

Synthesis and Characterization of the Conducting Polymer- Poly(p-phenylenediazomethine)

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Abstract

In the present study, a new conducting polymer based on glyoxal and p-phenylene diamine was synthesized in different solvents like methanol, toluene, DMF and m-cresol. The polymer was characterized by IR spectra, U.V Spectra, GPC and TGA. The effect of solvents on the degree of polymerization and hence on d.c. conductivity was studied. The effect of dopants like HClO₄, HCl and I₂ on conductivity of each sample was measured. The d.c. conductivity of the samples increased on doping with HCl, HClO₄ and Iodine. The polymer was found to be stable up to about 400°C. The density and thermal diffusivity of the pressed pellet were also determined.

Key Words: Conducting polymers, Doping, IR spectra, GPC, TGA, conductivity, density and thermal diffusivity

I. INTRODUCTION

Conducting polymers offer two potential advantages over the traditional inorganic materials used as conductors. First, processing of conducting polymers by moulding and other plastics processing techniques into various electrical and electronic devices and forms is easy compared to metallurgical processes used for inorganic conducting materials. Second, the lightweight property of polymeric materials would make certain types of applications more practical and economical. The biggest and most immediate potential application for conducting polymers is in lightweight rechargeable batteries for portable tools and vehicles. Conducting polymers would serve both current carrying and ion- conducting functions by replacing traditional electrode and electrolyte substances [3,5,6,7].

The structural requirement for a conducting polymer is a conjugated π electron system. Extended conjugation in the polymer backbone is attained in two ways, either by the interaction of electrons of the conjugated carbon- carbon double bonds or by the interaction of electrons of carbon-carbon double bonds with nonbonding electrons of heteroatoms, such as S, N, P, etc. present in the polymer chain. They can be easily oxidised or reduced by charge -transfer agents, which are called dopants. Electrons are removed from (p-doping) or added to (n-doping) the conjugated pi-electron system to form extra holes or electrons, respectively, which carry current through the polymer chain. In addition to oxidation or reduction, the dopants act as a bridge or connection for carrying current between different polymer chains [1,8].

Poly (azomethine)s, sometimes called poly(schiff bases), are a group of polymers which are catching more attention due to the following reasons. Aromatic poly(azomethine)s are highly thermo-stable in analogy to aromatic polyethers. Furthermore, poly (azomethine)s may possess a conjugated main chain and, after suitable doping, may show an attractive level of electric conductivity. Only a few poly (azomethine)s derived from aliphatic dialdehydes and aromatic diamines were described in literature, and most of them were prepared by solution condensation of diamines and glyoxal. High yields and satisfactory elemental analyses were reported, but no information on viscosity and molecular weights [2,4].

In the present study, a new conducting polymer based on glyoxal and p-phenylene diamine was synthesized. The synthesis of poly(p-phenylenediazomethine) was carried out in DMF. In-situ polymerization of glyoxal and p-phenylenediamine was done in DMF containing different amounts of PE. The d.c. conductivity and the effect of dopants like HClO₄, HCl and I₂ on conductivity of each sample was measured.

II. MATERIALS AND METHODS

2.1 *Materials*

p-phenylene diamine, Glyoxal hydrate (trimer), N,N-Dimethyl formamide (DMF), Toluene, Methanol, m-cresol, Hydrochloric acid (HCl), Perchloric acid (HClO₄), Iodine (I₂), acetone and CCl₄ was used in the present investigation.

2.2 *Synthesis of poly(p-phenylenediazomethine) in methanol*

0.1 mole of p-phenylene diamine was dissolved in methanol (300ml) and 0.1 mole glyoxal (40% solution) was added drop wise with continuous stirring for 2 hours. By that time, precipitation of the product takes place. The product was washed with water and then with methanol and dried well at room temperature under vacuum.

2.3 *Synthesis of poly(p-phenylenediazomethine) in toluene*

0.1 mole of p-phenylene diamine was added to 400 ml of toluene and was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling with continuous stirring, and was refluxed at the boiling temperature for 5 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colorless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at under vacuum

2.4 *Synthesis of poly(p-phenylenediazomethine) in m-cresol*

0.1 mole of p-phenylene diamine was added to 100 ml of m-cresol and was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. The precipitate was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 700⁰C under vacuum.

