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Study on Spectro-Electrochemical Behaviour of Thin-Layer Polymer of 3-(9H-Carbazol-9-yl)propanenitrile

H.E. Elkhidir^{1,*}, M.H. Awad², Adel M.M. Alkuha²¹Department of Chemistry, Faculty of Science and Technology, Shendi University, Shendi – 142/143, Sudan.²Department of Chemistry, College of Arts and Sciences-Kasr Khair, Elmergib University, Alkoms - 40414, Libya.

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ABSTRACT

A film of electrically active poly(3-(9H-carbazol-9-yl)propanenitrile) was prepared on platinum (Pt) electrode surface by oxidative electro-polymerization of 3-(9H-carbazol-9-yl)propanenitrile monomer. The polymerization reaction was performed in a reaction medium containing monomer, and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) mixture in acetonitrile (ACN) using repeated cycling at a scanning rate of 250 mV. Electrochemical polymerization of carbazole (Cz) and 3-(9H-carbazol-9-yl)propanenitrile (25 mM) were studied with cyclic voltammetry on both Pt and ITO electrodes. The structure of the poly(3-(9H-carbazol-9-yl)propanenitrile) was elucidated by nuclear magnetic resonance (¹H and ¹³C NMR) and Fourier transform infrared (FTIR) spectroscopy. The weight average molecular weight (M_w) of the electrochemically synthesized poly(3-(9H-carbazol-9-yl)propanenitrile) was determined using gel permeation chromatography (GPC), where it was found that the M_w of the polymer is equal to 37900 g/mol. The polymer was characterized using dry conductivity measurement, scanning electron microscopy (SEM) and UV-Vis spectroscopy, while the spectro-electrochemical studies indicated that poly(3-(9H-carbazol-9-yl)propanenitrile) films revealed a green color in the oxidized state and a high transmittance in the neutral state. Moreover the poly(3-(9H-carbazol-9-yl)propanenitrile) film is soluble in common organic solvents, like DMSO, THF, NMP and DMAC. The conductivity of poly(3-(9H-carbazol-9-yl)propanenitrile) was found to be 1.62×10⁻⁴ S/cm.

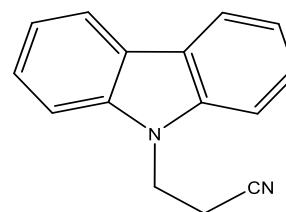
1. Introduction

The term “conducting polymers” was used after the Hideki Shirakawa, Alan J. Heeger and Alan Mc Diarmid in 1977 found that the polyacetylene with iodine confers the polymer's metallic properties. In the past thirty years the advanced industry such as microelectronics has required attention in research and new discoveries into newer materials having the required physical and chemical properties. A simple conjugated polymer can be converted into conductor through a so-called doping reaction which involved partial oxidation (p-type doping) or partial reduction (n-type doping) [1, 2]. The degree of conductivity of organic conductive polymers lies between two states of relative oxidation and reduction. In case of polymer loses itself electrons (partial oxidation) the polymer produces two positively charged polarons, if more oxidation occurs, more polarons will produced (doped form) [3].

Conductive polymers can be manufactured either by chemical or electrochemical polymerization methods. Electropolymerization is more advantageous as the reactions can be carried out at room temperature, the thickness of the films can be controlled, polymer films can be directly formed on the electrode surface, and it is possible to get homogeneous films [4, 5]. Therefore, conducting polymers are often synthesized by electrochemical polymerization. The electrolytic solution, consisting of the monomer, the supporting electrolyte, and the solvent, is taken into the cell and the electrolysis is carried out by applying a voltage between the working electrode (Pt, Au, C, etc.) and the counter electrode. Usually, the film of the conducting polymer is formed during anodic polarization [6]. The electrochemical preparation of a variety of electrochromic conducting polymers has been extensively investigated due to their electrical redox and photochemical properties and ability for a number of practical applications like smart windows [7], displays [8], and data storing devices and organic light emitting diodes (OLED) [9]. In the past thirty years, polycarbazole and their derivatives have been among those polymeric structures that have attracted great interest among researchers for the

