Synthesis and Characterization of a Copolymer: Poly(Aniline-*Co*-Fluoroaniline)

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ABSTRACT: In the present article, we report the chemical synthesis and characterization of poly(aniline-*co*-fluoroaniline) [poly(An-FAn)]. The copolymerization of aniline and 2-fluoroaniline was carried out by chemical method in acidic medium. The characterization of poly(aniline-*co*-fluoroaniline) was done using FTIR, UV-visible spectroscopy, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), scanning electron micrography (SEM), and a four-points-probe conductivity method. X-ray diffraction (XRD) and SEM characterization reveal crystalline nature of doped copolymer compared to undoped copolymer. The observed decrease in the conductivity of the copolymer relative to polyaniline is attributed to the incorporation of the fluoro moieties into the polyaniline chain. The chemically synthesized copolymer shows good solubility in common organic solvents, and is, therefore, technological useful. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1460–1466, 2001

Key words: poly(An-FAn); scanning electron microscopy; thermogravimetric analysis; X-ray diffraction

INTRODUCTION

The surge of interest in conducting polymers has recently resulted in a number of practical applications because of their unique electronic properties, diversity, ease of fabrication, and potentially low cost. These devices include field effect transistors (FETs), Schottky diodes, light-emitting diodes (LEDs),[1–3] etc. Undoped and doped conjugated polymers such as polyacetylene, polypyrrole, polyaniline, and polythiophene[4–6] have shown semiconducting behavior that can be used in device applications.

Polyaniline (PANI) is commonly referred to as the most stable material within the class of conducting polymers.[7,8] For instance, polyaniline has been proposed for use in electrochemical batteries,[9,10] electronic displays,[11] biosensors,[12,13] molecular electronics,[14] EMI shielding,[15] and opto-electronic devices.[16] However, the commercial exploitation of most of applications based on polyaniline is closely linked with its the ease of processability. The processability of this can be enhanced either by making substitution into the aromatic nucleus or copolymerizing in such a way that there is variation in torsion angle between adjacent phenyl rings of the polymer.

Copolymerization is the easy and powerful method of making systematic changes in the polymer properties, and is widely used in the production of commercial polymers including the fundamental investigations of structure–property cor-

relations.[17] Considerable efforts have been made towards the copolymerization of aniline monomers by some workers to improve processability of the polymer.[18–20] However, these polymers are unsuitable for device fabrication either due to low conductivity,[18] or amorphous nature,[19] or a large number of defects present in the polymer.[20] Keeping this in view, we have synthesized a copolymer that is shown to possess good conductivity and thermal stability, high solubility in organic solvents, partial crystallinity, and ability to produce free-standing films. In this article, we report the copolymerization of aniline with 2-fluoroaniline and the characterization of this conducting copolymer using electrical conductivity, FTIR, UV-vis, DSC, TGA, XRD, and SEM, respectively.

EXPERIMENTAL

Aniline and 2-fluoroaniline were procured from Sigma and Fluka, respectively, and used without further purification. Reagent-grade ammonium persulphate (APS), hydrochloric acid (HCl), and methanol were also used as received. 1-Methyl-2-pyrrolidone (NMP) of synthetic grade was received from Merck. Aqueous solutions were prepared using doubly distilled, deionized water (Millipore RO 10 TS).

Poly(An-FAn) was chemically synthesized by copolymerization of aniline and 2-fluoroaniline using ammonium persulphate [$(NH_4)_2S_2O_8$] as an oxidant. A mixture consisting of 2.80 mL of aniline (0.1 M) and 2.90 mL of 2-fluoroaniline (0.1 M) was dissolved in 150 mL of 1 M HCl. The temperature of solution was maintained at 0–2°C and constantly stirred for about 1 h. To this solution was added drop by drop another solution of 12.5 g ammonium persulphate in 100 mL distilled water. The reaction was continued for 24 h, after which a green precipitate was filtered. The filtrate was washed with 1 M HCl until it became colorless, followed by washing with methanol. The precipitate was dried in vacuum oven at 80°C for about 5 h. Undoped conducting polymer was obtained by treating the precipitate with aqueous ammonium hydroxide solution (pH = 12) and constantly stirring for about 48 h. The powder was then collected on a Buchner funnel and was washed with distilled water several times. The resulting powder was dried at 80°C for about 5 h in a vacuum oven. Similar procedure was followed to synthesize both polyaniline (PANI) and polyfluoroaniline (PFANI).

