



Electrical Conductivity Studies on Para Toluene Sulphonic Acid Doped Polyaniline

KEYWORDS

Poly Aniline; polymerization; emeraldine; conductivity

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ABSTRACT Polyaniline doped with hydrochloric acid (HCl) was prepared by chemical oxidative polymerization of aniline (ANI) in aqueous medium with ammonium peroxy disulphate as an oxidant. In the presence of oxygen, aniline undergoes polymerization rapidly and leads to the formation of scum like product. The deprotonation of the PANI:HCl samples were performed by stirring the PANI:HCl powder (emeraldine salt) in 0.1 M aqueous solution of ammonium hydroxide for 24 hours at room temperature, thus obtaining the polymer in the emeraldine base form. The redoping of the PANI (emeraldine base) with para toluene sulphonic acid was performed by mixing emeraldine base (EB) with para toluene sulphonic acid (PTSA) using a glass mortar and pestle to obtain the required doping levels ($Y = 0.5, Y = 0.3, Y = 0.1$). The prepared samples were pressed into pellets, and DC electrical conductivity was measured, using four-probe, with increasing temperature. The temperature dependence of electrical conductivity with increase in temperature followed Arrhenius equation. The electrical conductivity was observed around $10\text{-}2\text{ S cm}^{-1}$ for PANI- (PTSA)0.5, $10\text{-}3\text{ S cm}^{-1}$ for PANI- (PTSA)0.3 and $10\text{-}5\text{ S cm}^{-1}$ for PANI- (PTSA)0.1 respectively at $35\text{ }^{\circ}\text{C}$.

Introduction

Synthesis and electrical characterization of polyaniline has been the subject of extensive research during the past two decades since it was discovered that polyaniline could be made conducting (PANI-ES) by doping with acids like HCl, and then dedoped to the insulating state (PANI-EB) by treatment with a base like NH_4OH [Chiang A.C. et al (1986)]. The ease of synthesis with high yield, good stability in air, and the ability for reversibility to turn the conductivity to any value from the insulating to the metallic regime (several orders of magnitude) have made polyaniline a very desirable and the investigated conducting polymer [Nicholas J. Pinto et al (2005), Mohammad. F. (2000), Konklin J.A. et al (1998), Mc Andrews T.P. et al (1997), Gumbs R.W. (1994), Malhotra B.D. (1990)].

Conjugated polymers are semiconductors, but with doping they can change their properties into those of a metal. There are several types of doping – chemical doping, electro chemical doping, photo doping, interfacial doping etc. In this paper we report the chemical synthesis of polyaniline and its conductivity studies.

Experimental

2.1. Synthesis of emeraldine salt

9 ml aniline (0.1 M) was taken in a round bottom flask containing 150 ml of distilled water and 10 ml of concentrated hydrochloric acid. 11g (0.05M) of ammonium persulphate was dissolved in 100 ml of distilled water, and then added drop-wise to a stirred solution of 0.1 M of aniline dissolved in hydrochloric acid, pre cooled to $3\text{--}5\text{ }^{\circ}\text{C}$. Ammonium peroxy disulphate is added very slowly to prevent the warming of the solution. After the completion of this (nearly 30 minutes) stirring is continued for 2 hours to ensure completion of the reaction.

The time of initial colouration on mixing of reactants depends upon the temperature and protonic acid used. When HCl is used as a protonic acid, the colouration of the solution occurs almost after 1 minute at room temperature, and within 3 to 5 minutes at around $1\text{--}5\text{ }^{\circ}\text{C}$. The sequence of colouration is light blue \rightarrow blue green \rightarrow coppery tint \rightarrow green precipitates.

The precipitated emeraldine salt is filtered and washed with distilled water until the filtrate is colourless. The precipitate is then washed with methanol to remove oligomeric impurities. Finally it is washed with acetone, to remove water content,

and kept overnight for filtering. The precipitate is collected in a beaker and dried under dynamic vacuum at $70\text{ }^{\circ}\text{C}$ for 6 hours. The dried precipitate is then crushed into fine powder to get emeraldine salt.

