
Spectroscopic investigation of polyaniline co poly meta amino benzene sulfonic acid

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Abstract

Similar to metals, conducting polymers possess an extraordinary ability to conduct electricity due to their intrinsic properties. There has been considerable focus on the synthesis and development of such materials for a wide variety of applications. In this regard, polyaniline and its derivatives have versatile applications including use as active electronic material, fabrication of modified electrode, sensors, in secondary batteries and in microelectronic and electrochromic device. Introduction of potential polymers like PAN and PPY or PTF as conductive co-polymer, interpenetrating network or blends would be a challenging step towards the preparation of novel and cheap material with modified antistatic properties. In this work we used poly (m-amino benzene sulfonic acid) and poly aniline for the preparation of composite. Aniline and m-amino benzene sulfonic acid can be fast polymerized in water to yield conducting nano composites. The composites were easily water dispersable and showed prolonged stability.

Introduction

It is highly interesting to note that conducting polymers have strong ability to conduct electric current like conventional metals provided they compromise with other properties. During the last two decades, conducting polymer has received considerable research attention owing to its unique and useful properties. The synthesis and development of conducting polymers with the potential of replacing the expensive and rapidly depleting metal reserve have been one of the marvels of polymer chemistry¹⁻⁴. Thus, the lightness

of weight, easy processability and resistance against corrosion of organic polymer have led to many applications causing replacement of metals or to the creation of organic materials. Most of them, however, remain laboratory curiosities, but with tremendous potential for future scientific and technological development. The factors controlling the variation of conductivities over a wide range are mainly mode of synthesis, oxidant, reaction conditions, pH, time, nature of dopants and doping level etc. Among these organic polymers, polyanilines, polypyrrole, polythiophene etc have attracted special attention due to its high stability towards air and moisture, high electrical conductivity and unique redox properties. However, polyanilines are almost insoluble in common organic solvents especially in doped form, which causes difficulties in determination of molecular structure and restricts them to practical use. The technique has been applied in the more diverse field of research to get better applicable materials⁵⁻²².

Polyaniline and its derivatives have versatile applications including use as active electronic material, fabrication of modified electrode, sensors, in secondary batteries and in microelectronic and electrochromic device. To improve the processability thermal and environmental stability and to induce novel electronic and electrochemical properties substituted poly anilines being developed.²³⁻²⁶ Poly nuclear aromatic amines are new class of conducting materials of π - conjugated aromatic organic polymers e.g Poly (phenylene), Polyaniline, Polythiophene, Poly pyrrole.²⁷⁻³⁰ Of late considerable research attention has been paid to the preparation and evaluation of aqueous colloidal dispersion of different conducting polymer³¹⁻⁴⁰. Introduction of potential polymer like PAN and PPY or PTF as conductive co-polymer, interpenetrating network or blends would be a challenging step towards the preparation of novel and cheap material with modified antistatic and electromagnetic properties⁴¹⁻⁴⁷. The research thus appears to be of wide scope and further work in this series will be directed to this end.

Such types of composite are readily prepared by synthesizing the conducting polymer in presence of another conducting polymer commonly in aqueous medium. The monomers most widely used in this study are pyrrole (Py) and aniline (ANI). In this work we used poly (m-amino benzene sulfonic acid) and poly aniline for the preparation of composite. Aniline and m-amino benzene sulfonic acid can be fast polymerized in water

by FeCl_3 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$ to yield conducting nano composites. The composite can be dispersed in a stable aqueous dispersion medium.

Experimental

Materials

Aniline was purchased from SD chemicals (India). It was doubly distilled with Zn dust prior to polymerization. The monomer m-amino benzene sulfonic acid was purchased from SRL (India) and used without further purification. Ammonium persulfate from S.D. fine chemicals was used as oxidant without any purification. HCl purchased from SRL chemicals. For polymerization, conc. HCl (35.4 %, AR, sp. gr.1.18) was diluted to 1M solution.

