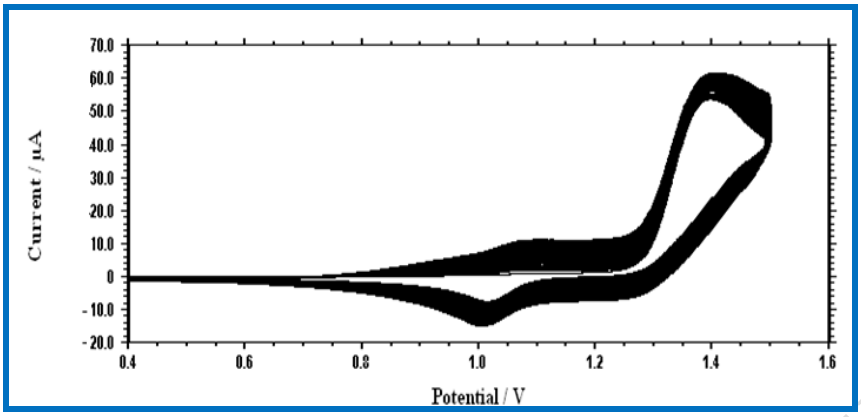



**Fig. 3 Cyclic voltammogram of 10Mm poly(2-(9H-carbazol-9-yl) acetic acid) (20 cycle) in 0.1M TBABF4+Acetonitrile, in HBF4 (25Mm), scan rate 100 mv. Ag/Ag+ as reference electrode, coil Pt as auxiliary electrode and Pt disk as work electrode.**

Fig. 4 shows that when we increasing the scanning cycles we found thick film appeared (dark green), and moreover in blank solution we can not seen it clear as we shwed below (Fig. 4) but indicates that the polymer was formed in blank solution.

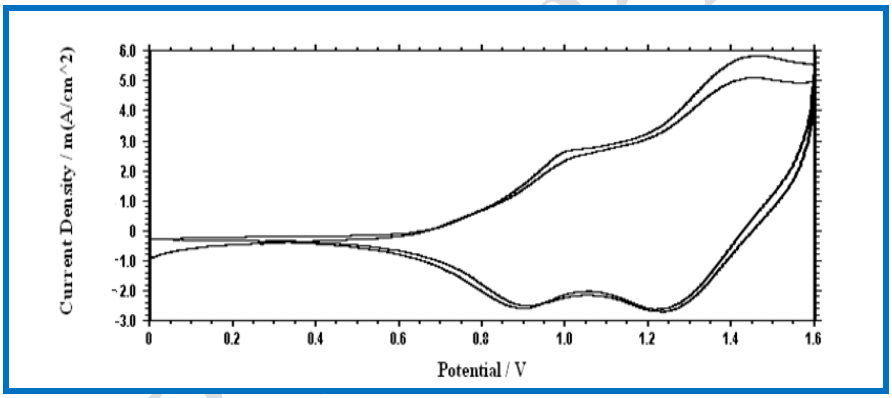



**Fig. 4 Cyclic voltammogams of poly(2-(9H-carbazol-9-yl) acetic acid) ( 10mM ) obtained from electrolysis in 25mM $HBF_4$ acidic media, in blank solution (0.05M $TBABF_4$ +ACN), at scan rate 100 mv/s.**

The dry conductivity of poly(2-(9H-carbazol-9-yl) acetic acid) was measured as $4.3 \times 10^{-2}$ S/cm using four probe point dry conductivity measurement technique.

**Table 1 comparison of $E_{pa}$(oxidation of monomer(V) ) and $E_{pc}$(reduction of poly carbazole) for carbazole and its derivatives.**

| | $E_{pa}$ (oxidation of monomer (V) ) | $E_{pc}$ (reduction of poly carbazole) |
|---|---|---|
| Carbazole | 1.5 | 0.90 |
| Polymer | 1.38 | 0.85 |

In Table we summarized and comparized the oxidation of momomer($E_{pa}$)and reduction of poly carbazole and its derivatives($E_{pc}$),we obtained slightly different oxidation potential for every

monomer as well as different reduction potential for polymers,so this due to N- subistitution moities of every monomer.