2.2. Preparation of emeraldine base

The prepared emeraldine salt (powder form) was taken in a round-bottomed flask containing 20 ml of ammonia solution and 80 ml of water, and was stirred continuously for 24 hours. The precipitated blue emeraldine base is filtered and washed with distilled water, methanol and finally with acetone. After keeping over night for filtering, the precipitates are collected and dried under dynamic vacuum at $70\text{ }^{\circ}\text{C}$ for 6 hours. The dried precipitate is then crushed in to fine powder to get emeraldine base. A flowchart of the preparation of emeraldine base is shown in Fig.1.

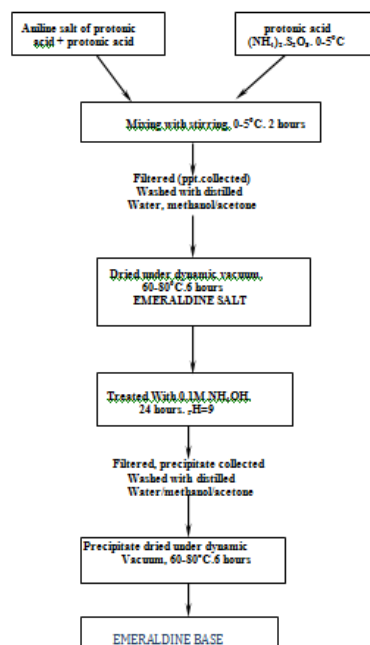


Fig. 1: Flow chart showing the various steps involved in chemical synthesis of polyaniline

2.3 Emeraldine base doped with para toluene sulphonic acid (PTSA)

In the present study, para toluene sulphonic acid (PTSA) was used as dopant. PANI-(PTSA)_y was prepared in three different doping levels (y = 0.1, 0.3 and 0.5). The molecular weight of PANI was estimated by viscometry method (Ostwald's viscometer).

PANI-(PTSA)_{0.5} was prepared by a thorough mixing of 0.012 M emeraldine base PANI with 0.006 M paratoluene sulphonic acid (PTSA) using a glass mortar and pestle. PANI-(PTSA)_{0.3} was prepared by mixing of 0.012 M emeraldine base PANI with 0.0036M PTSA, as explained above. For the preparation of PANI-(PTSA)_{0.1}, 0.012 M emeraldine base PANI was mixed with 0.0012M PTSA.

The prepared emeraldine salt powder was made into a pellet for conductivity studies using four probe apparatus. Electrical conductivity was calculated using the following equation [Instruction Manual of Resistivity Measuring Device].

where ρ is a correction divisor [it is a function of thickness of the sample as well as probe-spacing and equals to $\frac{4L}{\pi d}$] and where I, V, W and S are current (A), voltage (V), thickness of the pellete (cm) and probe-spacing (cm) respectively.

The conductivity was measured at different temperatures (from room temperature to 110°C). The current (I) was kept constant during the experiment.

3. Result and Discussion

The variation of conductivity with temperature of PANI-(PTSA)_{0.5}, PANI-(PTSA)_{0.3} and PANI-(PTSA)_{0.1} are summarized in table 1, 2 and 3 respectively and are shown in Figs. 2, 3 and 4 respectively. The temperature dependence of conductivity gives important information about the electrical conduction mechanism in the doped polyaniline. It can be seen from the figures that the conductivity of the sample increases linearly with temperature in all the three cases. Also, the conductivity is maximum for the doping level of 0.5M of PTSA. The increase linear increase in conductivity with temperature shows that para toluene sulphonic acid (PTSA) doped polyaniline (PANI) at different doping levels (y=0.5, 0.3 and 0.1) behaves like a semiconductor. On comparison with the standard values of electrical conductivity for traditional semiconductors, it is observed that the initial electrical conductivity of the PTSA doped PANI is well within the semiconductor region.

