Highly Conductive and Electroactive Fluorine-Functionalized Polyanilines

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ABSTRACT: A series of highly conductive and electroactive fluorine-functionalized polyanilines (F-Pans) (containing 28−131 mol % of F) have been successfully prepared via the concurrent reduction and substitution (CRS) method, by reacting the polyaniline emeraldine base with tetrabutylammonium fluoride in MeOH for 12 h. Although the conventionally prepared poly(fluoroaniline)s were in general found to be poorly conductive (10^{-6}−10^{-5} S/cm) with lowered molecular weights (4×10^3), significantly blue-shifted UV−vis absorption (with the exciton band appearing at 362−555 nm), and greatly increased oxidation potential (∼0.42 V vs SCE in 1 M HCl) in comparison with the similarly prepared unsubstituted polyaniline, the F-Pans obtained from the CRS method are not only highly conductive (3−0.1 S/cm) but also very much electroactive, with molecular weight, UV−vis absorption λ_{max}, and oxidation potentials comparable to those of the parent unsubstituted polyaniline. Such interesting new results accompanied with the CRS-prepared F-Pans suggest that the electronegativity of the F group alone could not be solely responsible for the poor conductivity associated with the conventionally prepared poly(fluoroaniline)s.

Introduction

Because of their unique electrooptical properties and market potential, polyanilines are one of the recent focuses in the field of conducting polymers.[1] However, as is common with other conjugated polymers, the application of polyanilines (Pans) is limited by their poor melt and solution processability. Improved solubility of polyaniline (Pan) can be achieved by introducing various alkyl and alkoxy substituents to the polymer backbone.[2,3] Because of such need, alkyl- and alkoxy-substituted Pans have been intensively studied. On the other hand, there are only scattering reports available for the Pans with electron-withdrawing substituents, such as nitro and halo. Among these limited studies, the F-containing Pans have received increased attention because of the unusual properties associated with the fluorine atom, such as high electronegativity, small atomic radius, high lipophilicity, and unique chemical reactivity.[4] However, the poly(fluoroaniline)s[5−8] prepared by the conventional chemical and electrochemical polymerization methods from fluoroanilines have been found to be poorly conductive (10^{-6}−10^{-5} S/ cm)[5,6,8] with lowered molecular weights (4×10^3),[6] significantly blue-shifted UV−vis absorption (with the exciton band appearing at 362−555 nm),[5,6] and greatly increased oxidation potential (∼0.42 V vs SCE in 1 M HCl)[6] in comparison with the unsubstituted Pans obtained under similar reaction conditions. These unusual aspects have been long attributed to the high electronegativity of the F substituent, which is believed to significantly reduce the electron density of the backbone and thus greatly impair their conductivity. However, in our previous studies,[9−12] we have found that the much lowered conductivities associated with the alkyl-, alkoxy-, and alkylthio-substituted polyanilines (prepared via oxidative polymerization from their corresponding monomers) arise from the higher extent of non-conjugated 1,3-linkage backbone structure due to the electron-directing placement effects of the substituent groups for the growing polymer chain,[12] instead of the generally believed steric hindrance effects of the substituent groups. Similarly, whether the characteristic problems (such as much lowered molecular weight, blue-shifted absorptions, and higher redox potentials) associated with the previously reported poly(fluoroaniline)s can be attributed solely to the electronegativity of the F substituent or to the defective backbone structure remains an open question.

To clarify the exact chemical roles that the F groups might have played during and after the growth of the poly(fluoroaniline) backbones, we have developed a feasible method for introducing the F substituent to the preformed polyaniline backbones via the previously reported concurrent reduction and substitution (CRS) method,[9] by reacting the half-oxidized emeraldine base form of polyaniline with fluoride nucleophile. After the reaction, the polyaniline backbone was found to be indeed substituted with fluorine and concurrently reduced to its leucoemeraldine base form. The advantage of this synthetic approach is that the backbone linkage structure of the fluorine-functionalized polyaniline (F-Pan) could be maintained the same as the parent unsubstituted Pan, thus totally eliminating the effects arising from the structural alternations of the backbone, so that the electron effect of the F substituent could be fairly evaluated. Surprisingly, the F-Pans prepared by the CRS method were found to be more conductive (after reoxidation and doping treatments) and electroactive than the poly(fluoroaniline)s prepared from the conventional oxidative polymerization (OP) method.[5] The results reported herein indicate the high electronegativity of the F group; although it does cast a negative impact on the conductivity and electron density of Pan, the effects however are not as dramatic as what the community have believed. Our study implies that the adverse effects that occurred to the previously reported poly(fluoroaniline)s may have mainly arisen from the electron-directing influence of the F group on the linkage placements between the neighboring repeat unit during the growth of the polymer backbone.

