Synthesis and Characterization of Fluoro-Substituted Polyaniline

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Abstract

Poly(2-fluoroaniline) was prepared by both chemical and electrochemical polymerization in acidic medium. Characterization of poly(2-fluoroaniline) was accomplished experimentally using ultraviolet-visible, Fourier transform infrared, differential scanning calorimetry, thermal gravimetric analysis, and X-ray diffraction techniques, respectively. Scanning electron microscopy studies revealed globular morphology of chemically synthesized poly(2-fluoroaniline). The cyclic voltammetric studies revealed diffusion-controlled phenomenon in electrochemically synthesized poly(2-fluoroaniline).

Index Entries: Poly(2-fluoroaniline); cyclic voltammetry; scanning electron microscopy; X-ray diffraction.

Introduction

Conducting polymers have recently attracted much attention. Among the various conducting polymers, the focus has been on polyaniline because of its projected applications in lightweight batteries *(1)*, electrochromic displays *(2)*, and so on. Polyaniline, however, has been found to be insoluble in the majority of organic solvents, which limits its use in many of the device applications. In addition, solubility is important from the characterization point of view. Processibility is considered to be an important requirement in conducting polymers for their possible commercial use. Various general approaches such as block copolymerization *(3)* and polymerization of substituted monomers *(4)* have been made to overcome the problem of intractability of conducting polymers. Processibility can be

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achieved either by copolymerization or preparation of composites *(5,6)* or by incorporation of certain functional groups in the chain structure.

Polymerization of substituted monomers is one of the most successful approaches for the synthesis of solution processible conducting polymers. Conducting polymers such as polyphenylacetylene *(7)*, poly(3-hexyl-thiophene) *(8)*, and poly(3-octylthiophene) *(9)* are some examples of such an approach. These conducting polymers have been found to be soluble in the organic solvents in their undoped states.

Substitution of polyaniline by, e.g., alkyl, aryl, and halogen groups has been investigated by several researchers *(10–16)*. The effect of withdrawing groups, such as fluorine and chlorine, on polyaniline has also been investigated *(13–16)*. Gruger et al. *(12)* have reported the results of raman and infrared studies on poly(2-fluoroaniline) indicating that localized polaronic moieties are perhaps responsible for the observed poor electrical conductivity. Snauwaert et al. *(13)* have shown, through photoelectron spectroscopic measurements that poly(2-fluoroaniline), degrades at 1.2 V. Kang et al. *(14)* have prepared poly(2-chloroaniline) and poly(2-fluoroaniline) by using chromic acid in aqueous 1 *M* HCl solution. Prasad et al. *(15)* have recently prepared poly(2-bromoaniline) and poly(2-chloroaniline) by chemical and electrochemical methods.

In this article, we report the result of our systematic investigations pertaining to the preparation and characterization of poly(2-fluoroaniline).

Materials and Methods

2-Fluoroaniline was obtained from Fluka and was used without further purification. Reagent grade ammonium persulfate (APS) and HCl were also used as received. Aqueous solutions were prepared in double-distilled deionized water (Millipore RO 10 TS).

Chemical synthesis of poly(2-fluoroaniline) was accomplished by employing a procedure used for polyaniline *(16)*. A 0.25 mol aqueous solution (100 mL) of ammonium persulfate was added drop by drop to 6.1 mL of 2-fluoroaniline (0.25 mol) dissolved in 1 *M* HCl followed by vigorous stirring. The solution was cooled to below 5°C by using a water bath (Julabo, Model F 10). As the reactants were mixed, the solution turned into a bluish green and the precipitate was obtained. After about 24 h, the precipitate was vacuum filtered and washed repeatedly with 1 *M* HCl until the filtrate became colorless. It was further washed with acetone, and the powder was subsequently dried in a vacuum oven at 80°C for about 5 h. To obtain undoped poly(2-fluoroaniline), the doped form was treated with aqueous ammonium hydroxide solution (pH 12.0) and was continuously stirred for about 12 h. This powder was then collected on a Buchner funnel and washed with distilled water several times. The resulting powder was dried at 80°C for about 5 h in a vacuum oven.

