Chemical Synthesis of Conductive Poly(methoxyaniline) in Hydroxyethylidenediphosphonic Acid

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The poly(orthomethoxyaniline)-hydroxyethylidenediphosphonic acid salt has been prepared by chemical polymerization method. It was characterized by UV-visible, infrared spectroscopy, thermogravimetric analysis and conductivity measurements. The solubility tests were also performed at room temperature for the doped and dedoped polymers in different solvents. The morphology of the polymer samples was studied by scanning electron microscopy monographs.

Key Words: Poly(*o*-methoxyaniline), Hydroxyethylidenediphosphonic acid, Doping, Electronic spectra, Electrical conductivity.

INTRODUCTION

Now-a-days electrically conducting organic polymers have attracted much attention in both science and technology. They also have numerous practical applications. Polyaniline is one such polymer whose synthesis does not require any special equipment of precausion and its has excellent environmental stability in the conducting form. The electrical conductivity of the polyaniline and substituted polyanilines is controlled through both oxidation and protonation[1-4]. The process doping distinguishes the polyaniline from other of polymer[5]. The ratio of amine to imine forms yields various structures to the polymer. Unlike other phenylene based conducting polymer[6-9], it has chemically flexible N-H group in its backbone and responsible for its interesting physical and chemical properties[10].

The present work is undertaken: (a) To synthesize the conducting polymer (both doped and dedoped polymer) using hydroxyethylidenediphosphonic acid by chemical polymerization method; (b) To characterize the synthesized conducting polymers by FT-IR spectra and UV-visible study; (c) To study the thermal properties of the polymers by thermal analysis; (d) To determine the molecular weight of the polymers by gel-permeable chromatographic method; (e) To measure the conductivity of the polymer samples by four probe technique; (f) To study the morphology of the polymers by scanning electron microscopy; and (g) To compare the solubility of doped and dedoped polymers in the solvents DMSO, NMP, toluene, $CHCl_3$ and ethanol.

EXPERIMENTAL

ortho-Methoxy aniline and dimethyl sulfoxide were distilled under vacuum and kept under nitrogen atmosphere in the dark. All other chemicals were AnalaR grade. Hydroxyethylidenediphosphonic acid was purchased from Merk (98 %).

Chemical polymerization of POMA-HEPA salt: Ice cooled 0.1 M aqueous solution of ammonium peroxydisulphate is added dropwise to a stirred ice cold 0.1 M solution of *o*-methoxyaniline dissolved in 1 M aqueous hydroxyethylidenediphosphonic acid pre-cooled to 0-5 ℃. Ammonium peroxydisulphate solution is added slowly to prevent the warming of the solution. After completion of the addition (0.5 h), stirring is continued for 2 h to ensure completion of the reaction. The precipitated POMA-HEPA salt (doped polymer) is filtered and washed repeatedly with distilled water until the filtrate is colourless. Finally the polymer is again transferred to a beaker containing 1 M aqueous solution of a hydroxy-ethylidenediphosphonic acid. After keeping overnight, the precipitates are filtered and dried 80 ℃ under reduced pressure to constant weight.

The freshly prepared doped polymer was dedoped using 1 % aqueous sodium hydroxide solution. A known amount of the doped polymer was added to sodium hydroxide solution and stirred for 6 h at room temperature and left overnight. The blue dedoped polymer (emeraldine base) was filtered, washed thoroughly with distilled water and dried at room temperature

for 24 h. Final drying was completed at 80 °C under reduced pressure to constant weight.