Polyaminobenzene sulfonic acid synthesis and composite preparation

Poly (m-amino benzene sulfonic acid) (PABS) was synthesized by chemical oxidation in protic acid medium, using aniline as initiator (15 mole %). m- Amino benzene sulfonic acid normally does not participate in homopolymerization possibly due to deactivating and bulky SO_3H substituent in the phenyl system⁴⁸. [Poly (m- amino benzene sulfonic)] The preparation procedure was mentioned else where⁴⁹. (PABS) acid was water soluble conducting polymer. Previously prepared a known quantity of PABS was placed in stoppered pyrex tube and dissolved in distilled water. After that measured quantity of aniline dissolved in 1M HCl solution added dropwise to the reaction vessel. Stirring was done for 30 mins. After that a solution of $(\text{NH}_4\text{S}_2\text{O}_8)$ in HCl was added to the solution over a period of 30-40 min at 0 °C. The reaction mixture was stirred again for 3 h. Then total contents of flask were centrifuged at 18, 500 rpm and centrifugate was separated from the residue. This process was repeated at least four times to remove adhered $(\text{NH}_4\text{S}_2\text{O}_8)$. This procedure was expected to dissolve out all surface adsorbed ammonium persulfate. Table 1 summarizes the results of the preparations. The separated black mass was washed by methanol and finally dried at 60 °C for 5 h under vacuum.

Table 1 Experimental details for the preparation of the composite

Entry	Weight (g) in feed	Time	% Polymer	Conductivity
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No	PABS	PAN	(h)		(S/cm)
1.	0.15	0.10	4	68	1.9×10^{-4}
2	0.15	0.15	4	71	1.8×10^{-4}
3.	0.15	0.20	4	74	2.4×10^{-4}
4	0.15	0.25	4	75	2.5×10^{-4}
5	0.20	0.20	4	71	2.9×10^{-4}
6	0.25	0.20	4	68	2.1×10^{-4}
7	0.30	0.20	4	66	2.3×10^{-4}
8	0.35	0.20	4	62	2.2×10^{-4}

Viscosity measurement

Intrinsic viscosities were determined in 96% sulfuric acid at 30 °C using polymer concentration between 0.05 and 0.1 g/dl with an ubbelohde capillary viscometer. As the exact molecular weight distribution could not be determined due to the unavailability of necessary experimental facilities (including GPC) a qualitative assessment of the molecular weight of prepared polymer relative to polyaniline was effect, based upon the measurement of intrinsic viscosities (η_{int}) of these polymers.

D.C. electrical conductivity

Conductivity measurements were made by two-probe technique using a Philips RP 9500 Bridges and Keithley 177 Micro voltmeter at room temperature. The sample was in the form of compacted disk pellets, 0.3 cm in diameter and different thickness. Four measurements were used to assure constant resistance for each of sample.

Infrared spectroscopic analysis

The IR spectra of polymer in KBr pellets were recorded on a Perkin-Elmer (model-833) infrared spectrometer by optically zero balancing in the range $400-4000 \text{ cm}^{-1}$ using 2-4 mg dry powder.

Thermal stability

Differential thermal analysis and thermogravimetric analysis of the above composites were carried out using Shimadzu DT-40 unit under static air. A heating rate 10 °C/min was used

Scanning electron microscopic analysis

Scanning electron micrographs of the polymer samples were taken on cam scans 2 DV units with variation of magnification. Powder samples of the polymers were deposited on the stubs by ultrasonic dispersion and then gold coated for studying the morphology of the samples.

Transmission electron microscopic analysis

The particle size of the composite was determined by transmission electron microscopy using Hitachi 600 instrument.

Results and Discussion

Polyaminobenzene sulfonic acid synthesis and composite preparation.

The addition of (NH₄S₂O₄) solution to monomer solution was accompanied by a gradual color change of the system from greenish blue to black, indicating formation of polyaniline. In general, the formation composite increases with increase aniline/ PABS ratio. Conversely with increase in PABS concentration, the total conversion to the composite gradually decreases because it merely acts as a diluent of (NH₄S₂O₈) and reduces its effective concentration as initiator.^{50, 51}

Viscosity measurement

Table 2 Solubility and Viscosity data of Polymer

Solvent	Composite	η_{ins} at 30° C (dL/g)
NH ₄ OH	Ss	
H ₂ O	I	
C ₆ H ₆	Ss	
THF	ms	
DMF	ms	

DMSO	ms	
H ₂ SO ₄	s	0.35

All the polymer powder was completely soluble in polar solvent like NMP and DMSO. All the composites are soluble in conc. H₂SO₄ (96%). So the viscosity measurements were carried out in H₂SO₄. The intrinsic viscosity data qualitatively indicate that the newly formed composites have quite low molecular weight compared to polyaniline (0.57 dl/g), which showed much higher viscosity. This was expected because the steric effects and also the deactivating influence of the substitute retard chain growth.

