Synthesis, Characterization and Conductivity Studies of Poly(p-phenylenediazomethine)/Polyethylene blends

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Abstract
The structural requirement for a conducting polymer is a conjugated π electron system. It can be easily oxidised or reduced by charge -transfer agents which are called dopants. In the present study, a new conducting polymer based on glyoxal and p-phenylene diamine was synthesized in DMF and was characterized by IR spectra, GPC and TGA. 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 $HClO_4$, HCl and I_2 on conductivity of each sample was studied. The D.C. conductivity of the samples increased on doping with HCl, $HClO_4$ and iodine while the D.C. conductivity of all blends decreased with increase in the amount of polyethylene.

Keywords: Conducting polymers, Doping, I R spectra, GPC, TGA, Conductivity.

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. Secondly, 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 are 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.[8,13, 15]

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. Conducting polymers 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 in 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.[6]

Poly(azomethine)s, sometimes caned 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 with no information on viscosity and molecular weights.[5,10]

Preparation of blends, composites and interpenetrating network has been widely used as an approach to combine electrical conductivity with desirable mechanical strength of polymers. Three principal approaches have been reported for increasing the processability of conducting polymers:

(1) Polymerizing appropriately substituted monomers so that the conducting polymers become soluble and still retain substantial conductivity (2) Preparing the polymer in dispersion form and (3) Polymerizing the monomers of the respective conducting polymer inside the matrices of conventional polymers leading to composite films.[1-4,7,9,12,14]

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 effects of dopants like $HClO_4$, HCl and I_2 on conductivity of each sample were measured.

Material and Methods
Materials: p-phenylenediamine, glyoxal hydrate (trimer), N,N-dimethylformamide (DMF), polyethylene (PE), hydrochloric acid (HCl), perchloric acid ($HClO_4$), iodine (I_2), acetone and CCl_4 were used in the present investigation.

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 and 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. The final drying of the sample was done at 100^0C 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 then dried well.

Synthesis of poly (p-phenylenediazomethine)-polyethylene blends: Polyethylene (5g) was dissolved in 400 ml of toluene by gentle heating along with continuous mechanical stirring. 0.1 mole of p-phenylene diamine was added to it and was dissolved by stirring. Then 0.1 mole of glyoxal was added and stirred well. The temperature of the reaction medium was increased slowly 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. Excess of toluene was allowed to evaporate until the precipitation of polyethylene started 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. The final drying of the sample was done at 100^0C in vacuum.

The same procedure was repeated by varying the amount of polyethylene in the reaction mixture. The dried samples were powdered well in a mortar and then pelletized for the measurements. For the spectral and thermal studies, the sample was extracted with acetone until the extract was colorless, and then it was dried well.

Doping: l g of each sample was put in 50ml each of 1M HCI solution, 1M $HClO_4$ solution and saturated solution of I_2 in

CCl_4 and kept for 24 hours. Then it was filtered, washed with a little amount of acetone and dried at 100^0 C under dynamic vacuum for one hour.

Polymer Characterization: The prepared polymer samples were characterized by IR spectra, TGA, and molecular weight determination (GPC).

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

Microwave conductivity and Complex permittivity: The dielectric properties and conductivity of the samples were measured using cavity perturbation technique.

Results and Discussion

IR spectra: IR spectra of the polymer prepared in DMF is given in the figure 1. Figure 1 shows the IR spectrum of the sample prepared in methanol. 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} show 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.

Effect of doping on the structure of the polymer was clear from the IR spectrum. Figure 2 shows the IR spectrum of the polymer doped with HCI. 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 as given in figure 1.
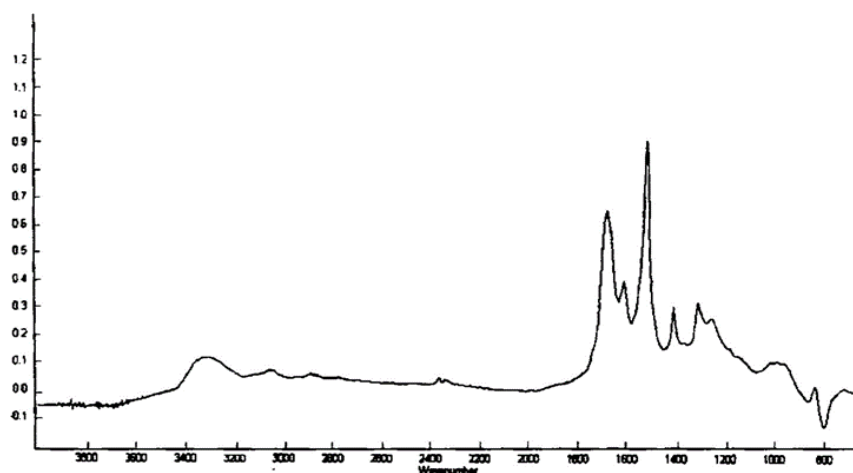

