

# Studies on polyaniline in methane sulphonic acid (MeSA)

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## Abstract

Polyaniline (PAn) exists in various forms distinguished by the number of protons bonded to nitrogen which determines degree of oxidation of the polymer. At a macroscopic scale, doping involves electron transfer as well as protonation of nitrogen hetero atom which stabilizes localized bound states to impart the electronic conductivity to the system. In this communication, we show that PAn can yield a conducting solution in methane sulphonic acid (MeSA) without any side reaction. We have studied the compatibility of this solution with poly methylmethacrylate (PMMA) to yield a conducting composite. © 1999 Elsevier Science S.A. All rights reserved.

**Keywords:** Polyaniline; Processibility; Methane sulphonic acid; Protonation; Cyclic voltammetry

## 1. Introduction

Elucidating the unique properties and characteristics of polyaniline (PAn) provides challenge of considerable current scientific interest. This polymer results from oxidative polymerization of aniline to yield (B–NH–B–NH) or (B–N = Q = N–) where B denotes benzenoid and Q denotes quinoid structure. Thus, the ratio of amine to imine gives the four forms, namely emeraldine base (neutral), leucoemeraldine (reduced) emeraldine salt (conducting) and pernigraniline (oxidised) [1–8]. The important aspect of PAn is its nonredoxable doping by protonic acids. Thus, the electronic conductivity is a function of level of protonation. However, the functionality present in the dopant determines the processibility of PAn [9,10] in its protonated form. The protonation involves the quinone diamine segment having two imine nitrogen,  $pK_{a1} = 1.05$  and  $pK_{a2} = 2.55$  [11]. Thus, any acid whose  $pK_a$  values fall in this range would be a suitable dopant for PAn [8]. The  $pK_a$  value of methane sulphonic acid (MeSA) is  $-1.86$  which is as strong as sulfuric acid, with only one dissociable proton and density is 1.48. The presence of electron releasing methyl group in MeSA can make this as a good solvent for PAn just like *N*-methyl-2-pyrrolidone, which has proved to be one of the best solvent for emeraldine base. However, MeSA would yield a solution of conduct-

ing form of PAn due to protonation during solubilization. Cao et al. [12] have shown that PAn is soluble in concentrated  $H_2SO_4$ . However, it has been pointed out that sulphonation of aromatic ring occurs to yield polymer having a 39 ring nitrogen. We failed to observe any such ring substitution using MeSA as solvent. In this paper, we present the results of electrochemical studies, viz. cyclic voltammetry and the spectroscopic analysis such as UV–Vis, FTIR, NMR, thermal analysis (TGA), viscosity and the X-ray diffraction (XRD) pattern of PAn–MeSA system.

## 2. Experimental

Aniline and dimethylsulfoxide (DMSO) were distilled under vacuum and kept under nitrogen atmosphere in the dark. All other chemicals were Analar grade. MeSA is of Merck (98%).

Pt electrodes were polished with increasingly finer grades of alumina ( $0.05 \mu m$ ) before use.

Polymerization of aniline in aqueous MeSA was carried out by two methods (i) chemical oxidative polymerization using ammonium peroxy disulphate and (ii) anodic polymerization at platinum (Pt) electrode using potentiodynamic technique.

### 2.1. Chemical polymerization

0.1 M aqueous solution of ammonium peroxy disulphate is added dropwise to a stirred solution of 0.1 M

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aniline dissolved in 1 M aqueous MeSA, precooled to 3–5°C. The stirring is continued for 2 h to ensure completion of the reaction. The precipitated emeraldine salt is filtered and washed repeatedly with distilled water and methyl alcohol until the filtrate is colorless. Finally, the polymer is again suspended in a beaker containing 1 M aqueous solution of MeSA for 24 h for achieving maximum doping. The doped polymer was recovered by filtration and dried under dynamic vacuum at 70°C for 8 h.

