

The Influence of Hydrogen Bonds on the Kinetics of Polymerization of Anilines and the Properties of the as-Produced Polyanilines

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Abstract The influence of hydrogen bonds, mediated either by hexafluorosilic acid (H_2SiF_6) or potassium fluoride, dihydrate ($\text{KF}\cdot 2\text{H}_2\text{O}$), in the oxidative polymerization of anilines is investigated. The reaction is conducted either under stirred or unstirred condition, in a glass or plastic vessel. The as-produced conducting polyanilines are analyzed by FT-IR, UV-Vis, cyclic voltammetry, SEM and elemental analyses. The electrical conductivity of the doped polyanilines was found to lie within the usual range of those synthesized through conventional methods. The kinetics of the polymerization are monitored via an open circuit profiling technique. The results indicate that fluoride ions can drastically slow down the reaction kinetics. And that both fluoride ions and H_2SiF_6 can impart nanomorphology in the bulk polyanilines whose fibers have an average diameter of ca. 100 nm.

Keywords Kinetics of aniline polymerization, Hydrogen bonds in polymerization of anilines, Influence of fluorides, Hexafluorosilicate ions or hexafluorosilic acid on polymerization of anilines, Hexafluorosilic acid as dopant of polyanilines, Nanofibers of polyanilines

1. Introduction

Polyanilines (PANI) is one of the most studied intrinsically conducting polymers because of its simple synthetic protocol, facile processability, good stability and relatively high electrical conductivity. The three commonly cited oxidation states of PANI are summarized in Fig. 1 where x , y and $1-y$ indicate the degree of polymerization, the reduced and oxidized repeat units, respectively. The completely reduced state of PANI is leucoemeraldine base (LEB) with $1-y = 0$. The fully oxidized state ($1-y = 1$) is pernigraniline base (PB) and that of the half-oxidized state is emeraldine base (EB) with $1-y = 0.5$ [1].

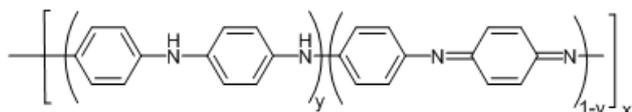


Figure 1. Structure of polyanilines (PANI)

Of these oxidation states of PANI, EB is the most interesting because it can be easily rendered electrically

conducting via protonic doping into its emeraldine salt (ES). The ES, in turn, can be reversibly switched back to its EB insulating state through deprotonation from its iminium ($=\text{N}^+-\text{H}$) or aminium radical cation ($^+\text{N}\text{H}$) as shown in Fig. 2.

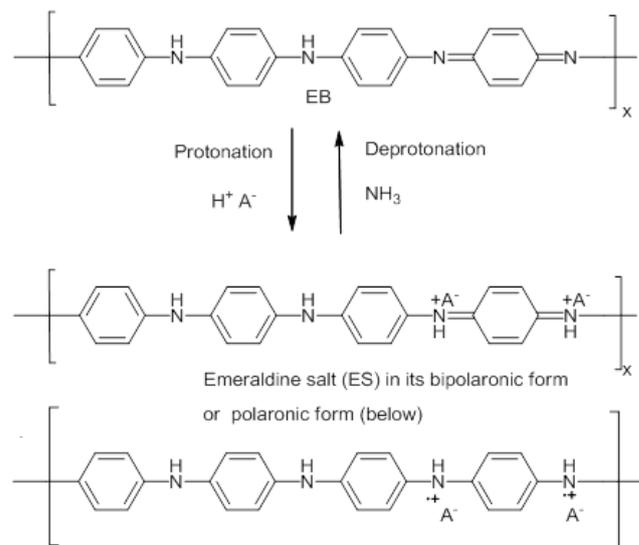


Figure 2. Processes of doping of EB with an acid and dedoping of ES with a base. In the ES structure, the A^- is the dopant anion

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The last three decades have witnessed a flurry of research on the syntheses of nanomaterials of intrinsically conducting polymers and the preparation of uni- or multidimensional nano-PANI have been reviewed [2]. Owing to the high aspect ratio of nano-PANI, their use as the key conducting component of devices can be found in electronic devices, chemical and biochemical sensors [3], [4].

The conventional preparation of PANI often calls for the use of water as the polar protic solvent in which monomeric anilines are oxidatively polymerized in an acidic medium, (typically HCl or H₂SO₄), with a strong oxidizing agent such as ammonium peroxydisulfate (APS). In this polymerization, extensive and complex, dynamic intermolecular hydrogen bond (H-Bond) exchanges are expected to take place between, e.g., water-aniliniums, APS-water-hydronium, aniline-anilinium [5]. To our knowledge, little study if any, has been conducted on the potential effect of H-bonds, in the polymerization of anilines in a medium containing compound with highly electronegative fluorine atoms or fluoride ions. Herein, we report the influence of either fluoride ions (from KF) or hexafluorosilicate (from the hexafluorosilicic acid, H₂SiF₆) on the kinetics of polymerization and on the morphology and properties of the as-prepared PANI. The choice of H₂SiF₆(aq) or HCl/KF (aq) is guided by their strong acidity which is a key requirement for good electrical conductivity of ES and the formation of specific nano-morphology [6].