Table: 1 Conductivity of PANI – (PTSA)_{0.5}

S. No	Temp (T°C)	Voltage volt x10 ⁻³	Temp T K	Resistivity ohm -cm	conductivity S/cm	1/T K x10 ⁻³	Log ρ
1	35	18.06	308	19.4757	0.05135	3.2468	1.28949
2	40	17.35	313	18.7101	0.05345	3.1949	1.27208
3	45	16.60	318	17.9013	0.05586	3.1447	1.25288
4	50	15.95	323	17.2003	0.05814	3.0960	1.23554
5	55	15.32	328	16.5209	0.06053	3.0488	1.21803
6	60	14.75	333	15.9062	0.06287	3.0030	1.20157
7	65	14.26	338	15.3778	0.06503	2.9586	1.18689
8	70	13.78	343	14.8602	0.06729	2.9155	1.17202
9	75	13.35	348	14.3965	0.06946	2.8736	1.15826
10	80	12.92	353	13.9328	0.07177	2.8329	1.14404
11	85	12.45	358	13.4259	0.07448	2.7933	1.12794
12	90	12.19	363	13.1456	0.07607	2.7548	1.11878
13	95	11.87	368	12.8005	0.07812	2.7174	1.10723
14	100	11.60	373	12.5093	0.07994	2.6810	1.09723
15	105	11.37	378	12.2613	0.08156	2.6455	1.08854
16	110	11.09	383	11.9593	0.08362	2.6110	1.07771

Table: 2 Conductivity of PANI – (PTSA)_{0.3}

S. No	Temp (T°C)	Voltage volt x10 ⁻³	Temp T K	Resistivity ohm -cm x10 ³	conductivity S/cm	1/T K x10 ⁻³	Log ρ
1	35	10.78	308	0.31657	0.003159	3.2468	2.5005
2	40	10.27	313	0.29773	0.003359	3.1949	2.4738
3	45	9.78	318	0.28352	0.003527	3.1447	2.4526
4	50	9.30	323	0.26961	0.003709	3.0960	2.4307
5	55	8.93	328	0.25888	0.003863	3.0488	2.4131
6	60	8.61	333	0.24961	0.004006	3.0030	2.3973
7	65	8.28	338	0.24004	0.004166	2.9586	2.3803
8	70	8.01	343	0.23221	0.004306	2.9155	2.3659
9	75	7.78	348	0.22554	0.004433	2.8736	2.3532
10	80	7.63	353	0.22120	0.004521	2.8329	2.3448
11	85	7.42	358	0.21511	0.004649	2.7933	2.3327
12	90	7.25	363	0.21018	0.004759	2.7548	2.3226
13	95	7.07	368	0.20496	0.004879	2.7174	2.3117

Table: 3 Conductivity of PANI – (PTSA)_{0.1}

S. No	Temp (T°C)	Voltage volt x10 ⁻³	Temp T K	Resistivity ohm -cm x10 ³	conductivity S/cm x10 ⁻³	1/T K x10 ⁻³	Log ρ
1	35	36.20	308	25.9168	0.0386	3.2468	4.4136
2	40	33.50	313	23.9838	0.0417	3.1949	4.3799
3	45	31.00	318	22.1940	0.0451	3.1447	4.3462
4	50	28.60	323	20.4757	0.0488	3.0960	4.3112
5	55	26.80	328	19.1870	0.0521	3.0488	4.283
6	60	24.80	333	17.7552	0.0563	3.0030	4.2493
7	65	23.20	338	16.6097	0.0602	2.9586	4.2204
8	70	21.90	343	15.6790	0.0638	2.9155	4.1953
9	75	20.30	348	14.5335	0.0688	2.8736	4.1624
10	80	19.30	353	13.8175	0.0724	2.8329	4.1404
11	85	18.10	358	12.9584	0.0772	2.7933	4.1126
12	90	16.80	363	12.0277	0.0831	2.7548	4.0802
13	95	16.00	368	11.4550	0.0873	2.7174	4.059
14	100	15.10	373	10.8106	0.0925	2.6810	4.0339

