Novel anodic oxidation of 1-amino-9-fluorenone and its electrochemical behavior

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Abstract

Electrochemical polymerization of 1-amino-9-fluorenone, AFO, was studied in CH_2Cl_2 solution with tetrabutylammonium perchlorate, $TBAClO_4$, as the electrolyte, via continuous cyclic voltammetry. The anodic oxidation of 1-amino-9-fluorenone was performed in organic solvents with the aim to prepare new conducting polymer materials. 1-amino-9-fluorenone anodic oxidation led to formation on gold electrodes of electroactive polymer films that were characterized by cyclic voltammetry. FT- IR spectra, FT- IR spectra of AFO by computational chemistry in density functional theory (B3LYP/3-21 G*), and UV-Vis indicates that films are mainly constituted of short chain oligomers also show that polymer present coupling on carbonyl group. The oligofluorenone is electrochemically active and the colour change from yellow to blue during polymerization, which provide potential application in fabrication of organic electronic displays electroluminescent devices and anti cancer drugs. PAFO films obtained from this media showed good redox activity and stability. Factors affecting film formation by successive potential scans like potential limits, scan rate, number of cycles, monomer concentration, and chronoamperometry.

Keywords: Polyaminofluorenone, Electrochemical polymerization, Electrochemical activity

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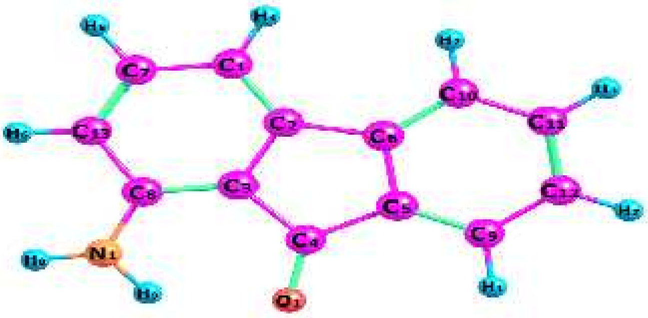
1. Introduction

Since the synthesis of the first polyfluorene by anodic oxidation of fluorene, a great deal of work has been performed leading to the synthesis of more than 20 different polyfluorenes. Electroactive polyfluorene films can be electrodeposited on platinum and glassy carbon electrodes both by anodic coupling from fluorene and by nickel-catalysed reduction of disubstituted fluorenes in acetonitrile, AN(1-3). Polyfluorenes are highly fluorecent and there exists quite a large number of works related to light emitting diode applications of fluorene based polymers(4-7). However, the reversible electroactivity of these polymers lies in a high potential range (i.e. 0.8-1.2V vs Ag/Ag+) thus, they cannot be synthesised and used as electrode modifiers in aqueous medium. Electrochemical polymerization of 9-fluorenone, FO, was studied in CH_2Cl_2 solution with tetrabutylammonium tetrafluoroborate, $TBABF_4$, as the electrolyte, via constant potential electrolysis, CPE. Prior to CPE, the redox behavior of FO was investigated in the same solvent/electrolytic medium using cyclic voltammetry, CV. CPE of FO yielded an insoluble polymer deposit on the electrode surface. The product was characterized by FTIR spectroscopy techniques. The redox and spectroelectrochemical, SPEL, behavior of the polymer were studied by CV and in situ UV–Vis spectrophotometric techniques at various potentials, respectively(8-16).

Poly(9-fluorenecarboxylic acid) (PFCA) was synthesized by electrochemical oxidation of 9-fluorenecarboxylic acid (FCA) using a mixture of nitromethane and boron trifluoride diethyl etherate as the solvent and tetrabutylammonium tetrafluoroborate as the supporting electrolyte. An insoluble and conducting brownish-orange film was deposited on the electrode surface, both during repetitive cycling and constant potential electrolysis at 1.15V (17-25). Characterization of the polymer film has been carried out using Fourier Transform Infrared spectroscopy technique and thermal behavior was studied via thermal gravimetric analysis. Structural analysis showed that the polymerization of FCA occurred at 2,7-position(26-33). Spectroelectrochemical behavior of the polymer film on indium tin oxide working electrode was studied by recording the electronic absorption spectra, in-situ, in monomer-free electrolytic solution at different potentials and it is found that the PFCA film can be reversibly cycled between 0.0V and 1.2V(34-39). Furthermore, a dual type electrochromic device based on PFCA was constructed and its spectroelectrochemical properties were investigated. The electrochromic device exhibits color change from transparent to dark blue with a good open circuit memory.