Fig. 5 shows that the strong band at 1703 $cm^{-1}$, 2927 $cm^{-1}$ are attributed to C=O group and C-H stretching vibration respectively in monomer. The band at 1597 $cm^{-1}$ attributed to $COO^-$ (carboxylate in neutral media) group in polymer. In acidic media, the band at 1727 $cm^{-1}$ attributed to COOH group in polymer. The band at 3586 $cm^{-1}$ is attributed to O-H group. The band appears between1050 to 1300 $cm^{-1}$ is assigned to C-O group [13]. The ring appears in range 1400 to 1600 $cm^{-1}$.

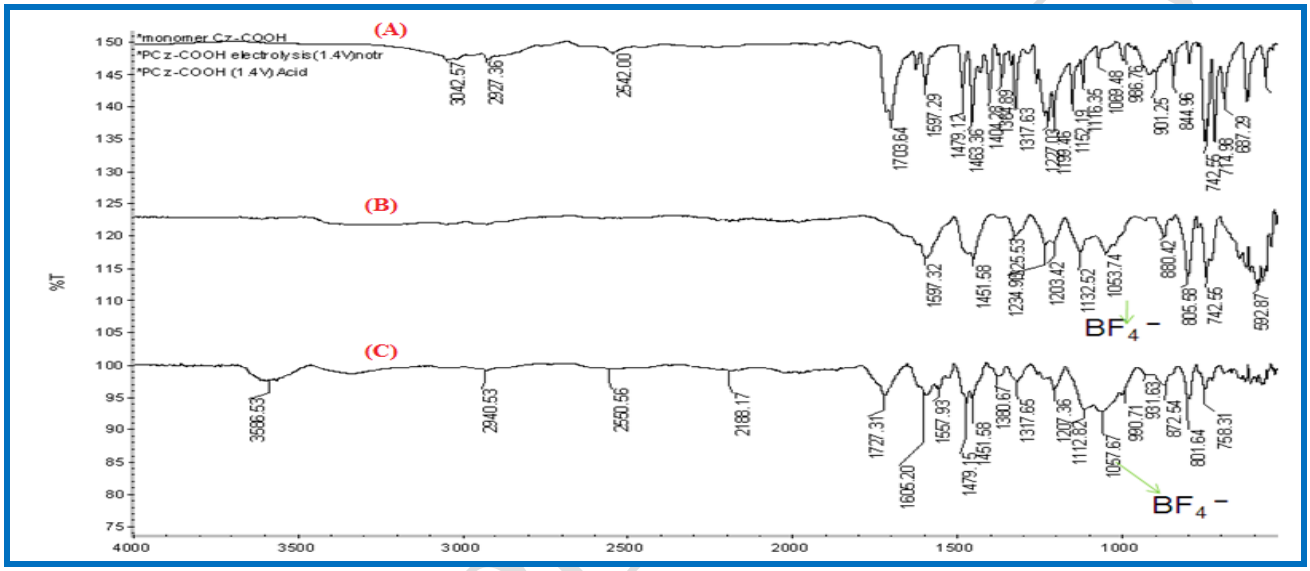



**Fig. 5 FTIR spectra of (A) 2-(9H-carbazol-9-yl) acetic acid monomer, (B) poly(2-(9H-carbazol-9-yl) acetic acid)(25mM) and (C) poly(2-(9H-carbazol-9-yl) acetic acid) in acid media film, which was electrodeposited from acetonitrile solution containing 50mM TBABF4 as supporting electrode.**

Fig. 6 shows the spectroelectrochemical behavior of monomer, and poly(2-(9H-carbazol-9-yl) acetic acid) in an acidic and neutral medium, we observed that the monomer (Fig 6a) was showed two small peaks at 350 nm , 370 nm, but after polymerization of 2-(9H-carbazol-9-yl) acetic acid in acidic medium we found that the peak appeared at 600 nm was belong to electronic transition $\pi - \pi^*$ (Fig 6b). For the polymer prepared in the neutral medium, a broad band peak appeared at 590 nm due to the absorption of charge transfer or polaron ions(Fig 6c), the two peaks have a high intensity and a longer wavelength when compared to monomer(Fig 6a). After polymerization of 2-(9H-carbazol-9-yl) acetic acid we observed that the tow peaks shifted to longer wave length (red shift) in both neutral(c) and in acidic media (b) Agreement with literature [14].

