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Synthesis and characterization of new azobenzenesulfonic acids doped conducting polyaniline

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Abstract

New azobenzene sulfonic acid dopants were synthesized by diazotized coupling reaction of sulphanilic acid diazonium salt with commercially available raw materials such as phenol, *m*-cresol and 4-phenylphenol. The structures of the dopants are confirmed by NMR and FT-IR. Polyaniline emeraldine base was doped by these new azobenzenesulfonic acid dopants in two different solvent medium such as methanol and *N*-methylpyrrolidinone to produce green emeraldine salt. The doping process was confirmed by FT-IR and UV–vis spectroscopy. The effect of composition of dopant on the conductivity of the polyaniline was investigated and the results suggest that the conductivity increases with the increase in the dopant concentration and attained maxima for more than 38% in the feed. The conductivity measurements reveal that all the dopants equally effective in producing in high conductivity in the range of 0.02 S/cm and the conductivity of the doped samples are insignificant to the structural difference in the dopant. WXRD and SEM analysis indicate that the doped samples are highly amorphous and porous in nature. The thermal analysis by TGA indicate that all the doped materials were highly stable up to 300 °C for high temperature applications.

Keywords: Polyaniline; Azobenzene sulfonic acid; Conductivity; Morphology; WXRD

1. Introduction

Conducting polyaniline has attained significant attraction for various applications in many high performance devices such as rechargeable batteries [1], chemical sensors [2], electromagnetic shielding [3], electrochemical and corrosion devices [4]. The interest in polyaniline based devices arises from the relatively economical polymer synthesis and processing techniques combined with wide range of electronic, optical, chemical and mechanical features [5]. The conducting state of polyaniline is easily obtained by simple protonation by reacting with acids and the process is also reversible. The availability of wide range of dopants such as mineral, carboxylic and sulfonic acids make the polyaniline chemistry much more interesting for controlling the various properties such as solubility, solid sate ordering, micro- and nano-sized materials, etc. [6–8]. The mineral acids doped polyaniline

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materials are very good conductors but their poor environmental stability is the main concern for long term applications. On the other hand sulfonic acid doped polyaniline materials are highly stable and the properties of the materials can also controlled by varying the structural parameters of dopants. Zeolite channels [9], track-etched polycarbonate [10], surfactants [11], micelles [12], liquid crystals [13], cyclodextrins [14] and polyacids [15] were employed as templates for the dopants such as dodecylbenzenesulfonic acid (DBSA) and camphorsulfonic acid (CSA). Commercially available aromatic sulfonic acids such as *p*-toluenesulfonic acid, 5-sulfosalicylic acid, 5-sulfoisophtalic acid, dinonylnaphthalenesulfonic acid, methanesulfonic acid and β-naphthalenesulfonic acid were applied as dopants for polyaniline [16–20]. We reported a systematic approach to produce ordered (crystalline), submicron size and uniform morphology PANI-doped materials using structurally different dopants in various polymerization methodologies such as interfacial and emulsion [21]. We have also reported a systematic approach for ligno sulfonic acid – a renewable resource based dopant for polyaniline and the conductivity and morphology of the doped materials are precisely controlled by varying the amount of dopant in the feed [22]. Recently, azobenzene sulfonic acids were successfully explored for synthesizing of polyaniline nano-fibers in a template free emulsion polymerization [23–25]. Qiu et al. reported a novel dopant 4-{*n*-[4-(4-nitrophenylazo)phenyloxy]alkyl}aminobenzene sulfonic acid for polyaniline nano-materials. The morphology and conductivity of the resulting nano-structures were strongly de-pended on the number of alkyl groups in the dopant molecule [23]. The azobenzene sulfonic acids have optically switchable cis–trans isomerization in addition to the doping, which is very useful for optical devices based on polyaniline. Therefore, design and development of new azobenzene sulfonic acid dopants are very attractive to understand their doping behaviors in polyaniline and also to study their structure–property relationship. Huang et al. had recently reported a synthesis of polypyrrole nano-fibers using azobenzene sulfonic acid dopants and the nano-fibers showed a high conductivity and photoisomerization [26].

The present work is emphasized to produce novel azobenzene sulfonic acids dopants from commercially available raw materials such as phenol, *m*-cresol and 4-phenylphenol, etc. and study the doping process of these new dopants for polyaniline in solution. The structures of the new dopant were confirmed by NMR and FT-IR spectroscopes. Polyaniline emeraldine base (Pani-EB) was doped using these new dopants in methanol as well as in *N*-methylpyrrolidinone. The doping processes were confirmed by FT-IR, UV–vis, conductivity measurements, wide-angle X-ray diffraction (WXRD), scanning electron microscopy (SEM) and thermo gravimetric analysis (TGA).

