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Electrical Properties and Thermal Stabilities Studies of Conducting Polyaniline Doped with Different Sulphonic Acids

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Abstract: Chemically prepared aniline was redoped with a range of sulphonic acids to examine the effect of chemical structure of dopants on the electrical properties and thermal stabilities. Although the initial electrical conductivities of sulphonic acid doped polyaniline were lower than HCl doped polyaniline, former were observed to be more stable towards oxidative degradation.

Abstrak: Polianilina yang didopkan dengan berbagai jenis asid sulfonik disediakan secara kimia. Kajian ke atas kesan struktur kimia dopan terhadap sifat pengaliran elektrik dan kestabilan haba telah dilakukan. Walaupun pengaliran elektrik polianilina berdop asid sulfonik adalah lebih rendah berbanding dengan polianilina berdop HCl, polianilina berdop asid sulfonik adalah lebih stabil terhadap penguraian secara pengoksidaan.

Introduction

Electrically conducting polymers in their pristine and doped states have been the materials of great interest for their applications in modern technologies. The non-linear response in undoped state whereas a large increase in electrical conductivity in doped state, has attracted many research groups in search of new systems with high conductivities and non-linearities [1]. Besides several other conducting polymers, polyaniline has also been studied extensively, during the last two decades [2-3]. Polyaniline has thus emerged as a potential conductive material due to its comparatively fair environmental stability, ease of preparation and wide areas for its applications such as rechargeable batteries [4,5], electromagnetic interference shielding [6], light emitting diodes [7], display devices [8], biosensors [9] and so on.

The electronic properties of polyaniline can reversibly be controlled by protonation as well as by redox doping [10]. Therefore, polyaniline could be visualized as a combination of reduced {-NH-B-NH-} and oxidized {-N=Q=N-} repeat units where -B- and =Q= denote a benzenoid and a quinoid unit respectively forming the polymer chain. Depending upon the oxidation state of nitrogen atoms which exist as amine or imine configuration, polyaniline can adopt various structures such as leucoemeraldine (fully-reduced form), emeraldine base (50% oxidized form), pernigraniline (fully-oxidized form) and the protonated form which is the conducting emeraldine salt [11]. Although, there have been many studies on polyaniline, no systematic work has been reported on comparative studies on polyaniline doped with different organic sulphonic acids. In this paper, we are reporting the effect of the structure of counter-ion on the electrical conductivity, FTIR spectra and thermal stability of polyaniline.

Experimental Details

Aniline (BDH), hydrochloric acid (BDH), potassium persulphate (Mallinckrodt) and ammonia (BDH) were used in the preparation of polyaniline. The redoping of polyaniline was performed by using methanesulphonic acid, sodium salt (Fluka), 1-butanesulphonic acid, sodium salt (Fluka), 1-octanesulphonic acid, sodium salt.monohydrate (Fluka), 1-dodecanesulphonic acid, sodium salt (Fluka), (±) 10-camphorsulphonic acid, sodium salt (Aldrich), benzenesulphonic acid, sodium salt (Fluka), xylenesulphonic acid, sodium salt (Aldrich), anthraquinone-2,6-disulphonic acid, disodium salt (Fluka), octylsulphate, sodium salt (Fluka) and dodecylsulphate, sodium salt (BDH) dissolved in hydrochloric acid (Table-1).

Polyaniline was prepared by reacting doubly distilled aniline (0.1 mol.) in 100 ml hydrochloric acid (1.0 M) with saturated solution of potassium persulphate in 100 ml of hydrochloric acid (1.0 M) at 0^oC [10]. The reaction mixture was kept under constant stirring for 5-6 h and then left at 0^oC for overnight. The dark green polyaniline (PANI:HCl) was filtered and washed with 250 ml of hydrochloric acid (0.1 M) in a Buchner funnel under suction. The excess acid in the polymer was washed with distilled water until the filtrate gave a negative test for hydrogen ions. The polymer so produced was thoroughly washed with acetone in a soxhlet to remove low molecular weight oligomers and then dried at 70^oC. Treatment of PANI:HCl with ammonia (0.1 M) produced blue color undoped polyaniline

(PANI) which was further washed with distilled water until filtrate gave negative test for hydroxide ions and then dried at 70^{o}C. As the salts could be converted to their corresponding acids by treatment with strong acids, PANI (0.5 g) was treated with sodium salts of different sulphonic acids (0.001 mol.) dissolved in 20 ml of hydrochloric acid (1.0 M) and left for 24 h for redoping. All the redoped polyaniline (PANI:A, PANI:B, PANI:C, PANI:D, PANI:E, PANI:F, PANI:G, PANI:H, PANI:I AND PANI:J) samples were washed thoroughly with excess of distilled water and then dried at 70^{o}C.

