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Effect of sulphuric acid on the properties of polyaniline–HCl salt and its base

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Abstract

The effect of H_2SO_4 on polyaniline–HCl salt and its base was studied for different concentrations of the acid (0.1, 1.0, 4.0, 8.0, 13.0 and 18.0 M) for a duration of one day and five days. The H_2SO_4 treated polyaniline samples were characterised by conductivity and UV–vis, FT-IR and EPR spectroscopic measurements. Due to the incorporation of H_2SO_4 in the polymer chain significant effects on polyaniline–HCl salt were observed, while for the polyaniline base doping occurs depending on the concentration of H_2SO_4. The extent of doping and the incorporation of the sulphate group in the polymer chain are revealed by the spectroscopic and conductivity studies. The conversion of polyaniline base to the salt form is less efficient by H_2SO_4 doping when compared to doping by HCl. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polyaniline has potential applications in secondary batteries and electrochromic devices [1]. Most of these applications require repeated injection and withdrawal of charge from the polymer by doping and undoping processes. The doping process, which is accomplished by the oxidation of polyaniline, produces positively charged polymeric species that are susceptible to nucleophilic attack by electrolytes and/or solvents resulting in the gradual degradation of the polymer. An understanding of the stability of conducting polyaniline in different media is desirable for its applications. Previous studies on polyaniline were chiefly concerned with its electrochemical and thermal stability. From these studies, both two- and three-step degradation processes have been proposed [2–5]. The electrochemical stability and degradation of conducting polyaniline at the anode has been briefly reviewed by Pud [6]. Recently, Ansari et al. [7] have reported that the electroactivity and conductivity of polyaniline are stable up to 150°C. Besides the stability under extreme conditions (i.e. at high temperatures or at high potentials), resistance to degradation under conditions that may be encountered in applications is of interest. Hence studies focused on the stability of polyaniline under acidic conditions are desirable. However, very few reports on the stability of polyaniline in acidic media are available. Pasquali et al. [8] found that the electrochemically prepared polyaniline undergoes degradation when stored in 1 M H_2SO_4–0.5 M Na_2SO_4. Kogan et al. [9] studied the redox reactions of electrochemically synthesised polyaniline in concen-

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trated H_2SO_4 (9–12 M) using cyclic voltammetry. Recently Neoh et al. [10] have investigated the chemical stability of polyaniline base in three organic acids; namely, toluenesulphonic acid, sulphosalicylic acid and dodecylbenzenesulphonic acid. In the present work, the stability of chemically synthesised polyaniline–HCl salt and its base in H_2SO_4 has been investigated. Polyaniline salt was converted into its base by dedoping in aqueous NH_40H. The polyaniline–HCl salt and its base were stored in 0.1, 1.0, 4.0, 8.0, 13.0 and 18.0 M H_2SO_4 for one day and for five days under vigorous stirring. The acid-treated polymer samples were characterised using spectroscopic and conductivity measurements.

2. Experimental

2.1. Materials

Aniline (Merck) was distilled twice. Ammonium persulphate (Ranbaxy), hydrochloric acid (Merck), and sulphuric acid (Merck) were analytical reagents and they were used as procured.

2.2. Preparation of the polymer salt

To a 1.5 M HCl solution containing 0.2 M freshly distilled aniline maintained at 0–3°C, an aqueous solution of ammonium persulphate (0.2 M) was added dropwise for 1/2 h. The total quantity of the reaction mixture was 2 l. During the addition of persulphate, the temperature of the reactants was maintained within ±1°C of that of ice bath and then kept at 10°C for 24 h. The polyaniline–HCl salt that precipitates was washed with 1.5 l of 1.5 M HCl and then with 250 ml of methanol. The precipitate was washed again using 1.5 l of 1.5 M HCl, followed by 250 ml of acetone. It was dried at room temperature for 72 h under vacuum.

2.3. Preparation of polymer base

The polymer salt prepared using the above procedure was dedoped using large excess of 0.5 M NH_40H to obtain the corresponding base. The NH_40H solution containing polyaniline–HCl salt was kept overnight under vigorous stirring and then filtered. The residue was washed with 500 ml of 0.5 M NH_40H. The polyaniline emeraldine base was dried for 72 h under vacuum.