The poly(An-FAn) films were prepared by casting a poly(An-FAn) solution in NMP on a Petri dish and drying under dynamic vacuum at 70–80°C. The solution-cast copolymer film was utilized to measure electrical conductivity and tensile strength.

The chemical synthesis was performed using a JULABO water bath (Model F 10) to maintain the temperature below 5°C of the solution. The conductivity measurements on pellets of doped and undoped samples of poly(An-FAn), PANI, PAFNI, and a 1 : 1 composite of polyaniline and polyfluoroaniline were conducted using a four-points-probe technique. Molecular weight of chemically synthesized poly(aniline-*co*-fluoroaniline) was carried out using a GPC/HPLC (Waters) after calibrating the system with polystyrene samples as standard. The spectroscopic characterization of each of the polymeric samples was carried out on a Nicolet FTIR (Model 510 P) and Shimadzu (Model 160A) spectrophotometer. Thermal studies of conducting polymeric samples were carried out on a Perkin-Elmer DSC 7 and Mettler 3000 at heating rate maintained at 20°C/min in inert (nitrogen) atmosphere. SEM micrographs of copolymer in powder form were taken on SEM (LEO 440).
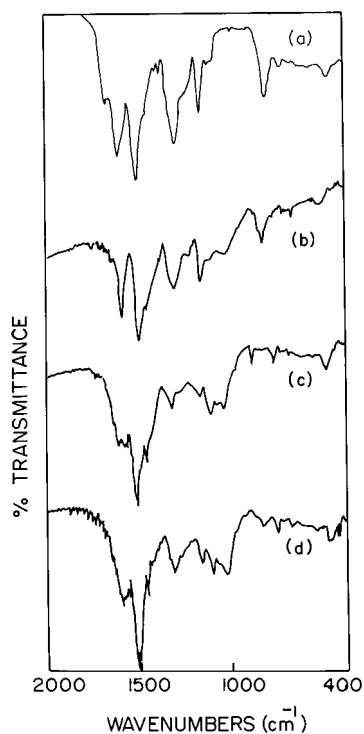
RESULTS AND DISCUSSIONS

Molecular Weight

GPC analysis of polyaniline and polyfluoroaniline (PFANI) shows the molecular weights of about 6
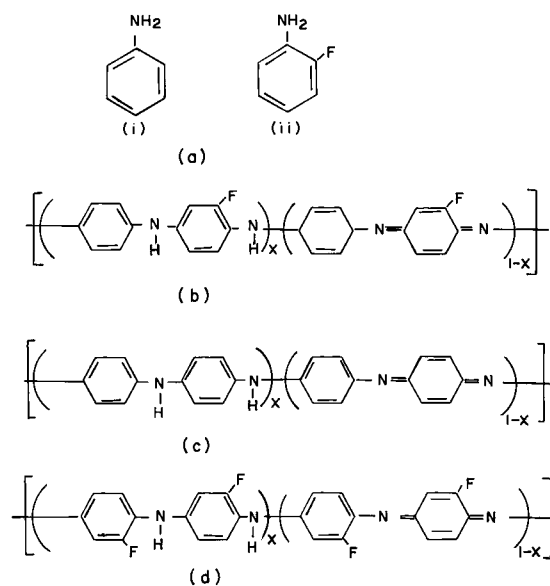
Figure 1   Structures of (a)(i) aniline (ii) fluoroaniline; (b) polyaniline-*co*-fluoroaniline (tentative); (c) polyaniline; (d) polyfluoroaniline (tentative).

Figure 2 FTIR spectra of chemically synthesized poly(An-FAn).