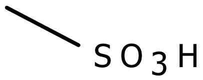
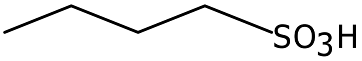
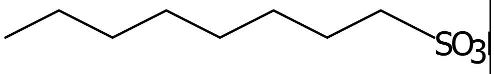
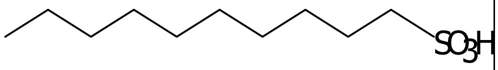
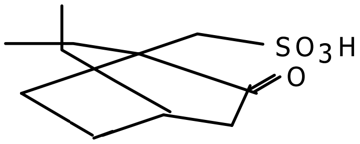
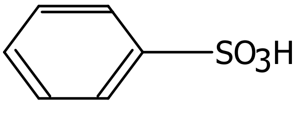
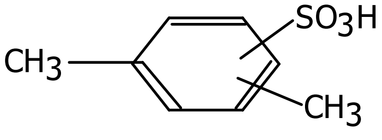
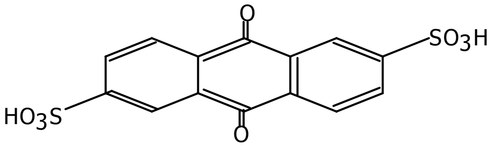
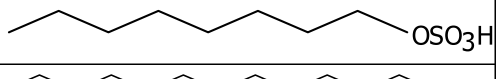
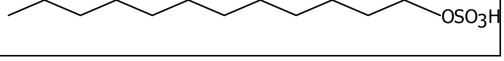
A Jandel (UK) four-probe DC electrical conductivity measuring instrument was used to measure the electrical conductivities of the redoped polyanilines on pressed pellets by using the following equation-

$$\sigma = I \ln 2/V \pi t \qquad (1)$$

where I = current in Amp., V = voltage in Volts and t = thickness of the sample in cm.

A Perkin Elmer FTIR (1725X) spectrophotometer was used to record the spectra from KBr pellets whereas thermogravimetric analysis was done in ambient air using Perkin Elmer TG7 thermogravimetric analyser.

Table 1. The chemical structures of different sulphonic acids used in the doping studies of polyaniline.

Symbol	Chemical Name	Chemical Formula	Chemical Structure
A	Methanesulphonic	CH_3SO_3H	
B	1-Butanesulphonic acid	$CH_3(CH_2)_3SO_3H$	
C	1-Octanesulphonic acid	$CH_3(CH_2)_7SO_3H$	
D	1-Dodecanesulphonic acid	$CH_3(CH_2)_{11}SO_3H$	
E	(±) 10-Camphor-sulphonic acid	$C_{10}H_{26}O_4S$	
F	Benzenesulphonic acid	$C_6H_5SO_3H$	
G	Xylenesulphonic acid	$(CH_3)_2C_6H_3\text{-}SO_3H$	
H	Anthraquinone-2,6-disulphonic acid	$C_{14}H_8O_8S_2$	
I	Octylsulphate	$CH_3(CH_2)_7OSO_3H$	
J	Dodecylsulphate	$CH_3(CH_2)_{11}OSO_3H$	

Results And Discussions

Polymer Preparation

When aniline is oxidized in acidic aqueous medium with potassium persulphate, the protonated conducting form of polyaniline (PANI:HCl) is produced as given in the following chemical reaction [12]-

$4\ Ph\text{-}NH_3^+ + 5\ S_2O_8^{2-} \rightarrow$
$2[\text{-}Ph\text{-}NH\text{-}Ph\text{-}NH^{\cdot +}\text{-}]\text{-} + 12\ H^+ + 10\ SO_4^{2-}$
(2)

Thus prepared dark green polyaniline was of high molecular weight as very little (< 0.5%) oligomers could be extracted on soxhlation for 24 h. The yield of polymer was more than 50% after washing and drying.