2. Experimental methods

2.1. Materials

Aniline (99.5%) (Aldrich chemicals) was purified by distilled under vacuum. Ammonium persulphate (98.5%), conc. HCl acid (35.0%), aqueous ammonia (25.0%), sulphanilic acid (99%), sodium nitrite (99.5%), sodium carbonate (98.5%), sodium hydroxide (97.0%), methanol (99.0%), phenol (99.0%), *m*-cresol (99.0%), 4-phenyl phenol (99.0%), *N*-methylpyrrolidone (99.5%) were purchased from Merck India company and purified by following the standard procedures [27].

2.2. Measurements

For conductivity measurements, the polymer samples were pressed into a 10 mm diameter disc using an IR pelletizer and analyzed using a four probe conductivity instruments by applying a constant current. The resistivity of the samples was measured at five positions and at least two pellets were measured for each sample: the average of 10 readings was used for conductivity calculations. Infrared spectra of the polymers were recorded using an Impact 400 D Nicolet FT-IR spectrophotometer in the range of 4000–400 cm^{-1}. For SEM measurements, polymer samples used for the conductivity measurements were further subjected for thin gold coating using JOEL JFC-1200 fine coater. The probing side was inserted into JEOL JSM-5600 LV scanning electron microscope for taking photographs. Wide angle X-ray diffractions of the finely powdered polymer samples were recorded by Philips analytical diffractometer using CuK-alpha emission. The spectra were recorded in the range of $2\theta = 0$–50 and analyzed using X' Pert software. UV–vis spectra of the drop cast polyaniline samples on glass plate are recorded using Perkin Elmer Lambda 35 Spectrophotometer. The thermal stability of the polymers was determined using TGA-50 Shimadzu thermo gravimetric analyzer at a heating rate of 10 °C/min in nitrogen.

2.3. Synthesis of 4(4-hydroxy-phenylazo)-benzenesulfonic acid (PABS)

Sulphanilic acid (51.9 g, 0.3 mol) and sodium carbonate (13.6 g, 0.13 mol) were taken in a 1000 ml conical flask. Water (500 ml) was added and heated to 60–70 °C to dissolve the entire solid. It was further cooled to 10–15 °C and a cooled solution of sodium nitrite (18.5 g, 0.29 mol) in water (55 ml) was added. The mixture was poured into ice (350 g) containing conc. HCl (53.2 ml) at 5 °C and stirred using mechanical stirrer for 30 min. The diazonium salt was added drop wise into a solution containing sodium hydroxide (30 g, 0.75 mol) and distilled phenol (23.5 g, 0.25 mol) in water (250 ml) at 5 °C. The coupling reaction was continued for stirring for 3 h in the ice cold condition using a mechanical stirrer. Conc. HCl (250 ml) in crushed ice (600 g) was slowly added into the reaction mixture for neutralizing and the neutralization was confirmed by pH paper. The red precipitate was filtered using Buchner funnel, washed with water and then dried in a vacuum oven for 24 h at 80 °C (0.1 mm of Hg). Yield = 70.0 g (93%). ^{1}H NMR (DMSO-d_6) δ: 7.83 ppm (d, Ar–H, 2H); 7.77 (s, Ar–H, 4H); 6.97 ppm (d, Ar–, 2H). FT-IR (KBr, in cm^{-1}): 3454.4, 1635.1, 1603.2, 1504.6, 1443.1, 1399.5, 1127.1, 1102.6, 1008.8, 847.2, 710.6, 631.4 and 572.1.

2.4. Synthesis of 4(4-hydroxy-2-methyl-phenylazo)-benzenesulfonic acid (MPABS)

Sulphanilic acid diazonium salt was prepared as described for PABS and added in to the solution of sodium hydroxide (30 g, 0.75 mol) and distilled *m*-cresol (27 g, 0.25 mol) in water (250 ml). The rest of the procedures are similar to that of PABS. Yield = 74 g (96%). ^{1}H NMR (DMSO-d_6): 7.76 ppm (b, Ar–H, 4H); 7.61 ppm (d, Ar–H, 1H); 6.80 ppm (s, Ar–, 1H); 6.74 ppm (d, Ar–H, 1H); 2.64 ppm (s, Ar–CH_3, 3H). FT-IR (KBr, in cm^{-1}): 3439.5, 2882.7, 1602.9, 1525.2, 1442.6, 1340.1, 1289.6, 1111.2, 1027.9, 1004.8, 864.3, 708.1, 623.2 and 587.1.