2.5 *Synthesis of poly(p-phenylenediazomethine) in N,N-dimethylformamide*

0.1mole of p-phenylene diamine was added to 300 ml of DMF and was dissolved by stirring. Then 0.1 mole of glyoxal was added to it and stirred well. The mixture was slowly heated to boiling, with continuous stirring, and was refluxed at the boiling temperature for 4 hours. By that time, the precipitation of the product takes place. It was then allowed to cool to room temperature and then poured into excess of ice-cold water. It was allowed to settle, filtered, washed with plenty of water until the filtrate was colourless. Then it was washed with methanol, and allowed to dry at room temperature in air for one day. Then the final drying of the sample was done at 700⁰C under vacuum.

The dried samples were powdered well, and, pelletized for the density and conductivity measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and dried well.

2.6 *Doping*

1g of each sample was put in 50ml each of 1M HCl solution, 1M HClO₄ solution and saturated solution of I₂ in CCl₄ and kept for 24 hours. Then it was filtered, washed with a little amount of acetone and dried at 700⁰ C under dynamic vacuum for one hour.

2.7 *Polymer Characterization*

The prepared polymer samples were characterized by IR spectra, U.V Spectra, TGA, and Molecular weight determination (GPC).

2.8 *Measurements*

2.8.1 *D.C. conductivity*

D.C. conductivity of the pressed pellets was determined by the two-probe technique.

2.8.2 *Density*

Density of the pressed pellets were determined using the equation, $D = M/V$, where 'M' is the mass of the pellet and 'V' is the volume of the pellet.

2.8.3 *Thermal diffusivity*

Thermal diffusivity was determined by photo acoustic technique.

III. RESULTS AND DISCUSSION

3.1 *IR spectra*

IR spectra of the polymer prepared in different solvents are given in the figure 1-4. The absorption band at 1678 cm⁻¹ should be assigned to carbonyl absorption, possibly carbonyl of an amide group. The absorption band at 3306 cm⁻¹ should be ascribed to a N-H stretching vibration. In literature the absorption of the — C=N group is found between 1675 and 1660 cm⁻¹. However, if it is conjugated to an aromatic ring it shifts to a lower wave number, between 1635 and 1625 cm⁻¹. The absorption bands at 1517 and 1609 cm⁻¹ shows the presence of an aromatic ring. The absorption band at 833 cm⁻¹ can be assigned to the C-H out of plane vibration of the aromatic ring.

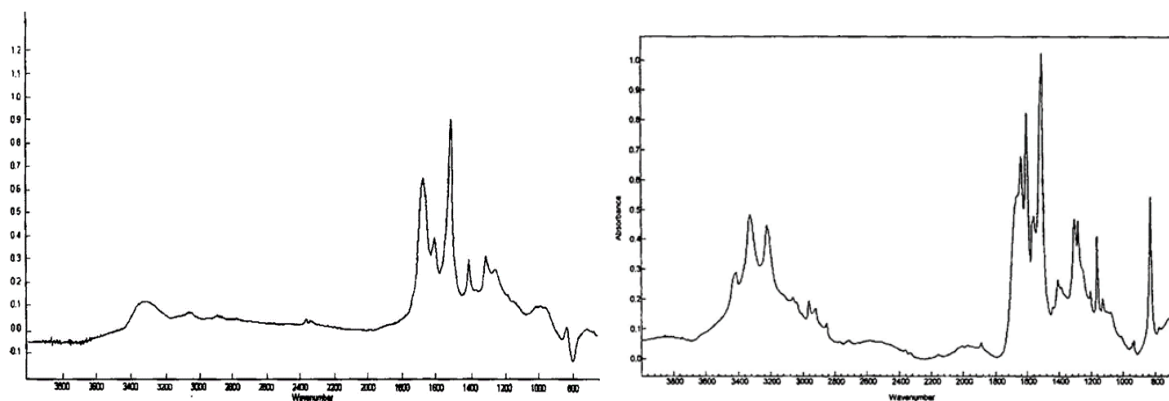


Fig. 1 IR spectra of the polymer prepared in Methanol **Fig. 2** IR spectrum of the sample prepared in Toluene

Figure 2 shows the IR spectra of the sample prepared in toluene. This spectrum shows various spectra! bands, which also occurs in the spectrum of p-phenylene diamine such as the bands at 3328, 3221, 1855, 1639, and 1130cm-1 . From the spectrum, it may be concluded that the reaction was not completed in toluene solvent, hence the molecular weight of the product was very low, and hence the conductivity also was very low. Figure 3 shows the spectrum of the polymer prepared in DMF. The absorption band at 1639 cm' I disappeared and a new band at 1625 cm-1 was present, which can be assigned to the —C=N- stretching vibration. Various spectral bands due to the presence of unreacted monomers disappeared in the spectrum of the polymer prepared in DMF.