Polyfluorene and its derivatives are an important class of electroactive and photoactive (40) materials from both fundamental and practical perspectives, i.e., they have exceptional electrooptical properties for applications in polymer light emitting diodes. Reductive aryl–aryl-couplings of dihaloaryls according to Yamamoto, aryl–aryl cross-couplings of aryldiboronic acids and dihaloaryls according to Suzuki, or of distannylaryls and dihaloaryls according to Still, have paved the way for chemical synthesis of polyfluorenes. Electrochemical polymerization can be achieved through cathodic or anodic methods, and the latter is more usually used with the following advantages. First, small monomer quantities are required while chemical polymerization requires substantial monomer quantities for polymerization, isolation, and characterizeation of the corresponding polymer(41-44).



Scheme. 1. Structure of 1-amino-9-fluorenone

2. Experimental

2.1. Chemicals

1-aminofluorenone (AFO), from (Sigma and Fluka, 97% pure), CH_2Cl_2(99%) and $TBAClO_4$ (97%) were obtained from Aldrich Co., and used without further purification. Hydrochloric acid (BDH) was used without further purification. Freshly distilled water was always used to avoid contamination with atmospheric CO_2.

2.2. Electropolymerization

Electrochemical measurements were carried out with a Voltalab potentiostat 006. Gold disk electrode (diameter:3mm) was used as working electrode. The reference electrode was Ag/Ag+ and Pt wire was used as an auxiliary electrode. The working electrode used in CV was polished before each measurement with alumina slurries (particle size 0.3µm). The electrode was then washed thoroughly with non- aqueous solutions, and dried in air. After that the electrode was dipped in methylene chloride solution containing(0.1M $TBAClO_4$) and 2×10^{-3}M of AFO for electropolymerization by potential cycling between 0V and 3V for defferent number of cycles at a scan rate of 100mV/s. The electrode obtained was denoted as polyaminofluorenone(PAFO)/Au, film electrode. The solubility of the formed polymer was tested by UV-Vis technique.

3. Results and Discussion

3. 1. Electrochemical study of monomer

The oxidation potentials of monomers were measured on gold electrode in $2x10^{-3}$M organic solutions, using cyclic voltammetry and the potentiostatic mode. The results of the monomer electrochemical studies are summarized in (Table.1). The potential scans of the monomer presented reversible waves. The anodic part of the AFO voltammograms exhibited two oxidation peaks observed at 1.77Vand 0.7V. The appearance of oxidation peak in AFO voltammograms suggests the probable existence of two oxidizable sites with different energies in the molecule this hypothesis is in agreement with the IR studies also indicate the presence of coupling sites. In all cases the peak current intensity varied linearly with the scan rate square root in the range 10-200mV. The results confirm that the redox processes are controlled by diffusion of electroactive species at the Au electrode. The oxidation potentials of all aminofluorenone derivatives are much lower than that of fluorene (Eox=1.8) (45,47). More over when compared with fluorene, the significantly lower potentials of AFO the respective electron-donating. The comparison of the cyclic voltammograms of fluorene, 2,7-diaminofluorene, fluorenone and aminofluorene (46,48)leads us to associate the last compounds first oxidation waves with E maximum to an electron abstraction on the fluorenic unit followed by a second electron abstraction, in the case of compounds, the polymerization is effective only after this second oxidation that leads us to think that the polymerization is performed only after the phenyl unit oxidation.