The electrochemical synthesis of poly(2-fluoroaniline) was carried out in a one compartment cell with a two-electrode configuration at constant

current density of 2 mA/cm². The total charge passed during the preparation of the film was about 1.2 C. A platinum plate was used as a reference and an indium-tin-oxide (ITO) glass plate as a working electrode. The effective area of the ITO glass plate was 1 cm². Since the electrochemical polymerization of 2-fluoroaniline in 1 *M* HCl resulted in poor-quality films, 4 *M* perchloric acid was used as the electrolyte solution.

The molecular weight of chemically synthesized poly(2-fluoroaniline) was estimated using a GPC/HPLC (Waters) after calibrating the system with polystyrene samples as standard. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet (Model 510 P) spectrometer. The ultraviolet-visible (UV-VIS) measurements were conducted using a UV-VIS spectrophotometer (Model 160 A; Shimadzu). The electrical conductivity of poly(2-fluoroaniline) was measured by four-points-probe technique. X-ray diffraction studies were carried out on an X-ray diffractometer (Philips PW, Model 3020). Scanning electron microscopy was carried out using LEO 440 (with SE1 detector). Perkin-Elmer DSC-7 and Mettler (TA 3000) were used for thermal measurements.

The cyclic voltammetry studies were undertaken for the spin cast films of chemical synthesized doped poly(2-fluoroaniline) in 1-methyl-2-pyrrolidone (NMP) and electrochemically synthesized poly(2-fluoroaniline) using electrochemical interface (Schlumberger Model SI 1286) by standard three-electrode configuration comprising of an ITO glass plate as a working electrode, a platinum plate (area = 1 cm²) as a counterelectrode, and Ag/AgCl as a reference electrode.

Results and Discussions

The number average molecular weight ($\overline{Mn}$) of undoped poly(2-fluoroaniline) obtained by gel permeation chromatography was observed to be about 4000.

FTIR spectrum of chemically synthesized undoped poly(2-fluoroaniline) in KBr matrix is shown in Fig. 1. The peaks seen at 880, 1153, and 1319 cm⁻¹ are characteristic of fluoroaniline. Typical aniline stretches observed at 1507 and 1455 cm⁻¹ are in agreement with the values reported in the literature *(8)*.

The UV-VIS spectrum of chemically synthesized doped and undoped poly(2-fluoroaniline) dissolved in NMP was recorded with the reference cell containing NMP alone. The solution spectra obtained for the doped and undoped poly(2-fluoroaniline) are shown in Fig. 2 (curves a and b). The absorption peak for the doped poly(2-fluoroaniline) seen at 570 nm indicates the presence of excitons owing to numerous quinine and diamine groups that remain unprotonated. The oscillator strength of benzenoid transition (π – π*) seen at 340 nm is as intense as in its corresponding base form. The presence of π – π* and exciton-like excitations at almost the same frequencies as in the case of emeraldine base form shows that in the polymer backbone, fully protonated and unprotonated domains coexist *(17)*.
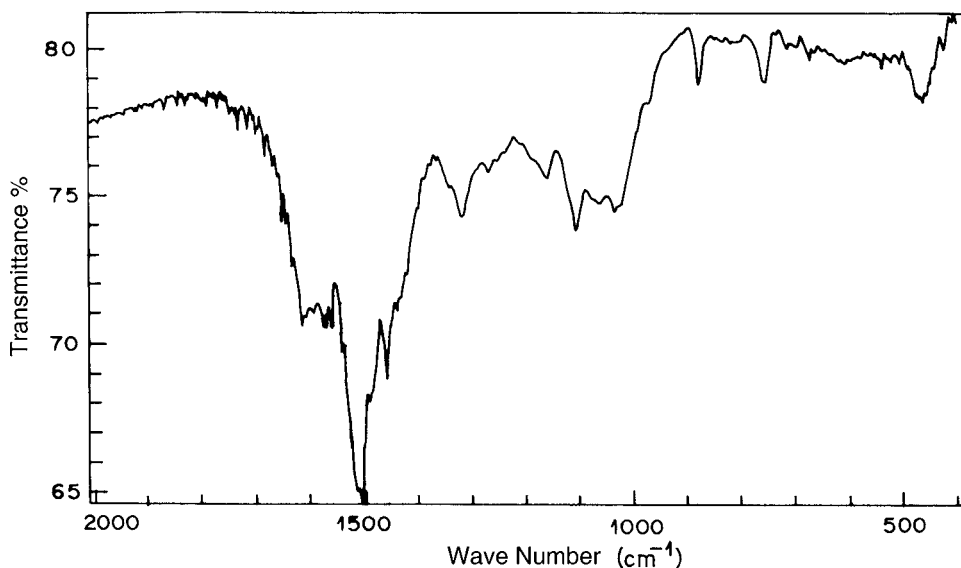
Fig. 1. FTIR spectrum of undoped poly(2-fluoroaniline).
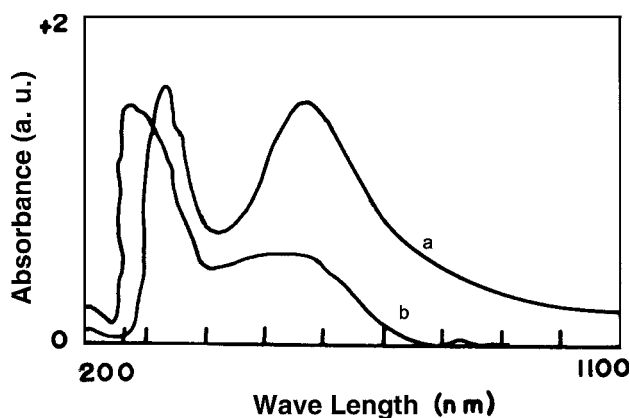