2.5. Synthesis of 4-(4-hydroxy-biphenyl-3-ylazo)-benzenesulfonic acid (BPABS)

Sulphanilic acid diazonium salt was prepared as described for PABS and added in to the solution of sodium hydroxide (12 g, 0.3 mol) and distilled 4-phenylphenol (17 g, 0.1 mol) in water (75 ml). The rest of the procedures are similar to that of PABS. Yield = 29 g (81%). ^{1}H NMR (DMSO-d_6): 8.01 ppm (d, Ar–H, 2 H); 7.98 ppm (d, Ar–H, 2H); 7.82 ppm (d, Ar–, 2H); 7.71 ppm (d, Ar–H, 2H); 7.55 ppm (m, Ar–CH_3, 1H) 7.47 ppm (d, Ar–H, 1H),7.37 ppm (d, Ar–H, 1H), 7.20 ppm (d, Ar–H, 1H). FT-IR (cm^{-1}): 3434.7 1619.9, 1511.4, 1482.8, 1426.8, 1356.3, 1263.8, 1122.9, 1036.5, 1007.9, 845.1, 761.8, 698.5 and 655.

2.6. Synthesis of polyaniline emeraldine base (Pani-EB)

Distilled aniline (25 ml, 0.274 mol) was dissolved in HCl (1 M, 500 ml) and taken in a 2000 ml three necked flask and cooled to 0 °C using ice. To this a pre-cooled solution of ammonium persulphate (78.1 g, 0.343 mol) in HCl (1 M, 250 ml) was added slowly very carefully (exothermic reaction). Immediate appearance of pink colour was noticed, which turned into deep blue. After 5 min, green colored polyaniline–HCl emeraldine salt was started to precipitate from the solution. The polymerization was further proceeded by stirring at 30 °C for 24 h. The precipitate was filtered, washed with 1 M HCl for three times and stirred in a flask containing 1 M aqueous ammonia solution (1125 ml 25% solution in water). The blue precipitate was stirred for 3 h at room temperature to ensure the completion of de-doping. The resultant blue emeraldine base was filtered, washed successively with water, methanol and acetone to remove the un-reacted starting materials and oligomers. The blue emeraldine base was dried in a vacuum oven at 80 °C for 12 h (0.1 mm of Hg). Yield = 21.1 g (84.4% yield). FT-IR (KBr, in cm^{-1}): 3236.7, 1586.9, 1492.5, 1307.6, 1164.5 and 829.5

2.7. Doping of Pani-EB with azobenzene sulfonic acid dopants

Typical procedure for doping PABS with Pani-EB in methanol (for **P-1**) is described below. 1.82 g of Pani-EB and 2.78 g of PABS were taken in a 100 ml RB flask with water condenser. 50 ml methanol was added and heated to 65–70 °C using an oil bath. Using magnetic stirrer the whole mixture was stirred for 3 h. It was filtered using Whatman filter paper, washed with methanol until the color disappears, and dried in vacuum oven at 50 °C (0.1 mm of Hg). The doped polymer weighed 1.96 g (43%). FT-IR (KBr, in cm^{-1}): 3230.6, 1574.7, 1489.7, 1294.9, 1130.3, 1026.1, 801.1 and 705.1. Similarly MPABS, BPABS were doped with Pani-EB using the same procedure either in methanol (**P-2** to **P-3**) and NMP (**P-4** to **P-6**). **P-2**: FT-IR (KBr, in cm^{-1}): 3230.7, 1569.3, 1486.9, 1240.1, 1116.6, 1023.4, 801.1 and 705.1. **P-3**: FT-IR (KBr, in cm^{-1}): 3228.3, 1566.5, 1484.2, 1294.9, 1113.8, 1026.1, 798.4 and 704.3. The FT-IR spectra of **P-4** to **P-6** were identical to that of **P-1** to **P-3**.