Table. 1. CV parameters obtained for electrochemical polymerization of AFO at the scan rate 100mV/s.

[M] mol/L	***I*pa µA/cm^2**	***I*pc µA/cm^2**	**% drop of I_{pa}**	**% drop of I_{pc}**
2×10^{-3}	101	-89	22	17
1×10^{-3}	83	-67	39	28
1×10^{-2}	60	-57	53	37
4×10^{-3}	89	-59	25	32
4×10^{-4}	60	-58	37	29

3.2. Electropolymerization studies

The electrochemical deposition of films on a Au electrode was carried out in organic solutions containing 2x10^{-3}M of monomer. Irrespective of the monomer chosen, films can be prepared by cyclic voltammetry (cv) and potentiostatic modes. Polymer solvents containing only 2x10-3M of monomer at this concentration and even in more diluted. The organic solvents used for electropolymerization were selected according to the physicochemical properties of deposited films, for instance the formed poly aminofluorenone films were completely soluble in dichloromethane for electropolymerization. The electropolymerization of AFO led to good quality, thin films, which were multicolor becoming, dark upon oxidation and bright upon reduction poly aminofluorenone (AFO). Poly AFO films were electro synthesized by the galvanostatic mode rather than by cv because polymer over-oxidation completed with monomer oxidation during the scans. The films were formed to give smoothly with time and exhibited oxidation and reduction processes. The films were obtained by cv in dichloromethane more easily than in acetonitrile solvent. The current intensity grew regularly with the number of cycles, and the polymer oxidation and reduction peaks appeared practically at the same potential values for any number of cycles. The film thickness could reach several microns without any film alteration. For the poly AFO voltammograms, the polymer over-oxidation, did not compete with monomer oxidation, neither with film growth, poly AFO films were dark blue in the oxidation state, and become yellow- grene in the reduced state. **(**Fig. 1.) shows a typical cyclic voltammogram of 2x10^{-3}M of AFO in CH_2Cl_2 containing 0.1M $TBAClO_4$ at gold disk electrode. The monomer electrooxidizes in two reversible peaks at 1.77V and 0.7V. The first oxidation peak is shift to more positive because of the presence of the electron-withdrawing carbonyl group present in AFO. The intensity of this reversible peak increases after each successive cycle a very thin and transparent film with blue colour covering the gold electrode surface was observed[ref]. The first peak(Ox1) could be attributed to the oxidation of the amino group to the corresponding radical cation ($NH_2^{\cdot +}$). The presence of carbonyl group in the fluorenone ring will increase the oxidation of flourenone as previously observed in the oxidation of AFO (ref). Therefore, the first oxidation peak is more positive than that of fluorene because of the presence of the electron-withdrawing carbonyl group present in AFO. This growth behaviour is in close agreement with that reported previously for the electropolymerization of 2-aminofluorene and fluorenone in methylene chloride in presence of $TBABF_4$ as supporting electrolyte and other fluorene derivatives(ref). The prepared modified electrode (ME) was removed from electrolysis medium, rinsed with methylene chloride to remove any monomer traces and then transferred to a pure aqueous 0.01M HCl solution to characterize the electrochemical response of the modified electrode(ME).