2. Experimental

2.1. Materials

All chemicals were purchased from Sigma-Aldrich Co. and were used as received except for aniline which was freshly distilled under reduced pressure prior to polymerization.

2.2. Instrumentation

FTIR and UV-Vis spectra are recorded with the use of a Nicolet iS10 (ThermoScientific Corporation) and UV-2550 spectrometers (Shimadzu Co.), respectively. Electrical conductivity of pelletized ES is measured with a four-probe device connected to a Lakeshore 120CS DC microcurrent source which is coupled to an auto-ranging multimeter 175A (Keithley/Tektronix Co.). Morphological characteristics of PANI are obtained via SEM (Zeiss Neon EsB, operating at 5 KV). The electron microscope is equipped with an energy dispersive X-ray spectrometer (EDS) operating at 10-15 KV. Prior to SEM analyses, the ES were briefly sonicated in DI water. A suspension was retrieved via pipet and placed on a silicon wafer. The sample was then air-dried. The kinetics of polymerization is monitored via an open circuit potential (VOC) profiling technique [7] using a concentrated agar/KCl(aq) electrolyte solution as the salt bridge (Pt electrode and SCE as reference). The electrolyte solution

(contained in a separatory funnel) is connected to the polymerizing solution via a plastic tubing with one end attached to an Eppendorf (plastic) pipette whose tip is immersed into the reaction bath. Quantitative elemental analyses are from Micro-Analysis, Inc. Cyclic voltammetry (CV) is conducted with a WaveNow 50-EDU potentiostat from Pine Instrument Co. (using pre-printed carbon electrodes with silver/silver-chloride as reference electrode). For CV experiments, aqueous solutions of the ES are briefly sonicated, then drop casted onto the working electrode and subsequently air dried. The electrode was then immersed in a 1.0 M aq.HCl (electrolyte) bath for voltammetry measurements (scan rate of 20 mv/sec).

2.3. Preparation of PANI in the Presence of Fluoride Ions in HCl (aq), a Mixed Halide Medium

Care is exercised when conducting the polymerization as etching agents are formed in-situ. Gloves and safety goggles are worn. All reactions are carried out in a well-ventilated fume hood. Typical experimental protocols are given below.

2.3.1. Polymerization under Stirred Condition

A mixture of 0.34 ml (3.77 mmol) aniline and 6.00g (64.00 mmol) of KF.2H₂O in 75 ml of 1.0M HCl (aq) was stirred in a 250-ml (glass or plastic) beaker for 15 min. Into this stirred solution was added, dropwise, a solution of 0.95g (4.16 mmol) APS in 70 mL of 1.0 M HCl (aq). The resulting mixture was further stirred for 4 h after which time it was suction filtered on a Buchner funnel. The deep green-, doped ES was sequentially washed with copious amounts of DI water and acetone until a colourless filtrate was obtained. The collected polymer was high vacuum dried at 50°C for 4 h and stored in a dessicator.

2.3.2. Polymerization under Unstirred Condition

The above reaction was repeated in a glass or plastic beaker. The anilinium in HCl(aq) containing 0.5g KF.2H₂O (5.31 mmol) was stirred briefly for a few minutes and the magnetic stir bar was then removed. This was followed by a dropwise addition of the APS (aq) solution from a separatory funnel. The resulting mixture was left undisturbed for 48h after which time it was suction filtered and worked up as described in 2.3 a above.

2.3.3. Polymerization of Anilines in aq. Hexafluorosilicic Acid (H₂SiF₆)

Into a 150-ml plastic beaker was placed 75 ml (ca. 160 mmol) H₂SiF₆ (20-30% in water), followed by a slow dropwise addition of 0.34 ml (3.77 mmol) aniline. Some white solid particulates precipitated out. They were pulverized with a spatula and the suspension is stirred until all solids dissolved. Then a solution of 0.95g (4.16 mmol) APS (aq) in 60 ml water was added dropwise in ca. 30 min. The resulting mixture was stirred for 4 h, suction filtered and worked up as described in 2.3a above.

2.3.4. Kinetic Study of Polymerization via Open Circuit Potential (VOC)

The experiment described in section 2.3.a above was repeated with 6.00g (64.00 mmol) $\text{KF}\cdot 2\text{H}_2\text{O}$ either in a plastic or glass vessel under stirring (500 rpm). A conventional polymerization (without KF) is also conducted in HCl (aq). In a separate polymerization, the experiment described in 2.3.c was also repeated in a plastic beaker. In all experiments, the solution of APS was added dropwise into the acidic anilinium solution in 5 min. The progress of the polymerization is monitored by recording the VOC change of the solution vs. time as soon as the first drop of the APS solution was added. The stirring was stopped when the voltage became constant.