Fig. 2. UV-VIS spectra of (a) doped and (b) undoped chemically prepared poly(2-fluoroaniline).

The band gap of the chemically synthesized poly(2-fluoroaniline) as determined from the absorption spectra (Fig. 2) has been found to be 2.76 eV and it is higher than that of doped polyaniline *(17)*.

The electrical conductivity of poly(2-fluoroaniline) measured on pellets of 13 mm diameter (thickness of ~0.9 mm) after applying 6 t of pressure by four-points-probe technique was found to be 3.53×10^{-5} and 1.58×10^{-8} S/cm for doped and undoped samples, respectively. This value of electrical conductivity is much less than that of the polyaniline in the doped form. This may perhaps be attributed to the presence of electron withdrawing group (fluorine) present in the polymer backbone that might suppress
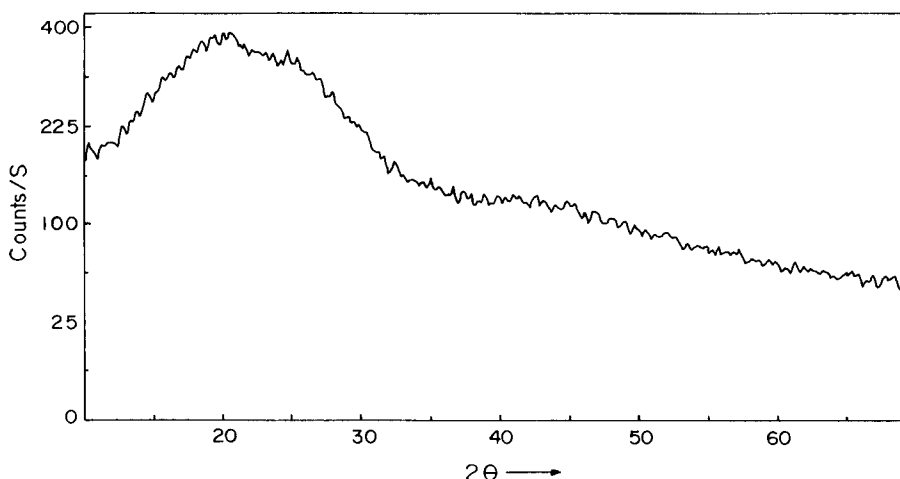
Fig. 3. X-ray diffraction pattern spectrum of doped poly(2-fluoroaniline).

the oxidation rate *(18)*. This value is also lower than that of 2.0 *M* H_2SO_4 doped poly(2-chloroaniline) *(19)*.

X-ray diffraction pattern obtained for the chemically prepared doped poly(2-fluoroaniline) is similar to that obtained for undoped polyaniline *(20)*. The broad hump seen in Fig. 3 indicates the presence of some microcrystalline regions in the chemically synthesized doped poly(2-fluoroaniline).