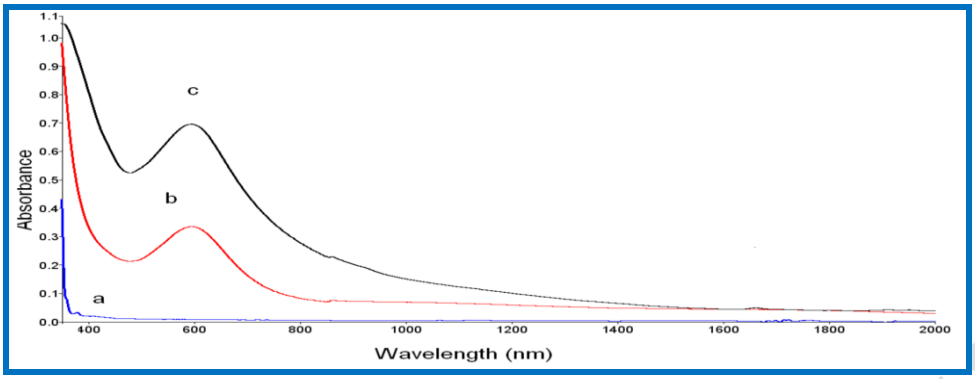



**Fig 6. Ex- situ UV–Vis/ NIR spectra of (a) 2-(9H-carbazol-9-yl) acetic acid (Cz-CH2-COOH) monomer, (b) poly(2-(9H-carbazol-9-yl) acetic acid) in acid media (PCz-CH2-COOH+HBF4), and (c) poly(2-(9H-carbazol-9-yl) acetic acid) (PCz-CH2-COOH ) (neutral).**

Spectroelectrochemical analysis of the PCz-$CH_2$-COOH film was studied in order to elucidate electronic transitions upon doping of the polymer (Fig. 7). The film was deposited on ITO electrode by electrochemical polymerization of 2-(9H-carbazol-9-yl) acetic acid in the 0.100 M TBABF4/acetonitrile. PCz-CH2-COOH coated ITO glass electrodes was investigated by UV-Vis spectroscopy in the monomer free electrolytic system via switching between +0.5 V and +1.6 V. In the reduced form, at 0.5 V, the film exhibited strong absorption assigned to π– π* transitions at wavelengths below 370 nm, but it was almost transparent in the visible region. As the applied potential became more anodic, new absorbance bands evolve at 390 nm and 750 nm due to the formation of charge carriers. The characteristic absorption peaks at 390nm and 750 nm agree with the previously reported data of polycarbazole derivatives. The broad band at 750 due transition involving polaronic state (charge - transfer absorption) and also improved the presence of dopants ($BF_4^-$ ions) that bounded to backbone of polymer.[15]

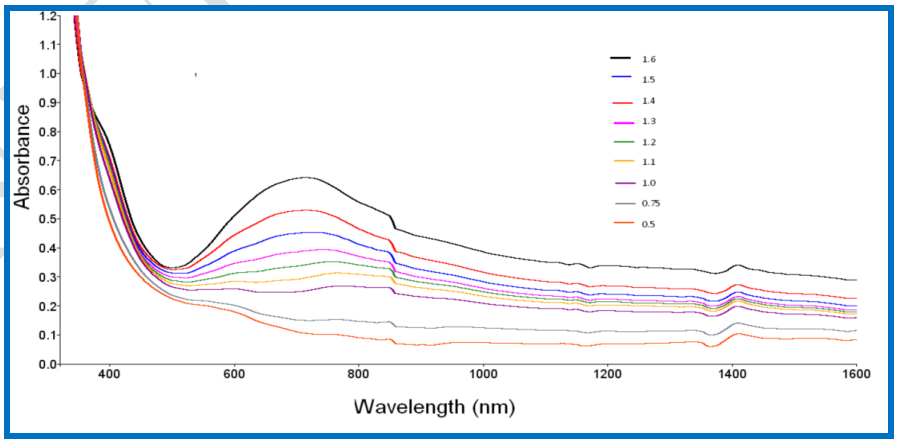



**Fig. 7 Spectroelectrochemical analysis of poly(2-(9H-carbazol-9-yl) acetic acid) under different potentials in (25mM) HBF4, and (0.1 M) TBABF4 / acetonitrile solutions (Voltage calculated versus SCE).**