3. Results and Discussion

3.1. Spectral Characterization

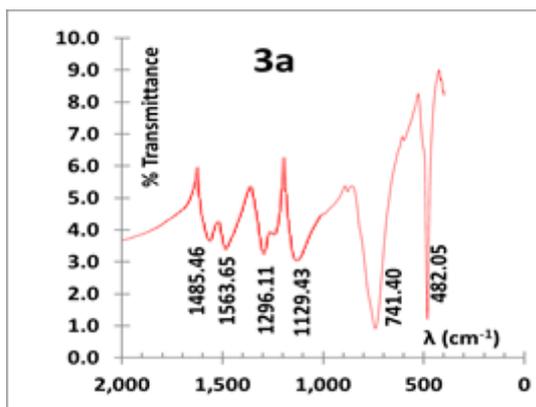


Figure 3a. IR of impure ES (prepared in 6g KF/HCl medium)

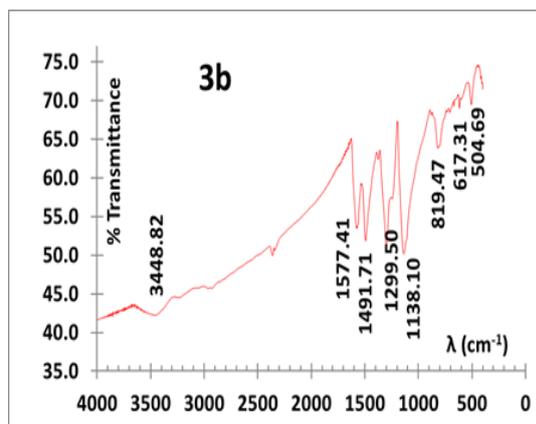


Figure 3b. IR of ES prepared in HCl medium (conventional method)

We first carried out a series of aniline polymerization in HCl (aq) in a glass beaker containing one of the following amounts of $\text{KF}\cdot 2\text{H}_2\text{O}$: 0.5, 2.0, 4.0 and 6.0 g. All isolated polymers exhibit the typical deep green colour which is a characteristic of PANI in its doped ES state. They are invariably mixed with some impure white/greyish particulates, referred here after as the “by-product”. A

representative IR spectrum of the impure ES is displayed in Fig. 3a. It shows vibrations with wavenumber (cm^{-1}) of 482.05, 741.40, 1129.43 (C-H in plane stretch), 1296.11 (C-N stretch, benzenoid), 1485.46 (C=C stretch benzenoid) and 1563.65 (C=C stretch, quinoid). The two prominent bands at 482.05 and 741.40 cm^{-1} are foreign to a conventionally synthesized ES, prepared in HCl (aq) whose typical spectrum (Fig. 3b) exhibits absorptions with wavenumber (cm^{-1}) of 504.69, 617.31, 819.47, 1138.10 (C-H in plane stretch), 1299.50 (C-N stretch, benzenoid), 1491.71 (C=C stretch benzenoid), 1577.41 (C=C stretch, quinoid) and 3448.82 (N-H stretch).

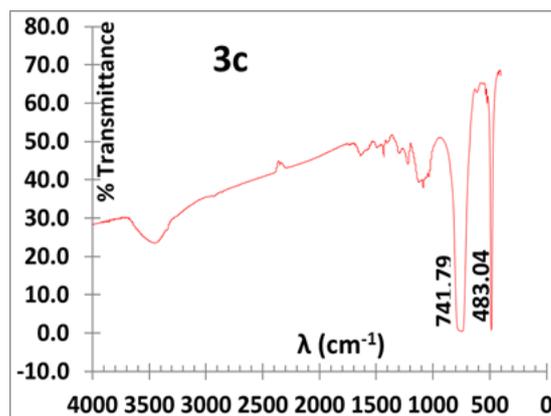


Figure 3c. IR of isolated by-product

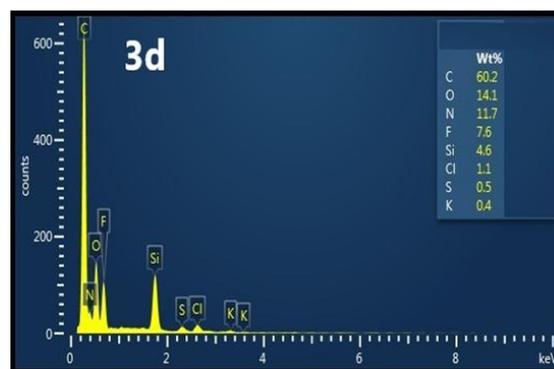


Figure 3d. EDS of an impure ES

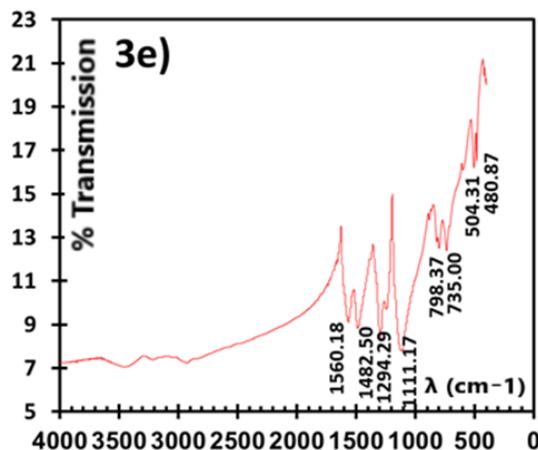
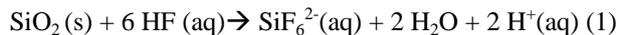
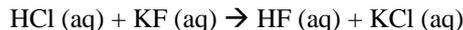