following reasons: Carbazole is a cheap raw material readily available from coal-tar distillation and various substitutes can be readily introduced into the carbazole ring [10-12]. Further carbazole-containing compounds show high thermal and photochemical stability. Moreover, the carbazole unit can be substituted at the 3- and 6-positions as well as at the 2- and 7-positions to give polycarbazole derivatives with different properties and potential applications [13]. Polycarbazole (PCz) is one of many relatively new conducting polymer groups with good electrochemical characteristics, and its conductive form can easily be obtained by the electrochemical method. Investigations related to chemical modification or copolymerization of carbazole with other monomers have led to the use of PCz and its derivatives as redox catalysts, photoactive devices, sensors, electrochromic display, electroluminescent devices and biosensors [14].

The present work is trying to electrochemical synthesis of a soluble conducting poly(3-(9H-carbazol-9-yl)propanenitrile) (25mM) polymer (Scheme 1). The work also aimed to investigate the electrochemical properties of poly(3-(9H-carbazol-9-yl)propanenitrile) polymer. Also, the aim extended to investigate the functional properties of polymer using electrochemical and spectroscopic techniques. The chemical synthesis of The work also aimed to investigate the electrochemical properties of poly(3-(9H-carbazol-9-yl)propanenitrile) has been previously described [15].



Scheme 1 Structure of monomer of 3-(9H-carbazol-9-yl)propanenitrile (or N-cyanoethyl carbazole)

*Corresponding Author: mubasherhashim@gmail.com(H.E. Elkhidir)

2. Experimental Methods

2.1 Synthesis of Poly(3-(9H-carbazol-9-yl)propanenitrile) (25 mM)

A mixture of the same weight (1.7 g) of carbazole and acrylonitrile was put into a conical flask. Then the mixture was immersed in an ice bath to cool for 15 min. Then benzyltrimethylammonium hydroxide (40% Triton B in MeOH) was added dropwise to the reaction medium. The mixture was heated up to 65 °C until the color of the solution changed from yellow to orange, and then the mixture was cooled until a green precipitate formed. Then, the green precipitate was recrystallized using acetonitrile.

2.2 FTIR, Raman and NMR Spectroscopic Measurements

FTIR spectra of monomer of 3-(9H-carbazol-9-yl)propanenitrile, poly(3-(9H-carbazol-9-yl)propanenitrile) (25 mM) and poly(3-(9H-carbazol-9-yl)propanenitrile) + HBF₄ (25 mM) films were acquired at room temperature from 400 to 4000 cm⁻¹ using Thermo model-NICOLET-1S 10 FTIR. Raman spectroscopy profiles were attained using surface enhancement Raman spectroscopy DeltaNu (SERS). The NMR data analysis were determined using NMR (Bruker 400 MHz AV NMR) spectrometer.

2.3 UV-Vis / NIR Spectra Analysis

UV-Vis/ NIR spectra with a scan rate of 2000 nm/min, of both 3-(9H-carbazol-9-yl)propanenitrile monomer and poly(3-(9H-carbazol-9-yl)propanenitrile) polymer in neutral and acid media were measured at room temperature using Lambda 75 spectrophotometer of Perkin Elmer.

2.4 SEM Analysis

The shape of synthesized oxidized poly(3-(9H-carbazol-9-yl)propanenitrile) was obtained by the scanning electron microscope (JEOL, Japan JSM 6390A) using different magnification (2000, 20,000 50,000x) with different picture width (μm).

3. Results and Discussion

Fig. 1 shows that the first two-cycle of oxidative electropolymerization of 3-(9H-carbazol-9-yl)propanenitrile emphasized that the thin-film of green color of 3-(9H-carbazol-9-yl)propanenitrile polymer produced or coated on Pt disc electrode. When the sweep segment cycle increased (20 cycle) it was observed that the formed film is very clear, but more soluble in blank solution in comparing with other derivatives. Solubility of this polymer was confirmed by the repetition of this work much time and carried out CVs with variable intervals and scan rates (Fig. 2).