2.4. H_2SO_4 treatment of polyaniline–HCl salt and its emeraldine base

100 ml each of six different concentrations, 0. 1, 1.0, 4.0, 8.0, 13.0 and 18.0 M, of H_2SO_4 were prepared. About 1 g of the polyaniline salt was added to each of the 100 ml of different concentrations of H_2SO_4. The same procedure was repeated for the polyaniline base. The H_2SO_4 solutions containing polyaniline–HCl salt or its base were kept under vigorous stirring for one day as well as for five days. The solutions were filtered and the residues washed with double distilled water. In the case of 18 M H_2SO_4 the samples were further precipitated using large quantities of distilled water (4 l).

2.5. Measurements

For recording the UV–vis absorption spectra a Hitachi U-3400 spectrophotometer was used. The sample solution in dimethylsulphoxide (DMSO) was used for recording the spectrum. The spectra were measured at three different concentrations and checked for consistency. The electronic spectra of the salt and the base were also measured in the solid state as KBr pellets. The FT-IR spectra of the samples were recorded using a BIO-RAD SPC 3200 instrument by the KBr pellet technique. The EPR spectra of the samples were recorded using a Varian E109 spectrometer operating in the X-band. The sample tube was evacuated before recording the spectrum to remove the moisture. To obtain the g value and spin concentration, the EPR spectra of the samples and charred dextrose as a standard were recorded under identical conditions of microwave frequency (9.05 GHz), microwave power (2 mW), modulation frequency (100 kHz), fieldset (3250 G), scan range (100 or 200 G), modulation intensity (1 Gpp), modulation time (0.064 s) and scan time (200 s). The spin concentration was determined by comparing the area under the EPR signal of the polyaniline sample with that of charred dextrose. The calculated areas are likely to be within 5% of the true value [11]. The electrical conductivity (dc) of the samples were measured at ambient temperature using the four-probe method (pressure contact) on pressed pellets obtained by subjecting the powder to a pressure of 50 kN. The error in the resistance measurements under galvanostatic condition using a Keithley model 220 programmable current source and a Kiethley model 195A digital voltammeter is less than 2%. The consistency in the measurements was checked by measuring the resistance twice for each pellet and for a batch of two pellets for each sample.

Table 1
Absorption maxima (λ_{max}, nm) of polyaniline salt and its base treated with H_2SO_4

H_2SO_4 treated	Salt				Base			
In solid state polyaniline	335	580	615	870	320		620	
In DMSO solution polyaniline	325	–	635	–	325	–	625	
For 1 day								
0.1 M	325	–	630	–	320	–	618	–
1.0 M	303	–	630	–	310	440	650	850
4.0 M	303	445	630	850	310	440	615	850
8.0 M	310	440	625	850	325	440	625	850
13.0 M	315	440	605	850	310	450	635	875
18.0 M	310	445	635	850	355	450	-	870
For 5 days								
0.1 M	325	–	630	–	320	–	625	–
1.0 M	325	–	630	–	315	440	650	860
4.0 M	320	440	635	860	315	435	620	830
8.0 M	320	445	625	850	305	435	620	850
13.0 M	305	440	–	850	325	445	–	850
18.0 M	330	435	–	860	330	420	–	843