Characterization of doped and dedoped polymer was carried out after thorough washing with distilled water and methyl alcohol and drying under dynamic vacuum for 8 h at 65 °C. The absorption spectra of the doped and dedoped polymers in DMSO solution were recorded using Hitachi-U-3400 UV-VIS near -IR spectrophotometer in the range of 250 to 1500 nm. Infrared spectra in KBr pellets were recorded in the 4000 to 400 cm^{-1} range on a Toshniwal-Simadzu FT-IR spectrophotometer 8000 series. Thermogravimetric analysis was 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. The conductivity of the polymer sample was measured by four probe technique (Scientific Equipment Model No. DFP-02). The polymer samples were pressed into pellets of 1 cm diameter at 3-ton pressure. The solubility of the doped and dedoped polymer was measured in different organic solvents at room temperature. The polymer samples were dissolved in tetrahydrofuran and the molecular weight was determined on a SIMADZU Gel Permeation Chromatography (GPC/LC-6A) equipped with two STYRAGEL columns and a differential refractometer detector. The morphology of the polymer was studied by scanning electron microscopic studies using SEM: Hitachi Model S-3000 H.

RESULTS AND DISCUSSION

UV-VIS-NIR spectroscopic studies: The electronic spectra of doped polymer (POMA-HEPA) chemically synthesized in DMSO and ethanol are shown by curves a and b respectively in Fig. 1. A DMSO solution of chemically synthesized POMA-HEPA shows absorption peaks at 306 nm and 559 nm, whereas an ethanolic solution of chemically synthesized POMA-HEPA shows absorption peaks at 317 nm and 532 nm.
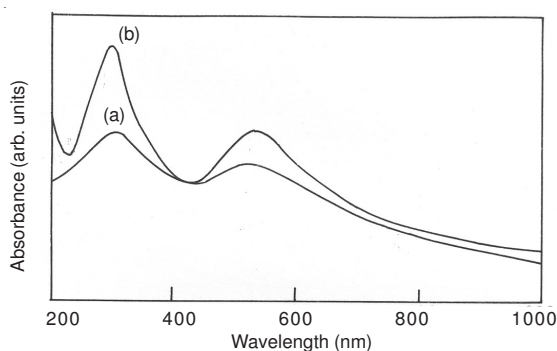

Fig. 1. UV-VIS-NIR solution absorption spectra; (a) Chemically synthesized doped polymer in C$_2$H$_5$OH; (b) Chemically synthesized doped polymer in DMSO

The electronic spectra of emeraldine base (EB) chemically synthesized in DMSO and ethanol are shown by curves a and b, respectively (Fig. 2). A DMSO solution of emeraldine base shows absorption peaks at 337 nm and 640 nm, whereas an ethanol solution of dedoped polymer shows absorption peaks at 320 nm and 637 nm. The λ$_{max}$ observed in the UV-VIS-NIR spectral studies of doped and dedoped polymer are given in Table-1.
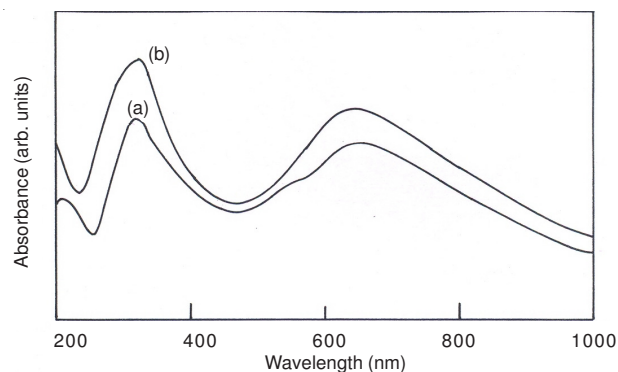

Fig. 2. UV-VIS-NIR solution absorption spectra; (a) Chemically synthesized dedoped polymer in C$_2$H$_5$OH; (b) Chemically synthesized dedoped polymer in DMSO

TABLE-1
ELECTRONIC SPECTRA OF DOPED AND DEDOPED POLYMER

S. No.	Polymer	Solvent		Assignments
		DMSO	C$_2$H$_5$OH	
1.	Doped polymer (POMA-HEPA)	306	317	π- π* Transition in benzenoid ring
		559	532	Cation radicals
2.	Dedoped polymer	337	320	π- π* Transition in benzenoid ring
		640	637	Cation radicals

The absorption peaks observed between 306 nm to 337 nm is assigned due to π-π* transition associated with benzenoid ring. The peak due to cation radicals lies between 532 nm to 640 nm. The electronic spectra of the doped and dedoped polymer show the blue shift to π-π* transition and red shift to cation radicals on adding dopant.