Experimental Section

Tetrabutylammonium fluoride (Acros), potassium fluoride (Aldrich), and potassium hydrogen fluoride (Showa chemical) were used as purchased. The polyaniline (Pan) thin films (∼0.1 or ∼1 μm) on electrodes were prepared either by electrochemical means

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Table 1. Preparation of Fluorine-Functionalized Polyanilines[a]

entry	Pan[b]	reagent/conc.	solvent	reaction time (h)	F %[c,d]
1	EB	KF/0.05 M	CH_3CN	24	N.R.
2	EB	KHF_2/0.05 M	CH_3CN	24	N.R.
3	EB	Bu_4NF/0.1 M	CH_3CN	24	N.R.
4	EB	KF/0.05 M	H_2O	24	N.R.
5	EB	KHF_2/0.05 M	H_2O	24	N.R.
6	EB	Bu_4NF/0.1 M	H_2O	24	N.R.
7	EB	KF/0.05 M	MeOH	12	16.7%
8	EB	KHF_2/0.05 M	MeOH	12	12.4%
9	EB	Bu_4NF/0.1 M	MeOH	12	28%
10	PB	Bu_4NF/0.1 M	MeOH	12	50%
11	PB	Bu_4NF/0.1 M	CH_3CN	12	N.R.
12	PB	Bu_4NF/0.1 M	H_2O	12	N.R.

[a] After the reactions, the resultant films were cleaned by rinsing and soaking with the same (fresh) reaction solvent. [b] EB and PB stand, respectively, for emeraldine base and pernigraniline base forms of Pan. [c] F % is the substitution degree of fluorine measured by XPS, based on the atomic ratio of F/N. [d] N.R. stands for "no reaction".

based on 0.1 M aniline solution using previously reported conditions and procedures[9] or by solution-casting from 0.5 wt % NMP solution of Pan. The emeraldine base (EB) form of Pan films was prepared by electrochemical forcing treatment in 0.5 M H_2SO_4 aqueous solution at 0.5 V (vs SCE) for at least 10 min, followed by the dedoping treatment with 0.1 N NaOH in MeOH. The pernigraniline base (PB) form of Pan films was prepared from the above resultant EB films by an additional electrochemical forcing treatment in 0.5 M $LiClO_4/CH_3CN$ solution at 0.7 V (vs SCE) for at least 20 min, followed by the dedoping treatment with 0.1 N NaOH in MeOH.[13]

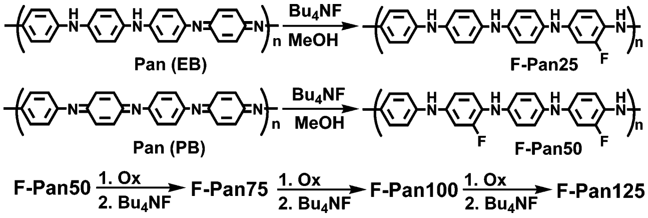
Preparation of Fluorinated Polyanilines (F-Pan25 and F-Pan50) via One Run of CRS Reaction. The above resultant unsubstituted polyaniline EB or PB films were soaked along with a fluoride salt (e.g., Bu_4NF) in a selected solvent (e.g., MeOH) for a predetermined time under N_2 at room temperature (summarized in Table 1). The resultant F-substituted films were rinsed with copious amounts of CH_3CN and then vacuum-dried at room temperature overnight. The depth profile studies with SIMS (secondary ion mass spectroscopy) for a series of control samples indicated that the fluorination happened evenly throughout the thickness of the films and was completed within ca. 10 h.

Preparation of Highly Fluorinated Polyanilines (F-Pan75, F-Pan100, and F-Pan125) via Multiple Runs of CRS Reaction. To prepare polyaniline containing more than 50 mol % of F, the above resultant F-Pan50 film (in its fully reduced leucoemeraldine base, LB, form) was electrochemically forced back to its EB form in 0.5 M $LiClO_4/CH_3CN$ solution at 0.7 V (vs SCE) for at least 20 min,[16] followed by the dedoping treatment with 0.1 N NaOH in MeOH. The resultant EB form of F-Pan50 was soaked with 0.1 M solution of NBu_4F in MeOH to repeat another run of CRS reaction to yield F-Pan75. The same electrochemical forcing treatment and CRS reaction can be repeated once more to yield F-Pan100, or twice more to yield F-Pan125.