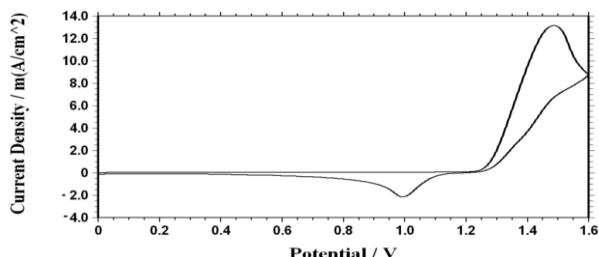


Fig. 1 Cyclic voltammograms of 3-(9H-carbazol-9-yl)propanenitrile (25 mM) (one cycle) in supporting electrolyte TBABF₄ (0.1 M) + ACN (25 mL) in nonaqueous media, scan rate 100 mV/s, Ag/AgCl as reference electrode, Pt wire as counter electrode, Pt disc as working electrode

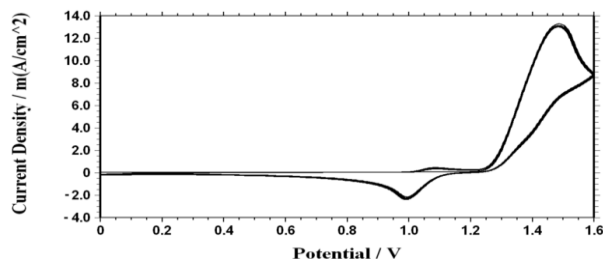


Fig. 2 Cyclic voltammograms (20 cycle) of 3-(9H-carbazol-9-yl)propanenitrile (25 mM) in supporting electrolyte TBABF₄ (0.1 M) + ACN (25 mL) in nonaqueous media, scan rate 100 mV, Ag/AgCl as reference electrode, Pt wire as counter electrode, Pt disc as working electrode

Solubility of poly(3-(9H-carbazol-9-yl)propanenitrile) seen clearly in blank solution, so the green colour of polymer disappeared when CV scanned in blank solution so that to ensure the poly(3-(9H-carbazol-9-yl)propanenitrile) is soluble. Electropolymerization of 3-(9H-carbazol-9-yl)propanenitrile carried out in (25 mM) HBF₄ acetonitrile at constant potential electrolysis (1.4 V) (Fig. 3). The polymer was obtained with good homogeneity and more stable in blank solution as exhibited in Fig. 4. It can be seen that two reversible peaks due to redox process in blank solution.

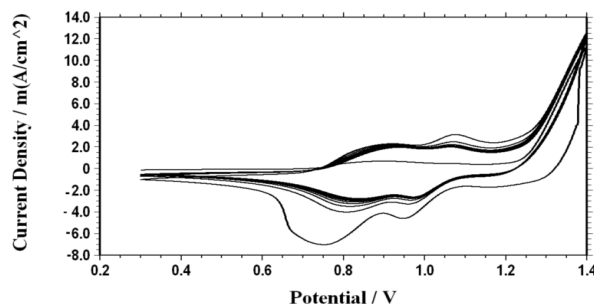


Fig. 3 Cyclic voltammograms (20 cycle) of poly(3-(9H-carbazol-9-yl)propanenitrile) (25 mM) in supporting electrolyte TBABF₄ (0.1 M) + ACN (25 mL) in 25 mM HBF₄, scan rate 100 mV, Ag/AgCl as reference electrode, Pt wire as counter electrode, Pt disc as working electrode

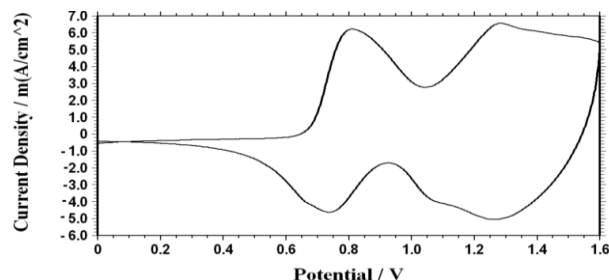


Fig. 4 Cyclic voltammograms of poly(3-(9H-carbazol-9-yl)propanenitrile) (obtained constant anodic potential 1.4 V) in blank solution TBABF₄ (0.1 M) + ACN, scan rate 100 mV/s

The dry conductivity of poly(3-(9H-carbazol-9-yl)propanenitrile) was measured as value of 1.62×10^{-4} S/cm using four probe point dry conductivity measurement technique. Table 1 shows a summarized and compared values of the oxidation (E_{pa}) of monomer (V) and reduction (E_{pc}) of poly carbazole for carbazole and 3-(9H-carbazol-9-yl)propanenitrile, obtained slight different oxidation potential for every monomer as well as different reduction potential for polymers due to N-substitution moieties of every monomer.