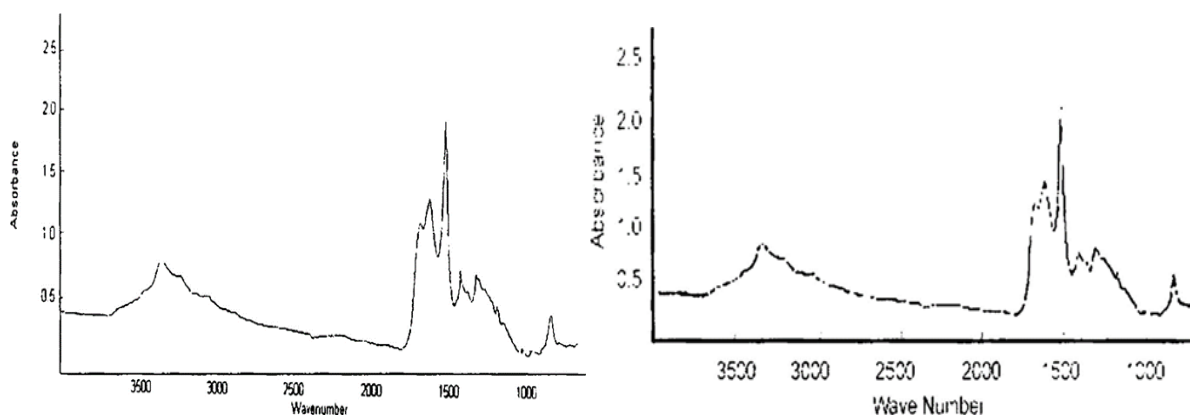


Fig. 3 IR spectrum of the sample prepared in DMF **Fig. 4** IR spectrum of the sample in m-cresol

Effect of doping on the structure of the polymer was clear from the IR spectrum. Figure 5 shows the IR spectrum of the polymer doped with HCl. The additional peaks at 1016, 1124, and 1203 cm⁻¹ can be assigned to be present due to the charge delocalization on the polymer backbone. Broad peak in the region of 2500 - 2800 cm⁻¹ was due to protonation on the polymer chain. Other peaks present in the spectrum were same as that present in the undoped polymer.

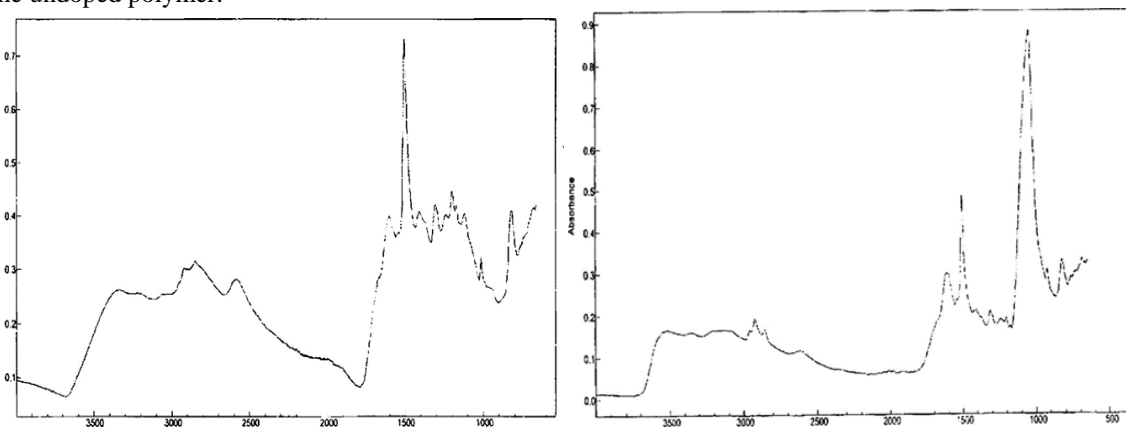


Figure 5 IR spectrum of the polymer doped with HCl.**Fig.6** Polymer doped with HClO4

Figure 6 shows the IR spectrum of the polymer doped with HClO_4 . The additional peaks at 1056 cm^{-1} can be assigned to be present due to the charge delocalization on the polymer backbone. Broad peak in the region of 3200 cm^{-1} was due to protonation on the polymer chain. The peak at 3300 cm^{-1} of the undoped polymer had been shifted to 3500 cm^{-1} . Other peaks present in the spectrum were same as that present in the undoped polymer as given in figure 1.