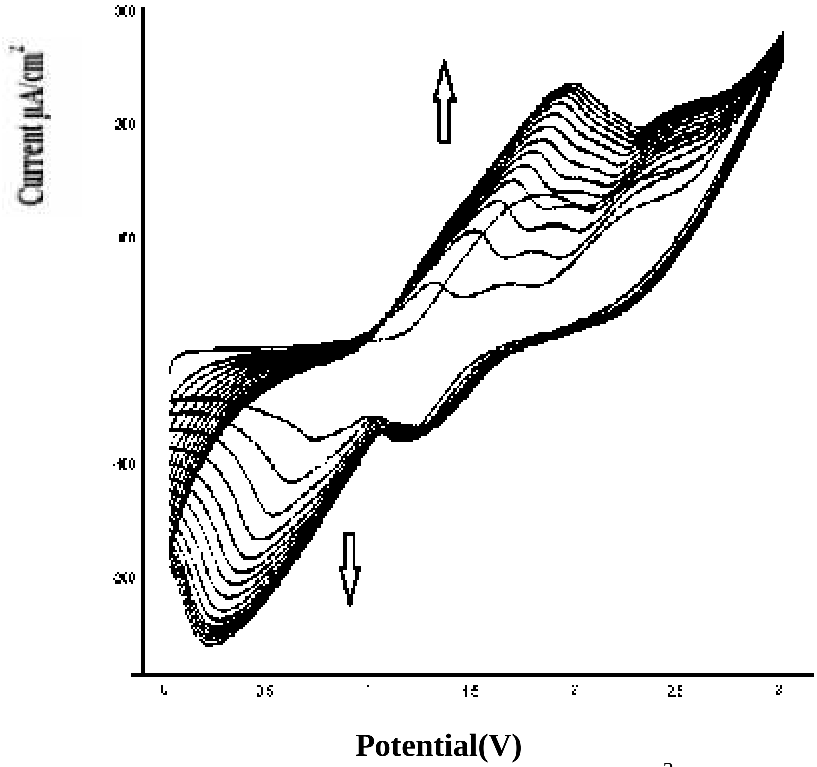


Figure. 1. Cyclic voltammmograms of 2 ×10^{-3}M of AF0/Au electrode in 0.1M $TBAClO_4$+CH_2Cl_2 solution at room temperature, ν: 100mV/s,15cycles.

3.3. Effect of monomer concentrations on the film formation

(Figure.2(a-d)) shows typical cyclic voltammograms recorded during the electrochemical geowth of poly(AFO) at gold electrode in CH_2Cl_2 solution containing 0.1M TBAClO4 and four different monomer concentrations4 ×10^{-3}M(a), 1 ×10^{-3}M (b) 1×10^{-2} (c) and 4×10^{-4}M (d) of AFO. AFO electrooxidzes reversibility and its oxidation appears peak (Ox1) at 1.77V,(Ox2) 2.25V during the first voltage scan before the potential reaches the upper limit 0f 3V. a reduction peak (Red1), (Red2) for the product formed during the anodic scan is observed (Red1) at 1.1V, (Red2) at 0.7V. Based on the comparison of the data with the previous results (ref) concerning the oxidation of other aromatic amines. The fact that cathodic peak corresponding to this anodic peak is rarely observed in this case indicates fast consumption of the electrogenerated monocation radicals by follow-up chemical reaction(ref). As the scan continues, the oxidation peaks for AFO shift in a more positive direction. The film formed during the first few potential cycles does not appear very electroactive, and thus the film formed during the early stages seems to incrase the overpotential for the oxidation of the monomer. This may be because products produced at the beginning may have smaller molecular weights and are poorly conductive. Upon further scaning, it was observed that the reversible oxidation peak (I) of the monomer with appearance of a new reduction system(IV) at 0.6V. The currents of this new system increase by continous cycling which indicates an accumulation of the electroactive polymer film on the electrode surface. These growth behaviours are in agreement with those reported (ref) for the electropolymerization of fluorene and fluorene derivatives, in acetonitrile at platinum electrodes. By oxidation of fluorene and its drivatives, the possibility that these products are polymer of AFO was considered.

