# An Overview Of Physical Properties Of Poly(Aniline-Co-2-Fluoroaniline)

**Umesh.S. Waware[1]*, Mohd Rashid[2]*, G. J. Summers[3]**
[1]Department of Mechanical and Industrial Engineering, Qatar University, P.O.Box 2713, Doha, Qatar.
[2,]Department of Applied Sciences, Vivekananda College of Technology and Management, Aligarh. India.
[3]Department of Chemistry, University of South Africa, P.O .Box 392, UNISA, Pretoria 0003, South Africa
Corresponding authors emails: Umesh S. Waware (uswaware@gmail.com), Mohd Rashid (rashidchem@gmail.com)

***Abstract*—Tubular and amorphous assemblies of copolymers of poly(aniline-co-2-fluoroaniline) have been synthesized by conventional chemical oxidation method. The molar feed ratio of monomers was varied to prepare copolymers of different compositions. The morphology, structural and physical properties of the as-synthesized copolymers were characterized by SEM, UV, IR-spectroscopy, electrical conductivity, solubility and thermogravimetric (TGA) analysis. The copolymers show different electrical conductivity and solubility depending upon the molar feed ratio. These copolymers are highly soluble in the some solvent such as NMP. The spectroscopic studies show that aniline and 2-fluoroaniline units are uniformly distributed along the main copolymer chain and the physical properties of copolymers can be tailored by varying the monomer in the feed ratio of copolymerization reaction. The electrical conductivity decreases upon increasing in the fluoroaniline in copolymerization reaction, the incorporation of functional group viz; flouro(–F) which reduces the conjugation in the polymer chain. The TGA reveals that poly(fluoroaniline) is thermally more stable than polyaniline; it is probably due to incorporation of –F atom along the polymer backbone.**

***Keywords—Poly(aniline-co-2-fluoroaniline); fluoroaniline);Solubility;Polyaniline; Conductivity***

## I. INTRODUCTION

Increasing use and applications of the conjugated polymer in the electronic devices have made them the material of the twenty-first century. They may be considered as “smart or active” polymers. Amongst the conjugated-conducting polymers, polyaniline (PANI) is being the most intensely and extensively studied polymer because of its highly incredible chemistry. In the Chemical synthesis of polyaniline by conventional method, an oxidant and a strong mineral acid as doping agent have been used [1]. It is stable and environmentally benign due to its aromatic and nitrogenous structural backbone. The polyaniline essentially possesses unique acid-base/doping-dedepoing behavior and relatively easy chemical processing. Only very few reports are published with electron-withdrawing groups for the functionalized PANI, Among these limited studies, the F-containing PANI have received much attention owing to the unusual properties of fluorine atom, such as small atomic size, high electronegativity and high chemical reactivity. The poly(fluoroaniline)s prepared by the conventional chemical and electrochemical polymerization methods from fluoroanilines have been found to be poorly conductive ($10^{-6}$-$10^{-5}$ S/ cm)[2-4].Fluorine functionalized highly conductive and electroactive polyanilines has been reported by Han and Chen[5]. Poly(aniline-co-fluoroaniline) has be reported as a biosensors for ammonia [6-8]. Many PANI derivatives have been reported based upon modification of oxidation state, dopants and polymerization conditions [9-13]. PANI on doping with protonic acid yields electrical conductivity in the range of $10^{-6}$- $10^{-2}$ S $cm^{1}$, depending upon the nature of doping acid and the processing conditions [12-14]. Some of the interesting characteristics of the PANI are its solubility, fusibility and dispersion ability for electrical devices. Substituted PANI such as Poly(aniline-co-fluoroaniline), [2,15-17] are more soluble and less conducting due to F substituent. Different approach have been applied to overcome these disadvantages viz; use of molecular design, modification of monomer structure, use of functionalized acid dopant, formation of blends/composites and copolymerization. In principle, copolymerization is the most accepted approach to provide greater dispersion ability to the PANI. The properties of copolymer can be tailored and modified by adjusting the molar ratio of monomers in the feed. The aim of the study is to investigate the as-synthesized copolymer to achieve improved physical properties viz; spectral, morphological and thermal stability and higher solubility in commonly used organic solvents such as DMSO, NMP, chloroform and rather higher electrical conductivity than polyaniline.