The $^{1}H$ NMR and $^{13}C$ NMR spectra were taken on a Bruker 400MHz AV NMR spectrometer and DMSO-$d_6$ was used as the solvent. An NMR spectrum, like infrared spectrum, seldom suffices by itself for identification of an organic compound. However, in conjuction with FTIR and UV spectra,also NMR is powerful and indispensible tool for the characterization of pure compound. NMR spectroscopy for quantitative work has been inhibited by cost of the instruments.In addition ,the probability of overlapping resonance becomes greater as the complexity of the sample increases. Also, NMR is often neither as sensitive nor as convenient as competing techniques[16].

Fig. 8 shows that the $^{1}H$ NMR of 2-(9H-carbazol-9-yl) acetic acid(H8), at 8.2(CH,d),7.6(CH,d), 7.45 (CH,t), 7.25 (CH,t). the $^{1}H$ NMR spectra of poly(2-(9H-carbazol-9-yl) acetic acid) in neutral medium(H7), at 8.65 (CH,S), 8.35(CH,d), 8.2(CH,d), 7.95(CH,d), 7.85(CH,d), 7.75(CH,d), 7.6(CH,d), 7.5(CH,t), 7.3(CH,t ), 7.15(CH,s), 7.1(CH,s), 5.8($CH_2$-N-ring,t), while $^{1}H$ NMR of poly(2-(9H-carbazol-9-yl) acetic acid) in acidic medium (H9), at 8.65 (CH,S), 8.35 (CH,d), 8.2 (CH,d), 7.95(CH,d), 7.85(CH,d), 7.75(CH,d), 7.6(CH,d), 7.5(CH,t), 7.3(CH,t ) 7.15(CH,s) 7.1(CH,s) 5.8 ($CH_2$-N-ring,t). Fig.8 shows that the $^{1}H$ NMR spectra of 2-(9H-carbazol-9-yl) acetic acid(H8) monomer showed four peaks (2 d, 2t),while the $^{1}H$ NMR spectra of the poly(2-(9H-carbazol-9-yl) acetic acid) in neutral (H7) and acidic(H9) medium consists of twelve peaks. After polymerization reaction occurred in neutral(H7) and acidic (H9) medium, the singlet peak appeared at 8.65(CH,s) and 8.5(CH,s), respectively due to hydrogen atom at positions 1 and 8, and this indicates that the polymerization reaction occurred at positions 2 and7, also in addition two weak singlet peaks were also appeared at 7.05 and 7.15 ppm for the poly(2-(9H-carbazol-9-yl) acetic acid) in neutral medium(H8) and at 6.9 and 7.0 for the poly(2-(9H-carbazol-9-yl) acetic acid) in acidic medium(H9) due to oxidized quinoidal structure (polaronic doped) of the polymer backbone.