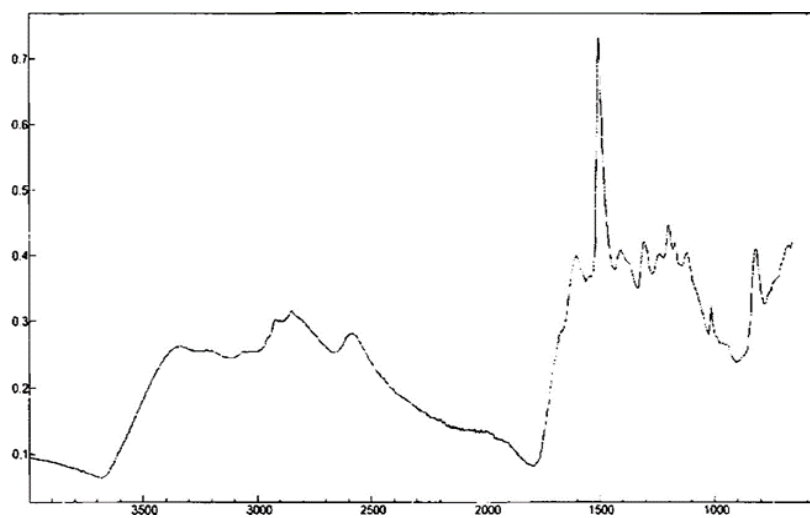**Fig. 1: IR spectra of the polymer prepared in DMF**

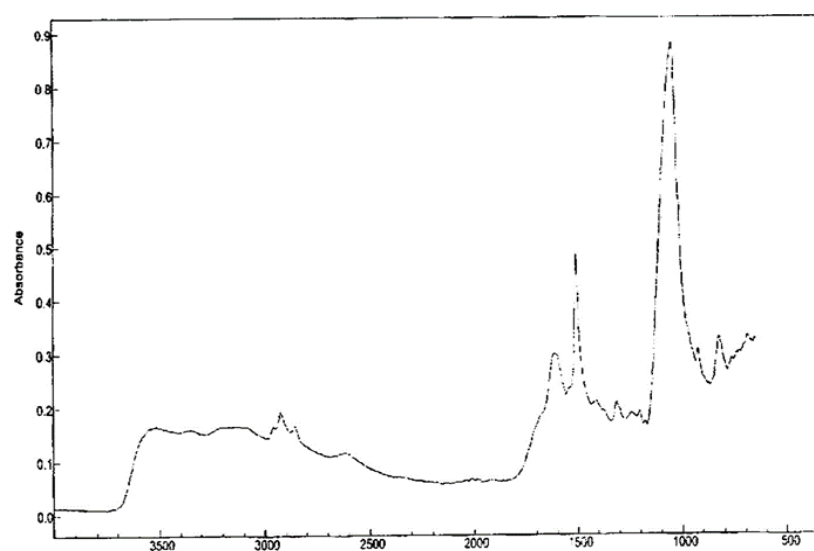**Fig. 2: IR spectrum of the polymer doped with HCl**