## II. *Experimental*

### *A. Material and Methed*

Aniline (Aldrich) was distilled twice prior to use. 2-Fluoroaniline (Aldrich), Ammonium persulphate, hydrochloric acid were of analytical grade and NMP, DMSO, DMF used were of spectroscopic grade. All aqueous solutions were prepared using double-distilled water. The Polyaniline (PANI) and poly(2-fluoroaniline) P-2-FA were synthesized by oxidation of aniline and 2-fluoroaniline separately with ammonium persulphate in 1M hydrochloric acid according to modified procedure reported [17]. Typical procedure involved in the synthesis of copolymer of P(A-co-2-FA) is given as follows. To the aqueous solution of aniline and 2-fluroroaniline in 1M HCl ,ammonium persulphate as an oxidant (molar ratio of monomers to oxidant 1:1) was added for oxidative coupling in order to obtained copolymers of different compositions, the mole fraction of 2-fluoroaniline in the reaction mixture was varied from 0.4 to 0.7. The steps involved in the copolymerization process are shown in scheme 1. Aniline (0.93 g) and 2-fluoroaniline (1.08 g) were dissolved in 200 ml of 1M HCl solution in a Elmyer flask. The solution was cooled to a temperature of 0-4 $^{o}$C. A precooled solution of ammonium persulphate (4.56 g) dissolved in 200 ml of 1M HCl was then added slowly in to the monomer solution with continuous stirring at the temperature of 0-4$^{o}$C under nitrogen atmosphere. The polymerization reaction was left for another 5 hrs. The reaction mixture was than kept for 24 hrs at room temperature; the precipitate of the as-synthesized copolymer was filtered off and subsequently washed with small volume of 1M HCl and dried in oven for 8 hrs at 80 $^{o}$C. A blackish green emeraldine salt was obtained. Emeraldine salt form of copolymer was converted into base form after treating with 1M $NH_4$ OH for 24 hrs. The precipitate of emeraldine base of copolymer was filtered and washed and dried in oven.

### *B. Charaterization*

The solubility of functionalized PANI derivatives in the powder form was confirmed by dissolving as-synthesized copolymer in NMP, 10 mg of polymer powder was allowed to disperse completely in 100 ml of solvent. The dispersion was kept for 24 hrs at room temperature of 25 $^{o}$C, the dispersion was filtered through sintered glass crucible (porosity 2 micron) and the room temperature solubility was determined. FT-IR spectra were recorded on a Perkin-Elmer 883 Infrared spectrophotometer. The room temperature electrical conductivity of compressed pellet of salt form of polymer was measured using two probe method using Keithley 617 electrometer. Thermal analysis was carried out with an instrument Auto Hi-Res Q500 Thermogravimetrical Analyszer by heating the polymer sample at a rate of 10$^{o}$C/min in nitrogen atmosphere. The morphology of polyaniline and the poly (aniline-co-fluoroaniline) nanostructure was investigated by a JEOL-6700 field emission scanning electron microscope (SEM).

## III RESULTS AND DISCUSSION

### *A. Solubility*

The solubility criteria of as-synthesized copolymers P(A-co-2-FA) of different monomer compositions was studied in the organic solvents viz; dimethylformamide (DMF), dimethylsulphoxide (DMSO), acetone, water, and NMP. The copolymer of P(A-co-2-FA) and P(2-fluroaniline) were highly soluble in NMP while the polyaniline showed sparingly soluble nature as shown in table I. P(2-fluoroaniline) (P-2-FA) and P(A-co-2-FA) show higher solubility in the non-polar solvents, that may be considered as an indication of copolymerization process in occurred in the polymers and there was an incorporation of 2-fluoroaniline unit in the backbone of the parent polymer and thus provide the higher solubility to the copolymer. P(2-FA) has relatively higher solubility than PANI [18]. The $F^-$ atoms, introduces flexibility in the rigid polyaniline backbone structure, thereby increasing the solubility of the copolymers. Another possible reason for the increased solubility might be the low molecular weight of polymer.