Figure 4A shows the scanning electron micrographs (SEMs) obtained for the surface of chemically synthesized doped poly(2-fluoroaniline) in powder form indicating globular morphology. The presence of small pits on the surface is indicative of a weak interaction between the chemically induced dopant with the polymeric backbone, which in turn may be related to the availability of electrons on the specific group available for interaction. This aspect can also be correlated to the observed low electrical conductivity in doped poly(2-fluoroaniline).

Figure 4B is the SEM of an undoped sample of poly(2-fluoroaniline) obtained on its treatment with ammonia solution. The presence of the clear hollow surface *(21)* points out the absence of dopant anions on the surface of undoped poly(2-fluoroaniline) powder.

Results of differential scanning calorimetry studies conducted on chemically synthesized doped and undoped poly(2-fluoroaniline) are shown in Fig. 5. The measurements were conducted up to 500°C at a heating rate of 20°C/min in an inert (nitrogen) atmosphere. In the case of doped poly(2-fluoroaniline), (Fig. 5, curve a), three endothermic peaks at 104, 229, and 364°C are observed. The peak at 104°C is understood to arise from the removal of water molecules present in the poly(2-fluoroaniline). The endothermic peak seen at 229°C occurs owing to the removal of Cl⁻ dopant ions from the polymeric backbone. The peak at 364°C is associated with the polymer degradation. Figure 5, curve b shows an endothermic peak at 83°C, which perhaps arises as a result of conformational changes in poly(2-
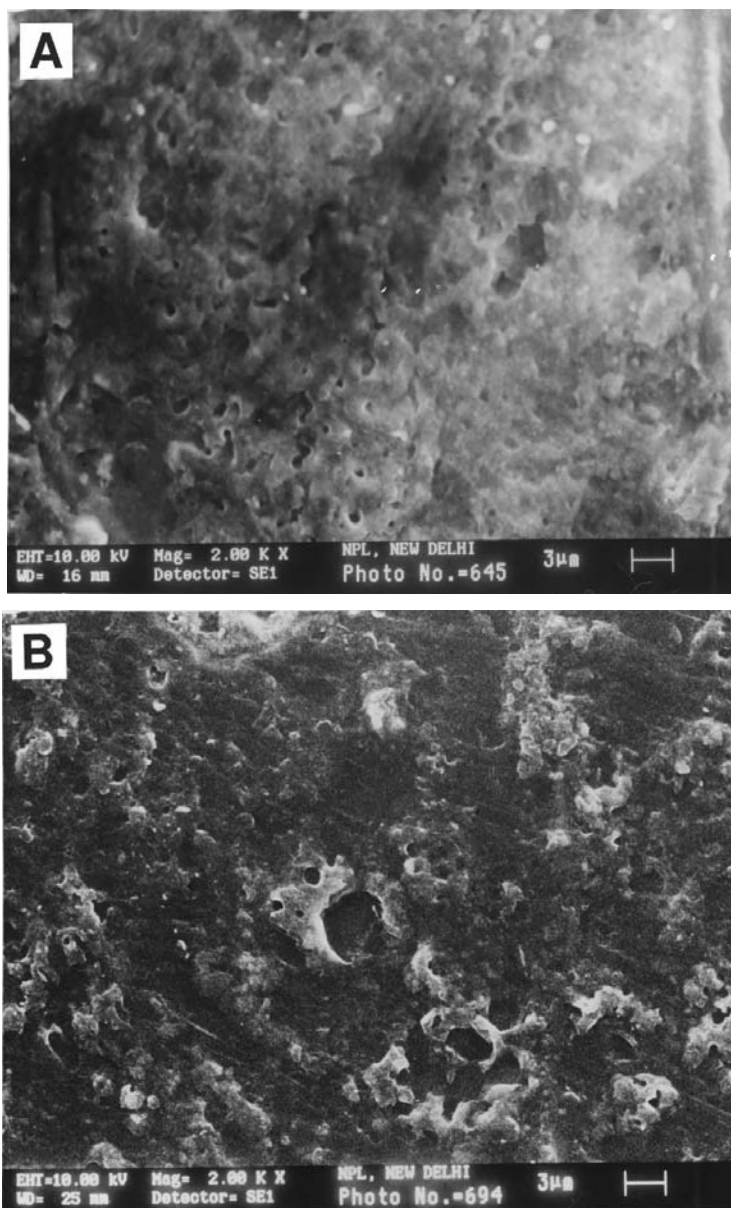
Fig. 4. SEM of **(A)** doped and **(B)** undoped chemically synthesized poly(2-fluoroaniline) powder.

fluoroaniline). The peak at 197°C is attributed to the interchain cross-linking in the polymer *(22)*. The peak observed at 418°C corresponds to the thermal degradation of the poly(2-fluoroaniline).