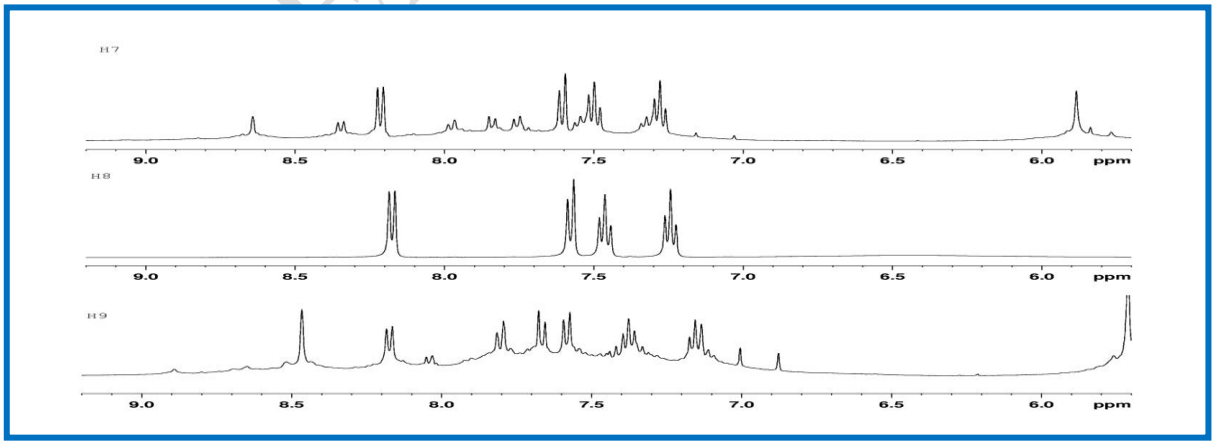



**Fig. 8 $^{1}H$ NMR (aromatic range) spectra of, 2-(9H-carbazol-9-yl) acetic acid monomer (80mg/ml)(H8), poly(2-(9H-carbazol-9-yl) acetic acid) (80mg/ml) in neutral (H7) and acidic HBF4 (25mM) (H9) solutions.**

Fig. 9 shows that the $^{13}C$ NMR( $\delta$ ppm; DMDO-$d_6$) spectra of 2-(9H-carbazol-9-yl) acetic acid monomer (H8), at 139.5 ($2C_a$),124.5($C_{2,7}$), 121.5 ($2C_b$), 119($C_{4,5}$), 118($C_{3,6}$), and 108($C_{1,8}$). The $^{13}C$ NMR ( $\delta$ ppm; DMDO-$d_6$) spectra of poly(2-(9H-carbazol-9-yl) acetic acid) in neutral medium(H7), at 139.5,139 , and 137.5 due to ($2C_a$), while 131.5 and 125($C_{2,7}$) the chemical shift in the absorption value of the carbon atoms of position 2 and 7 due to the occurrence of the polymerization reaction in them, 122, 121.5 and 121 due to ($2C_b$), 119 and 118.5 due to ($C_{4,5}$), 118 and 117 due to($C_{3,6}$), 109, 108.5and 108 due to($C_{1,8}$). while $^{13}C$ NMR ( $\delta$ ppm; DMDO-$d_6$) of poly(2-(9H-carbazol-9-yl) acetic acid) in acidic medium (H9), at 139, 137.5, 131.5, 125, 124, ,122, 121,5, 121, 119.2, 119, 118,117.5, 117, 109,108.5,108. The peaks in acid media is more intensity and the polymerization had been improved.

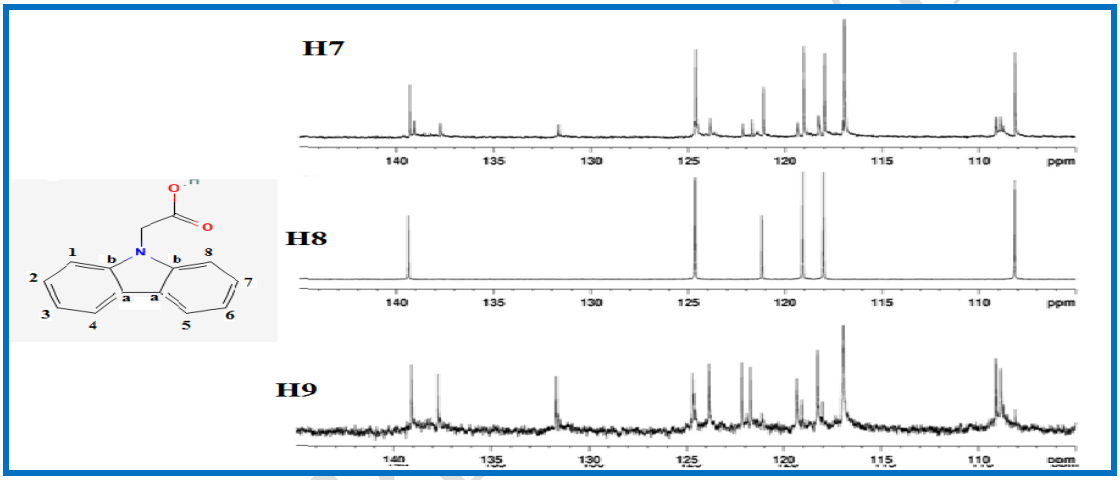



**Fig.9 $^{13}C$ NMR of (aromatic range) spectra, of 2-(9H-carbazol-9-yl) acetic acid monomer (80mg/ml) (H8), and poly(2-(9H-carbazol-9-yl) acetic acid) (80mg/ml) in neutral (H7) and in acidic HBF4 (25m M) (H9) solutions.**