Figure 3e. IR spectra of ES (prepared in H_2SiF_6)

A literature search reveals that the by-product bands at 482.05 and 741.40 cm^{-1} correspond to Si-F stretching and bending of the hexafluorosilicate (SiF_6^{2-}) anion, respectively [8]. We attribute the source of the by-product from the etching of the beaker glass walls by HF (aq) via the sequence of reactions [9]:



Although it is known that HF (aq) is commonly used in glass etching, its composition, however, is complex and is not well understood [10], let alone the influence of other ions found in our reaction medium. In addition, it was recently reported that the rate of silica etching is quite dependent on the rate of stirring, the presence of an oxidizing agent [11] and/or the concentration of species such as HF, HF_2^- formed in-situ during reaction [12]. For example, in our reactions, there is the possibility of etching of the beaker walls by ammonium bifluoride (NH_4HF_2), formed from pairing up the ammonium ion of APS with H_2F^+ resulting in the formation of SiF_4 according to Eq 2 below [13]:



This reaction, however, does not take place because the observed Si-F vibrations of the by-product in Fig 3(a) do not match those of the reported SiF_4 [14].

It has often been observed that in a conventional polymerization of aniline in HCl(aq), glass beakers are invariably covered to some extent with bits of green ES films [7], [15]. This is because aniline monomers and anilinium chloride can H-bond with glass as shown by IR spectroscopy [16]. And that polymerization does not necessarily start in solution, rather it could be initiated by anilinium seeds chemisorbed (via H bonds) on glass substrates [15,17]. In this work, such green films were not formed when fluoride ions were present, rather the glass walls were covered with frosts or whisker-like filaments (unremovable via mechanical brushing) resulted from the etching process. This observation suggests that the presence of fluoride ions either prevented the anilinium from H-bonding with the glass walls, or such bonds if formed, are displaced to favour the protonation of the silica oxygens by HF followed by dehydration and the subsequent fast formation of the highly stable SiF_6^{2-} according to Eq. (1) above. The nature of the counter cation of the SiF_6^{2-} anion in the by-product revealed to be K^+ ion which was confirmed through isolation of a small sample from the bulk of an impure ES product. Its IR spectrum (Fig. 3c) shows two prominent peaks at 483.04 cm^{-1} (Si-F stretching) and 741.79 cm^{-1} (Si-F bending) which closely match those of K_2SiF_6 whose spectrum also exhibits two oversized vibrations at 485 cm^{-1} and 740 cm^{-1} [18]. Since K_2SiF_6 is highly stable and essentially insoluble in water or acidic medium [19], it must have quickly precipitated out of the reaction medium once formed, i. e., before the APS oxidant was added. A semi quantitative determination of the elements of an impure ES sample was conducted via EDS analysis. Its spectrum (Fig 3d) confirms the presence of C, N,

O, K, Si, F, Cl, S and O. The latter two elements are derived from the reduction of the APS-peroxydisulfate anion (by anilines or oligoanilines) which is converted into HSO_4^- or SO_4^{2-} under acidic condition [20].

In another experiment, we have carried out a polymerization of anilines (in a plastic beaker) with hexafluorosilicic acid (aq) as the dopant. This acid is known to readily dissociates in water into $2\text{H}^+(\text{aq})$ and $\text{SiF}_6^{2-}(\text{aq})$. The IR spectrum of the resulting SiF_6^{2-} doped ES (Fig. 3e) shows absorption bands with wavenumber (cm^{-1}) of 480.87 (Si-F stretch), 504.31, 735.00 (Si-F bending) (instead of 741 cm^{-1} for the corresponding vibration in the afore-mentioned ES by-product), 798.37, 1111.17, 1244.18, 1294.29, 1378.76, 1482.50 (C=C stretch, benzenoid), 1560.18 (C=C stretch, quinoid), 3449.45 ($\text{N}^+\text{-H}$ stretch). It is noteworthy that the Si-F bands of this SiF_6^{2-} doped ES are much less intense than those found in the previously described impure ES (Fig. 3a) or those of the by-product (Fig. 3c). The result indicates that SiF_6^{2-} is not the main dopant anion of the afore-mentioned series of impure ES prepared in HCl(aq)/KF (glass beaker). The actual counter anion(s) of the series of isolated impure ES was determined via elemental analysis of a sample obtained from the polymerization of anilines in HCl/KF.2H₂O (plastic beaker). The results are as follows: 62.41% C; 4.86% H; 12.46% N; 8.09% Cl and 9.13% F. It is known that in a conventionally prepared ES with HCl (aq) as the dopant of anilines, the mol ratio of Cl/N is ca 1/2 (with 0.45 mol Cl⁻ and 0.92 mol N) [15]. Our results gave a Cl/N ratio of 1/4 implying that Cl⁻ and F⁻ are both counter anions of the impure ES.