To confirm the above mentioned results further, thermogravimetric analysis (TGA) was performed in an inert (nitrogen) atmosphere at 20°C/min on poly(2-fluoroaniline) in both doped and undoped states,
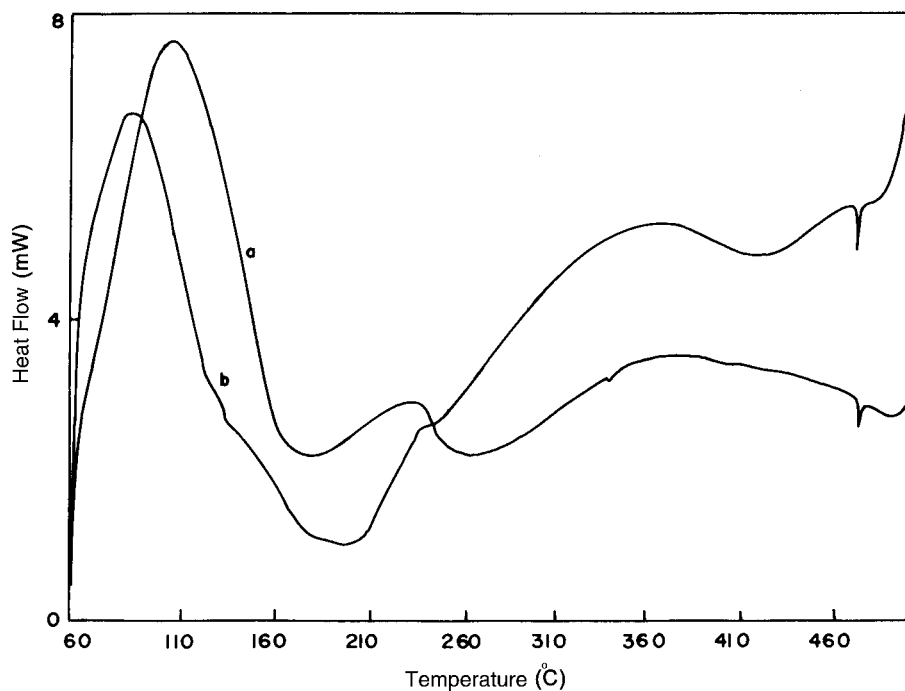
Fig. 5. Differential scanning calorimetry thermogram of (a) doped and (b) undoped chemically synthesized poly(2-fluoroaniline).
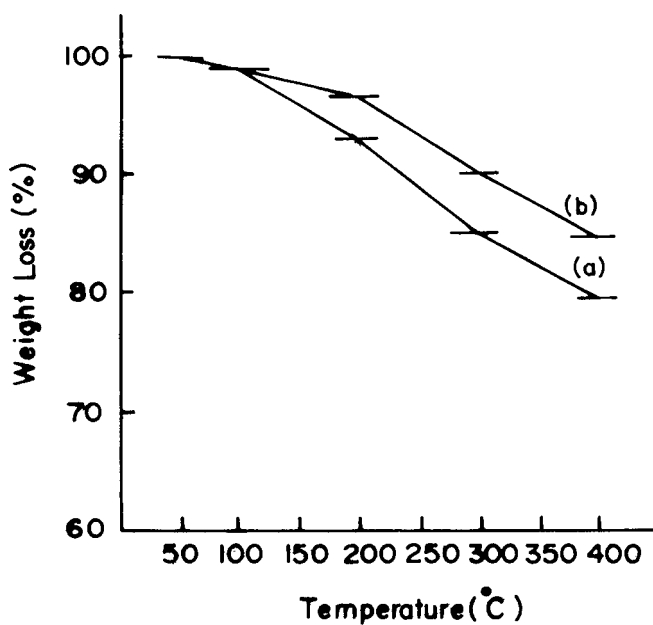