Raman measurements were carried out using surface enhancement raman spectroscopy (SERS) for poly(2-(9H-carbazol-9-yl) acetic acid). Fig. 10 shows that the Raman spectroscopy of monomer was exhibited the major respected peaks as we showed in Table 2. The peaks observed at both 1630 and 1544 $cm^{-1}$ are associated with the C=O stretching and C=C aromatic bonds, respectively. The peaks at 1351 and1021 $cm^{-1}$ due to aromatic C-H bend and C-O stretching respectively. Fig. 11 shows that after polymerization the peaks observed at both 1605 and 1520 $cm^{-1}$ are associated with the C=O stretching and C=C aromatic bonds respectively. The peaks at 1378 and 1016 $cm^{-1}$ due to aromatic C-H bend and C-O stretching, respectively with no significant different from monomer.

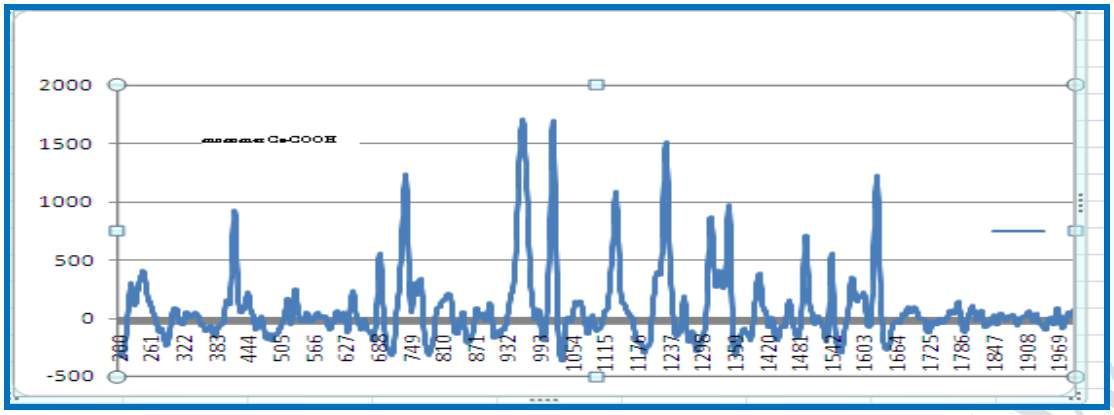



**Fig. 10 Raman spectrum of 2-(9H-carbazol-9-yl) acetic acid monomer ($cm^{-1}$)**

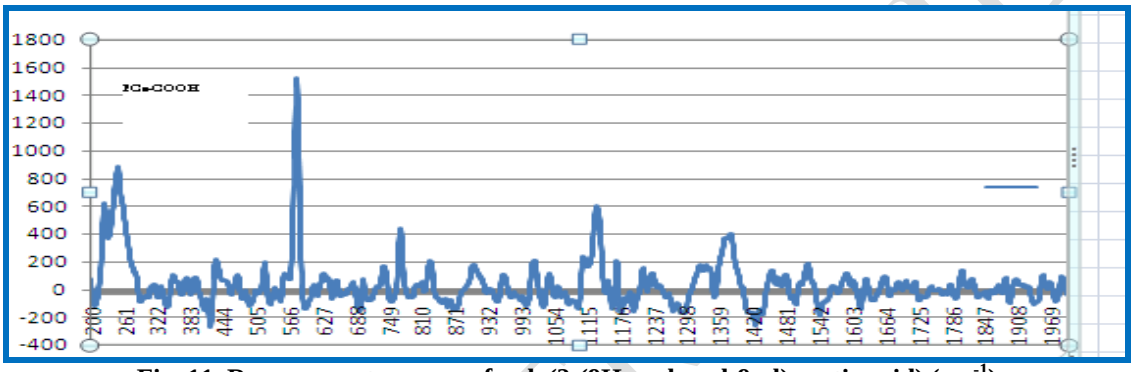



**Fig. 11 Raman spectroscopy of poly(2-(9H-carbazol-9-yl) acetic acid) ($cm^{-1}$)**

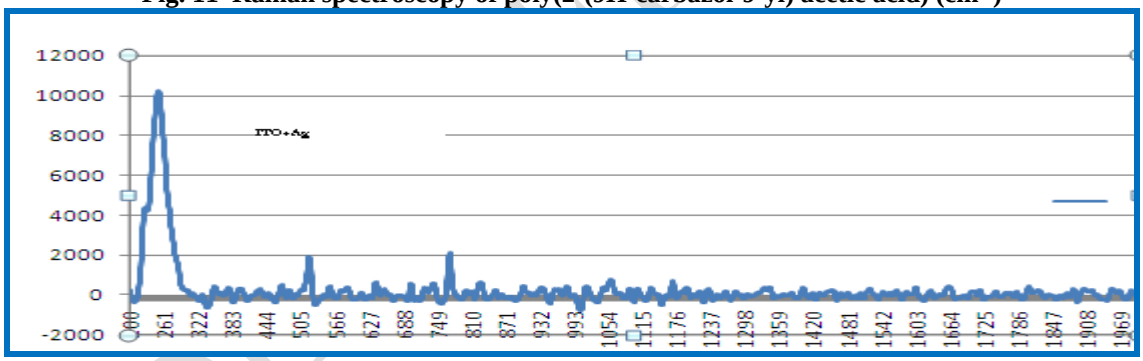



**Fig. 12 Raman spectroscopy of ITO + Ag (as base line).**

As we showed there are some different between Raman and FTIR in the value of peaks and spectrum is very complicated due to that some substances are inactive in IR but Raman active or vice versa ($CO_2$). 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 be occurred. However we used filters in Raman instrument the photo decomposition or fluorescence is very high [16]. The intensity of Raman peaks depend on intensity of the source, active groups and polarizability [16,17].