FT-IR spectroscopic studies: The principle absorption bands observed in the FT-IR spectra in the region of 4000-400 cm^{-1} for doped and dedoped polymer are presented in Fig. 3a and 3b. Table-2 gives the possible assignment of these IR bands. The bands at 1030 cm^{-1} is assigned to the symmetric PO$_4^{3-}$ stretching, and are the characterisitic bands of a phosphate group, present in the dopant. The band at 813 cm^{-1} indicates that there is a head to tail coupling in a polymer that is to say that monomeric units are linked at 1,4-position. This band shifts to 837 cm^{-1} in an dedoped polymer, indicating the strong influence of dopant on C-H$_{oop}$ vibration.
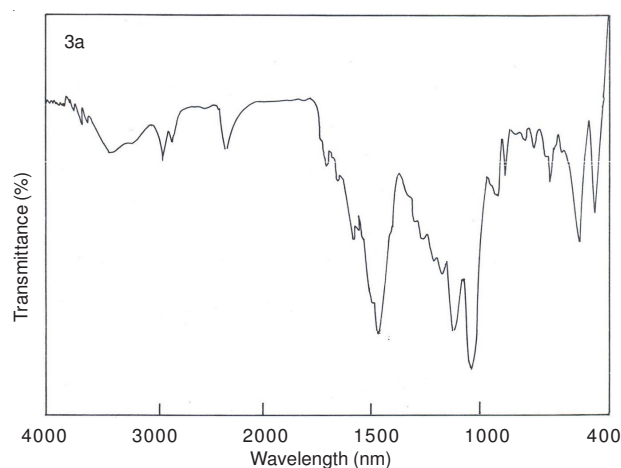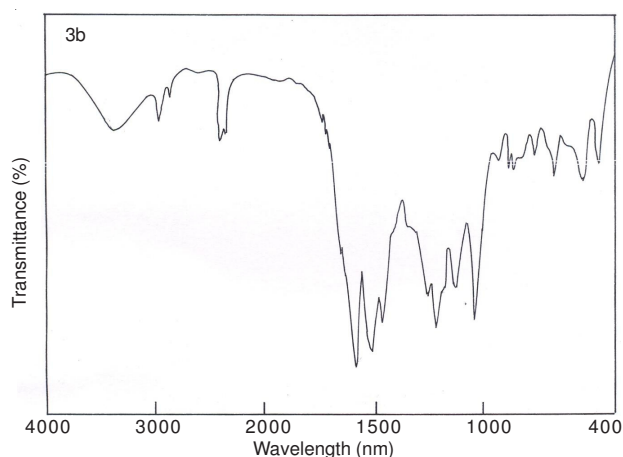

Fig. 3a. FT-IR Spectra of doped polymer

Fig. 3b. FT-IR Spectra of dedoped polymer

TABLE-2
FTIR SPECTRAL BANDS (cm^{-1}) OF DOPED
AND DEDOPED POLYMER

Doped polymer (POMA-HEPA)	Dedoped polymer (EB)	Assignments[a]
814	837	C-H$_{oop}$ of 1,4 ring
1030	-	Dopant –charge
1115	-	C-H$_{ip}$ on 1,4 ring
1225	1327	-C-N str
1460	1511	Str of N-B-N
1579	1591	-C-C str, str of N = Q = N
2854	2980	C-H aromatic
3400	3382	NH$_2$ sym str, NH str in B-NH-B

Thermal analysis: The thermal analysis of a polymer is crucial to define its performance during application. For conducting polymers[11-13] in particular, the deterioration of conductivity at temperatures above room temperature is a key factor to determine its potential application. Fig. 4a and 4b, show the thermogravimetric curves of the poly(*o*-methoxyaniline) doped with HEPA and emeraldine base (dedoped form).