Table 1 Comparison of E_{pa} (oxidation of monomer (V)) and E_{pc} (reduction of polycarbazole) for carbazole and 3-(9H-carbazol-9-yl)propanenitrile

Polymers	E_{pa} (oxidation of monomer (V))	E_{pc} (reduction of poly carbazole)
Carbazole	1.37	0.90
3-(9H-carbazol-9-yl)propanenitrile	1.47	1.05

Fig. 5 shows the IR spectra of monomer and polymer depicts a characteristic absorption peak at 2255 cm⁻¹ is attributed to nitrile group in monomer and shifted to 2243 cm⁻¹ in polymer. The band at 2956 cm⁻¹ and at 2869 cm⁻¹ are attributed to C-H stretching vibration mode in both monomer and polymer. The band at 1400–1600 cm⁻¹ spectral range assigned to aromatic ring. The band at 1325 cm⁻¹ is attributed to CH₂ group. The bands at 1049 and 828 cm⁻¹ attributed to BF₄⁻ dopant group. The band at 1191 cm⁻¹, 1325 cm⁻¹ in both monomer and polymer is attributed to C-N, and C-C group, respectively [16]. In acid media the polymerization improved and peaks became broader after polymerization.

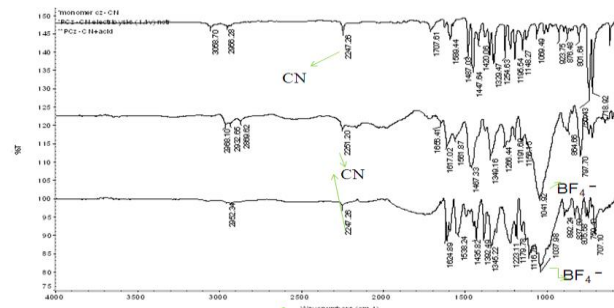


Fig. 5 FTIR spectra of monomer of 3-(9H-carbazol-9-yl)propanenitrile, poly(3-(9H-carbazol-9-yl)propanenitrile) (25 mM) and poly(3-(9H-carbazol-9-yl)propanenitrile) + HBF₄ (25 mM) films which was electrodeposited from acetonitrile solution containing 50mM TBABF₄ as supporting electrode

The spectroelectrochemistry studies give us more information about the electronic structure of the conducting polymer such as optical band gap. Fig. 6 shows that in the reduced form of the monomer of 3-(9H-carbazol-9-yl)propanenitrile, there is no strong absorption peak in the visible region and the monomer almost colorless. Therefore, a pale peak belongs to the $\pi-\pi^*$ was appeared at UV region at 327 nm, while the green color of neutral polymer solution showed broad band in visible region at 715 nm. The acidic polymer solution exhibited bathochromic shift behavior, as it showed maximum absorption at 872 nm.

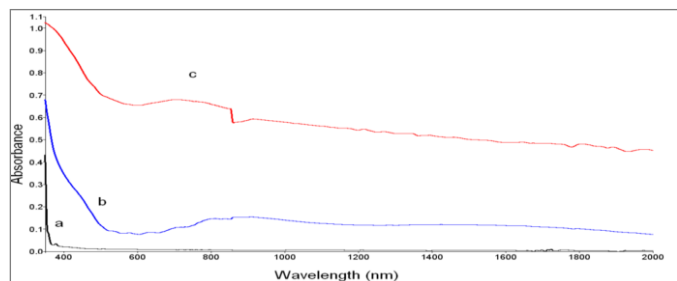


Fig. 6 Ex-situ UV-vis spectra of (a) monomer of 3-(9H-carbazol-9-yl)propanenitrile (Cz-CH₂-CH₂-CN), (b) poly(3-(9H-carbazol-9-yl)propanenitrile) in acid media (PCz-CH₂-CH₂-CN+HBF₄), (c) poly(3-(9H-carbazol-9-yl)propanenitrile) (PCz-CH₂-CH₂-CN) (neutral)