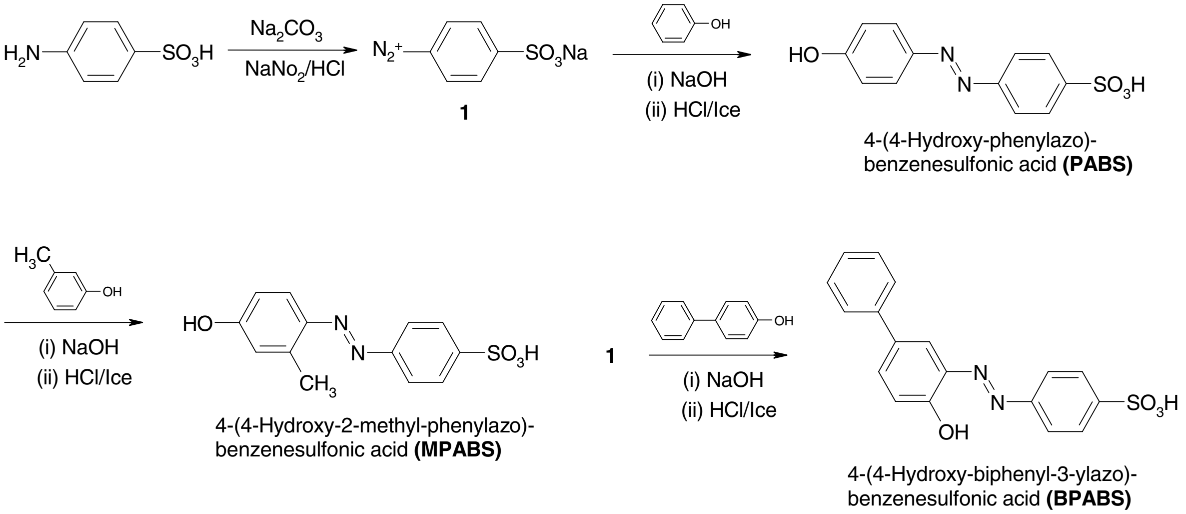
3. Results and discussion

New azobenzene sulfonic acid dopants were synthesized from commercially important phenols as shown in Scheme 1. Diazotized sodium salt of sulfanilic acid was reacted with sodium salts of phenol in water and subsequent neutralization to produce 4(4-hydroxy-phenylazo)-benzenesulfonic acid (PABS) [28]. Similarly *m*-cresol and 4-phenylphenol were reacted with sulfanilic acid to produce 4(4-hydroxy-2-methyl-phenylazo) benzenesulfonic acid (MPABS) and 4-(4-hydroxy-biphenyl-3-ylazo)-benzenesulfonic acid (BPABS), respectively. The yield and solubility of the new dopants were summarized in Table 1. The solubility of the dopant was checked in three different classes of solvents by dissolving 8–10 mg of the substances in 1 mL and the results are summarized for various solvent in Table 1. It is very clear from the table that the new dopants were freely soluble in alcohols and polar solvents like amides and *N*-methylpyrrolidone. The structure of the dopants was confirmed by NMR and FT-IR spectroscopy. The ^1H NMR spectra of the aromatic regions of PABS and MPABS are shown in Fig. 1 and the peaks are assigned for the representative protons. In PABS, three aromatic protons from the phenolic aromatic ring appeared as two clear doublets at 6.95 (d) and 7.8 ppm (c) whereas all four aromatic protons containing sulfonic acid ring appeared together at 7.75 ppm (a + b). In MPABS, the protons in the sulfonic acid aromatic ring appeared in the same position as in PABS, but the

Table 1
Yield, solubility, absorption and thermal properties of dopants

Dopants	Yield[a] (%)	Solubility[b]			λ_{max}[d] (nm)
		H_2O	THF	Polar[c]	
PABS	93	+–	–	+	359
MPABS	96	–	+–	+	366
BPABS	81	–	+–	+	339

[a] For isolated product.
[b] Measured for 8–10 mg in 1 ml of the solvent [(+) completely soluble, (+–) partially soluble and (–) insoluble].
[c] Solvents include *N*-methylpyrrolidinone, *N*,*N*-dimethylformamide and *N*-*N*-dimethylacetamide.
[d] Measured in NMP at 30 °C.



Scheme 1. Synthesis of new azo benzene sulfonic acid dopant.