$\times 10^4$ and 4×10^3, respectively, using polystyrene samples as standard. These values are in agreement with molecular weights reported earlier.[21,22] The molecular weight of undoped poly(An-FAn) by GPC analysis was found to be about 3.9 $\times 10^4$ using polystyrene samples as standard.

Spectroscopic Characterization

Figure 1 shows the structure of aniline and fluoroaniline and a schematic of various conducting polymers such as polyaniline, polyfluoroaniline, and poly(aniline-*co*-fluoroaniline) synthesized in the present work.

Figure 2(a) shows the infrared spectrum of poly(An-FAn). This curve shows the characteristic peaks at 1597, 1508, 1381, 1304, 1169, 1130, 827 and 752 cm^{-1}, respectively. The peak at 1597 cm^{-1} is due to the C=C double bond of quinoid
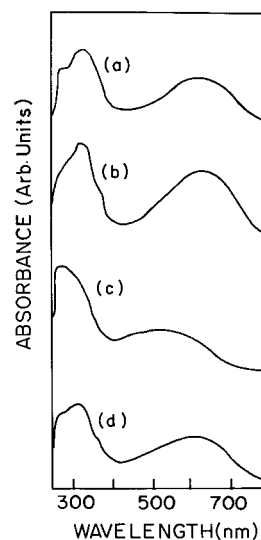
**Figure 3** UV-VIS spectrum of chemically prepared poly(An-FAn).

rings, whereas the peak at 1508 cm^{-1} arises due to vibration of the C=C double bond associated with the benzenoid ring. The peak at 1304 cm^{-1} has been attributed to a combination of C—N in quinoid and benzanoid sequences. The absorption peak observed at 1169 cm^{-1} has been associated with the presence of a halogen (fluoro) group in the copolymer. These vibration bands are also present in the infrared spectrum of PANI[23] [Fig. 1(b)] and PFANI [Fig. 1(c)]. However, a shift observed in the spectrum of poly(An-FAn) indicates the presence of fluoro moieties in the polymer chain.

Table I presents the IR bands observed for PANI, PFANI, copolymer of aniline and fluoroaniline, and 1 : 1 composite of polyaniline and polyfluoroaniline (COM PANI-PFANI). It is clear from the table that copolymer exhibits two additional peaks at 1381 and 1130 cm^{-1} in the IR spectra. This fact suggests that the synthesized polymer is a copolymer and not a mixture of homopolymers. This result is further confirmed by the IR spectra of the 1 : 1 composite of PANI and PFANI, which shows no such peaks.

The UV-VIS spectra of polymeric samples have been recorded at room temperature and are

Table I   IR Vibration Bands of Different Polymers

PANI	1593	1495	—	1305	1165	—	829	—
Poly(An-FAn)	1597	1508	1381	1304	1169	1130	827	752
PFANI	—	1508	—	1317	—	—	—	754
COM PANI-PFANI	1595	1508	—	1315	1169	—	830	753
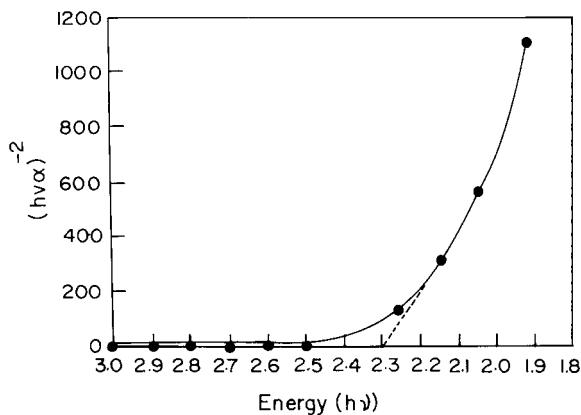
Figure 4 $(h\nu\alpha)^{-2}$ (vs $h\nu$) for the band gap of poly(An-FAn).

