

COUNTER ION EFFECT ON THE PROPERTIES OF POLY ANILINE AND POLY(PARA PHENYLENE)

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The results of the investigations on the polymerisation of aniline and benzene in protonic media reveals that functionalised protonic acids can induce solution processibility in polyaniline, whereas the flexibility and excellent mechanical properties are the feature of poly (paraphenylene) under such conditions.

Key words: Conducting polymers, polyaniline, poly (paraphenylene).

INTRODUCTION

The essential common feature of all organic conducting polymers is extended conjugation. The metallic conductivity in these materials originates from the mobility of charge carrier along the carbon conjugated backbone doping (oxidation or reduction). This doping is molecular doping and depending upon nature and level of doping, the range of conductivities from insulating to semiconducting to metallic can be obtained, the typical signature is the inherent anisotropic nature of conductivity.

Though, the world over the interest in conducting polymer was generated in 1977 with the discovery that poly acetylene could be obtained as a free standing film which could be doped by iodine to give a organic metal [1, 2]. However, the way back in 1911, McCoy and Moore [3], suggested that it should be possible for organic solid to conduct electricity [3]. It was only in 1954, Akamatu et al rthers [4] synthesised the first organic solid namely perylene-bromine charge transfer complex which had reasonable electrical conductivity. Since 1977, the participation of scientists from various disciplines in conducting polymer research has brought out many new applications to meet the demand of new growing technologies such as in dissipation of electrostatic charge [5], EMI shielding [6–8]. Light emitting diodes [9–10], bio-sensors [11–12], light weight rechargeable batteries [13–15] FET [16] Corrosion inhibitors [17] protective coatings and cathodic protections of metallic structures [18]. The trend indicates that there are only very few areas of technology where conducting polymers have not yet made any entry. The reason for their wide- range of applications are due to light weight, processibility, resistance towards corrosion and wide range of electronic conductivity which one can achieve by simple phenomenon of doping.

It is ironic that these materials are finding applications in new exciting technologies notwithstanding the fact that the basic structural aspects of these materials are not fully understood.

The majority of organic conducting polymers have been synthesised from aromatics except polyacetylene, which is one of the simple conjugated systems. The basic drawback of such a good system is its environmental instability making its practical application difficult, whereas aromatics offer advantage over polyacetylene by way of flexibility in structure and are environmentally stable, so that these can be used under ambient conditions. The major poly aromatic systems which have received greater attentions are:

- (i) Polyheterocyclics derived from five membered rings [19–21] like polypyrroles, polythiophenes, polyfurans
- (ii) Five membered heterocyclic ring condensed to benzene like

polyisothionaphthene, [22] polyindole [23] polyphenylquinoline [24] etc.

- (iii) Polyphenylenes. [25–28]
- (iv) Polyphenylenes having heteroatoms in polymer chain like polyaniline, [29–43] polyparaphenylene sulphide, poly(phenyleneoxides) [44]
- (v) New type of aliphatic polymer containing hetero atom. [45]

In this report we will briefly discuss some new results on polyaniline and polybenzene obtained in our laboratory.

POLYANILINE

Polyaniline [PAn], the polymer resulting from oxidative polymerisation of aniline has been known since 1862 [29]. Then after a gap of nearly 100 years in 1968, the electronic conductivity and its dependence on redox level, acidity and hydration was reported by Surville [46]. The polyaniline has aroused great interest over last few years due to its potential for applications in various optoelectronic devices [9, 10] and as an antistatic material [5–8], in spite of its nonprocessability by usual techniques. The polyaniline is particularly challenging because its conductivity and solubility in polar organic solvents depend not only on oxidation state but also on the degree of protonation and dopant. Polyaniline is built up from reduced (B-NH-B-NH) and oxidised (B-N=Q=N-) repeat units, where B denotes benzenoid and Q denotes quinoid ring. Thus the ratio of amine to imine yields various structures such as leucoemeraldine a reduced form, fifty per cent oxidised form is emeraldine base and fully oxidised form is pernigraniline. Unlike other phenylene based conducting polymers, polyaniline has a reactive –NH group in a polymer chain flanked either side by a phenylene ring which imparts it a very high chemical flexibility such as protonation and deprotonation in addition to adsorption through nitrogen which is having a lone pair of electrons. This very presence of –NH group is responsible for interesting chemistry and physics.

Protonation in polyaniline not only involves the ingress of protons but is also accompanied by ingress of anion to maintain the charge neutrality. The electrochemical behaviour of polyaniline not only depends on the pH condition but also the counter ion of the Brönsted acid used for doping. In this paper, we present our results on the polyaniline. Organic protonic acid system and compare its characteristics properties with other inorganic acids—PAn system reported earlier [14–15], without entering into the controversy of disputed mechanism of transport of protons and anion being migration or diffusion controlled.