Preparation of Homo- or Copolymers of 2-Fluoroaniline (P2FAs) via the Conventional OP Method. The homo- and copolymers of 2-fluoroaniline (P2FAs) were prepared using 1.25 equiv of ammonium peroxysulfate (APS) as the oxidant from a series of 0.2 M aqueous solutions of the monomer mixture of 2-fluoroaniline and aniline (containing 2.2 equiv of *p*-toluenesulfonic acid) with the fraction of 2-fluoroaniline in the monomer feed ranging from 1, 0.75, 0.5, 0.2, to 0. The polymerizations proceeded for at least 2 h. The resultant polymer powders were collected by filtration, rinsed with a copious amount of deionized water and MeOH, and then vacuum-dried overnight. The corresponding undoped polymer samples were prepared by an additional dedoping treatment with 5 wt % Na_2CO_3 solution.

Instrumentation. Conductivity measurements were performed with free-standing polyaniline films (~3 μm thick) after being fully doped with 1 M diphenylphosphate in CH_3CN for 10 h, based on a four-point-probe method using a Keithley 220 constant-current source and a Keithley 196 multimeter. XPS (X-ray photoelectron spectroscopy) spectra for the resultant polyaniline samples were collected with a ULVAC-PHI Quantera SXM, using Al K_α as the X-ray source. The excitation area was 100 × 100 μm; the step-sizes for survey and chemical state spectra were 1.0 and 0.050 eV, respectively. Attenuated total reflectance infrared (ATRIR) spectra of the resultant samples were monitored, using a Perkin-Elmer 2000 FTIR spectrometer equipped with a Graseby Specac single reflection diamond ATR accessory under a nitrogen atmosphere. UV−vis spectra of the resultant samples were recorded on a Hitachi U3501 spectrophotometer based on the NMP solutions of the polyaniline samples. The ^{19}F NMR spectra (d_6-DMSO, 470 MHz) of the samples were recorded with a Varian Unity Inova 500-MHz NMR spectrometer and externally calibrated with CCl_3F. The molecular weight analysis for the F-containing polyaniline samples was performed on a gel permeation chromatography (GPC) system equipped with four Waters Styragel columns (installed in a 60 °C oven) and a UV detector (at $\lambda = 330$ nm), using 1 mL/min DMF (containing 0.05 M LiBr) as the eluent. The molecular weight was calibrated against the polystyrene standards. The CV study for the F-containing polyaniline samples was performed with a CH Instrument (CHI-605A) in the CH_3CN solution of 0.5 M $LiClO_4$ at a scanning rate of 30 mV/s.

Scheme 1. Preparations of Fluorine-Functionalized Pans via the CRS Method



Results and Discussion

The preparations of the fluorine-functionalized polyanilines (F-Pans) via the CRS route[10] are illustrated in Scheme 1. We have first attempted to perform the CRS reaction between the polyaniline emeraldine base (EB) and F^- in an aprotic solvent medium (CH_3CN) to retain the maximum nucleophilicity of F^-.[14,15] However, the CRS reaction failed to go in 24 h at room temperature, despite using various F^- sources (such as KF, KHF_2, and Bu_4NF). Other attempts in performing the reaction in the aqueous solutions (to maximize the solubility of the fluoride salts) also proved futile. On the contrary, to our surprise, although it is generally believed that the nucleophilicity of F^- in a protic solvent could be very weak, the control experiments in MeOH worked reasonably well.

The result in Table 1 indicated that, under the same reaction conditions, the most soluble tetrabutylammonium fluoride (TBAF) actually gave the best result, leading to ~28 mol % (based on the aniline repeat units) of substitution. During the reaction period (12 h), the nontransparent dark blue polyaniline EB film changed gradually to a transparent colorless film, implying a possible transformation of the polyaniline backbone from the dark blue half-oxidized EB state to a colorless fully reduced and F-substituted leucoemeraldine base (LB) state.