Fig. 7 shows that the poly(3-(9H-carbazol-9-yl)propanenitrile) film exhibited a multi-chromic behavior under various applied positive potentials. The voltage field curves from 0.0 to 1.6 V showed intense bands in the visible light region corresponding to presence of a polaronic charge carrier. With increases the oxidation that leads to generation of bipolaronic bands on the polymer chains at longer wavelengths (red shift). The bathochromic shift produced new bands lead to different colorations for the conducting polymer films.

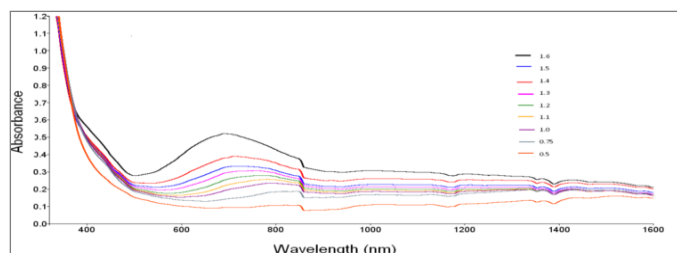


Fig. 7 Spectroelectrochemical analysis of poly(3-(9H-carbazol-9-yl)propanenitrile) (PCz-CH₂-CH₂-CN) + HBF₄ (25 mM) in 0.1 M TBABF₄, and in CH₃CN (Voltage calculated versus standard calomel electrode)

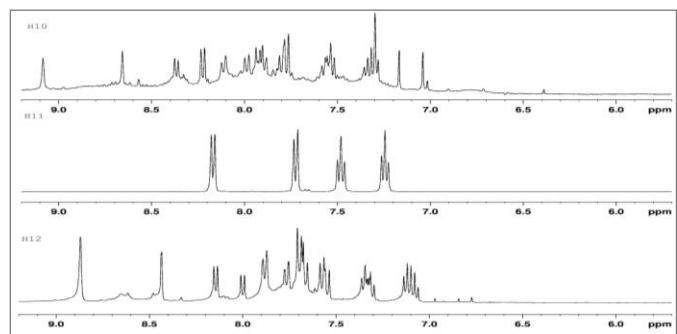


Fig. 8 ¹H NMR (aromatic range) of monomer 3-(9H-carbazol-9-yl)propanenitrile (H11) electrochemically deposited poly(3-(9H-carbazol-9-yl)propanenitrile) in acetonitrile neutral media (H10) (80 mg/mL) and in acetonitrile presence of HBF₄ (H12)

¹H NMR of the third derivative poly(3-(9H-carbazol-9-yl)propanenitrile) was more complicated than the two other derivatives as shown in Fig. 8. ¹H NMR of monomer of Cz-CH₂-CH₂-CN (H11), the two doublets at 8.17 and 7.67 ppm due to ¹H at 4, 5 positions, and 1, 8 positions respectively. The two triplet peaks at 7.48, and 7.24 ppm due to ¹H at 2, 7 position, and 3, 6 position respectively with expected integration ratios. From the ¹H NMR of PCz-CH₂-CH₂-CN (H10), the polymerization mainly may be occurred at 2, 6 position (Fig. 8). Because in this case two singlet peaks were appeared at 9.08, and 8.71 ppm due to 1, 5 position. The four doublets at 8.31, 8.21, 8.15, and 8.10 occurred due to 3, 4, 7, 8 positions. Also, the triplet at 7.75 ppm (CH, t), and the other multiplet (CH, m), at 7.35 ppm may be due to positive charge on doped conducting polymer backbone or to low molecular weight of carbazole polymeric structure. <https://doi.org/10.30799/jacs.241.21070303>

The other singlet peaks at 7.04 and 7.25 ppm due to different coupling. If the coupling at 2, 7 position singlet peaks at 8.71 ppm may be due to ¹H at 1, 8 position, the two doublet (CH, d) at 8.31, and 8.21 ppm due to ¹H at 4, 5 position and 3, 6 positions. The other optional polymerization may be occurred but the result was the same of the other derivatives. In acid media the value of peaks is variable as shown in Fig. 8. Also there are singlet peaks at 7.10 and 7.20 ppm confirmed that polymer formed or coupling at different positions but mainly at 2, 6 position. If there is coupling at the 3, 6, the singlet peak at 8.7 ppm must be attributed to 4, 5 position and the two doublet which mentioned above must be attributed to 2, 7 and 1, 8 positions.