## 2.2. Electrochemical polymerization

The electrochemical polymerization was carried out from 0.1 M monomer in 1.0 M aqueous MeSA solution by cycling the potential between –0.2 and 1.0 V vs. saturated calomel electrode (SCE) at Pt electrode at a scan rate of 50 mV/s by passing the charge of 0.32 C/cm<sup>2</sup>. Prior to polymerization, the solution was deoxygenated by passing argon gas for 30 min.

## 2.3. Characterization

Characterization of PAN was carried out after thorough washing with distilled water and methyl alcohol and drying under dynamic vacuum for 8 h at 70°C. However, for electrochemical measurements, the electrodeposited polymer was used after thorough washing with water and electrolyte (MeSA). The following methods were used for the characterization.

### 2.3.1. Electronic spectra

The absorption spectra of the solution was recorded using Hitachi-U-3400 UV–Vis near-IR spectrophotometer in the range of 250 to 1500 nm.

### 2.3.2. Infrared spectra

Infrared spectra in KBr pellets were recorded in the 4000 to 400 cm<sup>–1</sup> range on a Toshniwal-Simadzu FTIR spectrophotometer 8000 series.

### 2.3.3. NMR studies

Using DMSO-d<sub>6</sub> as a solvent and tetra methyl silane (TMS) as standard, the <sup>1</sup>H and <sup>13</sup>C NMR spectra of doped and undoped PAN were recorded using a 300-Unity NMR spectrophotometer at 25°C.

### 2.3.4. XRD powder patterns

XRD patterns were recorded using Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) on a Jeol JDX 8030 X-ray diffractometer.

### 2.3.5. Viscosity measurements

Viscosity of the PAN in MeSA was measured using Ubbelohde visometer at 25°C using 0.1% wt/wt solution in concentrated methanesulphonic acid (98%).

### 2.3.6. CHN elemental analysis

The percent composition of CHN values of the MeSA doped and undoped PAN was determined using Heraeus CHN–O rapid analyser.

### 2.3.7. Thermal analysis

Thermogravimetric and differential thermal analysis were recorded on a Polymer Laboratories Thermal Analyzer (STA-200). Nitrogen was used as the purge gas at a flow rate of 100 ml/min. The heating rate was 10°C/min.

### 2.3.8. Electrochemical measurements

Cyclic voltammetric (CV) studies were carried out using Wenking Potentiostat Model 75 M coupled with Wenking Voltage Scan Generator VSG72 and Rikadenki 201T X-Y/t recorder.

### 2.3.9. Conductivity measurements

The conductivity of the polymer sample was measured by four probe technique. The polymer samples were pressed into pellets of 1-cm diameter at 3-ton pressure.

## 3. Results and discussion

The polymerization of aniline to PAN in the presence of MeSA, which has an electron releasing methyl group and a –SO<sub>3</sub>H functional group having a pK<sub>a</sub> value of –1.86 [13] may bring some possible changes in the properties of PAN because PAN involves protonation as well as ingress of counter anions to maintain charge neutrality. A report in the literature suggest that protonation equilibria involve exclusively the quinone diamine segment of the polymer chain having two imine nitrogens with pK<sub>a1</sub> = 1.05 and pK<sub>a2</sub> = 2.55 [11].

It is generally accepted that protonation of PAN leads to formation of radical cations by an internal redox reaction which causes the reorganization of electronic structure to give two semiquinone radical cations (polaronic state). The degree of protonation and resulting electronic conductivity thus becomes a function of pH and pK<sub>a</sub> of a dopant. In this protonation process, it is essential that ingress of anions occurs to maintain charge neutrality in the resulting doped polymer. This implies that the nature of anions (size, crystal structure, etc.) should influence the properties of the resulting PAN.

In the present investigations, MeSA-doped PAN was found to be soluble in DMSO and MeSA (98%). The observations on solubility, spectral, viscosity, <sup>1</sup>H NMR and <sup>13</sup>C NMR and electrochemical studies suggest the possible interactions of dopant via electrostatic interactions with the chemically flexible –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 solubility  $\approx 12.5 \text{ g/l}$  is observed in DMSO

where the sulfoxide group is capable of interacting with the dopant, which is electrostatically attached to the polymer. Similarly the PAn was found to be soluble in 98% MeSA to the tune of 20% w/w.