The electrochemical stability of the PAn film at higher potential

TABLE I: Characteristics of PAN in different media

Medium	Method of preparation	Conductivity (s.cm^{-1})	IR absorption bands (cm^{-1})	wave length of absorption, λ	
					(nm)
 (SSA)	Chemical	0.2	1673, 1568, 1547, 1477, 1296, 1189, 1147, 1124, 1080 & 801		317 449 & 646
	Electro-chemical	1.0	1671, 1565, 1545, 1476, 1300, 1185, 1144, 1121, 1076 & 801	422 & 720	319 447 & 649
 (ESA)	Electro-chemical	2.0	1572, 1492, 1301, 1261, 1170, 1137, 1025 & 801	416 & 662	336 449 & 646
	Electro-chemical	5.0	1568, 1489 1302, 1260 1160, 1130, 1040 & 798	417.8 686	343 453 & 662
 (PTSA)	Electro-chemical	2.0	1570, 1481 1301, 1260, 1160, 1119 1020 & 801	419 & 682	303 332 447 & 639
	Electro-chemical	1.2	—	420 & 820	—

is essential for its possible use as electrochromic material and as catalytic electrodes. Similarly the soluble PAN is also required for many applications to facilitate post synthesis processing. The solubilisation can be achieved by two methods (i) pre-functionalisation of aniline as suggested by Genies [40] or (ii) by introducing functionalised dopant [35]. Since PAN has two acid functions, a strong and a weak one it is possible to achieve a complexation or rather a electrostatic interaction between the charges on the polymer and doping anion to yield a ternary system, whereby it is possible for the doped polymer to interact with the dipole end of the solvent to yield a solvated polymer [36–37].

Our present study aims at to achieve solubility of doped polyaniline of good conductivity and electroactivity in an organic solvent so that thin films on insulating substrates can be obtained either by dipping or spraying without affecting the basic molecular geometry of polyaniline.

Preparation of PAN

Aniline (Fluka, 99.5%) and dimethyl sulfoxide (99%) were distilled under vacuum and kept under nitrogen in dark. All other chemicals were analytical grade. Before use all solutions were thoroughly purged with argon.

Platinum electrodes were polished with increasingly finer grades

of alumina ($0.05 \mu\text{m}$). The conducting indium-tin oxide (ITO) were used without any such treatments but were rinsed thoroughly in acetone before use.

The polymerisation of aniline in aqueous organic protonic acids (OPA) was carried out by two methods: (i) Chemical oxidative polymerisation using ammonium persulfate; and (ii) anodic polymerisation at platinum (Pt), ITO and stainless steel anodes. The polymerisation was carried out at $303 \pm 1 \text{ K}$ and then characterised.

Characterisation

The characterisation of polyaniline was carried out after thorough washing with double distilled water and methyl alcohol/acetone mixture and dried under vacuum for three days at 323 K. However, for electrochemical measurement electrodeposited polymer was used after thorough washings with water and the electrolyte. The following methods were used to characterisation.

Electronic spectra: The electronic spectra of solution as well as the electrode surface were recorded in the range of 250 nm to 900 nm using Hitachi-U-3400 UV-Vis near IR spectrophotometer.

Vibrational spectra: The infrared spectra in KBr pellet were recorded in 4000 to 400 cm^{-1} range on Nicolet FTIR Spectrometer.

H-NMR of soluble PAN: Using DMSO- d_6 as a solvent and TMS as standard, the $^1\text{H-NMR}$ spectra of doped and undoped PAN with organic acids were recorded using 270 MHz, Pulse width 5 μs , spinning rate 20 Hz at room temperature on Bruker NMR spectrometer.

X-ray diffraction powder pattern: X-ray diffraction pattern for PAN-SSA, PAN-neutral and PAN- H_2SO_4 were recorded using $\text{CuK}\alpha\lambda = 1.5418 \text{ \AA}$ on JEOL JDX 8030 X-ray diffractometer.

Thermal analysis: Thermogravimetric (TGA) and Differential Thermal Analysis were recorded on Perkin Elmer-7 thermal analyser. Nitrogen was used as the purge gas at a flow rate of 100 $\text{ml}\cdot\text{min}^{-1}$. The heating rate was 20 $\text{K}\cdot\text{min}^{-1}$.