Figure 5 Electrochemical growth curve of poly(An-FAn) film.

shown in Figure 3. A shift is observed in the case of poly(An-FAn) [Fig. 3(a)] in comparison with PANI [Fig. 3(b)]. This may perhaps be attributed to the presence of electron withdrawing group (fluorine) present in the polymer backbone. In the case of poly(An-FAn), absorption peaks such as 331 and 625 nm are attributed to $\pi-\pi^*$ transition and polaronic band, respectively. The UV-VIS spectra of PFANI shows [Fig. 3(c)] the prominent absorption peaks at 290 and 555 nm for the $\pi-\pi^*$ transition and n–π^* transition, respectively. UV-VIS spectra of COM PANI-PFANI exhibit a bathochromic shift [Fig. 3(d)] to 305 and 606 nm, which are significantly different from that of poly(An-FAn). This fact also suggests that the synthesized material is a copolymer.

It is seen from earlier work that heavily doped polyaniline exhibits metallic behavior.[24,25] In the present study a low-level doping has been done, and hence, this exhibits a band gap. The band gap for chemically synthesized doped poly(An-FAn) has been calculated from the plot of $(\alpha h\nu)^{-2}$ vs. photon energy, shown in Figure 4. The energy band gap has been estimated to be 2.3 eV, which is lower than that of PFANI[22] and higher than that of PANI.[29]

Figure 5 shows the growth pattern of poly(aniline-*co*-fluoroaniline) at the scan rate of 50 mV/s in 1 *M* HCl. The shift in oxidation peaks to higher potential is due to the decreased conjugation length that is perhaps responsible for the lower value of electrical conductivity.[26,27] The cyclic voltammetry (CV) of this copolymer film at the same scan rate (50 mV/s) shows a shift (Fig. 6) in first oxidation peak (0.28 V) in comparison to polyaniline (0.12 V) and polyfluoroaniline (0.42 V). This suggests that the conjugation length and conduc-

tivity of the copolymer lie between that polyaniline and polyfluoroaniline.

THERMAL STUDIES

Differential Scanning Calorimetry Analysis

Differential scanning calorimetry studies (DSC) of all conducting polymeric samples were carried out in inert (nitrogen) atmosphere, at the scanning rate of 20°C per minute. In the case of undoped poly(An-FAn), two endothermic peaks are observed [Fig. 7(a)], one at 111°C, which arises due to the removal of water molecules present in the poly(An-FAn) and another endothermic peak at 333°C, which arises due to the degradation of the polymer. In addition, an exothermic peak at 208°C is also observed, which arises due to the interchain crosslinking in the copolymer.
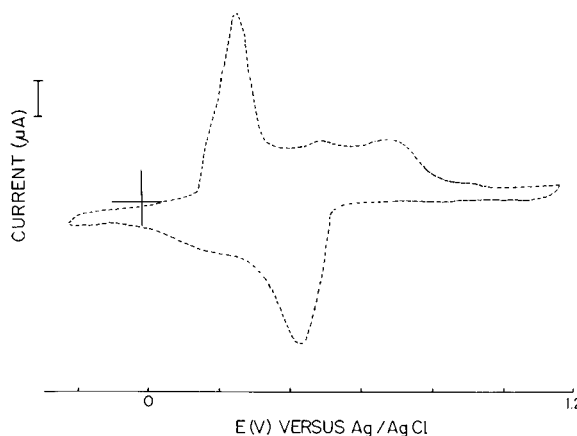

**Figure 6** Cyclic voltammetry of poly(An-FAn) film.
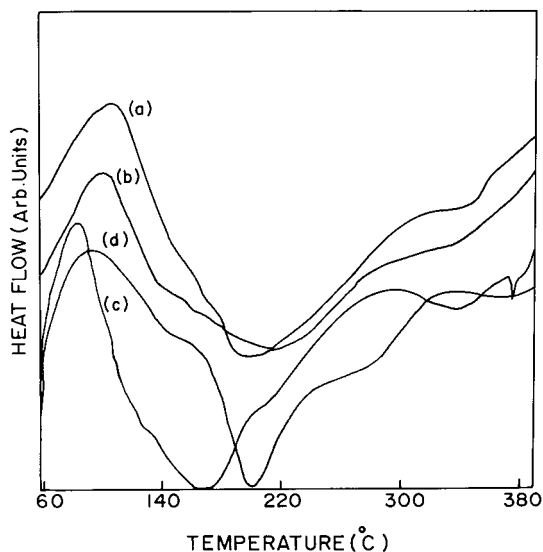
Figure 7 DSC thermograms of (a) polyaniline, (b) polyfluoroaniline, (c) poly(An-FAn) and (d) COM PANI-PFANI.