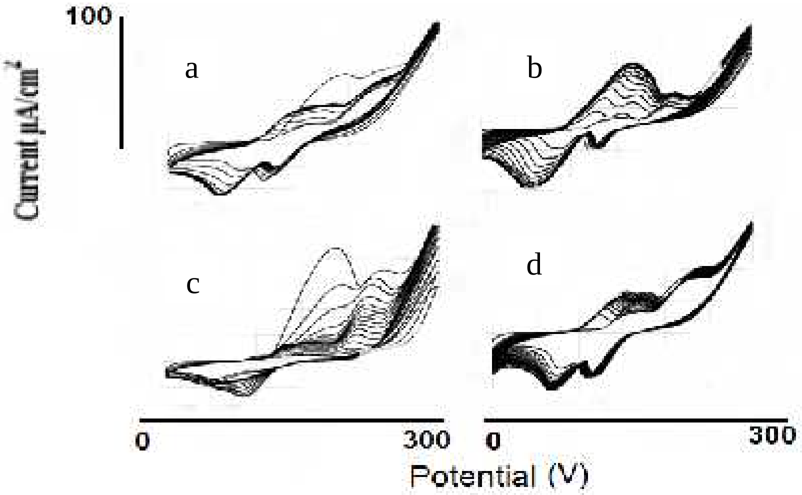


Figure.2. Cyclic voltammmograms of PAFO/Au electrode in 0.1M $TBAClO_4$+CH_2Cl_2 solution at 4 ×10^{-3}M(a) 1 ×10^{-3}M (b) 1×10^{-2}M (c) 4×10^{-4}M (d) AFO,ν: 100mV/s.

3.4. Electroactivity and stability studies

The poly(AFO) cyclic voltammograms, carried out in a monomer- free 0.1M TBAClO4 with a solvent solution, demonstrate that the films presented a good electroactivity, with well defined oxidation and reduction peaks. The current intensity of peaks varied linearly with the scan rate ranging between 10 – 200mV/s, with suggested a thin layer behavior (Fig. 3). The stability of polymer film was examined in monomer solution, when submitted to great number of cycles in the range of 0.7- 1.7V Ag/AgCl, the film exhibited electroactivity. The poly(AFO) film presented more stability with CH_2Cl_2 at 2x10^{-3}M of monomer than another concentrations. The electrochemical and electroactivity stability of the poly(AFO) films, the electrochemical behavior of the polymer films were studied in monomer free (Fig.4) and in hydrochloric acid (Fig.5) similarly to the results in the literatures (10) the steady-state cyclic voltammograms represented broad anodic and cathodic peaks. The peak current densities were both proportional to the scan rate, indicating the reversible redox behavior of the PAFO (poly-aminofluorenone) associated with the film were present in monomer free PAFO. The results was also can be found in the electropolymerization of 2-aminofluorene and fluorenone (8). Based on this discussion, the second process, at the higher potential was related to both protonic and electronic exchanges between the polymer and the electrolytic solution. In (Fig. 4) the anodic and cathodic peak potentials of PAFO film was depend on the scan rate, which suggested that these redox reactions were both reversible in diluted hydrochloric acid. The peak potential shift of conducting polymer is hardly explained by conventional kinetic limitations such as ion diffusion or interfacial charge transfer processes.

The main reasons accounting for this phenomenon are usually as follow(24), show heterogeneous electron transfer, effects of local rearrangements of polymer chains, show mutual transformations of various electronic species and the electronic charging of a sum of two interfacial exchange corresponding to the metal/polymer and polymer/solution interfaces. The poor stability of conducting polymer is one of the main obstacles to the application in polymeric and organic LEDs.

The relation between time and current curves under potentiostatic polymerization condition is given in (Fig. 6) the current decays as the electrolysis proceed to deplete the solution near the electrode of electroactive species. The mechanism of electrochemical polymerization of monomer is believed to proceed via a radical cation which reacts with a second radical cation to give a dimer to build up the polymer. The polymer chain built up by formation through conjugation of radicals of of two different monomers propagation (42). The higher applied potential, the higher current density, indicating the increase of the electro-polymerization rate and the amount of electroactive poly-aminofluorenone (PAFO) films deposited on the Au electrode(43).