Electrochemical measurements: The chronoamperometric studies of the polyaniline film obtained by potentiodynamic method were carried out a Bio Analytical system (BAS 100 A) Inc. USA, by switching the potential between -0.2 V to -0.8 V and -0.2 Volts .

The cyclic voltammetric studies were carried out using Tacussel bipad potentiostat coupled with X - Y recorder (BBL, Model SE 780) and universal programmer PARC 175.

DISCUSSION

It is generally accepted that protonation of PAN leads to the formation of radical cations by an internal redox reaction to cause the reorganisation of electronic structure to give two semiquinone radical cations (polaronic state). The degree of protonation and resulting electronic conductivity thus becomes the function of pH. In this protonation process it is essential that ingress of anion occurs to maintain charge neutrality in the resulting doped polymer. This implies that nature of anion (like size, crystal structure etc) should influence the properties of resulting polyaniline. The various properties of the PAN-systems are given in Table I.

In the present investigation, OPA doped PAN was found soluble in, dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and N-methyl-2-pyrrolidinone (NMP). The observation on solubility, spectral $^1\text{H-NMR}$ and electrochemical studies suggest the possible interaction of dopant via electrostatic interaction with chemically flexible $-\text{NH}-$ group of PAN. Therefore, dopant induced interaction of the polymer with the dipole end of the active solvent cannot be ruled out. Hence the maximum solubility ($11 \text{ g}\cdot\text{l}^{-1}$) is observed in DMSO where sulfoxide group is capable of interacting with the dopant which is electrostatically attached to the polymer. These types of interactions are less likely in the solvents devoid of active groups such as hydrocarbons or halogenated hydrocarbons.

Though the polyaniline obtained by both chemical and electrochemical methods has identical environmental stability, the electrochemical method leads to the formation of thin film on electrode surface which can find applications in electrochromic display and for various other electrochemical studies. For various other industrial application the chemical polymerisation is a preferred method for the synthesis, because large quantities can be prepared at a short notice since the conduction in polyaniline involves protonation, the chemical doping of a emeraldine base is a straight forward method and does not involve much elaborate arrangement.

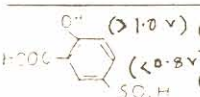
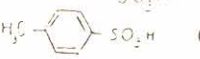
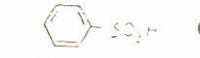
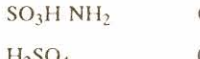
Electrochemical polymerisation

The electrochemical polymerisation of aniline in OPA medium was performed by cyclic potential sweep method by switching the potential from -0.2 to $+0.8 \text{ V(SCE)}$.

The redox potentials of the various peaks of the PAN systems in different electrolytes are tabulated in Table II. It is clear that polymerisation potential is essentially dependent on the electrolytic medium and hence a change in peak potentials of the redox couple is observed.

On comparing the results, it is found that in sulfuric acid medium

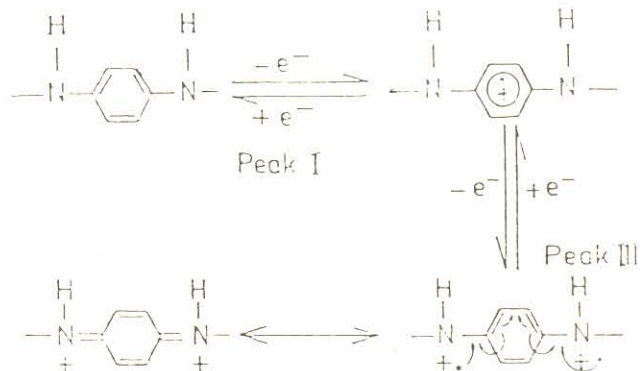
TABLE II: Redox potentials of Polyaniline film (vs SCE)

Electrolytes	I peak	II peak	—	III peak
	E_p ox (V)	E_p ox (V)		E_p ox (V)
	0.140 ($> 1.0 \text{ V}$)	0.460	—	0.720
	0.140 ($< 0.8 \text{ V}$)	—	—	0.720
	0.130	0.410	0.510	0.710
	0.10	0.40	0.480	0.70
$\text{SO}_3\text{H NH}_2$	0.125	0.40	—	0.67
H_2SO_4	0.09	0.36	—	0.625

the peak potential of the PAN film corresponding to I and III anodic peaks lies at 0.09 and 0.625 V SCE. The shift in peak potential can be attributed due to an interaction of the bulky dopant with the chemically flexible $-\text{NH}-$ of the polymer as is also evident from $^1\text{H-NMR}$ study. In all the three systems the polymerisation peak appears at more than 0.8V Vs SCE in the first cycle whereas corresponding peak in H_2SO_4 medium appears at 0.8V vs SCE. This suggests higher stability of aluminium radical cation in organic protonic acid media. In the subsequent cycles, new oxidation peaks II and III for the coupling of radical cations are observed at higher potential with increase in peak current further indicating the higher stability of the polymer formed under these experimental conditions.