Unlike, sulphuric acid as a solvent, no ring substitution and degradation of polymer was observed as indicated by electronic spectra and viscosity measurements (over a period of 3 months). The colorless filtrate obtained after isolation of PAn from MeSA by precipitation by adding water or methanol suggests that polymer does not degrade in concentrated MeSA medium.

### 3.1. CV studies

The electrochemical polymerization of aniline in MeSA medium by potentiodynamic method is shown in Fig. 1 in the very first cycle of polymerization the peak appearing at 0.95 V corresponds to the oxidation of aniline to anilinium cation. In subsequent cycles, the cyclic voltammogram assumes the shape consisting of number of peaks both in forward and reverse scan.

The growth rate of PAn films was monitored as the function of cycle number by measurement of the charge under cathodic portion of the CV [14], obtained for each growth cycle. The growth rate was taken as the difference between the preceding and following cycle number. The growth rate is increasing linearly with cycle number. After

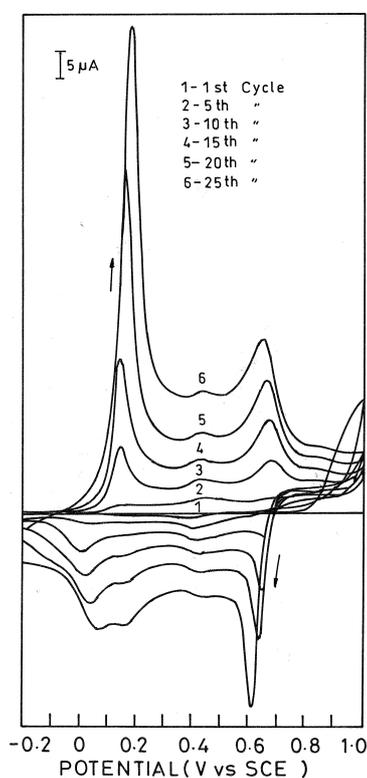


Fig. 1. Cyclic voltammogram of PAn formation, 1.0 M MeSA + 0.1 M Aniline, Sweep rate: 50 mV/s.

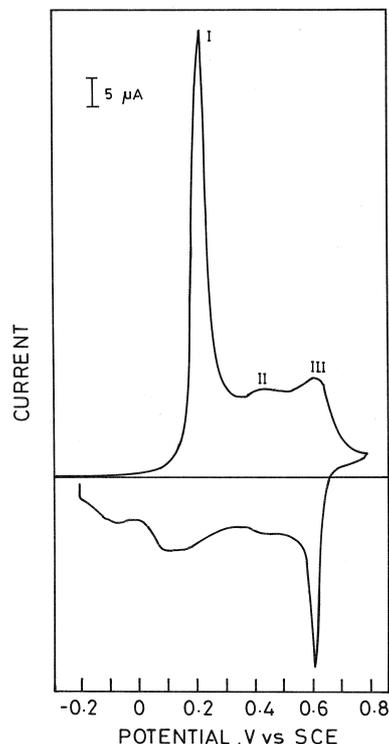
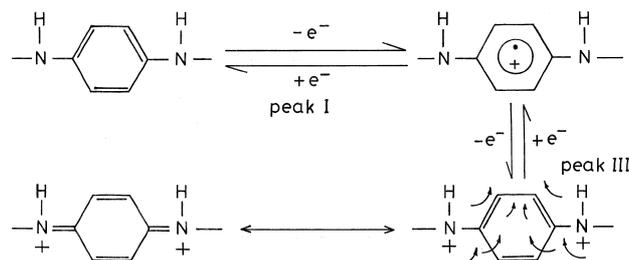


Fig. 2. CV behavior of PAn in MeSA, Sweep rate: 50 mV/s.

some cycling time, there was a negative deviation in the growth rates, which attains some maximum value. Hence, the growth rate decreases for the cycles for beyond maximum.