D. C. electrical conductivity

The conductivity data of Table 1 revealed that PABS-PAN composite exhibited a dc conductivity of the order 1.3×10^{-4} S/cm, which was quite improved from PABS (8.5×10^{-5} S/cm). The sulfonic acid groups substituted on the benzene rings caused an increase in band gap and decreased the conductivity due to their strong electron withdrawing nature and high substitution resulting in large steric strain.

Infrared spectroscopic analysis

The representative infrared spectra of the polymer composites are shown in Figure 1. The bands appeared at $3400-3430 \text{ cm}^{-1}$ were assigned to characteristic N-H stretching vibration for amine/ imine nitrogen.

Table 3 Characteristic infrared stretching vibration

Sample	Stretching Modes (cm^{-1})				
	Quinoid	Benzoid	C-N	SO ₂	C-S
1.	1586	1490	1123	1020	613
2	1595	1595	1123	1030	619
3	1580	1489	1124	1029	612
4	1576	1488	1124	1012	612
5	1584	1494	1123	1016	612

The characteristic quinoid and benzoid stretching bands appeared in PAN at 1589 cm^{-1} and 1498 cm^{-1} . The curve exhibited a characteristic strong Quinoid absorption at 1586 cm^{-1} and weak benzenoid vibration at 1515 cm^{-1} . The IR spectra showed that with increasing proportion of aniline both quinoid and benzoid stretching shift towards lower frequency. Symmetric stretching vibration (PABS) of SO_2 displayed at 1170 and 1028 cm^{-1} and peaks at 693 and 616 cm^{-1} are assigned to the S-O and C-S stretching modes. The asymmetric stretching of SO_2 (1300- 1320 cm^{-1}) may overlap with characteristic C-N bond vibration (1307 cm^{-1}) of PAN. The relative intensity of benzoid to quinoid absorption peak cannot be used here as an index of oxidation, on account of the difference in position asymmetric S=O stretching of PABS in this region and their possible overlap with other peaks. The absorption at 875-883 cm^{-1} and 792-798 cm^{-1} for C-H out of plane bending vibration.

Thermal stability

Figure 2a, 2b and .2c represented typical weight loss versus temperature data poly (m-amino benzene sulfonic acid), Polyaniline and composite respectively. Thermal analysis pattern showed that the relative stability of the polymer composite, poly aniline and poly amino benzene sulfonic acid. First two stages of weight loss can be attributed to the expulsion of free and bonded water molecule and the morphological changes of molecule. The thermogram was exothermic over the entire range of analysis.

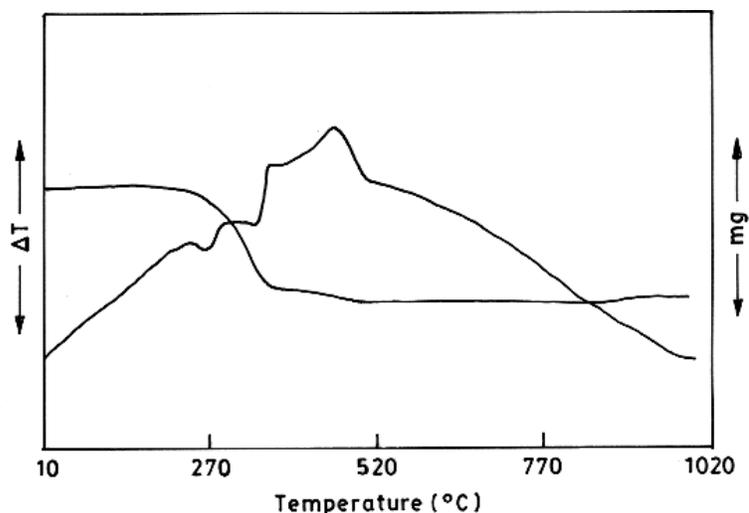


Figure 2a. TGA/ DTA diagram of m- amino benzene sulfonic acid.

