



Synthesis and Characterization of Poly(*o*-methoxyaniline)

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Poly(*o*-methoxyaniline) was prepared chemically from the monomer *o*-methoxyaniline using 2-chloroethylphosphonic acid. It was characterized by UV-visible, IR and TGA methods. The solubility tests were performed at room temperature for the doped and dedoped polymers in different solvents. The conduction of the polymer samples were determined at room temperature. The morphology of the polymer samples was studied by scanning electron microscopy.

Key Words: Poly(*o*-methoxyaniline), 2-Chloroethylphosphonic acid, Electronic spectra, Conducting polymer, Doping, Electrical conductivity.

INTRODUCTION

Conducting polymers have become foci in polymer science and material science due to their many known and envisaged technological applications, such as energy storage^{1,2}, electromagnetic interference (EMI) shielding^{3,4} electrochromic devices and sensors^{5,6}. Polyaniline has been categorized as an intractable material which is neither soluble nor fusible under normal conditions. The material is generally poorly ordered and its morphology is determined by the history of its synthesis. However, the polyaniline is difficult to process because it is insoluble in common organic solvents and is unstable at melt processing temperatures. These properties limit its applications. Several ring and N-substituted polyanilines which are soluble in common organic solvents have been prepared directly from polymerization of the corresponding aniline monomers⁷⁻¹¹. The incorporation of the side groups into the polyaniline has increased its solubility and processability and changed its properties. The present study aims at synthesizing poly(*o*-methoxyaniline) doped with 2-chloroethyl phosphonic acid (CEPA), its spectral characterization, solubility and its thermal stability.

EXPERIMENTAL

Chemical polymerization of POMA-CEPA 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 2-chloroethylphosphonic acid pre-cooled to 0-5 °C. 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-CEPA salt (doped polymer) is filtered and washed several times with distilled water until the filtrate is colourless. Finally the polymer is again transferred to a beaker containing 1 M aqueous solution of 2-chloroethylphosphonic acid. After keeping overnight, the precipitate is filtered and dried at 80 °C under reduced pressure to constant weight.

The freshly prepared doped polymer was dedoped using 1 % aqueous ammonium hydroxide (NH₄OH) solution. A known amount of the doped polymer was added to NH₄OH 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 polymer: 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 following methods were used for the characterization.

Electronic spectra: 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 250-1500 nm.

Infrared spectra: Infrared spectra in KBr pellets were recorded in 4000-400 cm⁻¹ range on a Toshniwal-Shimadzu FT-IR spectrophotometer 8000 series.

Thermal analysis: 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.

Conductivity measurements: 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.

Solubility measurements: The solubility of the doped and dedoped polymers was measured in different organic solvents at room temperature (Table-3).

Molecular weight determination: The polymer samples were dissolved in tetrahydrofuran (THF) and the molecular weight was determined on a Shimadzu gel permeation chromatography (GPC/LC-6A) equipped with two Styragel columns and a differential refractometer detector.

Scanning electron microscopy studies: 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: A DMSO solution of chemically synthesized (POMA-CEPA) shows absorption peaks at 383 and 610 nm, whereas an ethanol solution of the same shows absorption peaks at 375 and 656 nm. The λ_{max} observed in the UV-vis-NIR spectral studies of doped polymer is given in Table-1.

S. No.	Polymer	Solvent		Assignments
		DMSO	C ₂ H ₅ OH	
1	Doped polymer (POMA-CEPA)	383	375	π - π^* transition in benzenoid ring Cation radicals
		610	656	
2.	Doped polymer (EB)	337	320	π - π^* transition in benzenoid ring Cation radicals
		640	637	

The absorption peaks observed between 320-383 nm is assigned to π - π^* transition associated with benzenoid ring. The peak due to cation radicals lies between 610-640 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: Infrared spectroscopy is a powerful tool to determine the structural changes that occur during doping-dedoping process. It has been shown that the absorption frequencies are strongly influenced by the dopant¹²⁻¹⁶. Table-2 showed the key assignments of IR bands. The bands at 1021 cm⁻¹ is assigned to the symmetric PO₄³⁻ stretching and are the characteristic bands of a phosphate group, present in the dopant. The band at 774 cm⁻¹ indicates that there is a head to tail coupling in the polymer that is to say that monomeric units are linked at 1,4-position. This band shifts to 837 cm⁻¹ in dedoped polymer, indicating the strong influence of dopant on C-H_{oop} vibration.

Thermal analysis: Gupta and Umare¹⁷ have reported that the thermal stability of doped poly(*o*-methoxyaniline) strongly

Frequency (cm ⁻¹)		Assignments*
Doped polymer (POMA-CEPA)	Dedoped polymer (EB)	
774	837	C-H _{oop} of 1,4 ring
1021	—	Dopant -charge
1121	—	C-H _{ip} on 1,4 ring
1254	1327	-C-N str.
1493	1511	Str. of N-B-N
1581	1591	-C-C str., str. of N = Q = N
2963	2980	C-Haromatic
3452	3382	NH ₂ sym str., NH str. in B-NH-B

*Abbreviations: sym = symmetric, str. = stretching, ip = in-plane bending, op = out of plane bending, Q = quinoid unit, B = Benzenoid unit.

depends upon counter ion. Fig. 1(a-b), show the thermogravimetric curves of the poly(*o*-methoxyaniline) doped with 2-chloroethylphosphonic acid and emeraldine base (dedoped form).