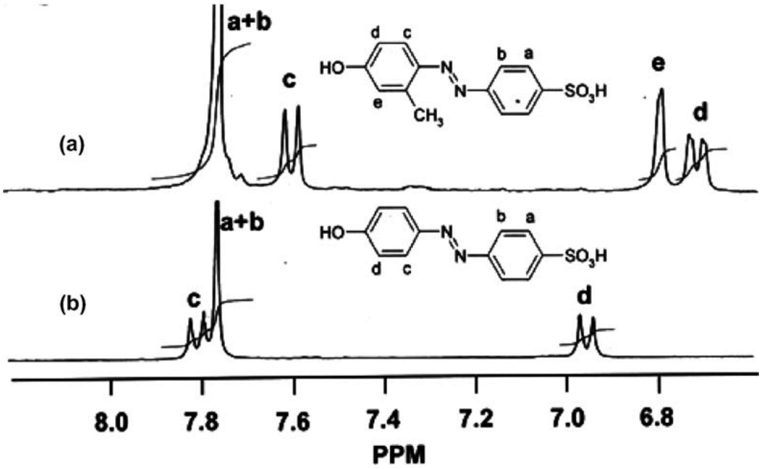


Fig. 1. ^{1}H NMR spectra of PABS (a) and MPABS (b) in d_6-DMSO. Only the aromatic region is expanded for simplicity.

three different types of aromatic protons in phenolic ring appeared as two clear doublets at 7.6 (c), 6.7 (d) and a singlet at 6.79 ppm (e). Similarly the structure of the BPABS was also confirmed by ^{1}H NMR (not shown). The intensities of the peaks are very well matched with the required number of protons and it confirms the formation of expected dopants. FT-IR spectrum (not shown) of the dopants showed a weak and broad peak at 3400 confirmed the phenolic-OH in the dopant. The new peaks at 1534, 1339 and 1237 cm^{-1} are corresponding to the trans N=N, O=S=O asymmetric and symmetric stretching vibrations, respectively. The appearance of these new peaks confirms the formation of azo-linkages in the dopant molecules. The UV–vis spectrum of the dopant were recorded in *N*-methylpyrrolidinone and shown in Fig. 2. The absorption spectra showed two clear maxima corresponding to the π–π* transition (lower region) for the trans-isomer and weak absorption at higher wavelength region for the n–π* transition for the cis-isomer of the azo linkage. The increase in electron density at the phenol aromatic ring increase the absorbance maxima in *m*-cresol compared to phenol. On the other hand the decrease in the conjugation in the phenylphenyl due to steric hindrance results in blue shift in the absorbance spectra. The increase in the steric hindrance also results in the formation of more cis-isomer in BPABS compared to other two dopants.

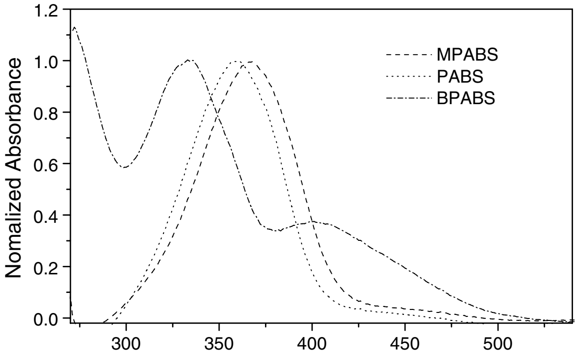


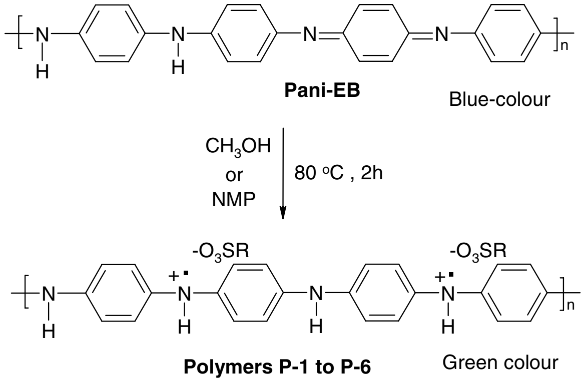
Fig. 2. UV–vis spectra of azobenzene sulfonic acid dopants in NMP at 30 °C.

Aniline in HCl was oxidized using ammonium-persulfate to produce a green color polyaniline–HCl emeraldine salt (Pani-ES), which was further converted into its corresponding emeraldine base (Pani-EB) by ammonium hydroxide. Three new azobenzene sulfonic acids were tested as dopants for polyaniline by reacting them with Pani-EB. In order to investigate the effect of doping condition and solvents on the properties of the resultant materials, two different solvents – methanol (for **P-1** to **P-3**) and NMP (for **P-4** to **P-6**) were selected (see Table 2). The dopants were freely soluble in both the solvents, but the Pani-EB insoluble in methanol and partially soluble in NMP. Therefore, one would expect a significant difference in the materials doped in either of the solvents. Typically the doping was carried out by dissolving the dopant in the particular dry solvent followed by adding finely powdered Pani-EB in to the dopant solution and vigorously stirring the for 2 h at 80 °C to produce their green colored doped emeraldine salts. The structure of the emeraldine salt is shown in Scheme 2 [21].