In case of doped poly(An-FAn), two endothermic peaks are present—one at 110°C arising due to the removal of water molecules present in the copolymer, and another endothermic peak at 303°C arising due to the removal of Cl^- dopants ions. An exothermic peak is also found at 206°C, which is assigned to the interchain crosslinking in the copolymer. The transition observed at 182°C has been designated as the glass transition temperature (T_g) of the doped copolymer. In the case of PANI, the endothermic peak seen at 100°C indicates [Fig. 7(b)] the evaporation of water from the polymer, while the exothermic peak at 260°C suggests the interchain crosslinking.[28–30] The thermogram of undoped PFANI[22] shows [Fig. 7(c)] two endothermic peaks, the peak at 83°C arises as a result of some conformational changes,
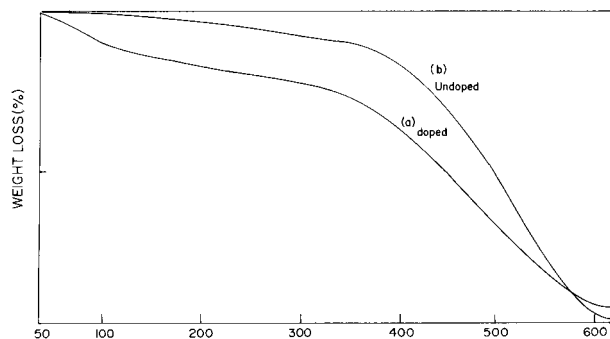
Figure 8 TGA thermograms of (a) doped and (b) undoped poly(An-FAn).
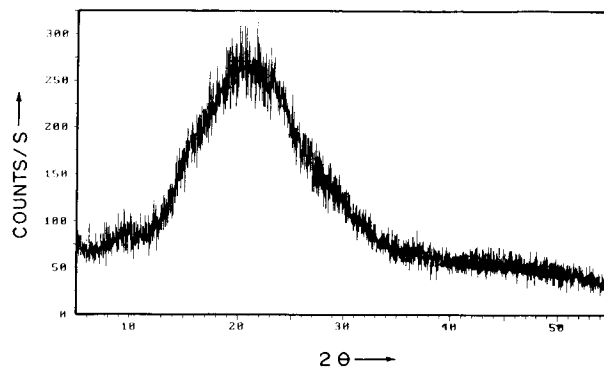
Figure 9 XRD pattern of doped of poly(An-FAn) powder.

and the peak at 197°C is attributed to the interchain crosslinking. The peak observed at 418°C corresponds to the degradation of the polymer.
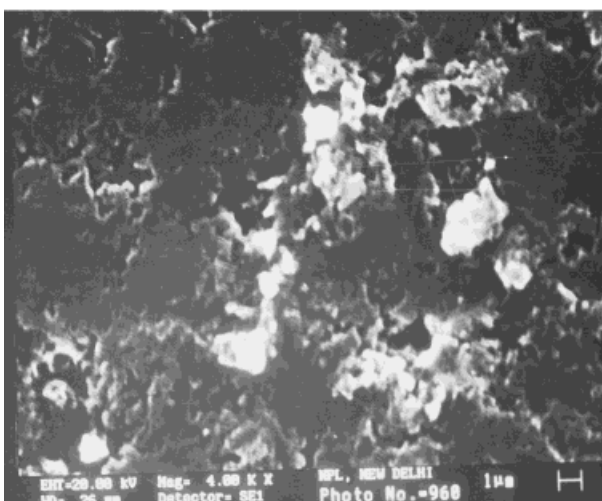
Thermogravimetric Analysis

Figure 8 reveals TGA curves of all polymers. It can be seen [Fig. 8(a)] that in the case of doped poly(An-FAn), 6.1% weight loss occurs up to a temperature of 100°C. A further weight loss of 10.2% occurs between 100 to 200°C. In the temperature range of 200–300°C, further weight loss of about 5.6% arises due to the removal of Cl^- ions. The total weight loss for doped poly(An-FAn) up to 500°C is about 63.7%, while that of undoped poly(An-FAn) is only about 51.1% [Fig. 8(b)]. In the case of undoped PANI,[28] the total weight loss at the same temperature range is about 21%, whereas, in the case of doped and undoped PFANI[22] it is 47 and 41%, respectively.