The cyclic voltammogram of polyaniline film obtained by potential sweeping in a blank organic acid media shows two main redox couples. (Table II).

Peak I appears at 0.140v for SSA 0.130 for PTSA and 0.10V for BSA while the peak III is seen at 0.72, 0.71 and 0.70V for SSA, PTSA and BSA respectively. Peak I is due to the formation of radical cations and their subsequent oxidation to imine occurs near peak III. The scheme can be represented in the following equation form.



Peak II in cyclic voltammogram can be assigned due to adsorption of quinone/hydroquinone generated during the growth of polymer film. The intensity of peak II further increases in the presence of quinone and hydroquinone added externally to the electrolyte conforming adsorption of quinone during synthesis of PAN and is not due to the degradation of PAN which begins only on exceeding potential limit of 0.8 V vs SCE in the present system.

Chemical Polymerisation

A thorough investigation was conducted to study the affect of various acids on yield of aniline polymerisation to polyaniline using ammonium peroxy disulphate in aqueous solutions. The acid concentration in terms of molality was kept constant at 1 molar and reaction temperature was 303 ± 1 K. The comparative data on yield of polyaniline along with the conductivity of a pressed pellet are recorded in Table III. It is strange to note that there is not much variation either in the yield or in conductivities of polymer on variation of acids having different pKa values except in the case of acetic acid whose pKa is 4.75 and conductivity is very low. The reason for low conductivity can be explained on the basis of PKa values of PAN which are 1.55 and 2.55. pKa of CH_3COOH is much higher than PAN and hence charge transfer complex formation of PAN with CH_3COOH is much weaker than the other acids.

TABLE III: Effect of protonic acid (Oxidant: $(\text{NH}_4)_2\text{S}_2\text{O}_8$)

Acid	p K _a	Yield (%)	Conductivity (s.cm ⁻¹)
HCl	-7.0	37	1.2
H ₂ SO ₄	1.82	30	0.7
HBF ₄	—	43	1.1
HF	3.17	43	0.5
AcOH	4.75	28	0.001
HClO ₄	—	41	5.0
NH ₂ SO ₃ H	1.04	36	0.2
BSA	—	36	0.1
PTSA	—	36	0.5
SSA	—	39	0.2

Similarly the study was undertaken to investigate the affect of various oxidising agents on the yield of PAN by oxidative polymerisation of aniline under aqueous acid solution of pH~1 and the data are recorded in Table IV. This study has been found to be highly unusual. For example in case of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ as oxidant whose E° is 2.00 V., the yield is 37% and conductivity (σ) is 1.2.s.cm⁻¹, whereas in case of $\text{K}_2\text{Cr}_2\text{O}_7$ yield is 41% and σ is 0.2. In the case of KMnO_4 under acidic condition, the yield is 6%. These data suggest that standard oxidation potential of the oxidant used cannot explain for low yield and high conductivity in certain cases and vice versa in others. To us it looks that the kinetics of redox couple is much more important than the E° of the oxidant. The reason for very low yield for KMnO_4 as oxidising agent, is ascribed to the fast decomposition of KMnO_4 under acidic conditions. It looks that initially whatever polymer forms it gets over oxidised by KMnO_4 to less conducting state and hence we observe a low conductivity of the polymer.

POLY (PARAPHENYLENE)

Poly(paraphenylene) (ppp) is the simplest aromatic polymer derived from oxidative coupling of benzene. The interest in PPP is of two folds (i) starting monomer benzene has a strong resonance stabilized structure (ii) The PPP has a very high thermal stability. The strong resonance stabilised structure of benzene, is responsible for very high oxidation potential and hence its polymerisation is a challenge to electrochemists. PPP was