¹H NMR of PCz-CH₂-CH₂-CN + HBF₄ (H12, at 8.9, (CH, s), 8.45 (CH, s), 8.15 (CH, d), 8.0 (CH, d), 7.9 (CH, d), 7.8 (CH, d), 8.0 (CH, d), 7.9 (CH, t), 7.8 (CH, t), 7.7 ppm (CH, t), 7.6 ppm (CH, t), 7.3 ppm (CH, m) (Fig. 8). The same observation for polymer of 3-(9H-carbazol-9-yl)propanenitrile were detected but noted that in acidic media the spectra were different in comparing with other derivatives and the peaks shifted to lower δ value may be due to high shielding occurred by doped polymer and observed that ¹H NMR spectra showed that the polymer chains were grown mainly via the coupling of the monomer at the C(2) and C(6) positions (Fig. 8). The polymerization in acidic media is better than in neutral acetonitrile, also there is a significant different in chemical shift (lower δ value and positive charge effected more in doped polymer).

¹³C NMR δ (ppm) (DMDO-d₆) of monomer of Cz-CH₂-CH₂-CN (H11), 140.5 ppm (quaternary a), 126.4 (C₂), 122.8 ppm (quaternary b), 120.9 ppm (C₄), 119.6 ppm (C₃), 110.0 (C₁). ¹³C NMR δ (ppm) (DMDO-d₆), PC-CH₂-CH₂-CN (H10), 140.57, 140.07, 139.26, 133.20, 132.53, 126.45, 126.30, 123.53, 122.74, 121.05, 120.74, 119.77, 119.45, 110.35, 109.93 (Fig. 9). ¹³C NMR δ (ppm) (DMDO-d₆), PCz-CH₂-CH₂-CN, (H12), 139.70, 138.51, 138.00, 131.61, 130.94, 130.57, 124.72, 124.03, 123.63, 123.31, 123.19, 122.27, 121.94, 121.48, 121.17, 119.47, 119.22, 118.25, 118.18, 117.84, 117.88, 117.23, 116.85, 115.40, 109.11, 109, 108.77 (Fig. 9). The peaks in acid media are observed as more intensity and the polymerization had been improved. Also in acid media new peaks appeared and some of peaks appeared in lower ppm than in neutral (without acidic media).

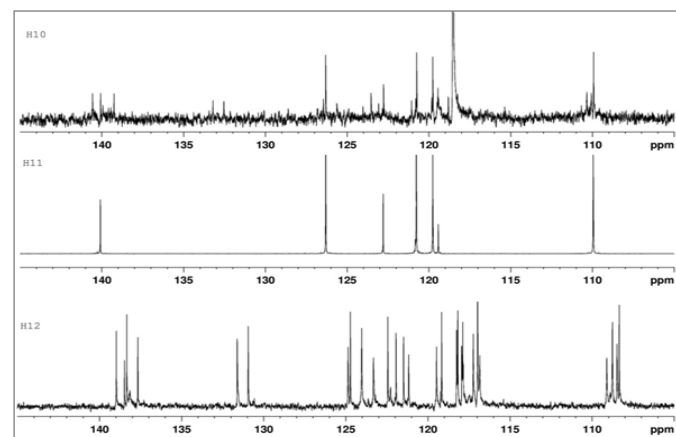


Fig. 9 ¹³C NMR of (aromatic range) of monomer of 3-(9H-carbazol-9-yl)propanenitrile (H11) electrochemically deposited poly(3-(9H-carbazol-9-yl)propanenitrile) in acetonitrile neutral media (H10) (80 mg/mL) and in acetonitrile presence of HBF₄ (H12)