3. Results and discussion

3.1. Spectroscopy

3.1.1. UV–vis spectra

The absorption spectrum helps to detect the presence or otherwise of the polyaniline–HCl salt and its base. The positions of absorption maxima for the spectra of polyaniline salt and its base recorded in solid and solution are given in Table 1. As representative of the systems, the spectra of polyaniline–HCl salt treated with 8 M H_2SO_4 for five days, polyaniline–HCl base and the base treated with 13 M H_2SO_4 for five days are given in Fig. 1. The absorption spectra for the polyaniline salt and base were also recorded in solid state in the form of a KBr pellet. In the solid state, the spectrum of the polyaniline base showed two absorptions around 330 and 620 nm, while that of the polyaniline salt exhibits four bands around 335, 580, 615 and 870 nm. The solution spectrum of the polyaniline base taken in DMSO also exhibits two bands around 325 and 625 nm, as observed in the solid state spectrum. However, unlike its solid state spectrum, the polyaniline salt in DMSO also shows two peaks at 330 and 630 nm in the same region as the polyaniline base. This indicates that some amount of polyaniline base is always present along with the polyaniline salt and that the more soluble polyaniline base gives rise to the absorption spectrum in solution. On the other hand, the spectrum obtained for the polyaniline base in DMSO acidified with HCl shows three bands near 325, 420 and 830 nm similar to that observed for the polyaniline salt, showing that the base is doped by HCl and is converted to the salt form. The absorption spectrum of the polyaniline salt should show bands at 420 and 830 nm. The sensitivity and position of the 620 nm band in a convenient region of the spectrum free from the solvent peaks makes it suitable for probing the polyaniline systems.

Although there is general agreement regarding the assignment of the 325 nm absorption band of the base

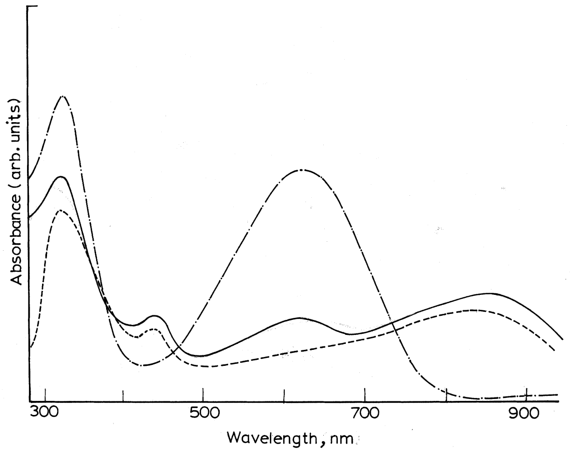

Fig. 1. Electronic absorption spectra of polyaniline–HCl base (—·—·—), polyaniline salt treated with 8 M H_2SO_4 for five days (– – –) and polyaniline–HCl base treated with 13 M H_2SO_4 for five days (—).

as arising from the π–π^* transition, there has been no unambiguous identification of the origin of the 620 nm absorption band. Duke et al. [12] on the basis of CNDO/S3 calculations have assigned it to the creation of a localised molecular exciton with the electron on a quinoid moiety and a hole on the two neighbouring benzenoid moieties. The molecular exciton is associated with a locally distorted segment of the polyaniline backbone. On the other hand, Kim et al. [13] have proposed that the optical absorption at 620 nm in the emeraldine base is due to n–π^* transition from the non-bonding nitrogen lone pair to the conduction (π^*) band. Recently Wan et al. [14] have attributed the peaks at 325 and 620 nm the excitation of the amine and imine segment respectively of the polyemeraldine chain. The bands around 430 and 860 nm are assigned as due to polaron transitions [15].

The UV–vis spectra of polyaniline–HCl salt and its base treated with different concentrations of H_2SO_4 were measured in DMSO. The spectrum of the polyaniline base treated with 0.1 M H_2SO_4 for both one day and five days exhibits two peaks, similar to that found for the untreated polyaniline base. This suggests that O.1 M H_2SO_4 does not cause doping. When the concentration of H_2SO_4 is increased to 1.0–13.0 M, four peaks were observed between 300 and 875 nm irrespective of the duration of H_2SO_4 treatment.

However, on increasing the duration to five days for 13 M H_2SO_4 only three peaks were found at 325, 435 and 850 nm (Fig. 1). The same observation was made for the polyaniline base treated with 18.0 M H_2SO_4 irrespective of the duration of treatment. The disappearance of the 630 nm peak indicates a greater conversion of the polyaniline base to the salt form.