Table 2
Dopant, doping solvents, conductivity, WXRD data and thermal properties of doped samples

Sample	Dopant	Solvent	Yield (%)	Conductivity σ (S/cm)[a]	WXRD peaks at 2θ	WXRD peaks d-spacing (Å)	T_D[b] (°C)
P-1	PABS	MeOH	43	9×10^{-5}	15.2, 19.9, 25.1	5.8, 4.4, 3.6	310
P-2	MPABS	MeOH	52	0.06	15.2, 19.9, 24.7	5.8, 4.4, 3.6	295
P-3	BPABS	MeOH	51	0.05	14.5, 19.9, 25.0	6.1, 4.4, 3.5	280
P-4	PABS	NMP	56	0.12	–	–	331
P-5	MPABS	NMP	54	0.05	15.2, 19.9, 24.7	5.8, 4.4, 3.6	293
P-6	BPABS	NMP	47	0.02	–	–	315

[a] Measured using four probe conductivity at 30 °C.
[b] On-set of degradation temperature (T_D) was determined by TGA at 10°/min heating rate in nitrogen.



Scheme 2. Synthesis of new azo benzene sulfonic acid doped polyaniline.

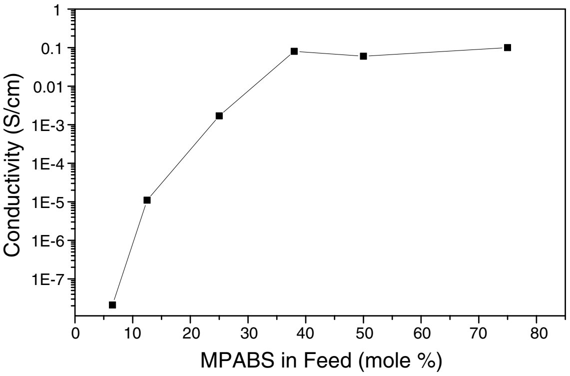


Fig. 3. Plot of conductivity versus MPABS in the feed for **P-2**.

In order to investigate the effect of amount of dopant on the conductivity of the polyaniline, MPABS was doped with Pani-EB at various mole ratios in the feed 6.5, 12.5, 25.0, 38.0, 50.0 and 75.0 (dopant/Pani-EB in mole ratio) using methanol as solvent. The conductivity of the doped samples were determined by four probe conductivity measurement unit by applying a constant current. The samples were compressed to 10 mm diameter and 0.5–0.8 mm thickness pellets for the measurements. The conductivity values of the samples were plotted against the amount of MPABS in feed and showed in Fig. 3. It is very clear from the plot that the conductivity of doped samples increases with increase in the amount of dopant in the feed and it attained a maxima for more than 38 mol%. It suggest that minimum 38 mol% of the dopant is required to obtain high conductivity of doped samples. Therefore, for comparing the doping ability of these structurally different dopants, the amount of dopant was fixed at 50 mol% equivalents to Pani-EB. All the doped materials are obtained in good yield. The conductivity of the APBS doped samples are highly selective to the doping solvent medium, the NMP seems to be a very good solvent for doping compared to that of methanol. All other two dopants produce a very good doped polyaniline with the conductivity in the range of 0.05–0.1 S/cm, irrespective of the solvent used for doping process. The reason for the different doping behavior of PABS is not very clear at present. We have also carried out multiple experiments by changing the mole ratio of the dopant versus Pani-EB and surprisingly there is no improvement in the conductivity of the doped samples. The optical properties of the polymers were studied by UV–vis spectroscopy (see Fig. 4). The UV–vis spectra of dye doped samples are shown in figure Pani-EB showed a peak at 650 nm corresponding to the π–π* transitions in quinoid ring. In doped polyaniline materials the peak at 650 nm is completely vanished and new peaks in the near-IR region are appeared above 800 nm corresponding to the formation of polaron species. The absorbance spectrum of **P-1** showed a weak peak in the range of 600–700 nm corresponding to the un-doped quinoid ring in the Pani-EB, which is in accordance to the conductivity measurements. The absorbance spectra of samples doped in NMP were almost identical to that of **P-2** and **P-3**

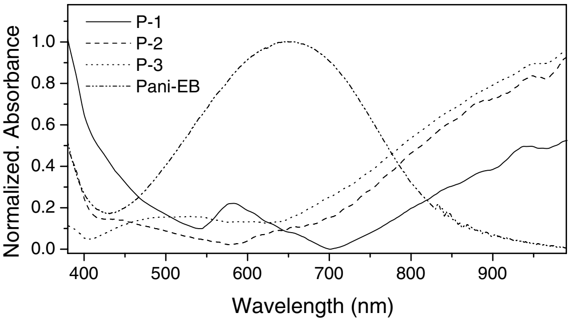


Fig. 4. UV–vis spectra of Pani-EB and azobenzene sulfonic acid doped samples in solid state.

showed in Fig. 4 and confirmed the high degree of doping.