Such hypothetical transformation of the polyaniline backbone from the EB to the LB forms was confirmed by the UV−vis study (Figure 1). The results indicate that after the reaction the exciton band at ~636 nm (Figure 1a) essentially disappeared, leaving behind only the $\pi-\pi^*$ transition band at ~344 nm (Figure 1b) and showing a spectral feature quite similar to the LB form of its parent unsubstituted Pan. The obtained LB form of F-Pan can be easily reoxidized chemically or electrochemically back to its EB form (Figure 1c), showing the $\pi-\pi^*$ transition (~328 nm) and exciton (~636 nm) bands at positions

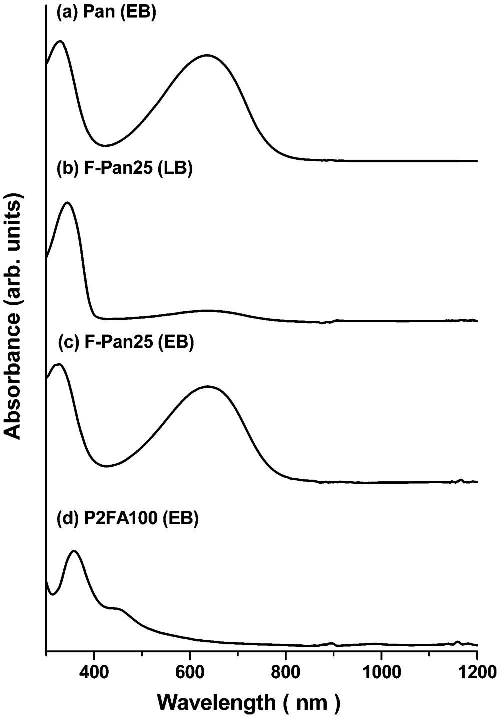
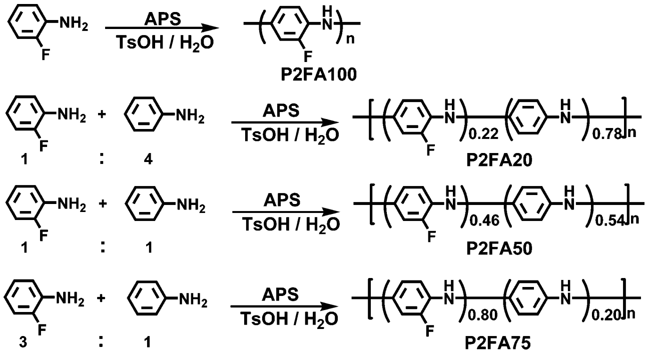


Figure 1. UV−vis spectrum for: (a) the EB form of the parent Pan film, (b) F-Pan25 film prepared from the Pan film in (a), (c) the EB form of the F-Pan25 film, and (d) the as-prepared poly(2-fluoroaniline) (P2FA100) film.

Scheme 2. Preparations of Homo- and Copolymers of 2-Fluoroaniline



similar to those of the original Pan (Figure 1a), whereas the control sample of poly(2-fluoroaniline) (denoted as P2FA100) prepared by us via the conventional oxidative polymerization (OP) method from 2-fluoroaniline (as illustrated in Scheme 2) showed a much blue-shifted exciton band at ~448 nm (Figure 1d), similar to the literature result.[5]

The presence of the new F group in the resultant film was confirmed by X-ray photoelectron spectroscopy (XPS). In addition to the original C 1s (284.5 eV) and N 1s (399.5 eV) lines, the XPS survey spectrum of the film (Figure 2b) also showed a newly appearing F 1s line at ~686.9 eV, consistent with the presence of a C−F covalent bond[16] instead of the left-over TBAF salt (~684.3 eV; Figure 2c). The measured atomic ratio of F/N (~0.28) suggested that the resultant F-Pan (denoted as F-Pan25) contained about ~28 mol % of F-substituent. In contrast, all of the F^- treated films in CH_3CN and H_2O media did not show any F 1s line. Furthermore, when a Pan film in its fully oxidized pernigraniline base (PB) form was treated with 0.1 M TBAF in MeOH for 12 h, the resultant F-Pan film (denoted as F-Pan50) was found to contain ~50 mol % of F group (Figure 2d). Both of the substitution degrees obtained in the MeOH medium (entries 9 and 10, Table 1) seem to agree, respectively, well with the theoretical amounts of the quinoid rings (as illustrated in Scheme 1) for the EB and PB forms of Pan. The depth profile studies with SIMS (secondary ion mass spectroscopy) confirmed that the F group was distributed evenly throughout the thickness of the films. The amount of F substituent on the polymer backbone can be further increased and tailored by performing repeated runs of CRS reaction on the same film, starting with any specific oxidation level as controlled by the electrochemical means. For example, when the obtained F-Pan50 film was further electrochemically forced[13] to 0.7 V (vs SCE) in 0.5 M $LiClO_4/CH_3CN$ for 20 min followed by a second run of CRS reaction, a F-Pan film (denoted as F-Pan75) containing ~76 mol % of F can be obtained. Likewise, the F-Pan100 and F-Pan125 films containing ~98 and 131 mol % of F, respectively, can also be obtained after repeating the third and the fourth runs of CRS reaction. The control experiments indicated that the amount and the nature of the F groups in the resultant films remained the same even after being soaked with 0.1 N NaOH in MeOH, reassuring us that the F groups in F-Pans were not present as the form of a HF dopant. The presence of the C−F bonds in the F-Pan films was confirmed by the newly appeared IR bands at ~1250 cm^{-1} (C−F stretching) and ~1050 cm^{-1} (X-sensitive band for the fluorinated aromatic ring) and was also supported by their ^{19}F NMR (d_6-DMSO, 470 MHz, externally calibrated with CCl_3F) peaks at δ −134.4 and −139.5, which are similar to that of 2-fluoroaniline (δ −135) but different from those of fluoride ions, such as F^- (~δ −102) and HF_2^- (~δ −143).