Polyaniline salt treated with H_2SO_4 shows similar spectral behaviour as those of the polyaniline base on H_2SO_4 treatment. Thus the spectra of polyaniline salt treated with 0.1 and 1.0 M H_2SO_4 for both one day and five days show, like the untreated polyaniline salt, two bands near 325 and 630 nm. When the concentration of H_2SO_4 was increased to 4.0–18.0 M and the duration of the treatment was for one day, four peaks around 320, 440, 630 and 850 nm were observed (Fig. 1). However, for salt samples treated with 13.0 and 18.0 M H_2SO_4 for five days, only three peaks were observed, closely resembling the spectra recorded for the polyaniline base in acidified DMSO.

A similar study to investigate the effect of $ZnCl_2$ (0.1–6.0 M) on the properties of polyaniline–HCl salt and its base has been reported earlier [16]. The results demonstrated that $ZnCl_2$ treatment leads to an increase in the solubility of the salt in DMSO. However, complete dissolution of the polymer salt in DMSO does not occur even at higher concentrations of $ZnCl_2$.

3.1.2. FT-IR spectra

The IR spectrum of the polyaniline base shows six principal absorptions at 1585, 1513, 1310, 1212, 1155 and 827 cm^{-1}. The peaks at 1585 and 1513 cm^{-1} are assigned to C–C ring stretching vibrations. The peaks at 1310 and 1212 cm^{-1} correspond to N–H bending and the symmetric component of the C–C (or C–N) stretching modes. The bands at 1155 and 827 cm^{-1} can be attributed to the in-plane and out-of-plane C–H bending modes, respectively [16]. The corresponding peaks for the polyaniline salt appear at 1612, 1555, 1378, 1305, 1175 and 800 cm^{-1}, respectively. The peaks for the polyaniline base and salt appear at the same region and with similar intensities except for marginal differences. The strong band at 1130 cm^{-1} in the base is much intense and broader in the salt spectrum and the band is also rather unsymmetric. In addition to the above peaks, the spectrum of the polyaniline salt also exhibits new peaks around 3382, 3220, 1664 and 706 cm^{-1}. The doping of the polyaniline base leads to the $-NH_2^+-$ group being formed which can be detected from the above peaks. This $-NH_2^+-$ group is similar to that present in the semicarbazide moiety [17]. The peaks at 3382 and 3220 cm^{-1} could be attributed as due to NH_2 stretching mode and the 1664 cm^{-1} band to the NH_2 bending vibration while the 706 cm^{-1} is assigned as due to NH_2 wagging. The intensity of these bands was found to increase depending on the strength of the acid.

The sulphate group shows characteristic ν_3 and ν_4 bands in the infrared spectrum near 1100 and 620 cm^{-1}, respectively. However, the spectrum of both the polyaniline–HCl salt and the base also have a strong broad band due to C–H in-plane bending near 1100 cm^{-1} except that this band is more intense and unsymmetrical in the polyaniline salt spectrum (Fig. 2c). In either case there is no band around ~620 cm^{-1}. Therefore, the 620 cm^{-1} band is diagnostic of the presence of the sulphate group. The IR spectra of polyaniline–HCl salt samples treated with higher concentrations (for example 4 M) of H_2SO_4 also shows an IR band of medium intensity at 615 cm^{-1} (Fig. 2d) indicating the incorporation of the sulphate group in the polymer chain.

The spectra obtained for the polyaniline base treated with different concentrations of H_2SO_4 resemble those of the polyaniline salt irrespective of the duration of treatment. It suggests that doping of the base by H_2SO_4 takes place. The bands due to polyaniline base shift towards lower frequencies on doping (Fig. 2b). With increase in the concentration of H_2SO_4 the shift towards lower frequency is somewhat greater. This shift towards lower wavenumbers is a signature of the conversion of the quinoid rings to the benzenoid form by H_2SO_4 induced spin-unpairing mechanism. The IR spectra of the base treated with higher concentration