Fig. 4a shows the TGA curve of the doped polymer (POMA-HEPA). It can be seen that the doped polymer is thermally less stable than the dedoped polymer. The first weight loss of *ca.* 2.5 % is obtained upto 100 ºC (due to loss of moisture), the second weight loss *ca.* 24 % is observed between 229 ºC and 324 ºC, which is equivalent to the weight of the dopant. The final degradation of polymer starts from 348 ºC and complete degradation occurs around 650 ºC. The thermogravimetric analysis of emeraldine base (dedoped) (Fig. 4b) indicates negligible weight loss *ca.* 2% up to 442 ºC. The degradation of emeraldine base starts from 448 ºC and complete degradation occurs around 774 ºC. The stability of a doped state becomes the function of dopant (counter ion) present.

Conductivity measurements: The conductivity of POMA-DTPA was found to be 0.9 S/cm at the 44 % doping level. The conductivity of POMA depends on the nature of the dopant, its orientation, electronegativity, functionality, purification, methods of synthesis, doping level and the process of doping. The dedoping process decreases the conductivity of the polymer due to decrease in number of carriers, the conductivity of the dedoped polymer was found to be in the order of 10^{-9} S/cm.
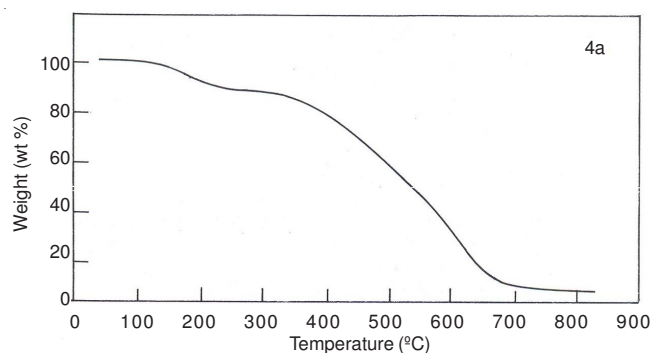

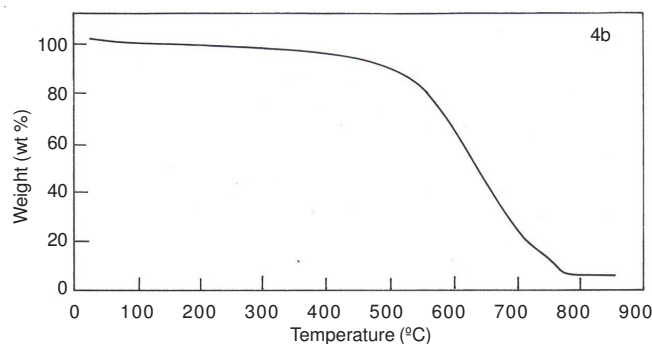Fig. 4a. TGA curve doped polymer

Fig. 4b. TGA curve dedoped polymer

Solubility of polymer: Solvation of polyaniline is a result of a number of interactions between polymer dopant and solvent. The change in structure is also possible due to restructuring of the solvent in the presence of ions. Born-type solvation depends on the dielectric constant of the solvent. Most dipolar aprotic solvents have dielectric constants in the range 35-50, resulting in a fairly constant contribution from the electrostatic ion-solvent interaction. Consequently, the other interactions assume greater importance in determining the relative stability of the system. Dipolar aprotic solvents are poor hydrogen bond donors because they do not contain hydrogen bonded to an electronegative atom. *i.e.*, oxygen or nitrogen. This is because the molecular polarizability of dipolar aprotic solvents is greater than that of water and other protic solvents and the solvent are able to interact with a large macromolecule such as polyaniline (Table-3).