The charge transfer becomes slower at longer oxidation times as can be seen from the increase in peak width at half height for the first anodic peak (peak I). This width changes from 60 to 70 mV, for the linear growth rate region, to well over 130 mV for the films at higher cycle number. This increase in the peak width at half height implies slower electron transfer kinetics as per principles of organic electrochemistry [15].

Fig. 2 shows the electrochemical behavior of PAn in a blank MeSA media, where two main redox couples at 0.21 V (peak I) and 0.65 V (peak III) and an ill-defined peak at 0.45 (peak II) are observed. The redox peak at 0.21 V (peak I) corresponds to the conversion of amine units to



Scheme 1.

Table 1

Peak potentials of polyaniline (Pan) film in presence of various organic proton acids (vs. SCE)

Name of the acid	Peak I $E_{p,ox}$ (V)	Peak II $E_{p,ox}$ (V)	Peak III $E_{p,ox}$ (V)	Reference
Methane sulphonic acid	0.210	–	0.650	This work
Sulpho salicylic acid	0.140	–	0.720	[9]
p-Toluene sulphonic acid	0.130	0.410, 0.510	0.710	[8]
Benzene sulphonic acid	0.100	0.400, 0.480	0.700	[8]
Sulphamic acid	0.125	0.400	0.670	[8]
Sulphuric acid	0.090	0.360	0.625	[8]

radical cations (interconversion of leucoemeraldine to emeraldine) and the redox peak at 0.65 V is due to the conversion of amine to imine (peak III) [16,17]. The middle redox peak (peak II) is due to the irreversible oxidation of PAN segments to benzoquinone species [18]. The peak current for the first redox process varies linearly with square root of sweep rate in the range 10 to 300 mV/s. The average of the peak potentials for the second redox process was found to be scan rate independent at lower scan rate but is dependent on the pH of the medium. The plot of  $E_{1/2}$  vs. pH is approximately  $-120$  mV/pH indicating that the redox reaction involves two protons and two electrons. Therefore second redox process is attributed to conversion of radical cation into fully oxidised PAN. The electrochemical behavior of PAN can be explained by invoking the formation of radical cations near peak I suggesting that at this potential electron transfer occurs in the polymer film. Near peak III, the oxidation of amine to imine occurs along with protonation [16–18]. This electrochemical behavior can be expressed by Scheme 1.

It has been observed that the position of peak I does not alter with pH of the medium. However, the peak III totally

vanishes when the pH of the medium is more than five and hence we believe that peak I is due to surface electron transfer (formation of the radical cation) and peak III is due to protonation. The pH variation was done with the help of the suitable buffer containing sodium salt of MeSA.

The middle peak (peak II) is observed as very small hump due to the quinoid structure of some segments of polymer chain via formation of pernigraniline as suggested by Trivedi [10]. The potential difference between redox peak I and redox peak III in the present study is only 0.44 V, whereas in the case of PAN in sulphuric acid it is 0.62 V vs. SCE. The lowering of difference can be rationalized by taking into account the electron donating property of  $-\text{CH}_3$  group present in the dopant. For comparison, the peak potentials of PAN in other media are given in Table 1.

### 3.2. UV-Vis studies

The absorption spectrum of PAN solution in MeSA recorded in the range of 250–1500 nm is shown in Fig. 3.