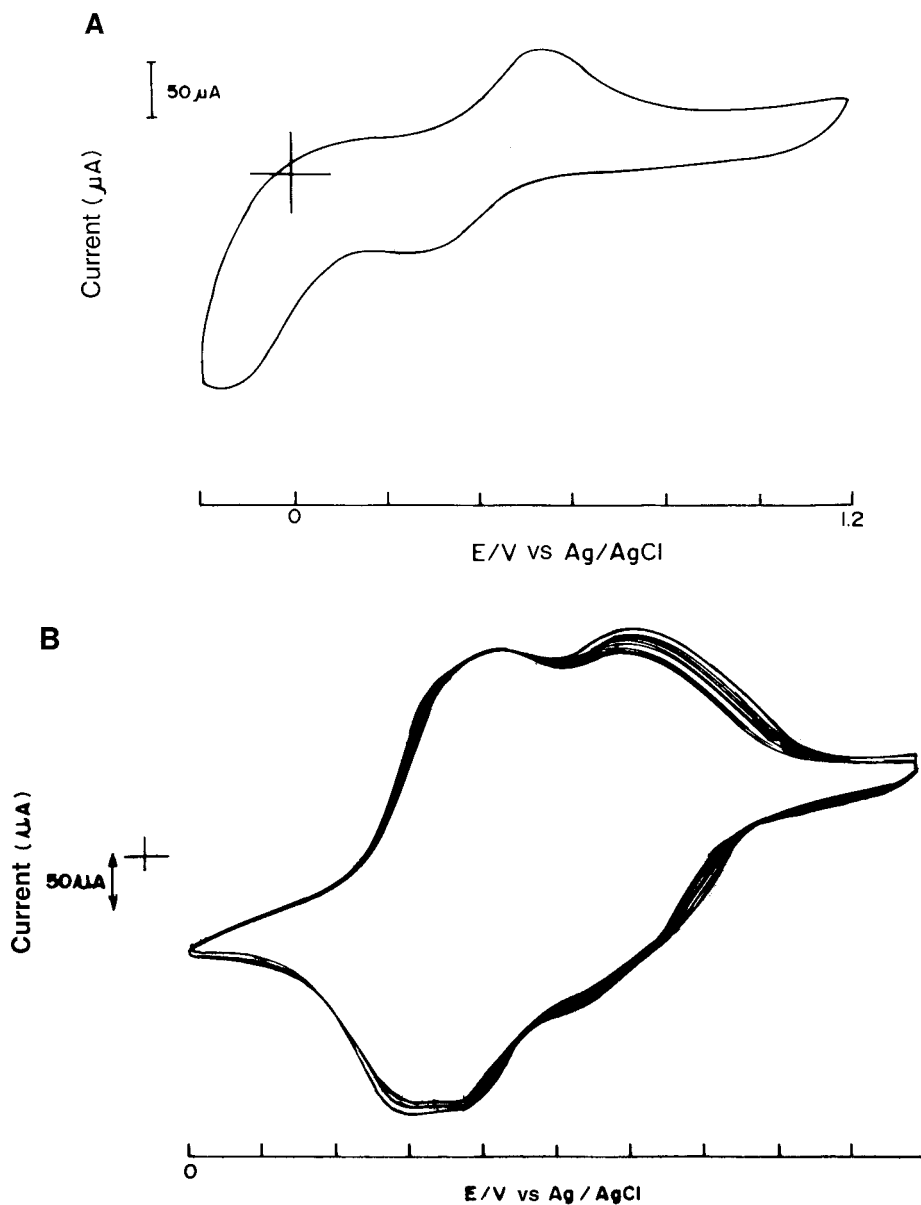Fig. 6. TGA thermogram of (a) doped and (b) undoped chemically synthesized poly(2-fluoroaniline).

A

50 μA

Current (μA)

0   1.2

E/V vs Ag/AgCl

B

Current (μA)

50 μA

0   1

E/V vs Ag/AgCl

Fig. 7. **(A)** Cyclic voltammogram of chemically synthesized poly(2-fluoroaniline) powder at scan rate of 50 mV/s. **(B)** Cyclic voltammogram of poly(2-fluoroaniline) film coated on ITO electrode in 4 *M* perchloric acid at scan rate of 50 mV/s.