TABLE IV: Effect of Oxidising agent on PAN Yield

Oxidant	E _{ox} (V)	Time (h)	Yield (%)	Conductivity (S.cm ⁻¹)
$(\text{NH}_4)_2\text{S}_2\text{O}_8$	2.0	4	37	1.2
$\text{K}_2\text{Cr}_2\text{O}_7$	1.33	12	41	0.2
KIO_3	1.09	20	27	0.3
FeCl_3	0.77	24	8	0.2
KMnO_4	1.49	24	6	0.00001
KClO_3	1.45	24	1	0.00001

first synthesised using slight variation of Friedal Craft reactions using anhydrous cupric chloride as oxidising agent and water as a catalyst [27]. The polymer so obtained is powdery and degree of conjugation is [12–16] phenyl rings. These drawbacks of chemical method led to the development of electrochemical polymerisation of benzene in acetonitrile containing $\text{R}_4\text{N}^+\text{BF}_4^-$ as an electrolyte [25]. This reaction is highly sensitive to concentration of the monomer. The polymer so obtained on anode surface has 21–24 monomer units and the conductivity of IO^{-2} S.cm⁻¹. Later a new electrochemical method was developed for polymerisation of benzene and its homologue using a room temperature melt. This room temperature melt had different properties as against other known room temperature melt in various respects such as (i) anodic polymerisation of aromatic benzene ring and (ii) there no deposition of metal on the cathode.

There is no anodic polymerisation and on cathode the discharge of Al^{3+} occurs resulting in deposition of aluminum metal.

The polymerisation reaction invariably proceeds via the generation of cation radical. The survey of the literature indicates that sulphonation of benzene proceeds via generation of and complexes. The formation of or complex is essential to bring down the oxidation potential. Therefore we carried out the polymerisation of 1 M benzene emulsified in 95–98% H_2SO_4 at 278–283 K. Prior to polymerisation, the solution was deoxygenated by passing nitrogen gas for 30 minutes. Polymerisation was carried out by galvanostatic and potentiostatic techniques. The growth of polymer film was also studied by sweeping the potential between 0 to 2.0V vs $\text{Hg}/\text{Hg}_2\text{SO}_4$ at various scan rates ranging from 10 mv.S⁻¹ to 200mv.s⁻¹. For the purpose of comparison all electrochemical potential are referred against Ag/AgCl reference electrode.

Characterisation

The characterisation of polymer was carried out after thoroughly washing with double distilled water and methyl alcohol/acetone mixture and dried under vacuum for two days at 353 K. However, for electrochemical measurement electrodeposited polymer was used after thorough washings with water and electrolyte. 1 M benzene emulsified in 98% sulphuric acid at 279 K gave a very typical cyclic voltammogram on sweeping the potential from 0.0V to 2.5V. In first cycle with no rise in current was observed up to 0.8V then suddenly there was a rise in current with maximum intensity at 1.44 V. In the reverse cycle the cyclic voltammogram merged with baseline, in second cycle the new peaks were observed at 0.91V and 0.22V in anodic scan. However, in cathodic scan, only one peak at 0.2V was observed. After several scans, the peak potential got stabilised at 0.27V and 0.91V in anodic scan and 0.15V in cathodic scan. These observations suggest the generation of radical cation in first cycle at 1.44V. But, after the initiation of polymerisation further coupling of intermediate radical cation

needs less energy and thereby polymerisation potential shifted to lower potential. The cyclic voltammogram of a brown polymer film in 1N H₂SO₄ was not well defined the peak in anodic region being observed at 80 mV and 850 mV. Similarly the peak at 20 mV was found in cathodic scan the anodic and cathodic peaks at 80 mV and 20 mV respectively are due to doping and undoping. The peak at 850 mV in anodic scan is due to the oxidation of benzenoid structure to the quinoid form.

TABLE V: Peak potentials in V vs Ag/AgCl of PPP synthesised in 98% H₂ SO₄

Medium	Anodic Peak (V)	Cathodic peak (V)
1 NH ₂ SO ₄	0.82, 0.0	0.010
36 NH ₂ SO ₄	+0.12, 0.32, 0.6, 0.92	0.19, 0.02
1 M LiClO ₄ 1N ACN	+0.40, 0.75,	+0.48

To understand the growth of benzene polymer in this medium the anodic deposition of polymer was carried out at different potentials by potential step technique. It can be seen from the time-current transient that when Polymerisation is carried out at 1.25 V a well defined current time transient is observed, with a fall in current first due to adsorption of organic molecules, and subsequently polymerisation to conducting state showing again the rise in current with time. However, at higher potentials, a continuous a full in current is observed indicating oxidation of benzenoid structure to quinoid structure which is less conducting. The resonance between benzenoid and quinoid in a rigid backbone structure further gets restricted because of energy difference in two forms being about 7.2 Kcal.mol⁻¹.

CONCLUSION

Our study has indicated that organic acids as dopants not only enhance electrochemical stability but also induce solution processibility in polyaniline—an important aspect from technological application view point. Similarly the study indicates that benzene polymerisation is still in its infant stage and needs thorough understanding of the reaction mechanism which might aid to achieving low band gap polymers.

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