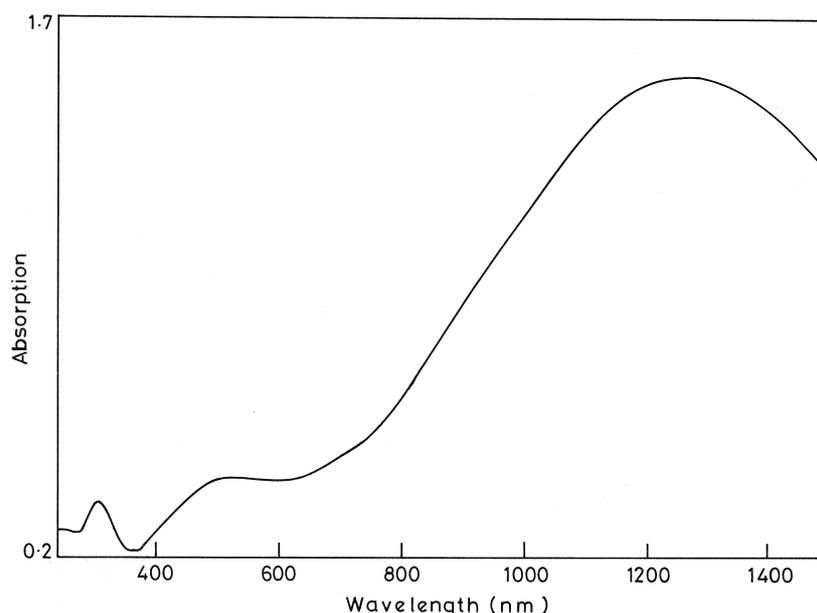


Fig. 3. UV-Vis solution spectra of PAN solution in concentrated MeSA.

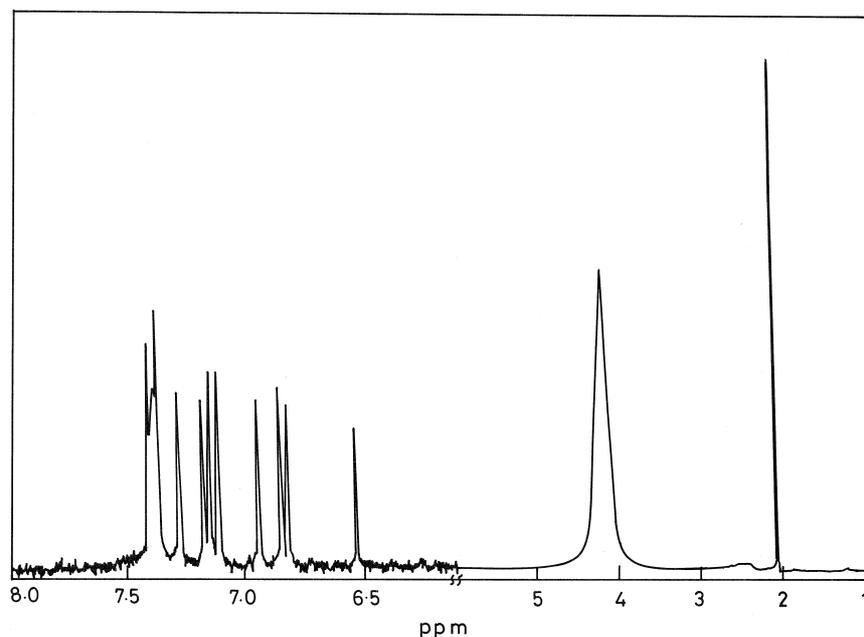


Fig. 4.  $^1\text{H}$  NMR spectra of PAN doped with MeSA.

The spectrum has three absorption bands at 317, 512 and 1274 nm. It can be seen from Fig. 3, that the continuous rise in absorption from 600 nm onwards, giving a maximum at 1274 nm, is due to the generation of bipolarons as charge carriers. If the conjugation is less, the absorption would have been occurred at lower wavelength, thus indicating that polymer does not degrade in MeSA medium.

The stability of polymer in MeSA is attributed due to the presence of the electron releasing methyl group in the dopant.

### 3.3. NMR spectra

The  $^1\text{H}$  NMR spectra of MeSA-doped PAN is shown in Fig. 4. The signals at 7.41 and 4.372 ppm are due to