respectively. The results are shown in Fig. 6. It can be seen (Fig. 6, curve a) that in the case of doped poly(2-fluoroaniline), 7% weight loss occurs between 50 and 200°C. Between 200 and 300°C, the weight loss of 8% arises owing to the removal of Cl⁻ ions. The 13% weight loss found between 300 and 400°C corresponds to the degradation of this polymer. Interestingly, a
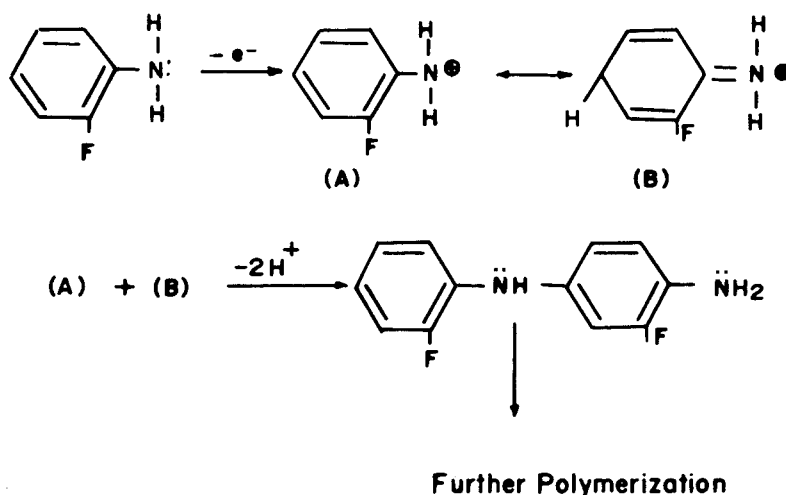
Fig. 8. Mechanism of formation of poly(2-fluoroaniline).

total weight loss of about 28% occurs between 50 and 400°C whereas it is about 20% (Fig. 6, curve b) in the case of undoped poly(2-fluoroaniline) in the same temperature range.

Doped and undoped forms of poly(2-fluoroaniline) have been found to be soluble in NMP and tetrahydrofuran. Therefore, it is possible to obtain the spin cast films of doped polymer. However, undoped poly(2-fluoro-aniline) was also found to be soluble in acetone. As compared to the undoped polyaniline, poly(2-fluoroaniline) is soluble in a number of organic solvents in both doped and undoped states. Solubility of undoped polymer in NMP was found to be 73 and 79% in its doped and undoped states, respectively. It should therefore be possible to cast films of desired dimensions of poly(2-fluoroaniline).

Figure 7A shows the cyclic voltammogram obtained for doped poly(2-fluoroaniline) films by the spin-coating method. The chemically synthesized polymer was dissolved in NMP and filtered well before use. The cyclic voltammogram was obtained in 1 M HCl at a scan rate of 50 mV/s. It can be seen that the voltammogram does not show any peak for radical cations whereas the second peak at 5.6 mV is obtained for radical anions. To compare the cyclic voltammogram with electrochemically synthesized films, we made an attempt to prepare films in 1 M HCl, but the quality of the films obtained was not good. Therefore, we used 4 M perchloric acid to prepare films electrochemically. Figure 7B is the cyclic voltammogram of poly(2-fluoroaniline) film obtained in 4 M perchloric acid. Anodic peaks at 0.42 and 0.63 V with complementary cathodic peaks can clearly be seen. These peaks have been attributed to the oxidation of the poly(2-fluoro-aniline) chain. Note that the shape of the cyclic voltammogram observed for electrochemically synthesized poly(2-fluoroaniline) film is found to be deformed with increasing potential cycling. Moreover, increasing the scan

limit to higher potentials leads to faster deterioration of the redox peaks, perhaps owing to the passivation of the poly(2-fluoroaniline) film. The anodic peak current i_{pa} and cathodic peak current i_{pc} scaled linearly with sweep rate, which is typical for a redox reaction involving surface-attached species, indicating a diffusion-controlled phenomenon.

The mechanism of polymerization of 2-fluoroaniline thought to arrive via head-to-tail coupling is shown in Fig. 8.

Conclusion

It has been shown that poly(2-fluoroaniline) can be prepared by chemical and electrochemical techniques. Chemically synthesized poly(2-fluoroaniline) was found to be soluble in common organic solvents, indicating that this conducting polymer can be utilized for technological applications. Attempts are presently being made in our laboratory to characterize the electrochemically prepared poly(2-fluoroaniline).

Acknowledgments

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