### *B. Electrical conductivitiy*

The electrical conductivity of individual copolymer measured by two-probe method is given in the table I. The electrical conductivity measured to the magnitude of $10^{-1}$ S cm$^{-1}$ for PA and to the order of $10^{-6}$ S cm$^{-1}$ for P(2-FA. The magnitude of electrical conductivity is different for different copolymer depends upon the molar feed ratio. The lower conductivity of P(2-FA is probably due to $F^-$ atom present at *ortho* position of aniline monomer. Fluorine atom present at *ortho* position produces a non-planar conformation which causes the disorder in the backbone of polymer [8], however, the mobility of electrons through the chain of polymer is restricted and thus, the conductivity of P(2-FA) gets lowered. The larger the content of 2-fluoroaniline in the copolymer composition, the greater the non-planarity in the copolymer chain which in turn results in the decrease of conjugation system and hence the electron delocalization and electrical conductivity decreases. The structural details of the conjugated homopolymer and the copolymer are shown in figure 1(a, b), respectively.

**Table 1.** Experimental values of solubility and electrical conductivity of homopolymers and copolymers.

| Polymers | Solubility (W/V %), ( g/dL) (NMP) | Electrical conductivity. σ, (S/cm) |
|---|---|---|
| PA | 07.40 x $10^{-2}$ | 1.25 x $10^{-1}$ |
| P(A-co-2-FA)70 | 80.46 x $10^{-2}$ | 5.23 x$10^{-5}$ |
| P(A-co-2-FA)50 | 77.31 x $10^{-2}$ | 5.81 x $10^{-5}$ |
| P(A-co-2-FA)25 | 75.04 x $10^{-2}$ | 6.27 x $10^{-4}$ |
| P(A-co-2-FA)10 | 73.11 x $10^{-2}$ | 6.42 x $10^{-4}$ |
| P(2-FA) | 84.37 x $10^{-2}$ | 3.40 x $10^{-6}$ |

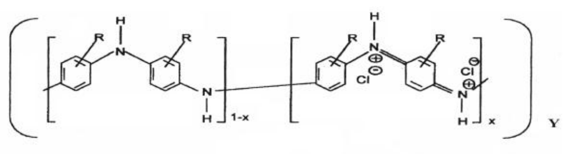

Fig. 1 (a). Repeat unit for homopolymers ( R = H for PA, R = F for P-2-FA)

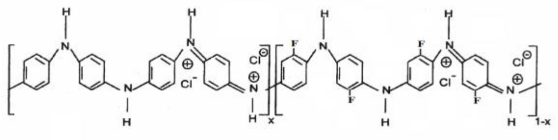

Fig. 1 (b). Repeat unit for copolymers.

### *C . Electronic spectra*

The electronic spectra of the homopolymers and copolymers taken in DMSO as shown in Fig 2.In fact, the UV-vis specra obtained for the poly(aniline-co-fluoroaniline) and polyanilne quite different from each other. UV-vis study has confirmed the transformation of Polyaniline backbone from the EB to the LB forms. The spectrum shows that the exciton band appeared at ~600 nm, and π- π*transition band at aprox 390 nm (Figure 1a).The UV-vis spectra for the EB forms of P(2-FA show a very low intensity exiton band at ~550 nm and a high intensity band due to π- π* transition at ~380-390 nm. Polyaniline copolymers containing different amount of F-content obtained from the oxidative polymerization methods. Upon increasing the degree fluorination the UV-vis spectra show obvious changes in the two absorption bands, the UV-vis spectra P(2-FA) showed prominent change in the bands, exciton bands lower shifted to lower wavelength from 600 to 480 nm and the intensity of exciton transition becomes very low (figure 1c-f).The the intensity ratio between the two absorption bands become very high upon fluorination. P(2-FA) prepared here by via the conventional oxidative polymerization method from 2-fluoroaniline as mentioned in Scheme 1, it shows less blue-shifted exciton band at ~480 nm (Figure 1b),different to the results reported by Han et.al.[5] and reported in the literature[17].