TABLE-3
SOLUBILITY MEASUREMENT OF POLYMERS
IN SELECTED SOLVENTS

S. No.	Polymer	Solubility (g/L)				
		DMSO	NMP	Toluene	CHCl$_3$	Ethanol
1.	Doped	7.3	6.2	5.3	1.8	1.8
2.	Dedoped	9.6	9.1	7.6	7.9	1.8

In the present case the solubility of the polymer was determined in five different organic solvents. Among the organic solvents tried, a maximum solubility was found in DMSO solvent. This can be explained by the ability of sulphoxide group of DMSO to interact electrostatically with the dopant attached to the polymer.

Molecular weight determination: The molecular weight of the doped polymer was determined as 12650.

Scanning electron microscopy analysis: The SEM micrograph of doped and dedoped polymer are shown in Fig. 5a and 5b. The porous globular sponge like structure shown in the figure 5a represents the SEM monograph of polyaniline doped with HEPA. The white spherical globes represent the dopants attached to the polymer chain and are responsible for the electrical conductivity of the doped polymers. The SEM monograph of dedoped polymer shown in the figure 5b reveals complete removal of the dopants from the polymer chain and hence exhibits less electrical conductivity.
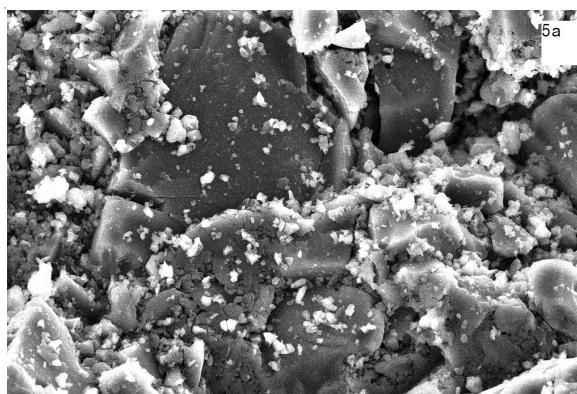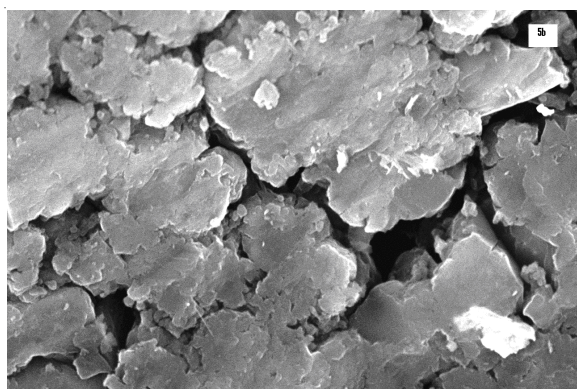
Fig. 5a. SEM micrograph of doped polymer

Fig. 5b. SEM micrograph of dedoped polymer

Conclusion

POMA-HEPA salt (doped polymer) has been synthesized from aqueous hydroxyethylidenediphosphonic acid medium.

The characterization by using IR and electronic spectra shows the formation of poly(*o*-methoxyaniline). The TGA study shows that the thermal stability of the polymer depends on the counter ions. Both doped and dedoped polymers show maximum solubility in DMSO. The dedoped polymer has more solubility than the doped polymer in DMSO. So the processability of the polymer made easy. Since both doped and dedoped polymers are soluble in ethanol, they can also be used as corrosion inhibitors.

Abbreviations

POMA	:	Poly(orthomethoxyaniline)
HEPA	:	Hydroxyethylidenediphosphonic acid
POMA-HEPA	:	Poly(orthomethoxyaniline) doped with hydroxyethylidenediphosphonic acid
EB	:	Emeralidine base (dedoped polymer)

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