From the Figs. 10–12 and Table 2, the Raman spectroscopy of monomer 3-(9H-carbazol-9-yl)propanenitrile exhibited the major respected peaks. The peaks observed at both 1629 and 1494 cm⁻¹ are associated with the C=O stretching and C=C aromatic bonds, respectively. Table 2 shows that peaks at 1236 and 1020 cm⁻¹ due to C-N stretching and C-O stretching respectively. After polymerization the peaks observed at both 1615 and 1469 cm⁻¹ are associated with the C=O stretching and C=C aromatic bonds, respectively. The peaks at 1277 and 955 cm⁻¹ due to C-N stretching and C-O stretching respectively with no significant different from monomer.

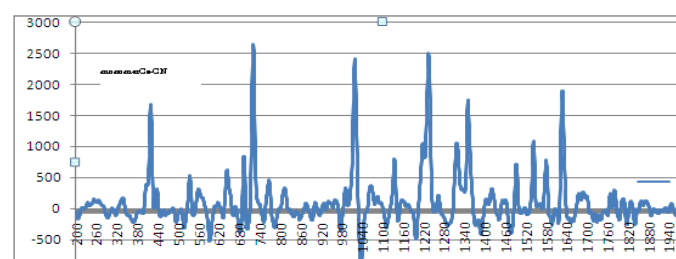


Fig. 10 Raman spectrum of monomer of 3-(9H-carbazol-9-yl)propanenitrile (cm⁻¹)

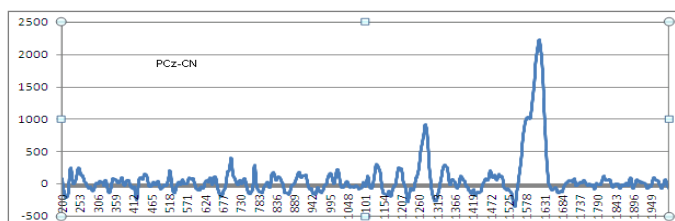


Fig. 11 Raman spectrum of poly(3-(9H-carbazol-9-yl)propanenitrile) (cm^{-1})

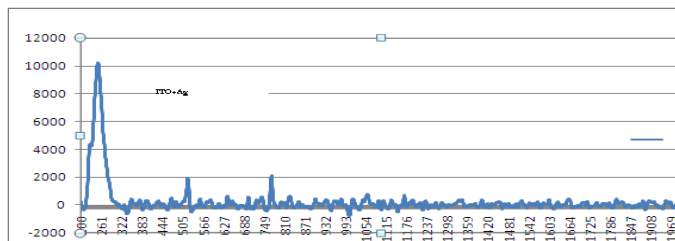


Fig. 12 Raman spectrum of ITO+Ag (as base line)

Table 2 Raman frequency of some functional groups of monomer 3-(9H-carbazol-9-yl)propanenitrile on ITO glass

ITO+Ag, Frequency, (intensity)	PCz-CH ₂ CH ₂ -CN Frequency, (intensity)	Monomer Cz-CH ₂ CH ₂ -CN Frequency, (intensity)
250(1132)	519 (162)	421 (1640)
520(1773)	701 (375)	535 (486)
771(1886)	900 (138)	644 (571)
	995 (1526) C-O str.	722 (2558)
	1131 (256)	767 (415)
	1197 (204)	710 (245)
	1277 (885) C-N str.	1020 (2400) C-O str.
	1332(242) Arom.C-H bend.	1136 (779)
	1469 (160) C=C	1236 (2436) C-N str.
	1615 (2216) C=O str.	1318 (1005)
		1352 (1722)
		1494 (708) C=C
		1544 (1021)
		1548 (705)
		1629 (1881) C=O str.

The surface morphology of the films deposited from electrochemical deposition were taken by SEM. The SEM images taken with homogenous films of aligned gold nanotubes to improve the optical sensing properties [17], using different magnification (2000, 20,000 50,000x) with different picture width (μm). Fig. 13 shows that the oxidized poly(3-(9H-carbazol-9-yl)propanenitrile) film of irregular particles with few clusters.