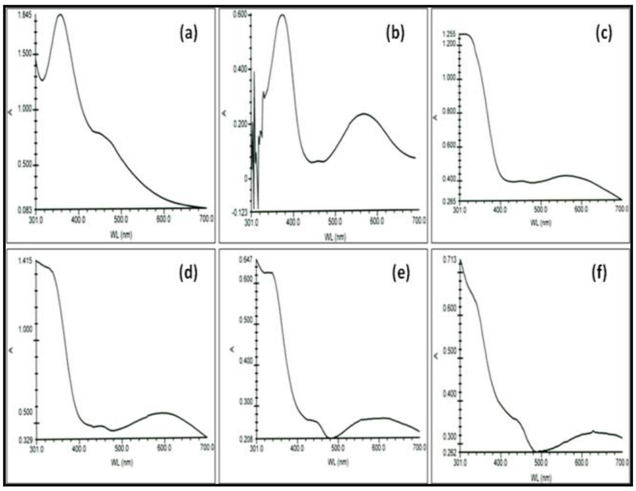

**Figure 2.** UV-vis spectra of (a) P-2-FA (b) PA (c) PA-co-2-FA70(d) PA-co-2-FA50 (e) PA-co-2-FA25 (f) PA-co-2-FA10 in DMSO

### *D. FTIR Spectra*

To elucidate the structural aspect of as-synthesized copolymers, FT-IR spectra are being recorded and compared with polyaniline in Fig 3. The comprehensive analysis of the IR spectral frequencies confirms the presence basic units of the copolymer in the backbone. The FT-IR spectra of PA salt (Figure 3a) exhibits band at 1574 and 1400 $cm^{-1}$ corresponds to the C-C ring stretching vibrations of the quinoid and benzenoid form. The peak of 1135 $cm^{-1}$ is assigned to C-H bending mode, absorption at 1297 $cm^{-1}$ is ascribed to the C-N stretching, 3152 $cm^{-1}$ -N-H stretching. The FTIR spectrum of P(2-FA) (Figure 3d), shows broad peak at 3401 $cm^{-1}$ characteristic of the N-H stretching. 1585-1466 $cm^{-1}$, assigned to the quinoid and benzenoid phenyl ring and C-F stretching occurs at 563 $cm^{-1}$. The spectral frequencies of copolymers and P(2-FA) homopolymers are almost similar to the corresponding PANI. The IR spectrum of copolymer P(A-co-2-FA) in (Figure 3 b, c, d) has been compared by observing the relative intensity of the peak at 600 $cm^{-1}$. Upon increasing the molar ratio of 2-Fluoroaniline in the copolymer P(A-co-2-FA), the intensity of C-F absorption band increases and absorption band shifted to the lower frequency. The IR spectrum of P(A-co-2-FA)50 (Figure 2c) almost resembles to P(2-FA) (Figure 3d) and the band attributed to C-F stretching observed as a strong peak. Thus, an increase in the molar ratio of 2-Fluoroaniline in the copolymer the intensity of the band C-F increases.