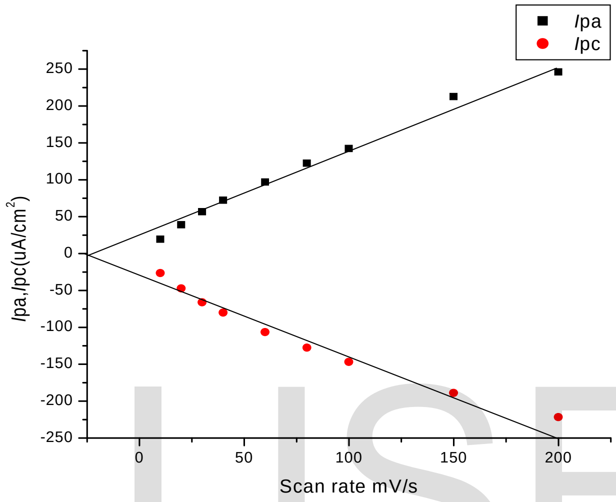


Fig. 3. Variation of current function ($I\mu A/c^2$) with voltage scan rate in mV/s for $2x10^{-3}$M AFO in 0.1M $TBAClO_4$+CH_2Cl_2 solution at a potential scan rate 200, 150, 100, 80, 50, 40,30, 20, 10 mV/s.

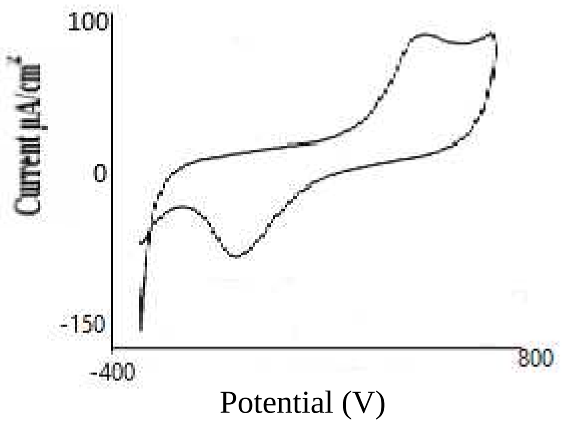


Fig. 4. Cyclic voltammmograms of 2×10^{-3}M PAFO/Au electrode in 0.1M $TBAClO_4$+CH_2Cl_2 solution free of monomer.

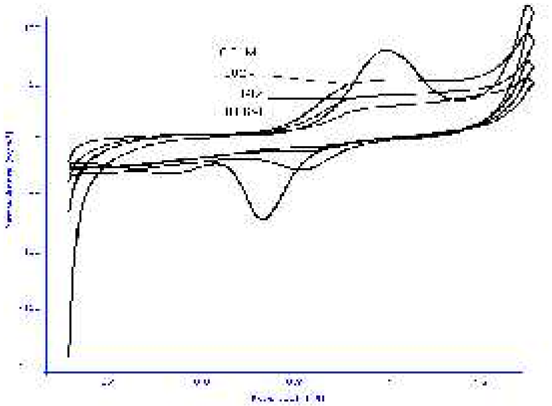


Figure.5. Cyclic voltammograms of PAFO/Au electrode in 0.01M HCl at different monomer concentrations, 2×10^{-3} M(1) 1×10^{-3} M (2) 4 $\times10^{-3}$ M (3)4×10^{-4} M (4) 1×10^{-2} M (5). 100mV/s, 15cycles.

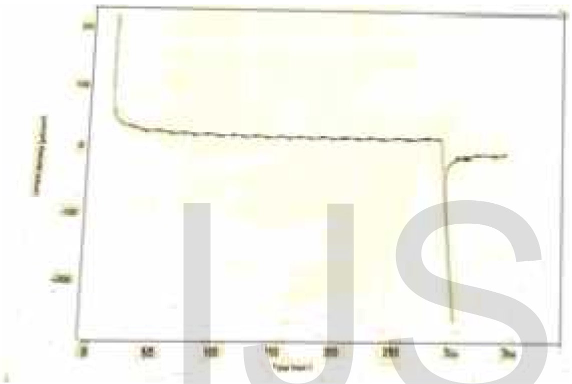


Figure. 6. Chronoamperometric curves of PAFO/Au electrode under potentiostatic polymerization, at 100mV/s, 15cycles.