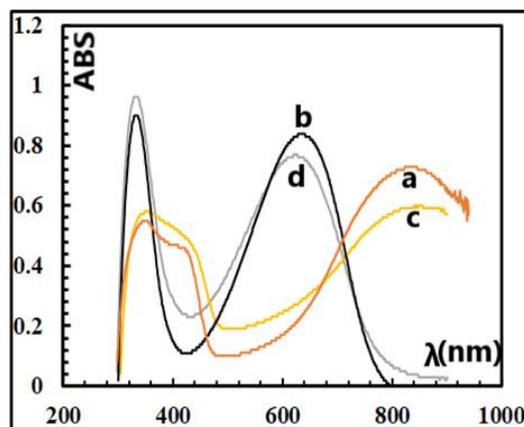


Figure 4. UV spectra of ES (4a) and EB (4b) prepared in H_2SiF_6 and those of ES (4c) and EB (4d) prepared in HCl/KF.2H₂O

Representative UV-Vis spectra of a sample of PANI prepared in aq. H_2SiF_6 (plastic beaker) are shown in Fig. 4. The doped ES (Fig 4a) exhibits bands at 361 nm ($\pi \rightarrow \pi^*$ transition), 438 nm (polaron $\rightarrow \pi^*$) and 846 nm ($\pi \rightarrow$ polaron, often referred to as the conducting free carrier tail) [21], [22]. The corresponding dedoped PANI (EB) in Fig 4b shows the typical bands at 334 nm ($\pi \rightarrow \pi^*$, benzenoid transition) and 623 nm ($\pi \rightarrow \pi^*$, benzenoid to quinoid transition) [23]. The wavelengths of these absorptions are close to those of a sample of PANI synthesized in HCl/KF.2H₂O (plastic

beaker). Their doped and dedoped spectra are displayed in Fig 4c and 4d, respectively.

3.2. Kinetic Study

The kinetics of polymerization are monitored through the change of the reaction-medium open circuit potential (VOC) vs time. The results are displayed in Fig. 5 along with the characteristics of the corresponding plots (Table 1).

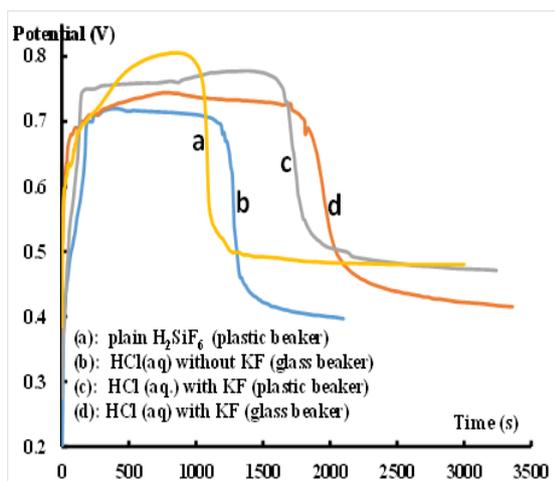


Figure 5. Potential vs. time profiles of aniline polymerizations

Table 1. Specific characteristics of the kinetic plots

Plot	Nature of Vessel used	Peak Potential (V)	Time needed to reach the end of potential plateau (s)
a	plastic	0.81	990
b	glass	0.72	1190
c	plastic	0.78	1650
d	glass	0.74	1833

Manohar et al. [7] have used the VOC technique to show that the polymerization of anilines transits through the formation of pernigraniline as the intermediate (the most oxidized state of PANI, Fig. 1). Its formation corresponds to the high “plateau” segment of the VOC vs. time plot. The intermediate then precipitates out at the terminal end of the plateau (indicated by the sharp drop in potential) to yield the final ES which is believed to be formed from the reaction of pernigranilines with residual aniline monomers.

In this work, the kinetics is assessed through the time needed for the polymerization to reach the end of the potential plateau (Table 1). The time revealed to be quite dependent on the acid dopant and the nature of the reaction vessel as indicated by the following decreasing order of polymerization rates: plain H_2SiF_6 (plot a, plastic beaker) > HCl without $\text{KF}\cdot 2\text{H}_2\text{O}$ (plot b, glass beaker) > HCl with $\text{KF}\cdot 2\text{H}_2\text{O}$ (plot c, plastic beaker) > HCl with $\text{KF}\cdot 2\text{H}_2\text{O}$ (plot d, glass beaker). The polymerization is fastest (shortest plateau, plastic beaker, plot (a)) with plain H_2SiF_6 as dopant because the preliminary step of glass etching does not take place and anilines or aniliniums do not form H-bondings with plastics, i. e. initiation of polymerization starts in solution not on the beaker walls. In addition, SiF_6^{2-} through

its fluorine atoms can form multiple H-bonds with the $\text{N}^+\text{-H}$ of the aniliniums, or $=\text{N}^+\text{-H}$ (iminium moiety) of the oligo or polyaniline chains. Precedents of similar type of H-bonds are found in reported X-ray structures of precipitated hexafluorosilicate salts of protonated nitrogen cations in e.g., tetramethylethylene diamines or derivatives of pyridines in which extensive H-bonds provided discrete cation-anion units with chain-like structures [24]. Since salts of monomeric anilinium hexachlorosilicates have limited water solubility (as shown in the experimental section 2.3 (c) above), the corresponding hexafluorosilicate doped oligo- and polyaniline salts are expected to have even lower solubility due to their higher masses (brought about by the high number of H-bonds). These salts are likely to precipitate out quickly, thereby ending the polymerization at a faster rate.