X-Ray Diffraction Study

The X-ray diffraction of doped and undoped copolymer in powder form reveals that the crystallinity of the doped copolymer is enhanced relative to undoped copolymer (Fig. 9). This feature was also confirmed by the SEM of the copolymer.

Scanning Electron Micrography (SEM)

As shown in Figure 10(a), the SEM of the doped copolymer reveals a small needle-shaped structure. This suggests that dopant moiety associated with the copolymer is attached through a strong intermolecular force. The needle-shaped appearances show a morphological change from the normal globular behavior of conducting copolymer. The constant formation of the needle-shaped

reason of lesser conductivity of the copolymer is due to the incorporation of the moieties of fluoroaniline into the polymer chain.

Solubility

The solubility of the doped and undoped form of poly(An-FAn), PANI, PFANI, and the 1 : 1 composite of polyaniline and polyfluoroaniline has been tested in 1-methyl 2-pyrrolidone (NMP), dimethyl fomamide (DMF), tetrahydrofuran (THF), and dimethyl sulphoxide (DMSO) at room temperature. The undoped poly(An-FAn) shows better solubility in NMP and THF. The doped PANI was, however, not soluble in NMP. Undoped PANI was soluble in the same solvent. Unlike PANI, both doped and undoped forms of polyfluoroaniline are soluble in NMP, THF, DMF, and DMSO. Thus, it is possible to cast film of the desired size of poly(An-FAn). A solution cast film of undoped poly(An-FAn) in NMP was also prepared at 80°C in a vacuum oven. The tensile strength of this film was estimated to be 27 mega pascal.

CONCLUSION

The synthesis of poly(aniline-*co*-fluoroaniline) has been accomplished using a chemical method. Spectroscopic studies (FTIR and UV-VIS), thermal studies (DSC and TGA), and scanning electron micrography (SEM) have revealed that poly(An-FAn) is a random copolymer. The electrical conductivity of the poly(An-FAn) has been found to be lower than that of PANI and higher than that of PFANI. Studies conducted on chemically prepared conducting copolymer have revealed that the conductivity behavior of the copolymer is perhaps due to the incorporation of fluoroaniline moieties in the PANI chain. It was

Figure 10 SEM micrographs of (a) doped and (b) undoped poly(An-FAn).

structures appears to be uniformly distributed on the polymeric matrix showing that doping has occurred uniformly. When the same copolymer is treated with aqueous ammonia, the needle-shaped dopants appear in the vacant globular empty spaces giving the amorphous morphology to conducting polymer [Fig. 10(b)]. The voids present in the surface show the leaching of dopant moiety from the bulk copolymer.

Electrical Conductivity

Room temperature electrical conductivity of all polymeric samples are listed in Table II. As indicated in the table, the electrical conductivity of the poly(An-FAn) and 1 : 1 composite of polyaniline and polyfluoroaniline is nearly the same, but lower than PANI and higher than PFANI. The

Table II Room Temperature Electrical Conductivity of Poly(An-FAn), PANI, PFANI, and COM PANI-PFANI

| Polymer | Conductivity (S/cm) | |
	Doped	Undoped
Poly(An-FAn)	3.51×10^{-3}	4.69×10^{-10}
PANI	1.2	3.27×10^{-9}
PFANI	3.53×10^{-5}	1.58×10^{-8}
COM PANI-PFANI	3.97×10^{-3}	3.6×10^{-10}

found that doped state of copolymer is more crystalline in nature compared to the undoped copolymer. The undoped copolymer exhibits good thermal stability and solubility in common organic solvents. The excellent characteristics of this copolymer could be utilized in development of devices.[31]

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