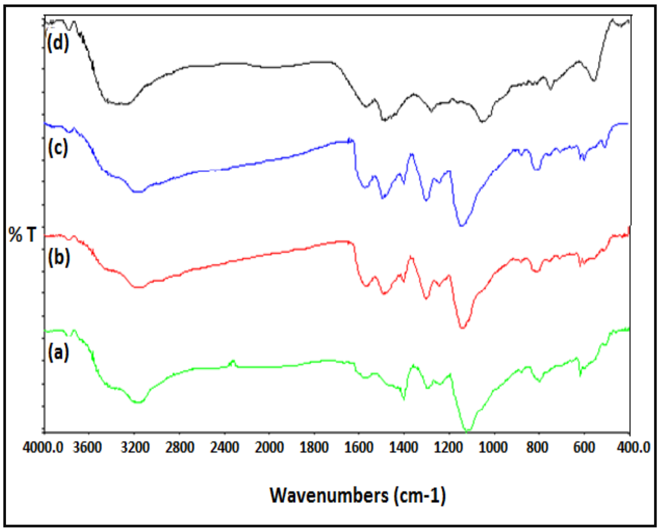

**Figure 3.** FTIR spectra of (a) PA, (b) P(A-co-2-FA)25, (c) P(A-co-2-FA)50, (d) P(2-FA)

### E. *Scanning electron microscopy*

Highly tubular and tubular assemblies of the polyaniline and of copolymers are shown by SEM images in Fig.4. The morphology of polyaniline and the composite polymer P(A-co-2-FA)50 which are synthesized by conventional chemical oxidative method dependent upon the molar ratio of fluoroaniline to aniline, which is represented by the [FA]/[ANI]. Green color polyaniline was readily obtained after appropriately mixing the aniline with oxidant. The change in the molar ratio affects the morphologies of the resulting polymer and copolymers. Pure polyaniline shows the uniform tubular morphology at the onset of the oxidation of monomgrber with the addition of oxidant to the reaction while the increase in the quantity of FA in the composite changes the morphology from tubular to cauliflower-like assemblies. The pure P(2-FA) has no uniform tubular morphology. Needle-shaped morphology was reported by Sharma el.at [18].The copolymer is primarily is amorphous in nature in this study.

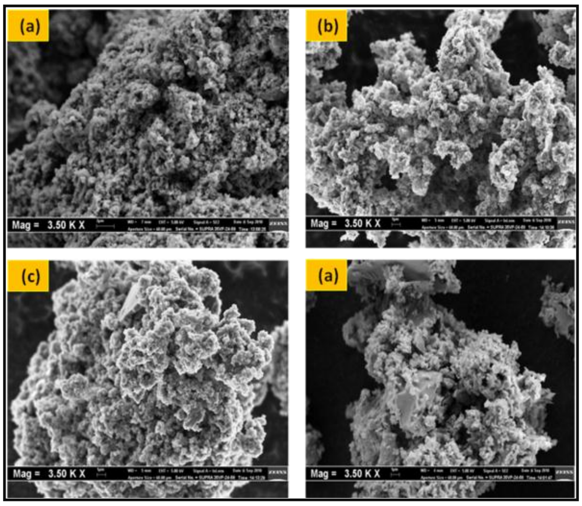

**Figure 4.** Scanning electron micrograph of at the magnification of 3.50x k, (a) PA (b) P(A-co-2-FA-50), (c) P(A-co-2-FA-25), (d) P(2-FA**).**

### *F. Thermogravimetic Analysis*

The thermal stability of the polymers was demonstrated by TGA analysis. The relative thermal stability of the doped PA, P(2-FA) and the copolymers in Fig 5. The thermal nature of copolymers in the thermogram of almost is similar to that of homopolymers.TGA thermogram shows two stages of weight loss in PA while copolymers show the initial weight loss at 200$^{o}$C approx. The gradual and continuous weight loss occurs after 250$^{o}$C because of –$NH_2$ group. At higher temperature approx. at 350$^{o}$C more rapid decomposition was observed. Thus the polymers are air stable. In order to compare the relative thermal stability of PA, P(2-FA) and their weight loss at 450$^{o}$C in percentage. It is observed that the P(2-FA) is more stable as compared to PA and copolymers. Upon increasing the content of 2-fluoroaniline in the composition, the thermal stability increases due to an increase of amorphous state in copolymer.