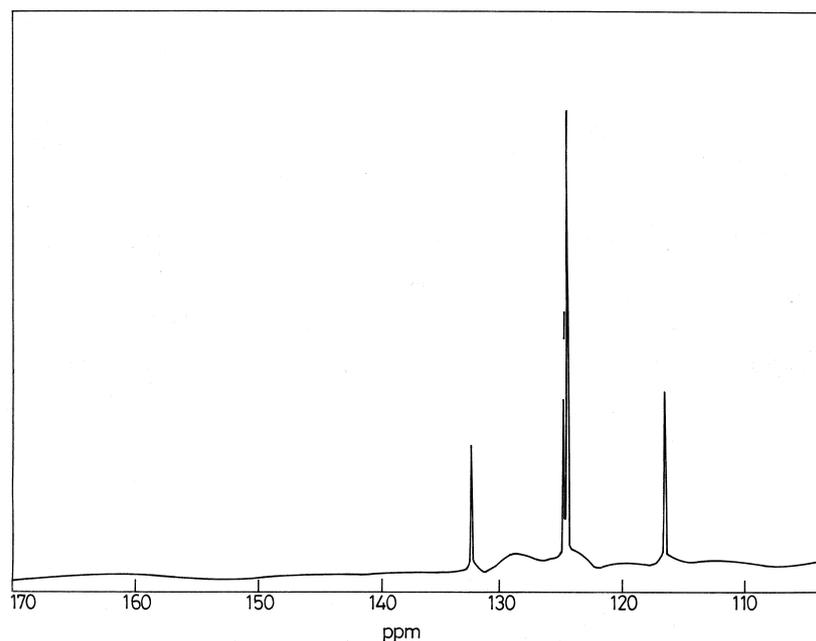


Fig. 5.  $^{13}\text{C}$  NMR spectra of PAN doped with MeSA.

Table 2  
 $^1\text{H}$  NMR data of PAN — chemical shifts with respect to TMS (ppm)

Organic acid	Aromatic proton (doped)	Aromatic proton (undoped)	N–H doped	N–H undoped	Reference
Benzene sulphonic acid	7.44	7.0	3.66	3.33	[8]
p-Tolulene sulphonic acid	7.59	7.0	3.77	3.34	[8]
5-Sulphosalicylic acid	7.36	7.6	3.89	3.34	[8]
Methane sulphonic acid	7.41	7.057	4.37	3.45	This work
Emeraldine base		7.0		3.3	

aromatic protons and the proton of N–H in the polymer [12,19], respectively. These signals are shifted to 7.057 and 3.454 ppm, respectively, on removal of the dopant. The signal due to the aliphatic proton of methyl group is observed at 2.064 ppm. No free proton signal of  $-\text{SO}_3\text{H}$  group (dopant) was observed indicating that the dopant present in the polymer is strongly bounded to the polymer matrix.

$^{13}\text{C}$  NMR spectrum of the doped PAN is shown in Fig. 5. For the emeraldine salt, two peaks were observed. A more intense line at 124.7 ppm is attributable to the proton-bonded carbons in the benzenoid rings and a weaker line at 132.8 ppm attributable to the nitrogen-bonded carbons in the benzenoid rings. The absence of the peak around 170 ppm [12] indicates the absence of quinoid impurities in the polymer sample.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR have been compared and are given in Tables 2 and 3.

### 3.4. FTIR studies

The FTIR spectrum of PAN–MeSA system in KBr medium is shown in Fig. 6 along with the possible assignments (Table 4). The large descending base line in the spectral region  $4000\text{--}2000\text{ cm}^{-1}$  has been attributed due to free-electron conduction in the doped polymer [19], this type of behavior was not observed in undoped polymer. The main absorption bands observed are  $1150\text{ cm}^{-1}$  (delocalization)  $1404\text{ cm}^{-1}$  (semiquinoid ring),  $1650, 1155, 1510\text{ cm}^{-1}$  (benzenoid) due to benzenoid structure. In the undoped PAN, two absorption bands of equally strong intensity have been observed at  $773$  and  $832\text{ cm}^{-1}$  due to C–C bending mode of benzenoid structure [20,21]. However, no absorption band due to quinone was observed indicating that the system is free from quinone impurities.

Table 3  
 $^{13}\text{C}$  NMR data — chemical shift with respect to TMS (ppm)

Organic acid	Aromatic C–H	Aromatic C–N	Reference
Methane sulphonic acid	124.8	132	This work
p-Tolulene sulphonic acid	133	165	[8]
5-Sulphosalicylic acid	133	170	[8]
Benzene sulphonic acid	128	137	[8]
Hydrochloric acid	138	157	[8]
Sulphuric acid	129.7	144.7	[8]
Emeraldine base (undoped)	120	137	[8]

The absorption bands due to the charge ( $1055\text{ cm}^{-1}$ ) and semiquinoid structure are also absent in undoped polymer.