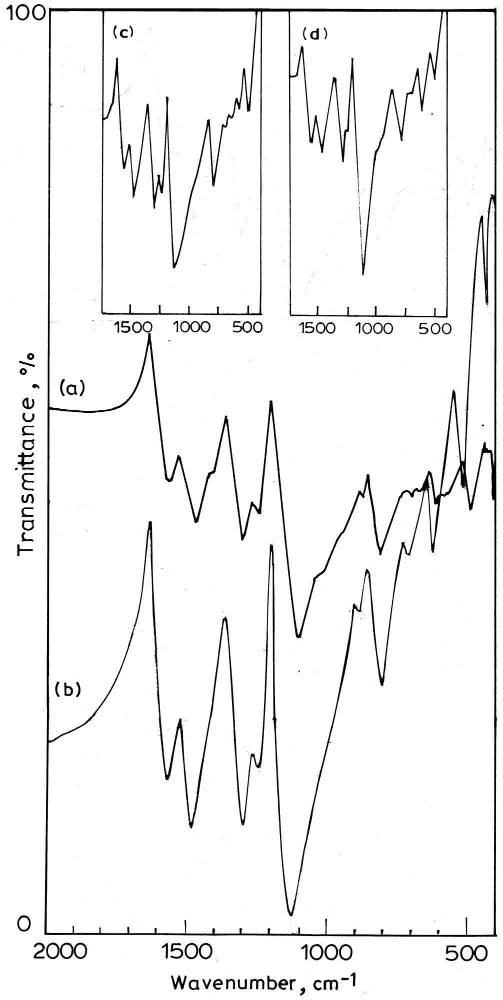

Fig. 2. FT-IR spectra of (a) polyaniline–HCl salt, (b) polyaniline–HCl base treated with 0.1 M H_2SO_4 for five days, (c) untreated polyaniline salt and (d) polyaniline salt treated with 4 M H_2SO_4 for five days.

of H_2SO_4 reveal the incorporation of the sulphate group.

3.1.3. EPR spectra

The ambient temperature EPR spectra of the polyaniline–HCl salt, its base and the samples treated with H_2SO_4 show a single signal without any hyperfine structure. The spectral data are given in Table 2. As a representative system, the EPR spectrum of the polyaniline–HCl base treated with 18.0 M H_2SO_4 for one day is shown in Fig. 3. The g value and the A/B ratio (that is, the ratio of the area of the positive to the negative peak) do not throw much light on the nature of the polymer (whether it is polyaniline salt or the base). They only reflect on the type of charge species

Table 2
EPR data for polyaniline salt and its base treated with H_2SO_4

H_2SO_4 conc.	Spins/g	g value	ΔH (G)	A/B ratio
Polyaniline salt	2.00×10^{20}	2.0042	2.5	1.0
1 day				
0.1 M	4.70×10^{18}	2.0038	6.0	1.0
1.0 M	4.85×10^{19}	2.0036	5.5	1.0
4.0 M	5.88×10^{19}	2.0032	5.2	1.0
8.0 M	$6.03 \times lO^{19}$	2.0041	4.5	1.1
13.0 M	7.16×10^{19}	2.0037	3.0	1.1
18.0 M	$8.57 \times lO^{19}$	2.0028	1.3	1.1
5 days				
0.1 M	8.12×10^{19}	2.0023	6.5	1.0
1.0 M	1.01×10^{19}	2.0030	5.8	1.0
4.0 M	2.54×10^{19}	2.0030	5.5	1.0
8.0 M	$2.01 \times 1O^{20}$	2.0033	4.2	1.0
13.0 M	3.00×10^{21}	2.0035	2.8	1.1
18.0 M	9.28×10^{19}	2.0030	2.0	1.1
Polyaniline base	7.20×10^{18}	2.0032	11.0	1.0
1 day				
0.1 M	1.49×10^{18}	.0054	13.0	1.0
1.0 M	3.44×10^{19}	2.0041	8.5	1.0
4.0 M	4.49×10^{19}	2.0029	3.5	1.0
8.0 M	1.57×10^{20}	2.0025	3.3	1.0
13.0 M	1.77×10^{20}	2.0025	2.0	1.1
18.0 M	$7.24x10^{19}$	2.0024	1.3	1.1
5 days				
0.1 M	8.06×10^{18}	2.0038	9.0	1.0
1.0 M	5.34×10^{19}	2.0036	6.0	1.0
4.0 M	6.00×10^{19}	2.0035	4.0	1.0
8.0 M	2.51×10^{20}	2.0030	2.23	1.0
13.0 M	6.51×10^{20}	2.0025	0.80	1.1
18.0 M	3.79×10^{19}	2.0029	2.0	1.1