Fig. 3: IR spectrum of the polymer doped with HC1O₄

Figure 3 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 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 quinonoid and benzenoid rings attached to N atom in the undoped polymer shifted to 1410 and 1505 cm^{-1} and 1413 and 1508 cm^{-1} respectively for HCl and $HClO_4$ doped samples. Figure 4 gives the IR spectrum of the conducting polymer composites with polyethylene. The spectral bands at 2918 and 2851 cm^{-1} were characteristic of polyethylene. Other spectral bands were due to the conducting polymer. Unreacted p-phenylene diamine was also present in the sample. The bands at 3328, 3221, 1855, 1639, and 1130 cm^{-1} were due to

unreacted p-phenylene diamine. Figure 5 compares the IR spectrum of the polymer with the blend. The intensity of carbonyl band at 1670 cm^{-1} was very low. The two spectra were similar. From these, we can conclude that conducting polymer was incorporated into the polyethylene matrix. By the action of temperature, and pressure, we can convert these blends into sheet form. So, the processability of the conducting polymer can be improved by making its blend with polyethylene without any chemical change in the polymer structure. Figures 6 and 7 show the IR spectra of the conducting polymer blend doped with HCl and $HClO_4$ respectively.

GPC (Gel Permeation Chromatogram): The molecular weight of the polymer was determined using hexafluroisopropanol as the eluent. Gel permeation chromatogram is shown in the figure 8. GPC distribution plot is given in figure 9 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.
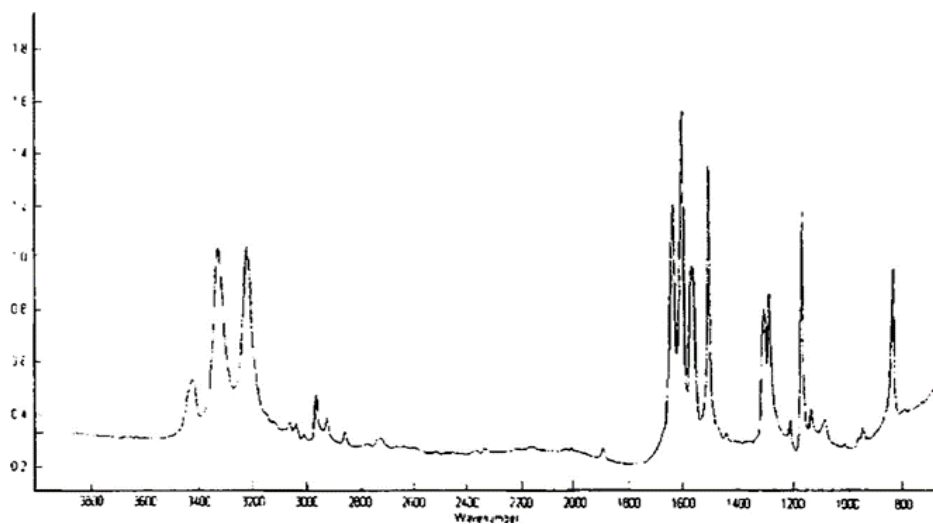
*Research Journal of Chemistry and Environment*_____Vol. **27 (8)** August **(2023)**

Res. J. Chem. Environ.

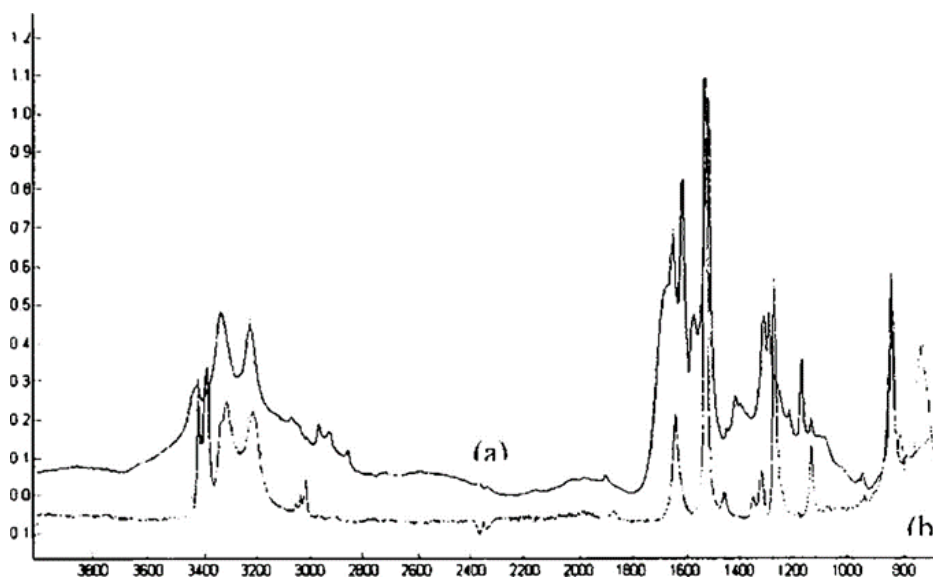**Fig. 4: IR spectrum of the conducting polymer composites with polyethylene**