The color change from dark green to sky blue is associated with the neutralization of positive charges on protonated PANI chains. The process may be treated as n-type of doping of a p-type doped polymer in which a polymer passes through an insulating state. Schollhorn and Zagefka [13] have suggested a redox reaction for ammonia or amine intercalation into layered metal chalcogenides which has been further supported by the work of Foot and Shaker [14]. On the basis of the disproportionation reaction of ammonia as suggested by above workers, an analogous reaction for the undoping of polythiophene (PTH) by water was also suggested by Mohammad [15]. The overall chemical reactions are given in the following equations-

$8\ NH_3 \rightarrow 6\ NH_4^+ + 6\ e^- + N_2$
(3)
$PTH^+\text{-}BF_4^- + NH_4^+ + e^- \rightarrow PTH + NH_4BF_4$
(4)
$6\ H_2O \rightarrow 4\ H_3O^+ + 4\ e^- + O_2$
(5)
$PTH^+\text{-}BF_4^- + H_3O^+ + e^- \rightarrow PTH + HBF_4.H_2O$
(6)
$HBF_4.H_2O \rightarrow HF + BF_3 + H_2O$
(7)

The charge neutralization reaction depends on the rate of chemical reaction between the polymer and dopant which in turn will depend upon the reactivity of polymer chain and the basic strength of dopant [15]. The basic strength of water is very low, hence does not act as undoping agent in case of polyaniline, however, an analogous neutralization reaction for polyaniline undoping by ammonia may be suggested as under-

$PANI^+\text{-}Cl^- + NH_4^+ + e^- \rightarrow PANI + NH_4Cl$
(8)

The color of polyaniline doped with different sulphonic acids was extremely dark, hence the change in color on redoping could not be properly observed.

Electrical conductivity and doping behaviour

As evident from Table-2, PANI:HCl possesses sufficiently high electrical conductivity of 3.216 S cm^{-1} that falls in metallic region and became an insulator on treatment with ammonia. An increase of about 8-10 orders of magnitude in electrical conductivity of PANI has been reported on doping with various doping agents [16]. It is observed that the size of counter-ion from the doping acids plays an important role in imparting the electrical conductivity to polyaniline. A continuous increase in electrical conductivity with increasing the size of the counter-ion from PANI:A to PANI:D and from PANI:I to PANI:J does support this concept. Polysulphonic acids could produce PANI of higher electrical conductivity than their mono- counterparts as evident from the case of PANI:H. It is also evident from the data that organic sulphates are as potent dopants as organic sulphonic acids.

The mol.ratio (number of moles of dopant/number of moles of PANI) is also an important factor controlling the electrical conductivity of conducting polymers [17]. The mol.ratio calculated from thermogravimetric data suggests that the doping process is diffusion dependent [18]. The extent of doping was low with acids of high molecular weight (mol.ratio=0.005 to 0.092 i.e. one dopant molecule per each 10-200 aniline units) whereas the doping was extremely efficient with low molecular weight acid (HCl, mol.ratio=0.3 i.e.one dopant molecule per each 3-4 aniline units). It may also be observed that the polymer doped with high molecular weight acids could produce materials of comparatively high electrical conductivity (PANI:D, PANI:F, PANI:H and PANI:J) than their low molecular weight counterparts.

Table 2. The four-probe DC electrical conductivity and mol.ratio of dopant in polyaniline doped with different sulphonic acids.

Polymer Sample	Electrical Conductivity (Scm^{-1})	Mol.Ratio of Dopant
PANI:A	4.48×10^{-3}	0.074
PANI:B	5.53×10^{-3}	0.033
PANI:C	5.99×10^{-3}	0.005
PANI:D	1.11×10^{-2}	0.005
PANI:E	6.55×10^{-3}	0.082
PANI:F	1.06×10^{-2}	0.013
PANI:G	3.57×10^{-3}	0.032
PANI:H	1.21×10^{-2}	0.022
PANI:I	2.90×10^{-3}	0.074
PANI:J	1.37×10^{-2}	0.092
PANI:HCl	3.216	0.305

Note: Mol.Ratioes are calculated from TGA data.