On comparing the two spectra, from the intensity of the additional peaks due to the dopant molecules, we can say that HClO_4 is a more stable dopant than HCl . The absorption bands at 1408 cm^{-1} and 1511 cm^{-1} due to the quinoid and benzenoid rings attached to N atom in the undoped polymer are shifted to 1410 and 1505 cm^{-1} and 1413 and 1508 cm^{-1} respectively for HCl and HClO_4 doped samples.

3.2 GPC

The molecular weight of the polymer was determined using Hexafluoroisopropanol as the eluent. Gel permeation chromatogram is shown in the figure 7. GPC distribution plot is given in Figure 8 and the results are given in Table 1. The number average molecular weight of the polymer was 25660 and the weight average molecular weight was 69123. The result shows that polymerization reaction takes place to a great extent.

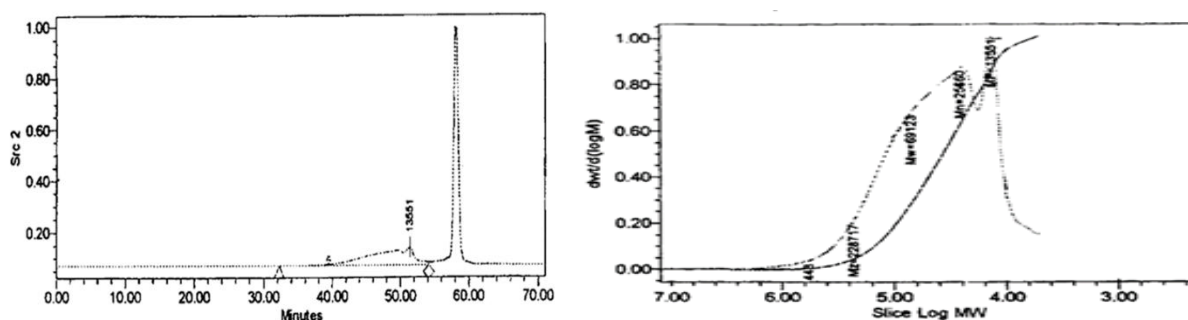


Fig.7 Gel permeation chromatogram of the polymer Fig. 8 GPC distribution plot

Table 1 GPC results

M_{peak}	M_n	M_w	M_z	M_w / M_n	M_z / M_w
13551	25660	69123	228717	2.694	3.309

3.3 TGA

In the thermogravimetric analysis of the sample (fig.9), there was about 10% weight loss at 300°C and about 20% weight loss at 400°C and as the temperature was increased, there was continuous weight loss. The initial weight loss may be due to volatilization of water molecules and the weight loss at high temperature was related to the degradation of the polymer backbone due to the production of gases such as acetylene and ammonia.