Table 2. Conductivity Study[a]

entry	polymer[b]	F %	conductivity (S/cm)	remark
1	Pan	0	2−3	this work
2	F-Pan25	28	2−3	this work
3	F-Pan75	76	0.5	this work
4	F-Pan100	98	0.1	this work
5	P2FA100	97	$\sim 10^{-6}$	this work
6	P2FA100		3×10^{-5}	refs 5,6
7	P2FA50	46	3×10^{-4}	this work
8	P2FA50		3×10^{-3}	ref 6

[a] Conductivity study of this work was performed by a four-point-probe method based on the fully doped (with 1 M diphenylphosphate in CH_3CN) polyaniline films. For the reference works, HCl was the dopant. [b] Emeraldine polyaniline films were used for entries 1 and 5−8. For F-Pans in entries 2−4, their leucoemeraldine polyaniline films obtained after the CRS reaction were used directly.

The conductivity of these F-Pan films was studied by a typical four-point-probe method based on their fully doped films (with 1 M diphenylphosphate in CH_3CN for 10 h). To our surprise, the F-Pan25 containing 28 mol % of F was as conductive (2−3 S/cm; entry 2 of Table 2) as its original parent Pan film (2−3 S/cm; entry 1). Most interestingly, even for the F-Pans that contain an appreciable amount of F, such as 76 and 98 mol %, the conductivity was still as high as 0.5 and 0.1 S/cm, respectively, which are much higher than the homopolymers of 2-fluoroaniline (P2FA100; 10^{-6}−10^{-5} S/cm; entries 5 and 6) and the copolymers of aniline/2-fluoroaniline (1:1) (P2FA50; 10^{-3}−10^{-4} S/cm; entries 7 and 8) prepared from the conventional oxidative polymerization (OP) method (Scheme 2). The high conductivity results for the CRS-prepared F-Pans suggest that the electronegativity of the F group alone could not be solely responsible for the poor conductivity associated with the previously reported poly(fluoroaniline)s.[5,6,8]

The CV traces (with 0.5 M $LiClO_4$ electrolyte in CH_3CN) of these CRS-prepared F-Pan films look quite similar to that of their parent unsubstituted Pan with the first redox potential $E_{1/2}$