**Table 2. Raman Frequency of some Functional Groups of monomer, and poly(2-(9H-carbazol-9-yl) acetic acid) on ITO glass.**

| IT0 +A g, Frequency,(intensity) | PCz-$CH_2$-COOH Frequency,(intensity) | Monomer Cz-$CH_2$-COOH Frequency,(intensity) |
|---|---|---|
| 250(1132)<br>520(1773)<br>771(1886) | 250 (866)<br>431 (198)<br>521 (179)<br>581 (1526)<br>771 (403)<br>824 (163)<br>904 (155)<br>1016 (183) C-O str.<br>1132 (583)<br>1171 (210)<br>1218 (136)<br>1320 (132)<br>1378 (387) Arom. C-H bend.<br>1453 (109)<br>1605(110) C=O str.<br>1520(151) C=C | 248 (391)<br>421 (901)<br>428 (266)<br>535 (299)<br>520 (142)<br>643 (223)<br>695 (559)<br>742 (1187)<br>819 (181)<br>962 (1663)<br>1021 (1688) C-O str.<br>1138 (938)<br>1233 (1509)<br>1317 (855)<br>1351 (943) Arom. C-H bend<br>1407 (365)<br>1496 (707)<br>1544 (513) C=C Arom ring<br>1582 (326)<br>1630 (1223) C=O str |

The surface morphology of the films deposited from electrochemical deposition were taken by SEM. Fig. 13 shows the surface morphology of the films deposited from electrochemical deposition were takenby SEM, the images showed homogenous films of aligned gold nanotubes to improve the optical sensing properties [18], using diffrent magnification (2000, 20,000, and 50,000x) with diffrent picture width (µm). We can see important surface roughness evens if, electrodeposited films are homogeneous in naked eyes.