The above rate sequence also indicates that under the conventional condition, the polymerization in plain HCl/glass beaker, (plot b) is faster than those conducted in the HCl(aq)/ $\text{KF}\cdot 2\text{H}_2\text{O}$ (a mixed halide medium) using a plastic or glass beaker (plot c and d, respectively). The slower kinetics in the mixed halide medium can be attributed in part to the stronger H-bonds of the smaller F^- with hydroniums [25] which deliver its protons to the aniline monomers or oligo anilines at a slower rate. That is, proton transfer is faster in a medium where only the larger Cl^- is present as its H-bonds with the hydroniums is weaker [25]. The polymerization in HCl/ $\text{KF}\cdot 2\text{H}_2\text{O}$ (glass beaker, plot (d)) is the slowest of all displayed plots. It is slower to the corresponding reaction conducted in a plastic vessel (plot c). This could be due to the additional, preliminary step during which fluoride ions mediate the anchoring of anilines/aniliniums (via H-bonds) on the glass walls, i.e., prior to the addition of APS, substitution of OH in silica by F^- [26] in the acidic medium forms the strong Si-F bond on the glass walls. This new bond could have facilitated H-bondings of aniliniums on the walls as follows: $\text{Si-F}\dots[\text{HNH}_2\text{Ph}]^+$ (where the dotted line indicates H-Bond). These anchored species are eventually displaced as the glass is etched away resulting in the precipitation of K_2SiF_6 .

Since the H-bonds taking place between $\text{N}^+\text{-H}$ (of aniliniums or $=\text{N}^+\text{-H}$, iminium of the oligo/polyanilines) and F^- or SiF_6^{2-} are stronger than the corresponding bonds with Cl^- [27], [28], higher potential values of the resulting monomeric or oligo/polymeric species are to be expected when F^- or SiF_6^{2-} are counter/dopant anions of the ES. This is evidenced by the data in Table 1 (derived from Fig 5). For example, the use of a plastic vessel should provide more H-bonds between reagents since there are no H bonds between the vessel and the reagents. And H_2SiF_6 , having six fluorine atoms, should provide more H-bonds than fluoride ions per mole of reacting species. Therefore, the following decreasing order of peak potentials is observed: H_2SiF_6 (plastic beaker, plot a, peak potential: 0.81V) > HCl/ $\text{KF}\cdot 2\text{H}_2\text{O}$ (plastic beaker, plot c, peak potential: 0.78V) > HCl/ $\text{KF}\cdot 2\text{H}_2\text{O}$ (glass beaker, plot d, peak potential: 0.74V) > plain HCl (glass beaker, plot b, peak potential: 0.72V). We note that reports relating potential shifts involving ligand H-bonds

with F⁻ have been described in ferrocene/ferrocenium system [29] and in enols [30].

3.3. Cyclic Voltammetry

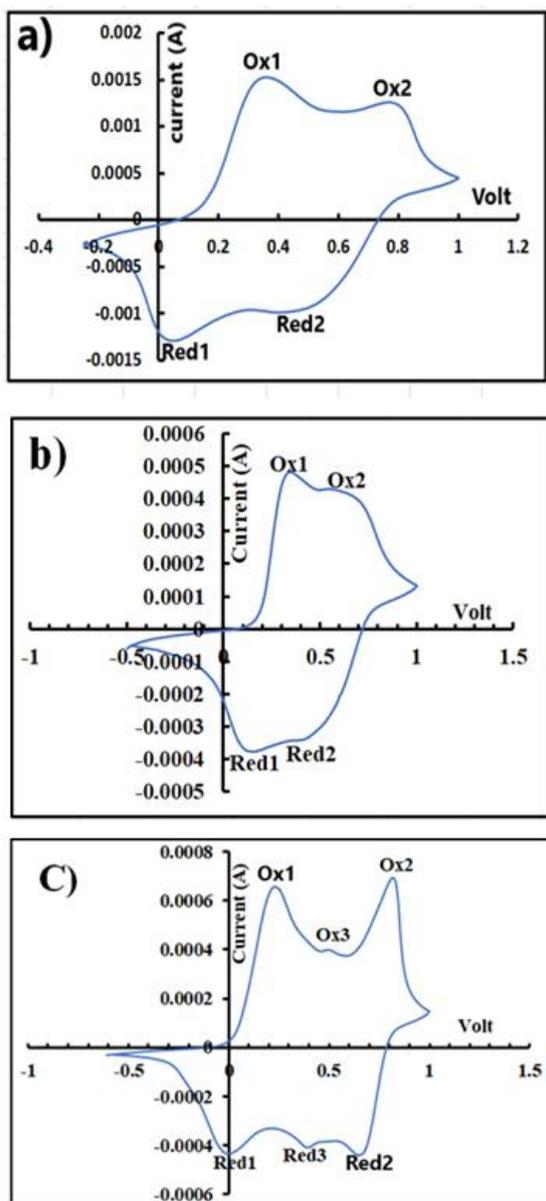


Figure 6. Voltammograms of an ES sample prepared in a) HCl (aq), b) HCl(aq)/KF.2H₂O, c) H₂SiF₆ (aq)