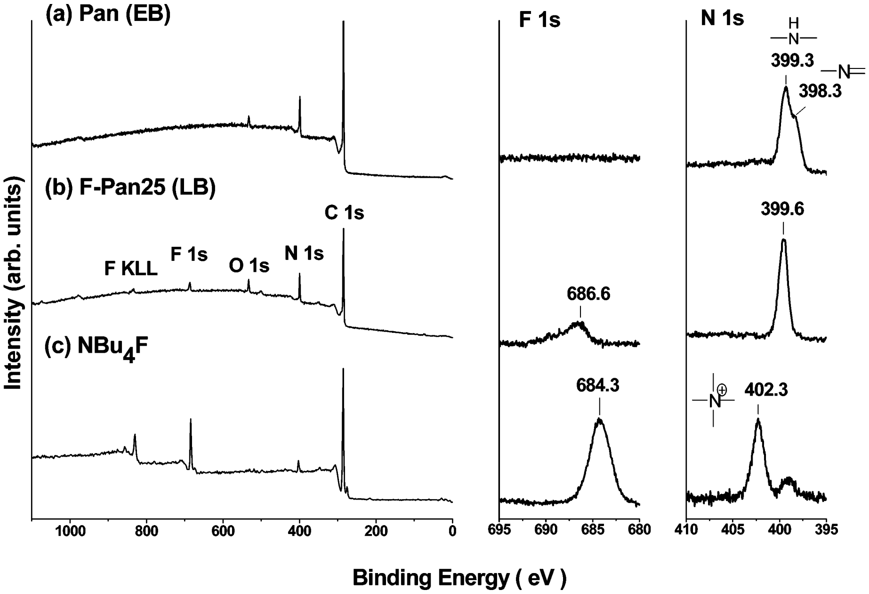


Figure 2. The XPS spectrum for: (a) the EB form of the parent Pan film, (b) the F-Pan25 film prepared from the Pan film in (a), and (c) the Bu_4NF salt residues being intentionally left over the surface of the Pan film by skipping the cleaning steps after the reaction.

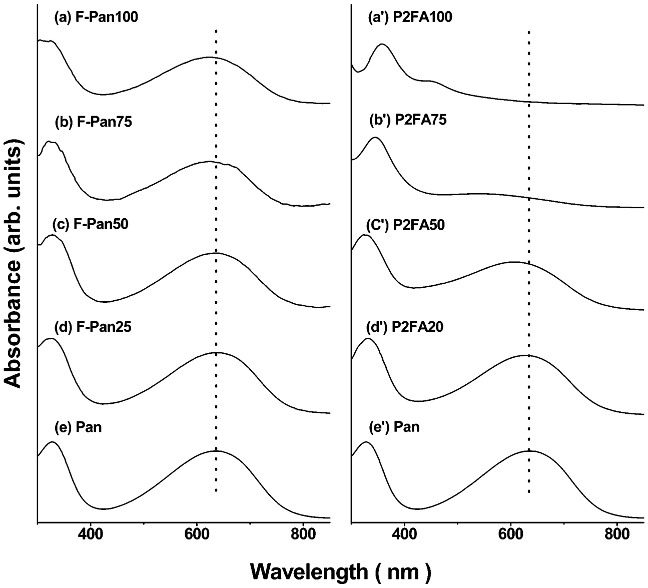


Figure 3. The UV−vis spectra for the EB form of the F-substituted Pan samples: (a−d) the F-Pan samples with 98, 76, 50, and 28 mol % of F substituent, respectively; (a′−d′) the P2FA samples with 97, 80, 46, and 22 mol % of F substituent, respectively. The broken lines are placed at 636 nm, which is the λ_{max} for the exciton band of the unsubstituted Pan.

(for transforming between the LB and EB forms) being increased only slightly from ~0.16 V to less than 0.19 V as the substitution degree of F increased from 0 to 131 mol %. On the other hand, the previously reported poly(2-fluoroaniline) prepared by the conventional OP method was found to show a much larger increment (~0.3 V) in $E_{1/2}$ from their similarly prepared polyaniline.[6]

The GPC study confirmed that CRS-prepared F-Pan samples all have similarly high molecular weights (M_w = 32 000 for F-Pan25, 31 800 for F-Pan50, and 24 200 for F-Pan100) as that of the original parent Pan (M_w = 28 900). The small variations in M_w may be caused by the differences in their hydrodynamic volumes arisen from the respective chemical modifications. On the other hand, the OP-prepared poly(2-fluoroaniline) (P2FA100) showed a much reduced M_w (~2700). The GPC result indicated that, although poly(2-fluoroaniline) has a much lower M_w, it still contained a reasonable size of polymerization degree. The GPC result together with both conductivity and CV results imply that the much poorer electroactivity associated with the previously reported poly(fluoroaniline)s may be alternatively attributed to the changes in their backbone structures, due to the formation of a significant extent of non-conjugated 1,3-linkage structures as induced by the electronic influence effect of the F group on directing the placement for the next jointed repeat unit. The presence of such conjugation defects can greatly reduce the effective length of the conjugation segments, leading to much blue-shifted UV−vis absorptions and significantly reduced redox capability.

The UV−vis spectra (Figure 3) for the EB forms of various F-containing polyaniline samples having different amounts of F obtained from both the CRS and the OP methods are closely compared.