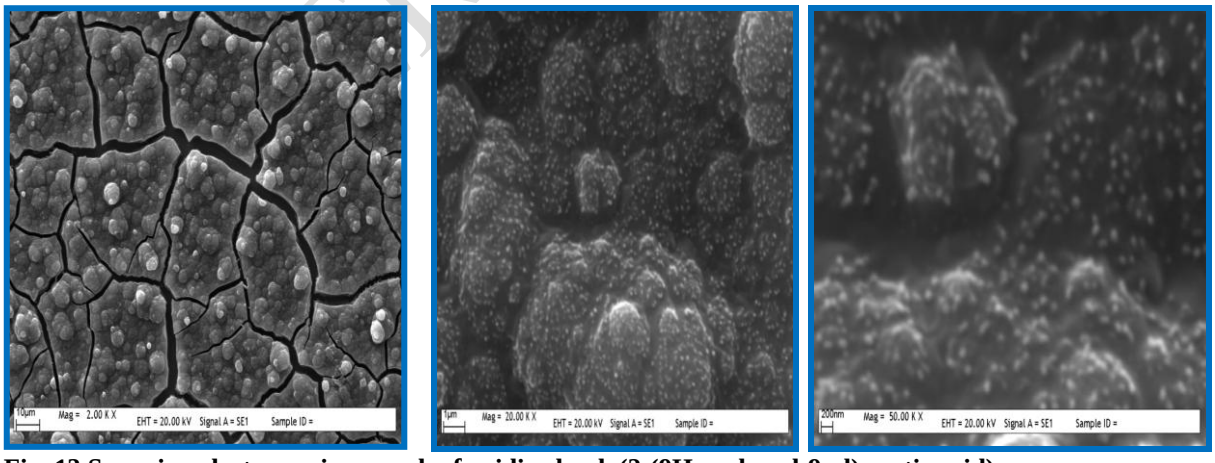


**Fig. 13 Scanning electron micrograph of oxidized poly(2-(9H-carbazol-9-yl) acetic acid).**

**Table 3. The Molecular weight of poly(2-(9H-carbazol-9-yl) acetic acid) in neutral, and acidic medium**

| Polymer | Average molecular weight (Mw) | dispersity |
|---|---|---|
| PCz-$CH_2COOH$(n) | 130900 | 1.33 |
| PCz-$CH_2COOH$ +$HBF_4$ | 58200 | 1.84 |

The weight average molecular weight (Mw) of poly(2-(9H-carbazol-9-yl) acetic acid) synthesized in neutral and acidic medium was determined using gel permeation chromatography (GPC), when using tetrahydrofuran (THF) solvent and polystyrene (PS) It was used as a standard in GPC analysis. Table 3 shows that the PCz-CH2COOH(n) has Mw equal 130900 Da, and number average molecular weight (Mn) 98421.1 Da with dispersity value equal 1.33.

**Table 4. The solubility tests (mg/ml) of poly(2-(9H-carbazol-9-yl) acetic acid).**

| Polymers | NMP | DMSO | ACN | THF | DMAC |
|---|---|---|---|---|---|
| PCz-$CH_2COOH$(n) | 4mg/ml | 75mg/ml | 1.6mg/ml | 3.0mg/ml | 3.6mg/ml |
| PCz-$CH_2COOH$+$HBF_4$ | 2.6mg/ml | 65mg\ml | 1.2mg/ml | 2.6mg/ml | 3.2mg/ml |

Table 4 shows that the solubility (mg/ml) of poly(2-(9H-carbazol-9-yl) acetic acid) in some organic solvents such as N-methyl-2-pyrrolidone (NMP), dimethyl sulphoxide (DMSO), Acetonitrile (ACN ) , Tetrahydrofuran (THF), and N,N-dimethylacetamide (DMAC).

## 4.Conclution

These newly prepared 2-(9H-carbazol-9-yl) acetic acid monomer was electrochemically polymerized to give a novel poly(2-(9H-carbazol-9-yl) acetic acid) which backbone consisted of carbazole.This new polymer classified as conducting polymer with agood soubility in some organic solvents .We have reported here a novel electrochromic system which gives strong green color in oxidation state and transparen in reduction state indicates the possibility of anew materials. The electrochemical and spectroscopic data obtained above give strong evidence that polymerization of poly(2-(9H-carbazol-9-yl) acetic acid) was occurred upon electro-oxidation of the monomer. The formed polymer film was further characterized by FT-infrared , UV–Vis, Spectroelectrochemical analysis, NMR, Raman spectroscopy, and SEM.

**COMPETING INTERESTS DISCLAIMER:**

**Authors have declared that no competing interests exist. The products used for this research are commonly and predominantly use products in our area of research and country. There is absolutely no conflict of interest between the authors and producers of the products because we do not intend to use these products as an avenue for any litigation but for the advancement of knowledge. Also, the research was not funded by the producing company rather it was funded by personal efforts of the authors.**

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