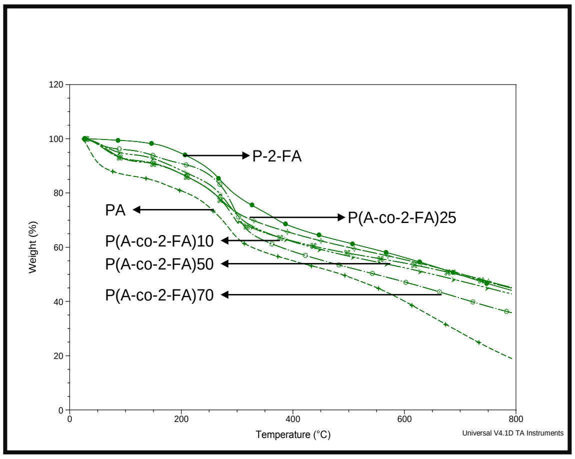

**Figure 5.**Thermograms(TGA) of PA, P(2-FA), P(A-co-2-FA 70), P(A-co-2-FA 50),P(A-co-2-FA 25),P(A-co-2-FA 10)

## IV. CONCLUSIONS

To summarize, as-synthesized copolymer of poly(aniline-co-flouroaniline) is different from polyaniline in respect of that physical properties viz; solubility, electrical conductivity, thermal stability and morphology. FTIR and UV-studies have revealed that the as-synthesized copolymers are characteristically distinct in structure from polyaniline. The copolymer P(2-FA) possesses high solubility measured in NMP. The solubility increases upon increasing the degree of fluorination in the copolymers. Copolymers have relatively better solubility and lower conductivity due to the presence of F$^{-}$ atom in the backbone of copolymer. Different copolymers of poly(aniline-co-flouroaniline) have different electrical conductivity depending upon the F atom, larger the flouroaniline monomer content in composition, lower is the electrical conductivity. The copolymer P(2-FA) is thermally more stable than polyaniline as shown TGA thermograms and SEM micrograph clearly depict amorphous nature of the copolymer and its is due to the incorporation of fluorine atom into the polymer backbone.

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## References

[1] K Y Jen, G G Miller and R L Elsenbaumer J. Chem. Soc. Chem. Commun. 1986, pp.1346
[2] A. Go¨k, B. Sari and M. Talu, Synth. Met. 2004, 142, 41.
[3] A.L. Sharma, V. Saxena, S. Annapoorni and B.D. Malhotra, .J.Appl. Polym. Sci. 2001, 81, pp.1460.
[4] D.P. Kang and M.S. Yun, Synth. Met. 1989, 29, E343.
[5] Chien-Chung Han and Hsin-Yu Chen Macromolecule 2007,40, 8969-8973( references therein).
[6] J Anand, S Palaniappan and D N Sathyanarayana Prog. Polym Sci. 1998, 23:993
[7] P Chandrashekher, B.J.Zay,T.McQueeney, A Scara, D Ross and G C. Birur. Synth Met 2003, 135:23
[8] A. L. Sharma, P. Kumar and A. Deep, Polymer-Plastics Technology and Engineering, 52: 737–742, 2013
[9] A. G. MacDiarmid and A. J. Epstein. Chem. Soc 1989, 88:317
[10] Y Wei, R Hariharan and S. A Patel. Macromolecules 1990, 23:3
[11] J. Yue and A. J. Epstein. J. Am. Chem. Soc. 1990, 112: 2800
[12] Y Cao, P. Smith and A. J. Hegger Synth Met 1992, 65:103
[13] M. C. Gupta and S S. Umare. Macromolecules 1992, 25:138
[14] A.J.MacDiarmid and A.J. Epstein, Synth Met, 1994, 65:103
[15] A..L. Sharma, V. Saxena,S. Annapoorni and B. D. Malhotra J. of Applied Polymer Sci, . 81, 1460–1466 (2001)
[16] A.Cihaner and A.M.Onal Eur.poly J. 37,2001,1767.
[17] Angela H. Kwon, Jeanine A. Conklin, Michael Makhinson and Richard B. Kaner , Synthetic Metals 84,1997,95.
[18] S Ye, N T Do, Dao, L.H and A K Vijh Synth. Met,1997 88: pp.65
[19] J.Anand, S. Palaniappan and D.N. Sathyanarayana. J Poly Sci Poly Chem 1998 36: pp.2291
[20] J. L.Bredas, G.B. Street, B. Themans and J.M. Andre. J. Chem. Phys. 1995, 83: pp.1323
[21] S.Ghose and V. Kalpagam. Synth Met, 1989, 33, pp.13
[22] J.M Ginder, and A J. Epstein,., Phys. Rev. B 1990, 41,15 pp.10674
[23] W. S. Zho, K.Cromak and A.G. MacDiarmid, J. Am. Chem. Soc.,1991, 113,pp.2665