### 3.5. Viscosity measurements

The inherent viscosity of the PAN base in concentrated MeSA (98%) was used as an indicator of the molecular weight. The PAN synthesized had an inherent viscosity of  $1.25\text{ dl/g}$  at  $25^\circ\text{C}$ .

The materials were fractionated for the molecular weight dependence. The sample with  $\eta_{\text{in}} = 0.22\text{ dl/g}$  were made from the low molecular weight fraction extracted from the same batch, i.e., the fraction soluble in DMSO. Sample with  $\eta_{\text{in}} = 1.7\text{ dl/g}$  were made from then fraction which is insoluble in DMSO. The fraction that was insoluble in DMSO was soluble in concentrated MeSA, is not cross-linked, but has relatively high molecular weight.

The fraction of the sample which gives  $\eta_{\text{in}} = 1.7\text{ dl/g}$  has the molecular weight (as estimated from the Marak–

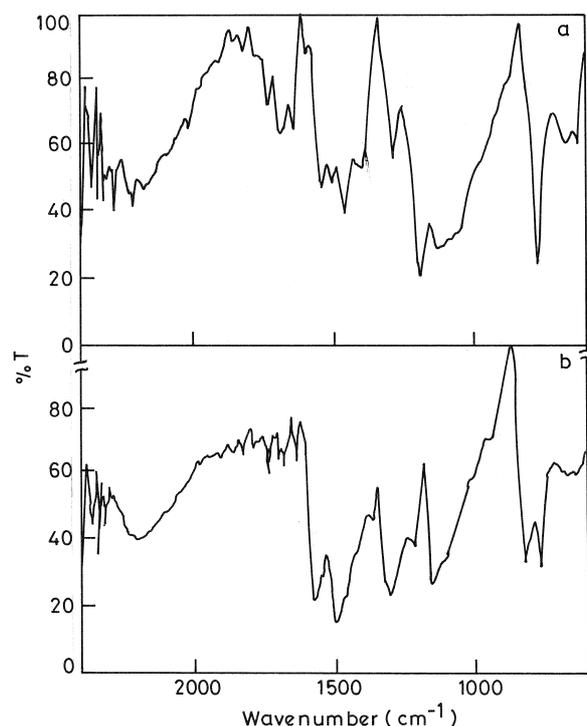


Fig. 6. FTIR spectra of PAN (a) doped with MeSA (b) undoped.

Table 4

FTIR data of the MeSA-doped PAN. Possible assignment of the FTIR spectra of PAN (Ref. [20])

Frequency (cm <sup>-1</sup> )	Assignments <sup>a</sup>
627	Dopant, aromatic deformation
773	C–H <sub>op</sub> of 1–4 ring
1055	Dopant-charge
1196	C–H <sub>ip</sub> on 1,4 ring
1298	–C–N str in BBB
1404	–C–N str Q–B–Q
1510	Str of N–B–N
1546	–C–C str
1651, 1687	–C–C str, str of N = Q = N
3120	=NH str
3440	NH <sub>2</sub> sym str, NH str in B–NH–B

<sup>a</sup>Abbreviations: sym = symmetric, str = stretching, ip = in-plane bending, op = out of plane bending, Q = quinoid unit, B = Benzenoid unit.

Houwink relations [22,23] in the range 16000 (rigid chain limit) to about 63000 (flexible chain limit).

The stability of PAN solution in MeSA was monitored with respect to the specific viscosity of the PAN solution over a period of 3 months and the results are shown in Table 5. It indicates that there is no degradation of polymer in MeSA. The change in viscosity is only 3% over a period of 3 months.

Since the conformation of PAN in the solution state is not established and as result, viscosity data are difficult to interpret. Therefore, we have carried out the viscosity measurements as described earlier Andreatta et al. [24].