Representative cyclic voltammograms of ES samples prepared in plastic beakers, doped either with plain HCl, HCl/6g KF.2H₂O or plain H₂SiF₆ (aq), are displayed in Fig 6 (a), (b) and (c), respectively. The plots resemble those of the ES reported by Jugovic *et al* [31] who polymerized anilines on graphite electrodes. They exhibit the two sets of anodic and cathodic current peaks, typical of conducting PANI. The first set (ox1 and red1) is associated with the conversion of the fully reduced leucoemeraldine to the partially oxidized emeraldine and the second set (ox2 and red 2) corresponds to the conversion of the emeraldine state to the fully oxidized pernigraniline state [32]. In the case of ES doped with H₂SiF₆,

its voltammogram shows one additional redox couple (ox 3 and red 3). This redox couple could be due to a) the degradation of by-products of PANI such as benzoquinone or hydroquinone [33] or b) the presence of either PANI containing insoluble quinonic groups or polymers from ortho-coupling of phenazine containing units [34].

3.4. Electrical Conductivity

The electrical conductivity of representative ES samples was measured via the four-probe technique. For samples prepared in HCl (aq) containing KF.2H₂O (glass beaker). The results are as follows: 3.00 S/cm, (0.5g), 0.61S/cm, (2g); 0.44S/cm (4g) and 0.60S/cm (6g). Those of the ES synthesized in plain HCl (glass vessel) and plain H₂SiF₆ (plastic vessel) are 1.10S/cm and 4.80 S/cm, respectively. Overall, the conductivity values are comparable to and fall within the usual reported range (10⁻² to 10² S/cm) of most ES prepared under the conventional method [20].

3.5. Morphological Analyses of PANI via SEM and Elemental Analyses via EDS

We have explored various experimental conditions that might influence the morphology of the ES. Representative SEM pictures of the synthesised polymers prepared in HCl/KF are displayed in Fig 7. With 0.5 g of KF.2H₂O, the ES, obtained under unstirred conditions for 48 h, are composed mostly of nanofibers whose average diameters are less than 100 nm (Fig 7a and 7b). The nature of the vessel (glass vs plastic) does not seem to significantly affect the morphology of the polymers. This supports our previous findings that the by-products formed from glass etching processes must have precipitated quickly at the initial stage of the polymerization and they do not influence the polymer growth/final morphology. With 2g of KF.2H₂O (stirred conditions, 3.5 h), the as-formed ES is essentially nanofibrous in nature (Fig 7c) although slightly shorter than those described earlier. With 4g of KF.2H₂O, the ES gradually becomes less homogeneous as larger/globular features are formed along with the nanofibers (Fig 7d). The morphology became much less regular when the reaction was conducted in the presence of 6g of KF.2H₂O (Fig 7e). This observation suggests that the first formed ES had served as templates for secondary polymeric growth as evidenced by the presence smaller grains deposited on the surface of the fibers.

An SEM picture of an ES sample doped with H₂SiF₆ (plastic vessel) is also presented in Fig 7f. The fibers are by far more homogeneous in their average lengths and diameters (<80nm in average diameters) than those of its counter parts presented earlier. This is evidenced by the presence of thin and elongated nanofibers. In summary, we believe the afore-mentioned numerous H-bonds taking place, during polymerization, between F⁻ or H₂SiF₆ and the monomers or oligo- or polyanilines, are instrumental in producing chain like structures which then direct the elongation of the polymers to eventually yield the observed

nanomorphology. Without these strong H-bonds, only granular PANI is formed (Fig 7 g) as has frequently been observed under the conventional, stirred polymerization condition (glass beaker) [35], [36]. While we have not investigated the influence of temperature on morphology of ES, it has been reported that the polymerization of anilines in plain HF (aq) at 5°C produced an ES with porous film like morphology [37].