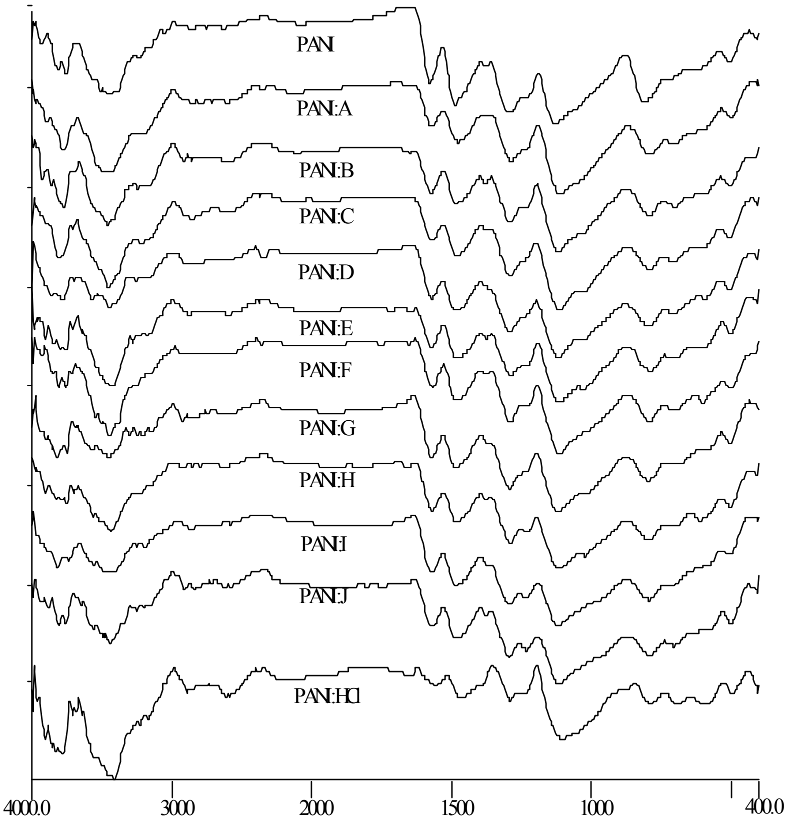


Figure-1: FTIR spectra of polyanilines doped with different sulphunic acids

FTIR Spectroscopy

The details of FTIR spectra of polyanilines are given in Table-3 and Figure-1. The FTIR spectrum of undoped polyaniline (PANI) showed the usual absorption bands slightly at lower positions than the reported ones which may be due to high molecular weight of the polymer [16].

The assignments from ref.10 have been followed. The band corresponding to out of plane bending vibration of C-H bond of p-disubstituted benzene rings appears at 815 cm^{-1}. The bands corresponding to stretching vibrations of N-B-N and N=Q=N structures appear at 1488 cm^{-1} and 1578 cm^{-1} respectively where –B- and =Q= stand for benzenoid and quinoid moieties in the polymer. The bands corresponding to vibration mode of N=Q=N ring and stretching mode of C-N bond appear at 1132 cm^{-1} and 1295 cm^{-1}. The FTIR spectrum supports the presence of benzenoid as well as quinoid moieties in the PANI. A lowering in 1132 cm^{-1} (10 to 19 cm^{-1}) corresponding to quinoid moieties was observed on doping with different sulphonic acids. There was comparatively little lowering (2 to 11 cm^{-1}) in the absorption band at 1488 cm^{-1} corresponding to bezenoid moieties. This suggests that the treatment of PANI with sodium salts of sulphonic acids caused doping of PANI and it occurred mainly on quinoid moieties. However, HCl doping caused a large shift of 29 cm^{-1} and 20 cm^{-1} in the 1132 cm^{-1} and 1488 cm^{-1} bands corresponding to quinoid and bezenoid moieties respectively. This may be reason of high electrical conductivity of PANI:HCl.