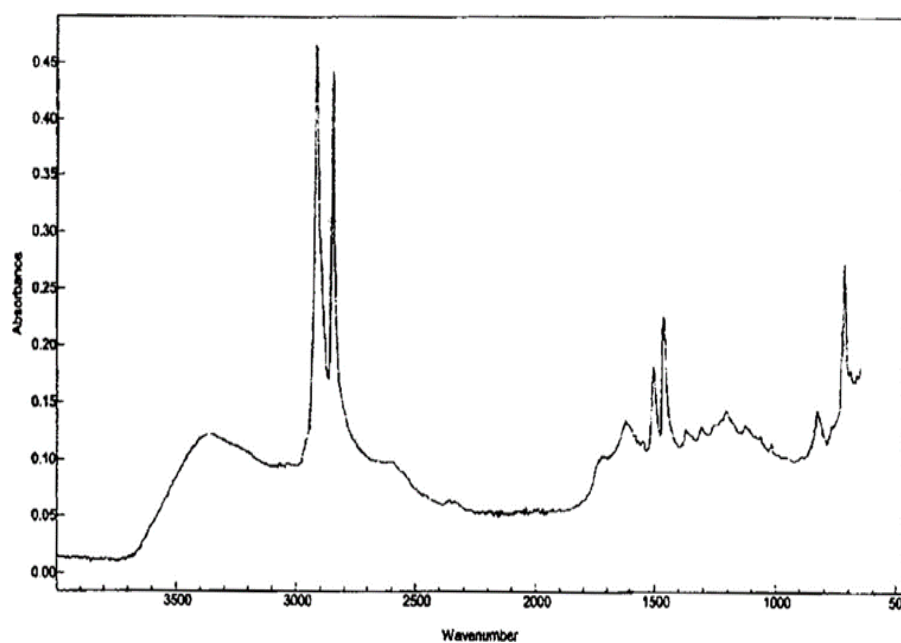**Fig. 5: IR spectra of (a) conducting polymer and (b) its polyethylene blend**

Fig. 6: IR spectrum of the conducting polymer-polyethylene blend doped with HCI
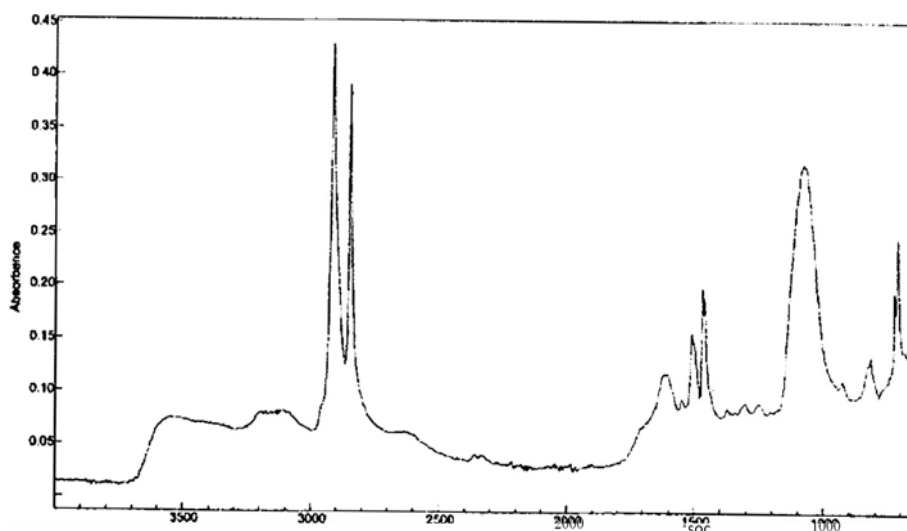
*Research Journal of Chemistry and Environment*_____Vol. **27 (8)** August **(2023)**

Res. J. Chem. Environ.