The results clearly show that as the fluorination degree increases from 0 to 100 mol %, the UV−vis spectra of the CRS-prepared F-Pans showed only small changes in their λ_{max} of the exciton bands (from 632 to 622 nm) and maintained a similar intensity ratio between the exciton and the $\pi-\pi^*$ transition bands, whereas the UV−vis spectra for the OP-prepared P2FAs showed dramatic changes in both the λ_{max} of the exciton band (blue-shifted considerably from 632 to 448 nm) and the intensity ratio between the two absorption bands.

The much poor redox ability (or electroactivity) associated with the OP-prepared P2FA samples was further demonstrated by the air oxidation studies, based on the NMP solutions (~10^{-5} M) of their fully reduced LB forms. The oxidation degrees were monitored by the λ_{max} intensity ratio between the exciton band and the $\pi-\pi^*$ transition band with UV−vis spectrometer. The results summarized in Figure 4b indicate that the air-oxidation ability of the LB forms for the OP-prepared homo- and copolymers of 2-fluoroaniline was found to be significantly impaired as the fraction of 2-fluoroaniline in the monomer feed increased from 0 to 100 mol %. In contrast, the CRS-prepared F-Pans (Figure 4a) can all undergo air oxidation similarly well (with quite similar reaction rates and extents) as their parent unsubstituted Pan, despite that they also contained similar amounts of F groups as their corresponding P2FA counterparts. The results suggest that the much poorer redox capability

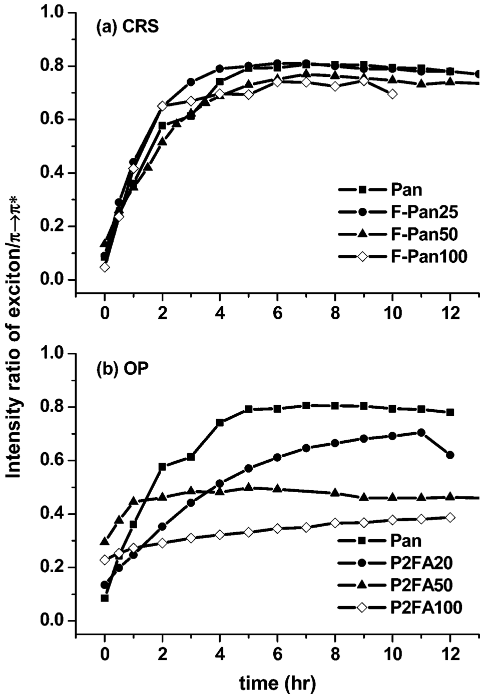


Figure 4. The air oxidation study for the LB samples of the F-substituted polyanilines, based on their NMP solutions ($\sim 10^{-5}$ M): (a) the F-Pans having 0, 28, 50, and 98 mol % of F substituent; and (b) the P2FAs having 0, 22, 46, and 97 mol % of F substituent. The UV−vis absorption $\lambda_{\max}$ intensity ratios between the exciton band and the $\pi\rightarrow\pi^*$ transition band of the corresponding samples are monitored and plotted against the reaction time. The LB samples of P2FAs were prepared by treating their EB powders with an excess amount of hydrazine for 8 h, while the LB samples of F-Pans obtained from the CRS reactions were used directly.

associated with P2FAs was unlikely to be caused by the electronegativity of the F groups alone. Instead, the results imply that the effective conjugation extent of the backbone of P2FAs might have been much reduced as the feed fraction of 2-fluoroaniline increased, caused by the electron-directing placement effect of the F group that led to the formation of a higher extent of conjugation defects on the polymer backbones. The much shortened conjugation segments could result in much lowered redox ability and electroactivity.

Conclusions

In conclusion, a feasible CRS method for making F-Pans with various amounts (28−131 mol %) of F-substituent in a conveniently controllable fashion has been successfully developed. Surprisingly, the resultant F-Pans are found to be highly conductive (3−0.1 S/cm) and show electroactivity similar to that of the parent unsubstituted Pan, whereas the homo- and copolymers prepared from 2-fluoroaniline via the conventional OP method are found to be poorly conductive (10^{-4}−10^{-6} S/cm), showing significantly lowered M_w and greatly reduced electroactivity, which may be attributed to the formation of non-conjugated 1,3-linkage structure due to the electron-directing placement effect of the F groups during the growth of the polymer chains.

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