FT-IR spectroscopy is a powerful tool to analyze the structures of doped polyaniline samples. FT-IR spectra of Pani-EB and **P-1** to **P-3** are shown in Fig. 5. The five peaks in Pani-EB at 1587, 1485, 1317, 1155 and 831 cm^{-1} are in accordance with earlier reports [21,29]. The two peaks at 1587 and 1485 are corresponding to the quinoid and benzenoid ring C=C stretching ring deformations, respectively. The peak at 1317 and 830 are corresponding to C–N stretching and C–H out-of-plane vibrations of 1,4-disubstituted benzene ring, respectively. The appearance of new peaks in the doped samples at 1317 and ~670 cm^{-1} are attributed to symmetric and un-symmetric stretching vibrations of O=S=O and S–O groups. The peak at 1026 cm^{-1} is corresponding to $NH^+ \cdots SO_3^-$ interactions between the polymers chain and the dopant. The FT-IR, UV–vis and conductivity measurements confirm the doping of Pani-EB by the new azobenzene sulfonic acid dopants. The thermal stability of the doped samples were analyzed by thermo gravimetric analysis and the representative TGA plots for the polymers are given in Fig. 6. It is very clear from the plot that all the doped materials are highly stable up to 300 °C and can be used for various high temperature applications.

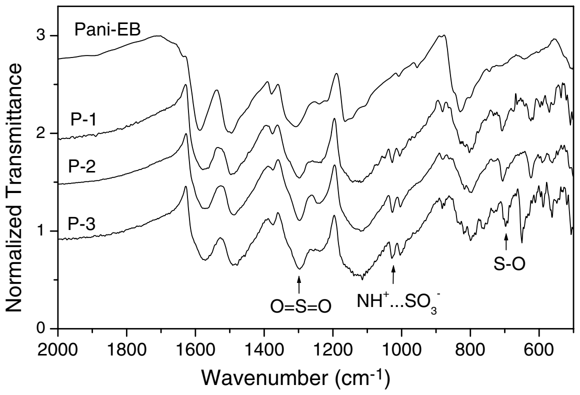


Fig. 5. FT-IR spectra of Pani-EB and azobenzene sulfonic acid doped samples.

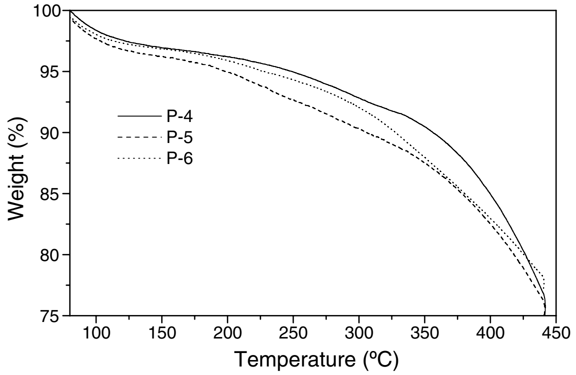


Fig. 6. TGA plots of doped samples azobenzene sulfonic acid doped samples in NMP.

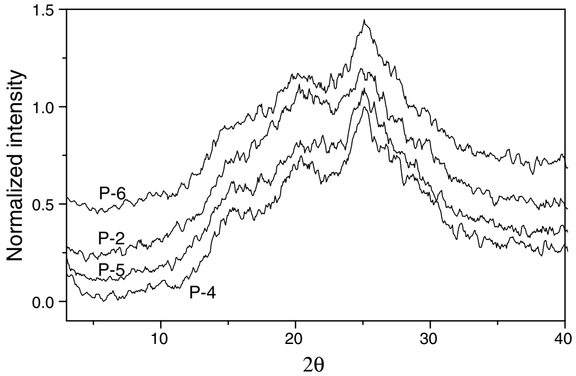


Fig. 7. WXRD patterns of azobenzene sulfonic acid doped samples in solid state.