Fig. 7: IR spectrum of the conducting polymer-polyethylene blend doped with HClO4
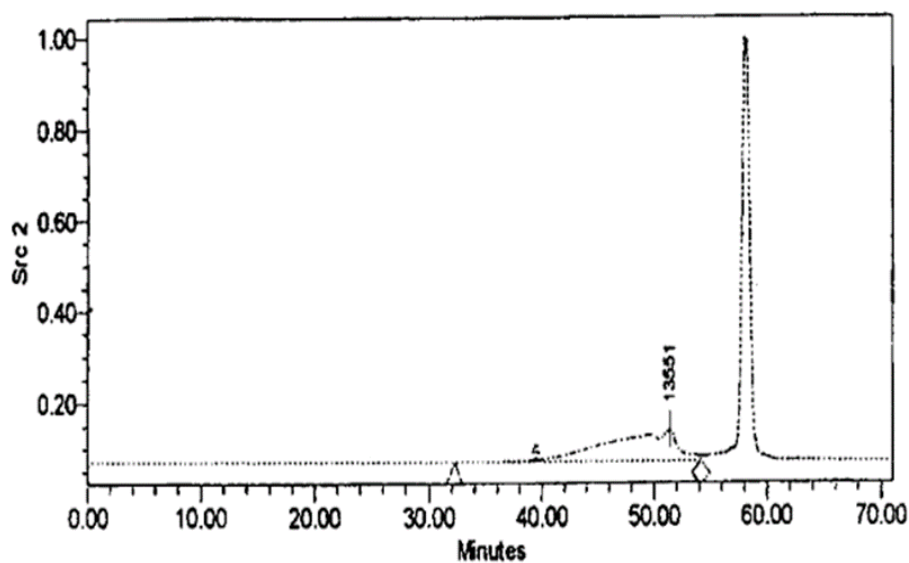
Fig. 8: Gel permeation chromatogram of the polymer

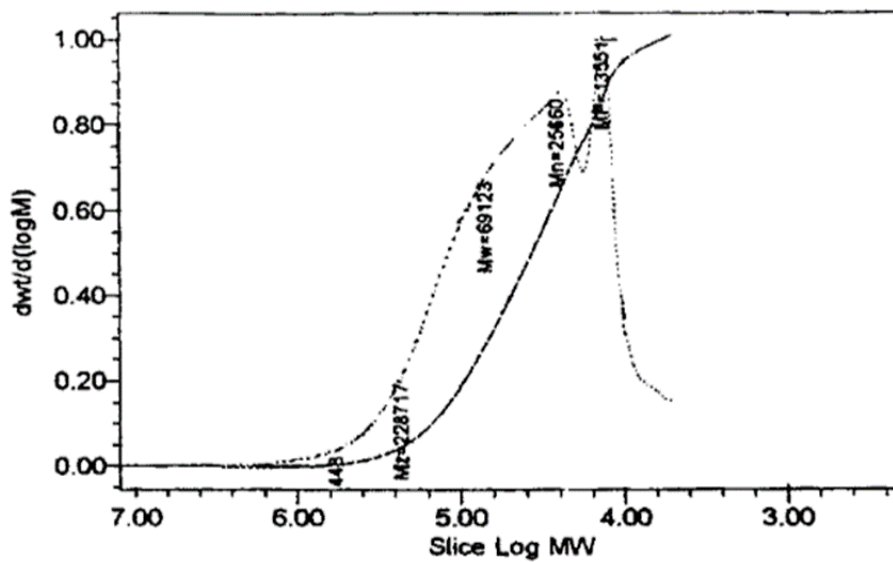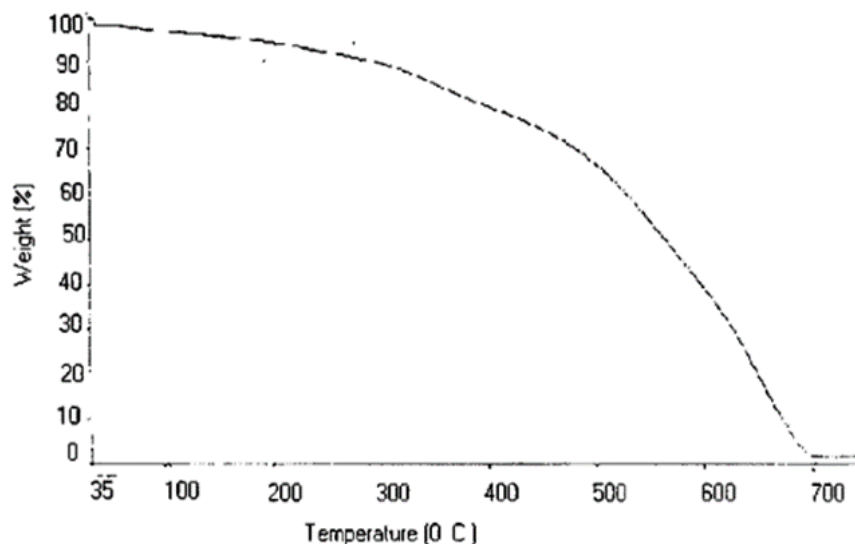**Fig. 9: GPC distribution plot of the polymer**