### 3.6. CHN elemental analysis

The protonation level of MeSA-doped PAN was determined by elemental analysis. The percent composition of the CHN values are very well in agreement with the 50% protonation level (maximum). The values are in agreement with the empirical formula of C<sub>24</sub>H<sub>18</sub>N<sub>4</sub> · 2.1CH<sub>3</sub>SO<sub>3</sub>H.

### 3.7. Thermal analysis

The Thermogravimetric analysis (TGA) of emeraldine base indicates that the degradation of polymer begins around 442°C, while in doped polymer, the first weight loss of 3% is obtained up to 100°C (due to moisture), the second weight loss (35%) is observed in between the temperatures 282 and 350°C, which is equivalent to the weight of the dopant. The final degradation of polymer

Table 5

Change of specific viscosity with time

Sl. number	Time	$t_0$	$t_1$	$T_1 - T_0$	$\eta_{sp} = t_1 - t_0 / t_0$
1	Fresh	85.97	109.72	23.78	0.2766
2	30 days	85.97	109.57	23.60	0.2745
3	45 days	85.97	109.48	23.51	0.2735
4	90 days	85.97	109.28	23.32	0.2713

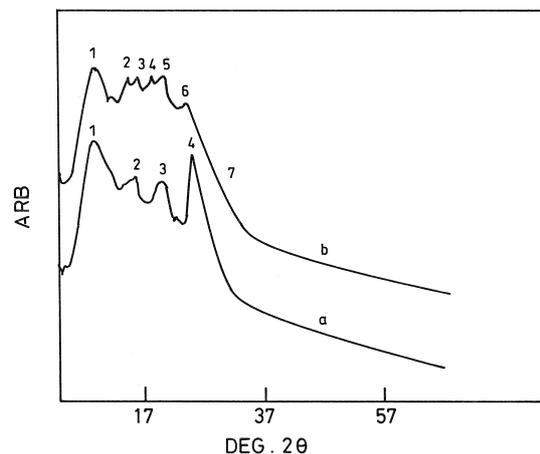


Fig. 7. XRD powder patter of PAN (a) doped PAN (b) undoped PAN.

starts from 360°C and complete degradation occurs around 600°C.

### 3.8. XRD studies

The XRD powder pattern of PAN is shown in Fig. 7. The X-ray data of PAN-MeSA system is compared with the PAN-H<sub>2</sub>SO<sub>4</sub> system in Table 6. The peaks observed are at lower value of 2θ indicating that PAN is having better crystallinity.

### 3.9. Conductivity measurements

The conductivity of the MeSA-doped polymers samples were found to be in the order of 1 S cm at 50% protonation level.

### 3.10. Composite formation

20 w/w solution PAN in MeSA was found suitable to yield a homogeneous composite with poly methylmethacrylate (PMMA). Depending upon the loading level, PMMA in PAN conductivity observed varied from 10<sup>-1</sup> to 10<sup>-4</sup> S cm. Those composites were highly flexible. The detailed study would be discussed elsewhere.

Table 6

XRD powder pattern (Cu, Kα, λ = 1.518 Å)

Peak number	PAN-MeSA		PAN-H <sub>2</sub> SO <sub>4</sub>		Undoped	
	2θ	d	2θ	d	2θ	d
1	8.400	10.517	19.05	4.655	8.900	2.838
2	15.700	5.640	24.35	3.652	4.700	3.690
3	20.300	4.371	25.00	3.559	16.100	4.287
4	24.900	3.573	25.75	3.457	18.400	4.818
5	–	–	–	–	20.700	5.501
6	–	–	–	–	24.100	6.021
7	–	–	–	–	31.500	2.838

#### 4. Conclusions

The present investigation reveals that PAN can be obtained as 20% W/W solution in concentrated MeSA (98%). The viscosity measurements and absorption studies over the period of 3 months indicates that there is a negligible or no degradation of polyniline in MeSA solution occurs and it is possible to prepare a PMMA composite of PAN using MeSA as the medium.

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