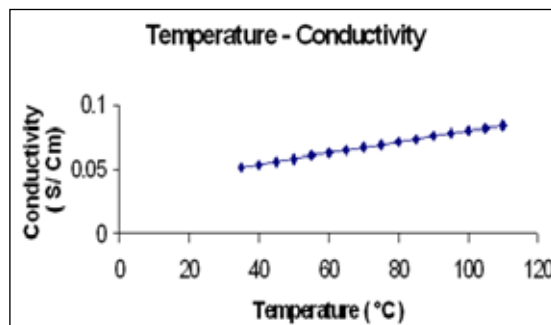


Fig. 2. Change in conductivity with temperature of PANI-(PTSA)_{0.5}

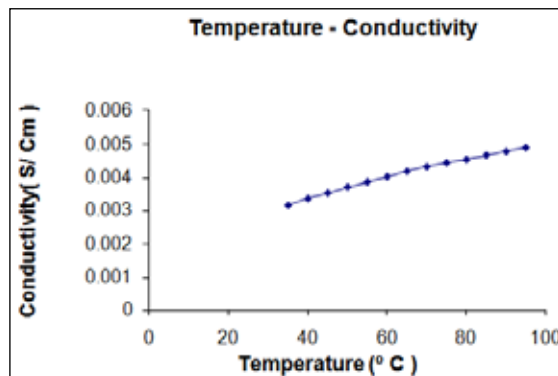


Fig.3. Change in conductivity with temperature of PANI-(PTSA)_{0.3}

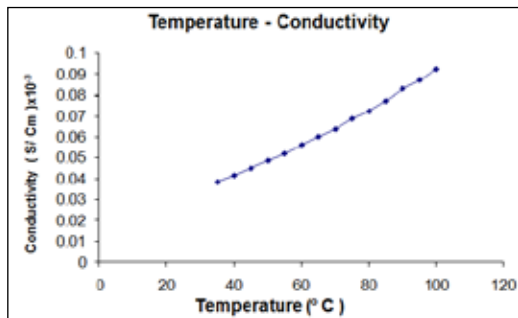


Fig.4: Change in conductivity with temperature of PANI-(PTSA)_{0.1}

The initial electrical conductivity was observed around 10^{-2} S cm^{-1} for PANI-(PTSA)_{0.5}, 10^{-3} S cm^{-1} for PANI-(PTSA)_{0.3} and 10^{-5} S cm^{-1} for PANI-(PTSA)_{0.1}, at 35°C. However, the temperature dependence of electrical conductivity of PTSA doped PANI (in all the three doping levels) increases with increase of temperature, which suggests its thermal stability in the presence of oxygen.

The temperature dependence of resistivity was fitted to Arrhenius type equation and measured values were plotted logarithmically as a function of reciprocal of temperature. Figures 5, 6 and 7 show the variation of $\log(\rho)$ with inverse temperature of PANI-(PTSA)_{0.5}, PANI-(PTSA)_{0.3} and PANI-(PTSA)_{0.1} respectively.

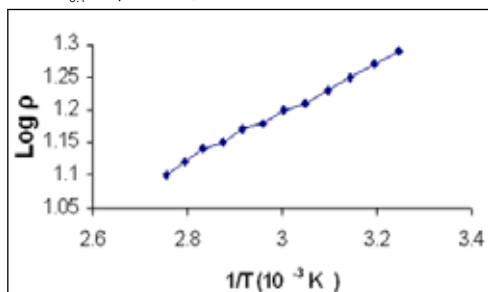


Fig.5 . Change in logarithmic resistivity with inverse temperature of PANI-(PTSA)_{0.5}

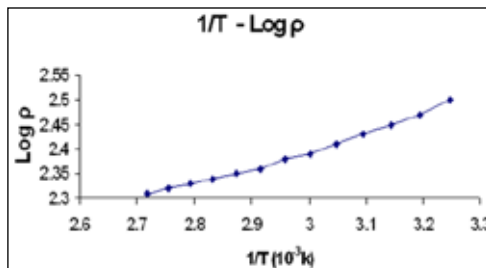


Fig. 6: Change in logarithmic resistivity with inverse temperature of PANI-(PTSA)_{0.3}

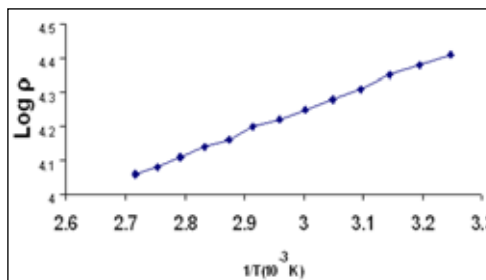


Fig.7 Change in logarithmic resistivity with inverse temperature of PANI-(PTSA)0.1

4. Conclusions

Polyaniline was prepared and doped with Para Toluene Sulphonic Acid at three different molar ratios. Thermal conductivity and electrical conductivity of the sample were measured. From the temperature vs conductivity plots for the three samples, it is seen that the electrical conductivity increases linearly with temperature, showing the semiconducting nature of the sample. Also, the conductivity is maximum for maximum doping concentration.

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