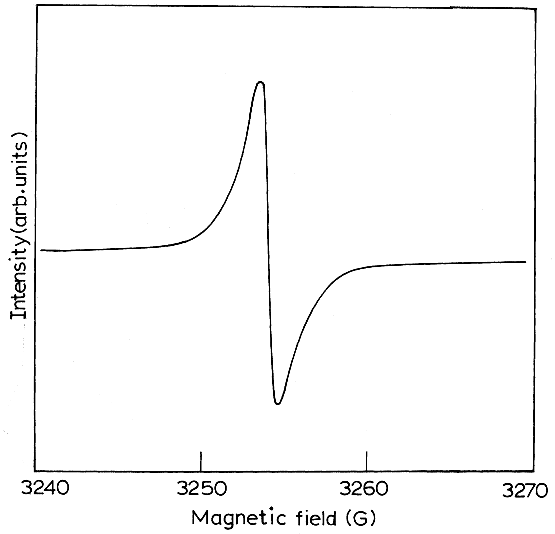

Fig. 3. The EPR spectra of polyaniline–HCl base treated with 18 M H_2SO_4 for five days.

that is involved in conduction. The actual differentiation between the salt and the base in polyaniline comes from the spin concentration and the ΔH values. In the case of polyaniline salt, the spin concentration is around of 10^{20} spins g^{-1} while the ΔH value for a typical polyaniline salt is in the range of 2.0–3.0 G. For the polyaniline base, the spin concentration is about 10^{18} spins g^{-1} and the ΔH values lie in the range 8.0–12.0 G [11]. The g value of the polyaniline base samples treated with H_2SO_4 for both one day and five days, lies in the range 2.0024–2.0054 close to that of the free electron. The g value marginally decreases with increase in H_2SO_4 concentration. The A/B peak ratios are nearly 1.1 indicating that the spins are free electron type. The line widths of samples treated with H_2SO_4 decrease with increase in the concentration of H_2SO_4 which suggests progressively increased doping of the polyaniline base. Thus the spin concentration of the polyaniline base treated with H_2SO_4 for one day increases from 1.49×10^{18} to 1.77×10^{20} spins g^{-1} for the concentration of H_2SO_4 increasing from 0.1 to 13 M. This result is in agreement with the absorption spectral studies. The results in Table 2 show that a longer duration of H_2SO_4 treatment leads to an increase in the spin concentration of polyaniline–HCl base. There is however, a slight decrease in the spin concentration at 18.0 M. As noted from the absorption studies and the conductivity measurements, 0.1 M H_2SO_4 is too low for doping of the polyaniline base.

The EPR spectral properties (namely g value, A/B ratio, line width and spin concentration) of the polyaniline salts treated with H_2SO_4 are similar to those of the base treated with H_2SO_4. The spin concentration of the polyaniline salts treated with H_2SO_4 for one day is lower than that of the untreated polyaniline salt. From Table 2, it can be noted that the spin concentration of the salt samples on H_2SO_4 treatment is found to increase with the increase in the concentration of H_2SO_4. However, the spin concentration of the H_2SO_4 treated polyaniline salt samples is found to be lower than that observed for the untreated salt. An increase in the duration of the treatment to five days for the same concentration of H_2SO_4, leads to greater spin concentrations than for the untreated polyaniline–HCl salt (8 and 13 M H_2SO_4), indicating that the duration of the treatment has a considerable role which is again consistent with the results of the conductivity studies discussed below.

3.2. Electrical properties

3.2.1. Conductivity

The conductivity values of polyaniline salt, its base and these compounds treated with H_2SO_4 measured using the four-probe technique are given in Table 3. The conductivity of the polyaniline salt is ~10 S cm^{-1} while that of its base is less than 10^{-8} S cm^{-1}. The conductivities of the polyaniline base treated with various concentrations of H_2SO_4 is much greater than that of the polyaniline base irrespective of the duration of the treatment, which reveals that doping takes place. The conductivity of the polymer samples increases with H_2SO_4 concentration. The conductivity of the samples treated for five days is slightly higher than those treated for one day supporting the above result that the duration of H_2SO_4 treatment has a mild influence on the conductivity of the base samples.