3.5. Physicochemical analysis of the polymer

3.5.1. UV-Visible spectra

UV-visible spectra of PAFO polarized at 2.0V vs gold electrode in a solution of AFO and $TBAClO_4$ dissolved in CH_2Cl_2 (Fig.7). Electronic absorption spectra of the polymer film were recorded. The polymer film has three absorption bands: at 305, 470nm and 545nm. The first absorption band is related to the π- π* transition of the polymer backbone, the absorption spectrum of polymer presents onlytwo strong bands at 305 and 470nm and the spectrum tailed off to about 545nm, which is mainly due to the increase of the conjugated chain length. The PAFO results formed the soluble part of the sample prepared in the mixed electrolyte was mainly composed of the polymer with repeated AFO units. The fluorescence spectrum of aminofluorenone exhibits a broad band with several fine structure at 370, 415nm, excited at 305nm while only one strong and broad fluorescence band at 545nm excited at 435nmwas observed in the spectrum of poly-aminofluorenone solution. Furthermore, the fluorescence intensity of polymer is stronger that than of AFO in the solutions with the same concentrations relative to fluorenone repeat units. The spectral results described above indicate that the electrochemically synthesized polymer FO have longer effective conjugated lengths and can emit much stronger and more unitary colored fluorescence light than those of monomer, a large absorption band corresponds the (ref).

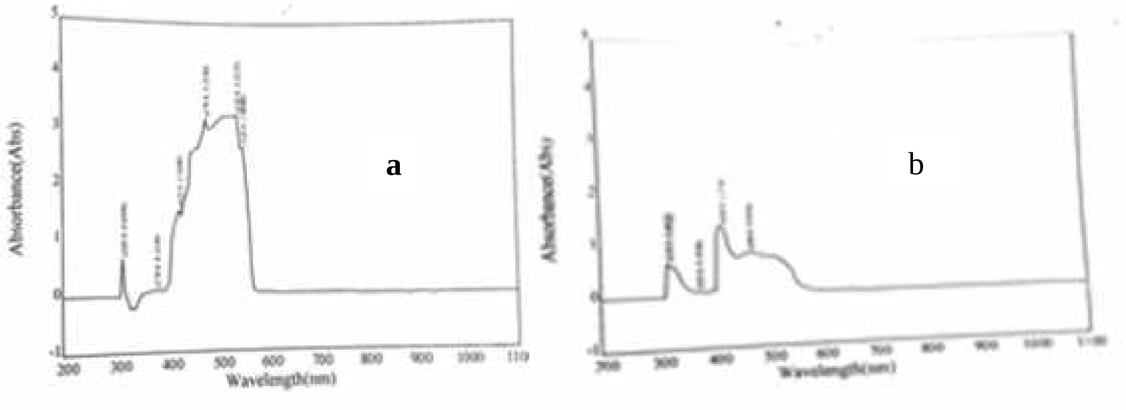


Figure.7. UV-Vis spectra of 2 ×10^{-3}M of AF0/Au electrode in 0.1M $TBAClO_4$+CH_2Cl_2 solution at room temperature, ν: 100mV/s,15cycles at AFO(a) polymer-AFO(b).

3.5.2. IR-spectroscopy

FTIR spectra of aminofluorenone and dedoped polyaminofluorenone (PAFO) films. A compound has hydrogen bonded to sp2 carbons in the benzene ring. The absorption obtained at 3000cm-1in the polymer (Fig. 8) indicates that hydrogen's attached to sp2 carbons. N-H bending vibration occur at 1607cm-1 in the monomer, whereas obtained at 1634cm-1 in PAFO, N-H stretching at 3210cm-1 in monomer and obtained at 3170cm-1 in PAFO, C-C absorption bond in monomer at 955, 1221, 800cm-1, whereas the absorption band in PAFO at 918, 1038, 1101cm-1. C-H bending vibrations for hydrogen bonding's bonded to sp2 carbons gives rise to absorption bonds in the 1381cm-1 in monomer and at 1447cm-1 in polymer. The absorption band for the carbonyl group (C=O) obtained at 1678cm-1 and at 1699cm-1 in polymer.