Table 3. The peak positions (cm^{-1}) in the FTIR spectra of polyanilines doped with different sulphonic acids.

Sample→ Peak No.↓	PANI	PANI :A	PANI :B	PANI :C	PANI :D	PANI :E	PANI :F	PANI :G	PANI :H	PANI :I	PANI :J	PANI :HCl
1	410	-----	-----	-----	406	-----	-----	-----	-----	-----	406	402
2	508	-----	508	509	508	504	504	506	505	507	503	500
3	-----	-----	-----	-----	-----	-----	603	-----	-----	-----	-----	-----
4	-----	-----	-----	-----	-----	-----	-----	-----	614	-----	-----	-----
5	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	704	694
6	-----	792	793	792	796	791	793	797	795	794	792	789
7	815	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
8	-----	-----	-----	-----	-----	-----	-----	-----	1024	-----	-----	-----
9	1132	1113	1121	1117	1120	1116	1114	1122	1117	1122	1117	1103
10	-----	-----	-----	-----	-----	-----	-----	-----	-----	1235	1233	-----
11	1295	1289	1294	1293	1295	1291	1293	1295	1293	1296	1295	1292
12	1377	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
13	1488	1477	1486	1481	1484	1484	1485	1486	1485	1486	1486	1468
14	1578	1572	1574	1571	1573	1573	1570	1572	1571	1572	1571	1560
15	-----	-----	-----	-----	-----	-----	-----	-----	1660	-----	-----	-----
16	-----	-----	-----	-----	-----	-----	-----	-----	-----	1808	-----	-----
17	-----	-----	-----	-----	-----	-----	-----	1935	1913	-----	1929	-----
18	2091	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
19	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	2184
20	-----	-----	-----	-----	2359	-----	-----	-----	-----	-----	-----	-----
21	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	2580	-----
22	-----	-----	-----	-----	-----	2603	-----	-----	-----	-----	-----	-----
23	-----	-----	2620	-----	-----	-----	-----	-----	-----	-----	-----	2619
24	2868	2859	-----	2868	-----	-----	-----	-----	-----	2864	2842	-----
25	-----	-----	-----	-----	2906	-----	-----	-----	-----	-----	-----	-----
25	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	2914	-----
27	-----	-----	-----	-----	-----	-----	-----	2926	2926	-----	-----	-----
28	-----	-----	-----	-----	-----	-----	-----	-----	-----	3197	-----	-----
29	-----	-----	-----	-----	-----	-----	-----	3210	-----	-----	-----	-----
30	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3258	-----
31	-----	-----	-----	-----	-----	-----	-----	3306	-----	-----	-----	-----
32	-----	-----	-----	-----	-----	3417	-----	-----	-----	-----	-----	3407
33	3460	-----	3463	3454	3445	-----	3453	3452	3438	-----	3439	-----
34	-----	-----	-----	-----	-----	-----	-----	-----	-----	3484	-----	-----
35	-----	-----	-----	-----	3570	-----	-----	3573	-----	-----	-----	-----
36	-----	-----	-----	-----	-----	-----	-----	-----	-----	-----	3651	-----
37	-----	-----	-----	-----	-----	-----	-----	-----	3704	-----	-----	3714
38	3762	-----	3772	-----	3786	3757	3764	3754	3753	3742	3763	3787
39	3812	-----	-----	3807	-----	-----	3814	3827	-----	3824	3814	-----
40	-----	-----	-----	-----	-----	3908	-----	-----	3907	-----	3889	3909
41	3943	-----	3933	-----	-----	-----	3935	-----	-----	-----	3943	-----
42	-----	-----	-----	-----	-----	3994	3997	3992		-----	3997	3998

Thermogravimetry

In presence of atmospheric oxygen, the polymers containing low dissociation energy bonds are the most susceptible to oxygen attack whereas polymers containing phenyl group, C-F, fused rings etc. are expected to show higher oxidative stability at elevated temperatures. Another reason for lower thermal stability of polymers than usually expected is due to accidental inclusion of weak linkages in the main chain. While the presence of aromatic moieties in polyaniline will impart a better oxidative stability, the presence C-N linkages will make it susceptible to oxygen attack. It is observed as may be predicted that the oxidative stability of pristine polyaniline is somewhere in between polyparaphenylene and polythiophene (PTH) and much much higher than polyacetylene. The doped of polyaniline, like other p-type doped conductive polymers, would be expected to be stable to oxygen but will be susceptible to the reaction with doping agent [16,19].