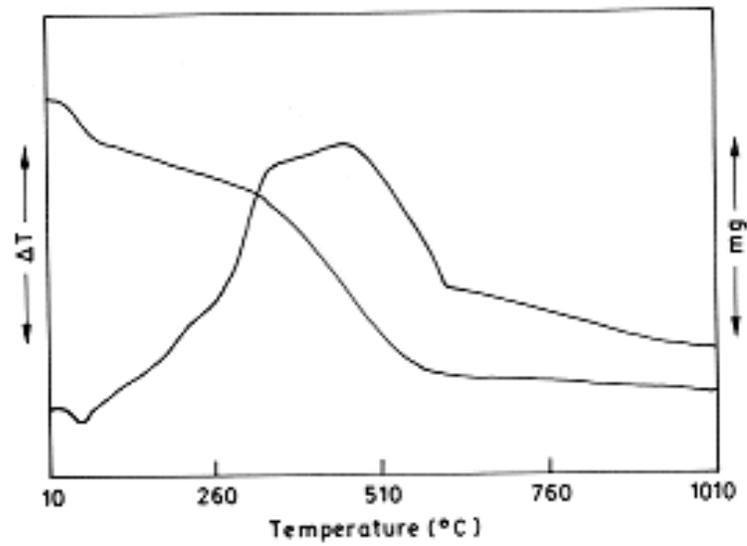


Figure 2b. TGA/ DTA diagram of poly aniline.

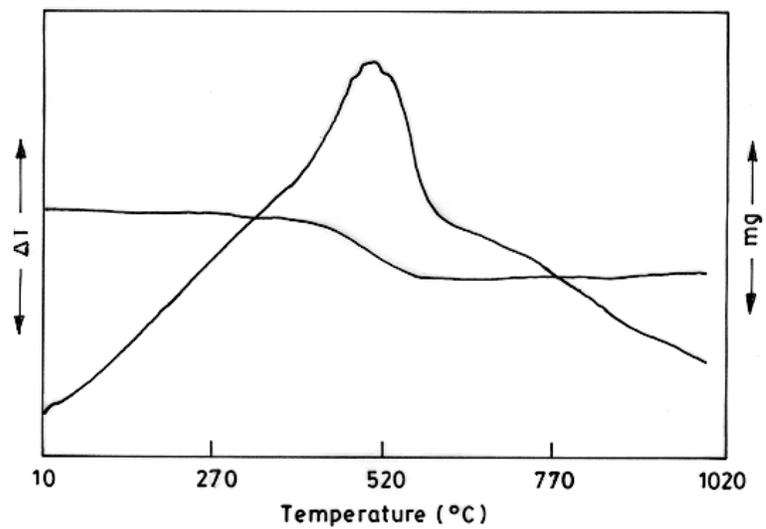


Figure 2 c Thermal diagram of composite

Table 4 Thermal analysis diagram of polymer composite

Sample	Mass Loss (%)			Range of decomposition
	Up to 200 ^o C	Up to 400 ^o C	Up to 600 ^o C	
PAN.	22	7-18	80	100-499
PABS	0.0	0-30	66	298-560
Composite-2	0.0	0-7	65	322-655
Composite-4	3-4	5-10	66	100-997

Such exothermic behaviour of the composite has been attributed to cross linking of polymer chain and rearrangement and degradation of side chain. And the final weight loss (Table 4) was due to the thermal degradation of the polymer backbone. The thermal analysis data did not indicate any pronounced stability difference between two composites (having different proportion of two polymers). Though they were more stable than that of PAN and PABS as indicated by their decomposition temperatures. The PABS-PAN composite showed maximum thermal stability. It exhibited highest decomposition temperature and low weight loss prior to the final degradation. The final stage of thermal degradation took place in different stages. The thermal changes prior to final decomposition were likely to be a composite of a number of events including loss of water (Endothermic), H-bonding (Exothermic) bond rupture, cross linking, rearrangement and degradation of side chains (exothermic). The significant thermal stability of the composite may be rationalized. The experimental results at the present level however do not warrant a detailed explanation.