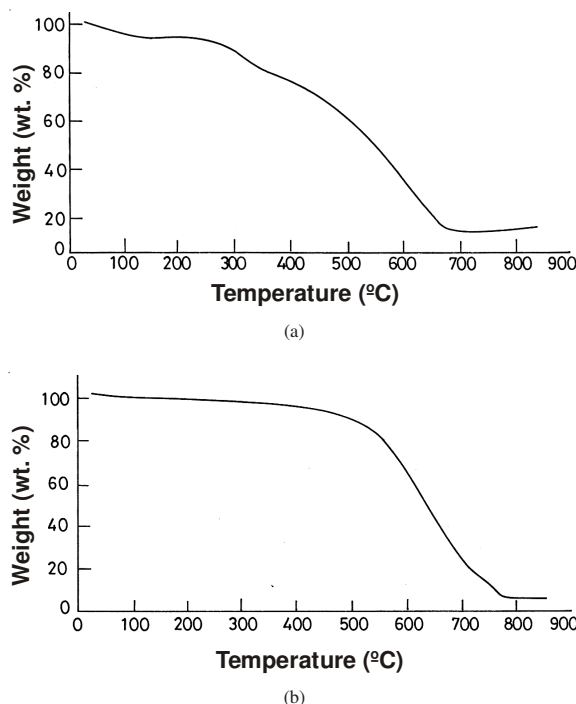
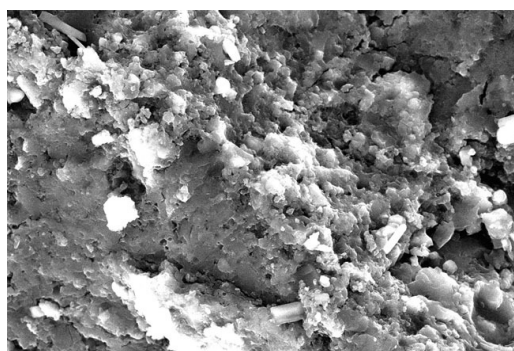


Fig. 1. TGA curve of POMA (a) doped polymer (b) dedoped polymer

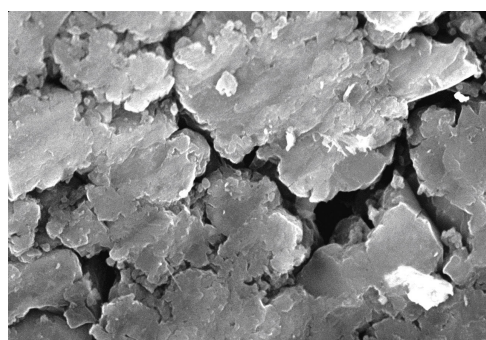
Fig. 1a shows the TGA curve of the doped polymer (POMA-CEPA). It is observed that the doped polymer is thermally less stable than the dedoped polymer. The first weight loss of ca. 4.5 % is obtained upto 100 °C (due to loss of moisture), the second weight loss ca. 21 % is observed between 236 and 345 °C, which is equivalent to the weight of the dopant. The final degradation of polymer starts from 360 °C and complete degradation occurs around 663 °C. The thermogravimetric analysis (TGA) of emeraldine base (dedoped) (Fig. 1b) indicates negligible weight loss ca. 2 % up to 442 °C. The degradation of emeraldine base starts from 448 °C and complete degradation occurs around 774 °C. The stability of a doped state becomes the function of dopant (counter ion) present.

Conductivity measurements: The conductivity of POMA-CEPA was found to be 0.7 S/cm at the 43 % 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. The molecular weight of the polymer is 12,346.

Scanning electron microscopy analysis: The SEM micrograph of doped and dedoped polymer are shown in Fig. 2(a-b). The porous globular sponge like structure shown in the Fig. 2a represents the SEM monograph of polyaniline doped with CEPA. The white spherical globes represent the dopants attached to the polymer chain which are responsible for the electrical conductivity of the doped polymers. The SEM monograph of dedoped polymer shown in the Fig. 2b reveals complete removal of the dopants from the polymer chain and hence exhibits less electrical conductivity.



(a)



(b)

Fig. 2. SEM micrograph of POMA (a) doped polymer (b) dedoped polymer

Conclusion

Poly(*o*-methoxyaniline) has been synthesized from aqueous 2-chloroethylphosphonic 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. The dedoped polymer has more solubility than the doped polymer in DMSO (Table-3). So the processability of the polymer is made easy. Since both doped and dedoped polymers are soluble in ethanol, they can also be used as corrosion inhibitors.

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	1.6	1.6
2	Dedoped	9.6	9.1	7.6	7.9	1.8

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