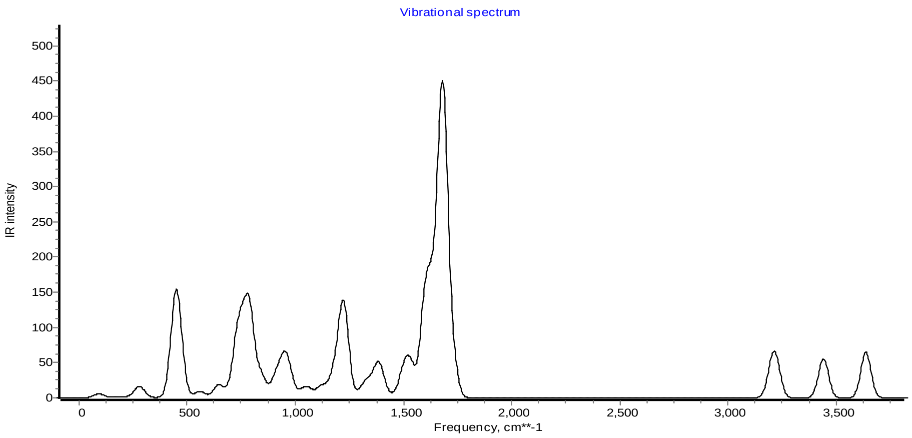


Figure.8a. FT-IR spectra of AF0 on DFT-B3LYP.

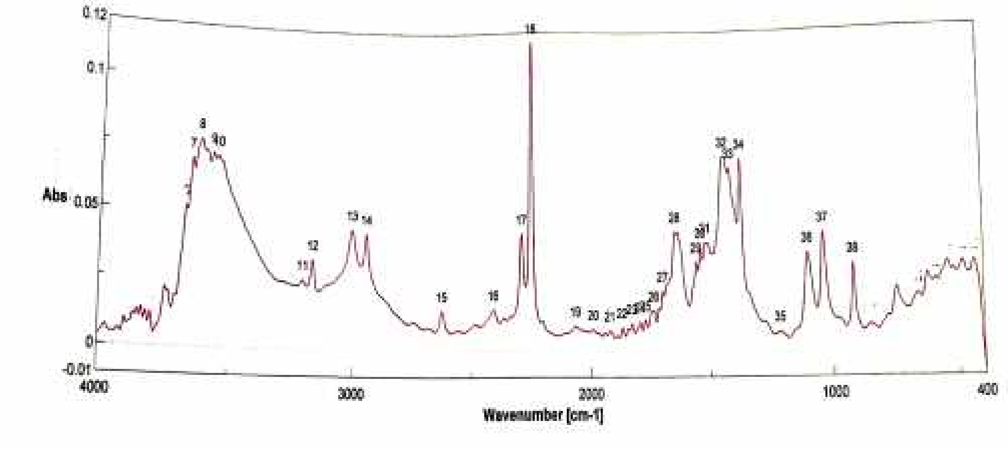


Figure.8b. FT-IR spectra of 2 ×10^{-3}M of AF0/Au electrode in 0.1M $TBAClO_4$+CH_2Cl_2 solution at room temperature, v: 100mV/s,15cycles at PAFO.

3.6.. Conclusion

I conclude that films of poly(AFO) could be prepared by repeated cycling in CH_2Cl_2 containing 0.1M $TBAClO_4$. The films prepared show electroactivity both in organic solvents and in diluted acidic medium(0.1M HCl). The electrochemical behavior of PAFO resembles that of polyaminofluorene, polyfluorenone(PFO) polyaniline synthesized in the same medium. The electrochemical characterization of the PAFO, such as UV-Vis spectra, IR-spectra, chronoamerometry, show the electro-polymerization of other NH_2 group-containing aromatic compounds and we can supposed the mechanism on its polymerization

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