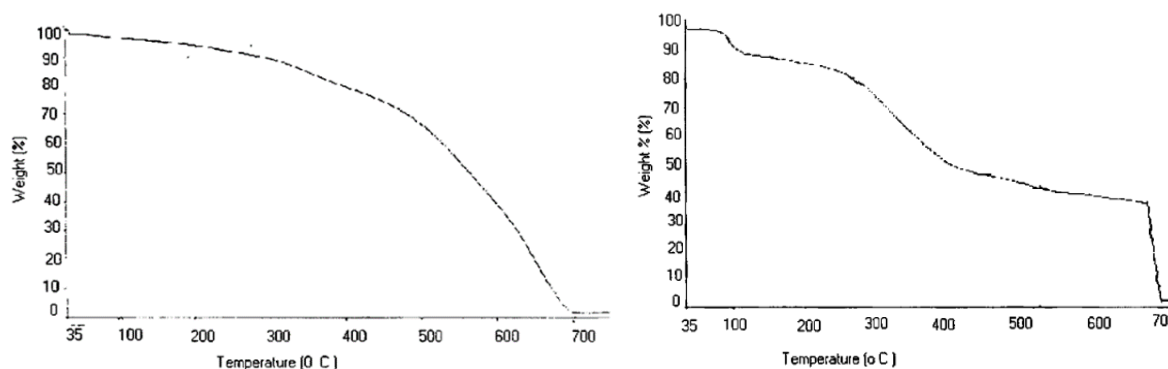


Fig.9 TGA of the polymer prepared in DMF

3.4 D.C. Conductivity

The d.c. conductivity and density of the prepared samples are given the Table 2. Conductivity of the undoped samples was changed with the solvent in which the reaction was carried out. The variation in conductivity may be due to the difference in the degree of polymerization in different solvents. The conductivity of the sample prepared in DMF was greater than other samples. DMF is a polar aprotic solvent and the polymer formed were more soluble in DMF than in toluene and methanol, that helped to increase the degree of

polymerization, which in turn increased the conjugation length and hence the conductivity was increased. In methanol and toluene, precipitation of the product takes place easily and hence further reaction may not take place. So the conductivity is very low in the samples prepared in methanol and toluene. The conductivity of the undoped sample prepared in m-cresol is similar to that prepared in DMF.

The conductivity of the doped samples was more than that of the undoped samples. This was because, after doping, more charge carriers were introduced into the polymer chain, which helped to increase the conductivity. Conductivity of acid doped samples was more than that of I₂ doped samples. This may be due to the attachment of H⁺ ions to the N atom of the polymer using the lone pair of electrons, which results in the oxidation of the polymer chain. Charge delocalization on the polymer chain helped to increase the conductivity, which was evident from the IR spectra of acid doped samples. The low conductivity of the I₂ doped samples may be due to the fact that the oxidation of the polymer chain by iodine was very low. Also, on drying the samples, the action of heat and vacuum may be removing the iodine easily.

Table. 2 Density and conductivity of poly(p-phenylenediazomethine)

Solvent	Density (g cm ⁻³)	Conductivity(S/m)			
		Undoped	Dopants		
			HCl	HClO ₄	I ₂
DMF	1.0906	1.164 x 10 ⁻⁴	8.604 x 10 ⁻²	2.801 x 10 ⁻³	1.019 x 10 ⁻³
m-Cresol	0.7096	2.415 x 10 ⁻⁵	3.663 x 10 ⁻²	6.061 x 10 ⁻³	4.082 x 10 ⁻⁵
Toluene	1.1309	6.25 x 10 ⁻⁶	2.463 x 10 ⁻⁴	9.709 x 10 ⁻³	9.009 x 10 ⁻⁴
Methanol	1.1432	3.597 x 10 ⁻⁸	2.198 x 10 ⁻⁵	8.422 x 10 ⁻⁵	3.086 x 10 ⁻⁵

3.5 Thermal diffusivity

Thermal diffusivity of the polymer samples prepared in different experimental conditions is given in Table 3. The thermal diffusivity of poly(p-phenylenediazomethine) prepared in m-cresol solvent was very high and it was in between that of Al and Fe. So poly (p-phenylenediazomethine) was a good conductor of heat.

Table 3. Thermal diffusivity of poly(p-phenylenediazomethine)

Solvent	Thermal diffusivity (cm ² S ⁻¹)
Methanol	0.0536
Toluene	0.0368
DMF	0.5037
m-Cresol	0.5088

IV. CONCLUSION

1. Condensation reaction took place between glyoxal and p-phenylene diamine to form the conducting polymer poly(p-phenylenediazomethine).
2. The molecular weight of the polymer prepared in m-cresol solvent was, Mn = 25660 and Mw = 69123.
3. The polymer was thermally stable up to about 400^oC.
4. D.C. Conductivity of the polymer prepared in DMF was more than that of other samples prepared in m-cresol, methanol and toluene.
5. Doping increased the d.c. conductivity of the polymers prepared by the condensation reaction between glyoxal and p-phenylene diamine.
6. HClO₄ was a better doping agent for poly(p-phenylenediazomethine) compared to HCl and I₂
7. Thermal diffusivity of the polymer was in between that of Al and Fe. So it was a good conductor of heat.

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