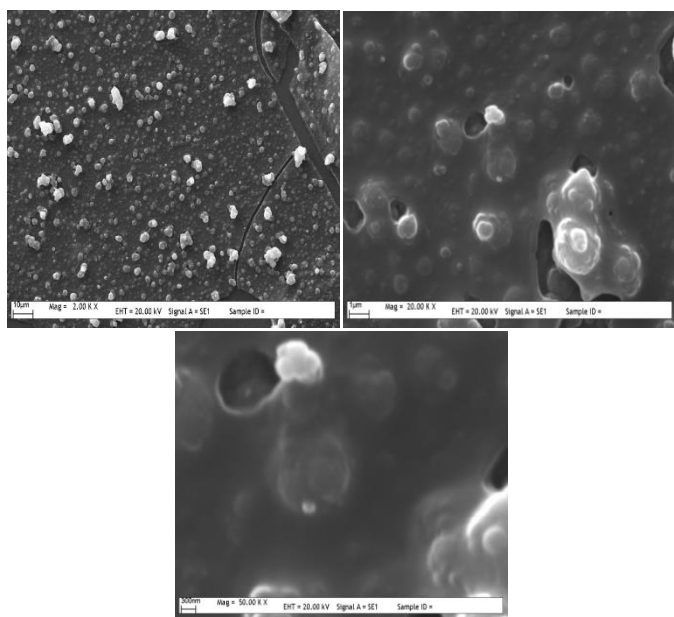


Fig. 13 Scanning electron micrograph of oxidized poly(3-(9H-carbazol-9-yl)propanenitrile)

The doped PCz-CH₂CH₂-CN films were carried out in some solvents such as DMSO, THF, NMP, ACN and DMAC as shown in Table 3. Gel permeation chromatography (GPC), usually with refraction index and viscosity detectors, is the most common way to obtain information about the molecular weight distribution and the results are provided in Table 4. The average molecular weight has been determined by gel permeation chromatography (GPC) and tetrahydrofuran (THF) was used as the solvent and eluent in the GPC analysis. The polystyrene (PS) was used as standard [18]. The sample is dissolved in a suitable solvent, e.g., tetrahydrofuran (THF), by shaking carefully. Under no circumstances, it was dissolved in an ultrasonic bath. When necessary, the sample solution is purified by normal filtration to purify it through a membrane filter with a pore size of 0.2–2 μm . In this study, the reason for the insolubility of the prepared particles was attributed to their high molecular weight. Samples were prepared as reduced (0.0 V) films and dissolved in (7.5 mg/5 mL) THF.

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Table 3 The solubility tests (mg/mL) of 3-(9H-carbazol-9-yl)propanenitrile

Polymers	DMSO	NMP	THF	Acetonitrile	DMAC
PCzCH ₂ CH ₂ -CN(n) (mg/mL)	80	2.4	2.0	2.8	4.0
PCzCH ₂ CH ₂ -CN +HBF ₄ (mg/mL)	70	1.8	1.8	1.6	1.2

Table 4 The molecular weight of poly(3-(9H-carbazol-9-yl)propanenitrile)

Polymer	Average molecular weight (Mw)	dispersion
PCz-CH ₂ CH ₂ -CN(n)	29500	1.03
PCz-CH ₂ CH ₂ -CN +HBF ₄	37900	1.03

4. Conclusion

In this work, newly prepared monomers were electrochemically polymerized to give a new polymer which backbone consisted of carbazole. This new polymer classified as conducting polymer with a good solubility in some organic solvents. These findings reported here a novel electrochromic system which gives strong green colour in oxidation state, and a transparent in reducing state indicates possibility of a new materials. The electrochemical and spectroscopic data obtained give strong evidence that polymerization of poly(3-(9H-carbazol-9-yl)propanenitrile) was occurred upon electro-oxidation of the monomer. The formed polymer films were also characterized by FTIR, UV-Vis, spectroelectrochemical analysis, NMR, Raman spectroscopy and SEM. The average molecular weight of the polymer was determined using GPC with THF as a solution, and it was found that the polymer possesses a high molecular weight, and the insolubility behavior of the polymer can be attributed to its high weight.

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