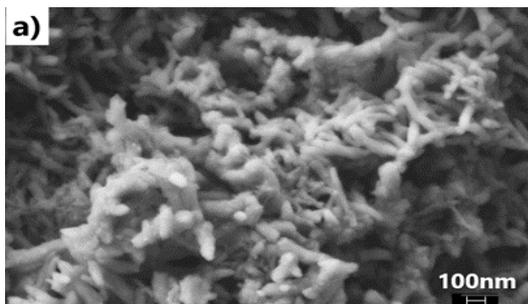


Figure 7(a). with 0.5g KF in HCl (unstirred, glass beaker 48 h reaction)

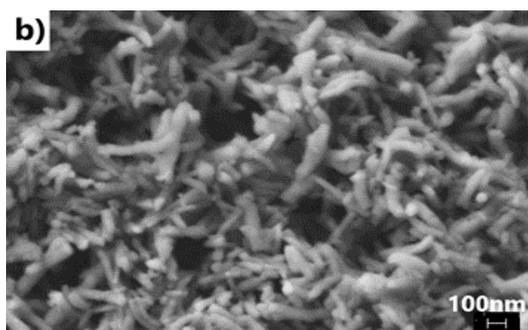


Figure 7(b). with 0.5g KF in HCl (unstirred, plastic beaker, 48 h reaction)

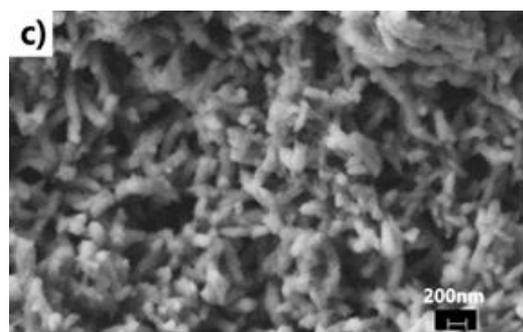


Figure 7(c). with 2g KF in HCl (stirred, glass beaker, 4 h reaction)

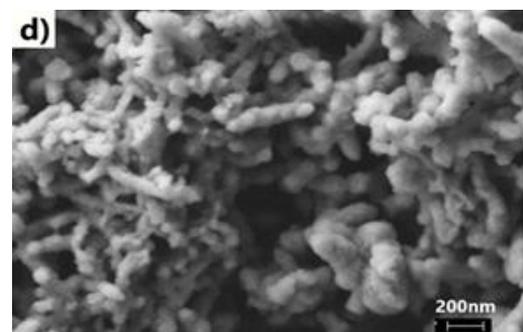


Figure 7(d). with 4g KF in HCl (stirred, glass beaker, h reaction)

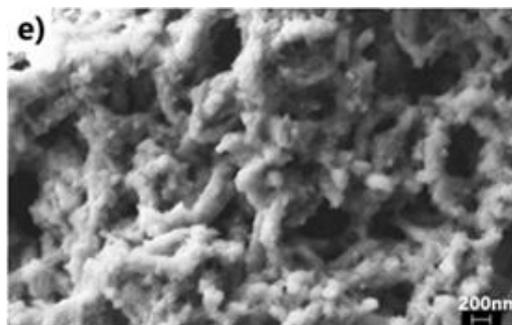


Figure 7(e). 6g KF in HCl (stirred, glass beaker, 4 h Reaction)

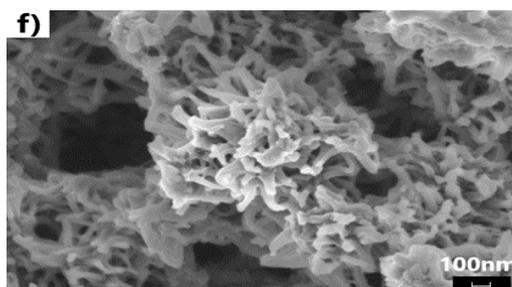


Figure 7(f). In plain H_2SiF_6 (stirred, plastic beaker, 4 h reaction)

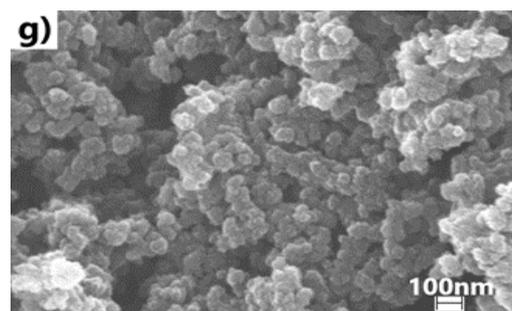


Figure 7(g). In plain HCl (stirred, glass beaker, 4h reaction)

4. Conclusions

The influence of H-bondings from either fluoride ions or hexafluorosilicic acid on the kinetics of the polymerization anilines and the morphology of the as-formed PANI has been assessed. It is found that the morphology of PANI, prepared under the conventional condition (in plain HCl), is granular while those prepared in plain hexafluorosilicic acid or in a mixed halide medium (F^- and Cl^- from HF and HCl) are essentially nanofibrous at low concentration of fluorides or in plain hexafluorosilicic acid. Despite the etching of glass beaker when HF (aq) is present, it is found that the morphology of the PANI produced is independent of the vessel used (glass or plastic beaker). However, etching and H-bondings between reagents and/or glass walls affect the kinetics of polymerization and the oxidation potential of the reacting species as evidenced by open circuit potential vs time profiling of the polymerization. The results indicate that the polymerization is a) fastest in plain hexafluorosilicic acid (plastic beaker) and b) slowest in HCl(aq)/HF (aq) medium (glass beaker). The electrical conductivity ($0.10 \text{ S/cm} < \sigma$

<10 S/cm) of all prepared PANI lies within the usual range of that of a conventionally prepared sample.

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