It has been reported that undoped polyaniline is stable up to as high as 650^{o}C whereas PANI:HCl showed three steps degradation in thermogravimetric analysis. First step for the removal of water, second for removal of HCl from 230^{o}C to 300^{o}C and third for oxidative degradation of PANI backbone. 3-pentadecylphenyl-phosphoric acid doped PANI showed one step degradation with onset of 280^{o}C whereas the blend of PANI with the doping acid showed two steps starting from 240^{o}C and 350^{o}C. PANI doped with camphorsulphonic acid showed appreciable changes whereas the film produced from PANI:HCSA powder dissolved in m-cresol showed no effect in its Raman spectra on heating up to 150^{o}C. Electrochemically prepared poly(o-methylaniline) lost all its dopant by 320^{o}C and lost all its weight by 680^{o}C. It is also reported that toluenesulphonic acid doped p(o-methoxyaniline) is more stable than PANI:HCl. There was four step gradual loss of H_2O, SO_3^- and sulphonic groups before the breakdown of sulphonated PANI backbone [16,19]. In summery, two-, three- and four-steps in the degradation and variable stabilities of PANI have been observed in the thermogravimetric studies.

Table-4. Thermogravimetric analysis of polyaniline doped with different sulphonic acids.

SAMPLE	FIRST STEP UPTO (^{o}C)	WEIGHT LOSS (%)	SECOND STEP (^{o}C)	TO (^{o}C)	WEIGHT LOSS (%)	THIRD STEP (^{o}C)	RESIDUE AT 900^{o}C (%)
PANI	116	8.2	211	371	2.2	371 (460)	59.0
PANI:A	129	11.2	197	337	6.3	337 (371)	44.0
PANI:B	124	6.6	194	275	4.4	275 (396)	43.0
PANI:C	125	6.0	204	239	1.4	239 (239)	35.0
PANI:D	125	5.8	200	248	2.0	248 (248)	28.5
PANI:E	118	9.8	216	418	13.7	418 (425)	40.5
PANI:F	122	6.0	197	276	3.0	276 (280)	43.2
PANI:G	122	5.6	214	338	8.1	338 (348)	43.2
PANI:H	126	8.7	213	284	2.9	284 (290)	52.6
PANI:I	120	6.0	176	373	18.7	373 (436)	42.5
PANI:J	127	4.3	179	365	26.8	365 (403)	32.5
PANI:HCl	115	8.7	152	387	13.4	387 (440)	39.0

Note: In the third step, the temperature gives the beginning of decomposition whereas the temperature in the parenthesis gives the onset of fast decomposition.

Although, we observed three-step degradation in all PANI polymers, some compositions showed very clear and broad step-2 (PANI:G, PANI:I, PANI:J and PANI:HCl)), some of them showed a very small step-2 (PANI, PANI:A, PANI:B and PANI:F) while the rest of the compositions showed unclear step-2, superimposed over step-3 (PANI:C and PANI:D) as evident from table-4 and figure-3. There are variable reports on the removal of HCl from PANI:HCl but we observed the removal of HCl starts at around 152°C. The sulphonic acid doped PANI showed the removal of doping acids in the range of 176°C (for PANI:I) and 214°C (PANI:G). It is evident that sulphonic acid doped PANI expected to be more stable in retaining its electrical properties as step-2 corresponds to the removal of doping acids. The onset of step-3 corresponding to the oxidative degradation of PANI backbone is in the similar range for PANI:A (337°C), PANI:G (338°C), PANI:I (373°C) and PANI:J (365°C) as that for PANI:HCl (387°C) but falls in the lower range for PANI:B (275°C), PANI:C (239°C), PANI:D (248°C) and PANI:F (276°C). The extent of doping in terms of mol.ratio is also calculated as given in table-2 from TGA data.

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