The conductivity of the polyaniline salt treated with different concentrations of H_2SO_4 is less than that of the untreated polyaniline salt. This indicates that the deprotonation of polyaniline–HCl salt occurs causing a decrease in conductivity. However, this decrease is partially compensated at higher concentrations of H_2SO_4, which may be due to the incorporation of the sulphate group in the polyaniline chain as noted from the infrared studies. The conductivity of the samples treated with H_2SO_4 for five days and that of the samples when the duration of treatment is one day is similar. There is a slight drop in conductivity when the concentration of H_2SO_4 is increased from 13.0 to 18.0 M, which may be attributed to the degradation of the polymer chain.

Similar studies carried out with varying concentrations of $ZnCl_2$ on polyaniline samples [16] also showed lower conductivity for the treated samples indicating that the deprotonation of the salt occurs. Both $ZnCl_2$ and H_2SO_4 treatment of the polyaniline base samples leads to an increase in conductivity, showing that polyaniline–HCl base is converted to the salt form (doping) on treatment with $ZnCl_2$ or H_2SO_4.

Table 3
Conductivity values for polyaniline salt and its base treated with H_2SO_4

H_2SO_4 Conc.	Conductivity (S cm^{-1})			
	Polyaniline salt		Polyaniline base	
	1 day	5 days	1 day	5 days
0.0 M	10.6	$< 10^{-8}$		
0.1 M	3.98	4.18	0.17	0.30
1.0 M	4.88	4.91	0.74	0.89
4.0 M	5.94	6.09	0.90	5.10
8.0 M	8.97	9.23	1.70	3.31
13.0 M	9.65	9.89	4.65	5.62
18.0 M	1.26	1.64	435	6.32

4. Conclusions

In conclusion, the conductivity of polyaniline–HCl salt treated with H_2SO_4 up to 13.0 M does not vary significantly from that of the untreated salt. Treatment with H_2SO_4 results in doping for the polyaniline base. The incorporation of the sulphate group is observed for both polyaniline–HCl salt and its base when treated with higher (4.0 M) concentrations of H_2SO_4.

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References

[1] Kitani A, Kaya M, Sasaki K. J Electrochem Soc 1986;133:1069.

[2] Kulkarni VG, Campbell LD, Mathew WR. Synth Met 1989;30:321.

[3] Chan HSO, Ho PKH, Khor E, Tan MM, Tan KL, Tan BTG, Lim YK. Synth Met 1989;31:95.

[4] Amano K, Ishikawa H, Kobayashi A, Satoh M, Hasegawa E. Synth Met 1994;62:229.

[5] Yue J, Epstein AJ, Zhong Z, Gallagher P, MacDiarmid AG. Synth Met 1991;41–43:765.

[6] Pud AA. Synth Met 1994;66:1.

[7] Ansari R, Price WE, Wallace GG. Polymer 1996;37:917.

[8] Pasquali M, Pistoia G, Rosati R. Synth Met 1993;58:1.

[9] Kogan YAL, Shunina IG, Savchenko VI. Synth Met 1990;37:63.

[10] Neoh KG, Pun MY, Kang ET, Tan KL. Synth Met 1995;73:209.

[11] Anand J, Palaniappan S, Sathyanarayana DN. J Phys Chem 1995;99:10324.

[12] Duke CB, Conwell EM, Paton A. Chem Phys Lett 1986;131:82.

[13] Kim YH, Foster C, Chiang J, Heeger AJ. Synth Met 1989;29:285.

[14] Wan M, Yang I. J Appl Polym Sci 1995;55:399.

[15] Tzou K, Gregory RV. Synth Met 1993;53:365.

[16] Anand J, Rao PS, Palaniappan S, Sathyanarayana DN. Synth Met 1998;95:57.

[17] Sathyanarayana DN, Volka K, Geetharani K. Spectrochim Acta 1977;33A:517.