All the polymer samples were subjected to Wide angle X-diffraction using Cu-α radiation source and scanned from $2\theta = 0$–50. Polyaniline emeraldine is having a highly rigid structure and is reported to be amorphous and upon doping with sulfonic acids the dopant–polymer interactions may tend to organize the polymer chains. The diffraction patterns for the doped materials are shown in Fig. 7 and the peak values are summarized in Table 2. The WXRD spectra of the **P-1** to **P-6** were free from their dopants and only peaks corresponding to the polyaniline backbone were observed [30]. A broad diffraction pattern was obtained for

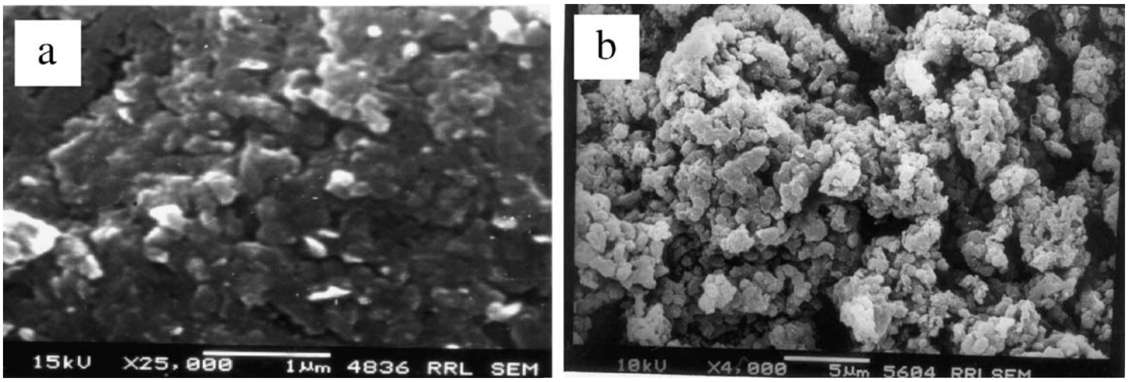


Fig. 8. SEM images of Pani-EB (a) and MPABS doped sample (**P-2**) in methanol (b).

Pani-EB due to its typical amorphous nature (not shown). The doping of Pani-EB by the sulfonic acids via protonation reaction induces ordering in the polyaniline chains resulting the formation of new peak at $2\theta = 25.1$ (d-spacing $= 3.5$ Å). The peak at $2\theta = 19.5$ and 15.2 ($d = 4.4$ and 5.5 Å, respectively) in sulfonic acid doped sample is same as that of observed earlier by other groups for PANI-dopant complexes [21]. It is originated by the increasing inter planar distance followed by the inclusion of dopant molecules. The WXRD patterns for the MPABS doped in methanol (**P-2**) and NMP (**P-5**) were almost identical, which suggests that the influence of solvent on the solid sate ordering of polyaniline for azobenzene sulfonic acid doped samples were almost insignificant. In all the doped materials, the sulfonic acid is almost behaved like simple dopants even though it has one free phenolic groups to effectively undergo hydrogen bonding with polyaniline chains. The morphology of the doped materials were analyzed by SEM and their photographs are shown in Fig. 8. The sample preparation was done by compressing the polymer powders into 1 mm thick pellets, followed by depositing gold on the probing side by electroplating technique. It is very clearly observable from the photographs that there is no significant difference in the morphology of the materials. The doped materials exhibits (Fig. 8(b)) a disordered porous morphology with larger particle size distribution in the range of 0.5 μm.

4. Conclusion

In summary, we have designed and synthesized three new azobenzene sulfonic acid dopants and successfully utilized them for doping in polyaniline. Two different solvent methanol and NMP were used to study the difference in the doping behavior. PABS showed a significant difference in the conductivity depending up on the solvent employed for the doping process whereas other two dopants almost showed identical behavior for methanol and NMP. The conductivity of the samples increases with increase in the dopant concentration and a higher conductivity of 0.1 S/cm was obtained. WXRD and SEM reveal that the doped materials are highly amorphous and porous morphology was obtained. The reason for the porous structure may be due to that the azobenzene sulfonic acids are not highly efficient in penetrating the amorphous polyaniline emeraldine chains for inducing high ordering. However, good morphology is possible in the in situ doping of polyaniline using these azobenzene sulfonic acids along with aniline. Currently the work is in progress in utilizing the azobenzene sulfonic acids in various in situ polymerization such as interfacial, emulsion and dispersion, which will be published elsewhere.

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