Scanning electron microscopic analysis

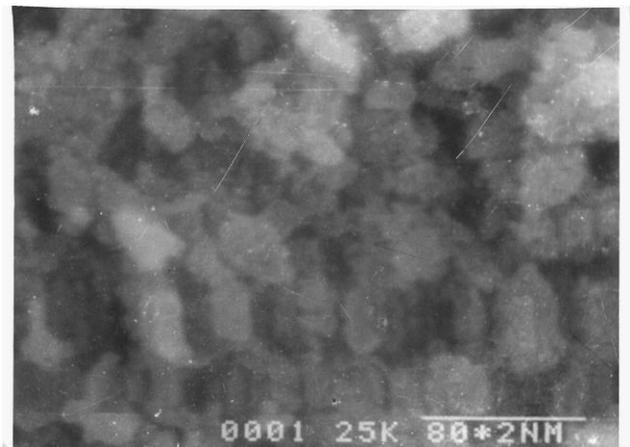
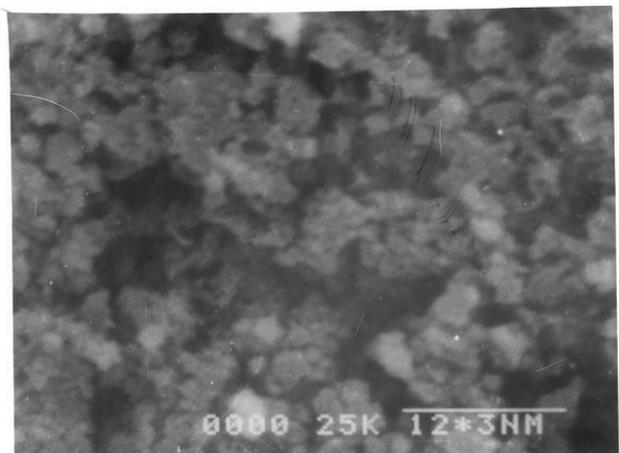


Figure. 3 SEM micrograph of composites

The SEM photographs (Figure .3) showed typical features for above-mentioned composites. They were mainly composed of irregularly arranged rhombohedral blocks with sharp edge and interspersed with smaller granular form. Simultaneously the structure looks more porous.

Transmission electron microscopic analysis

Figure 4 presented two typical TEM micrographs of this composite. The lighter region in the background of the TEM picture was due to polyaniline particle and the darker region was due to poly (m-amino benzene sulfonic acid) particles. The average particle diameter for the composite as calculated from the TEM photographs was 70nm respectively.

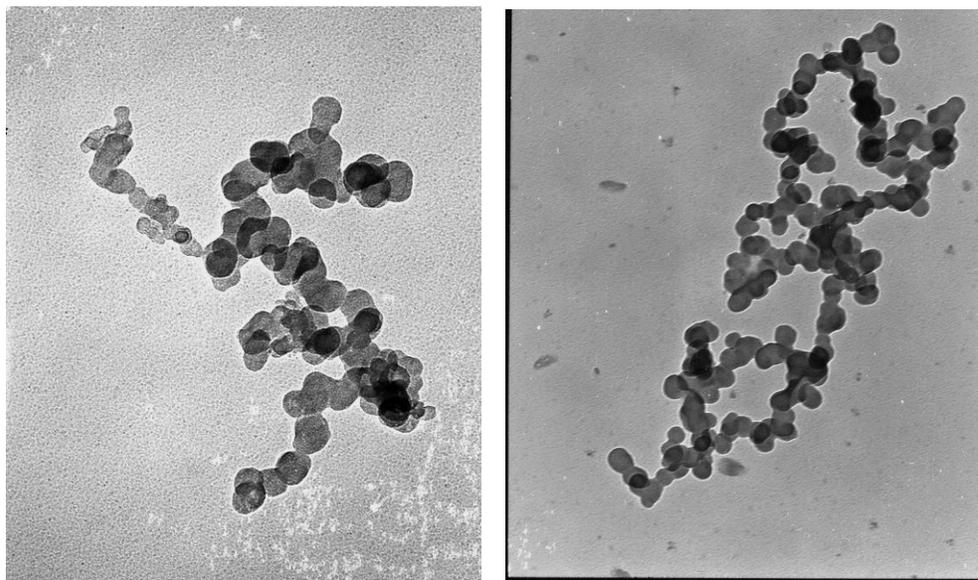


Figure 4. TEM picture of PABS-PAN composite

Conclusion

We present a simple method of preparation of polyaniline and poly (4-aminobenzenesulphonic acid) by oxidative polymerization protocol. Composites are consistent as per IR, DSC, SEM and TEM data.

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