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Res. J. Chem. Environ.
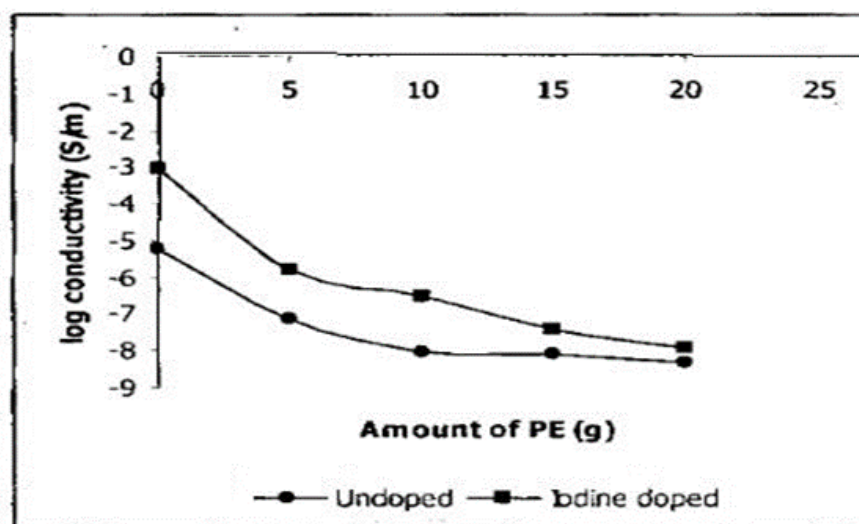

Fig. 10: TGA of the polymer prepared in DMF

Fig. 11: D.C. conductivity of the conducting polymer/polyethylene blends doped with I$_2$
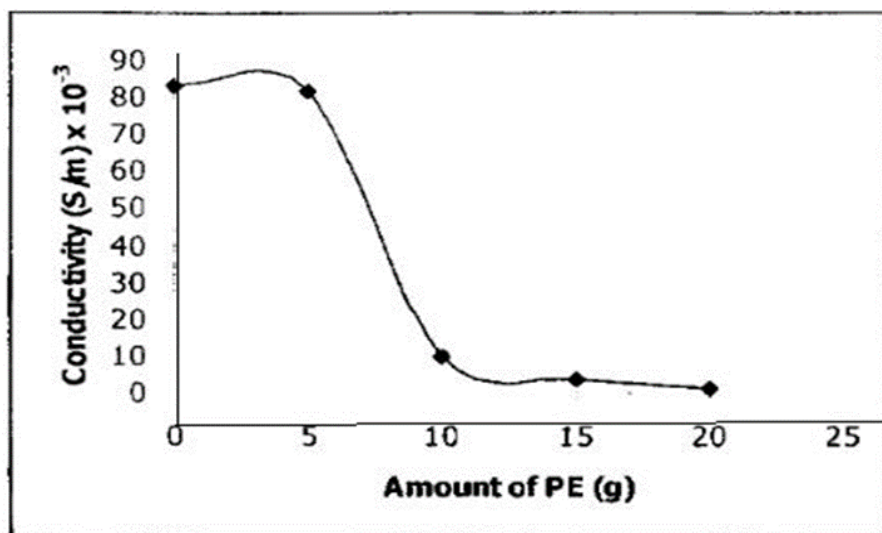

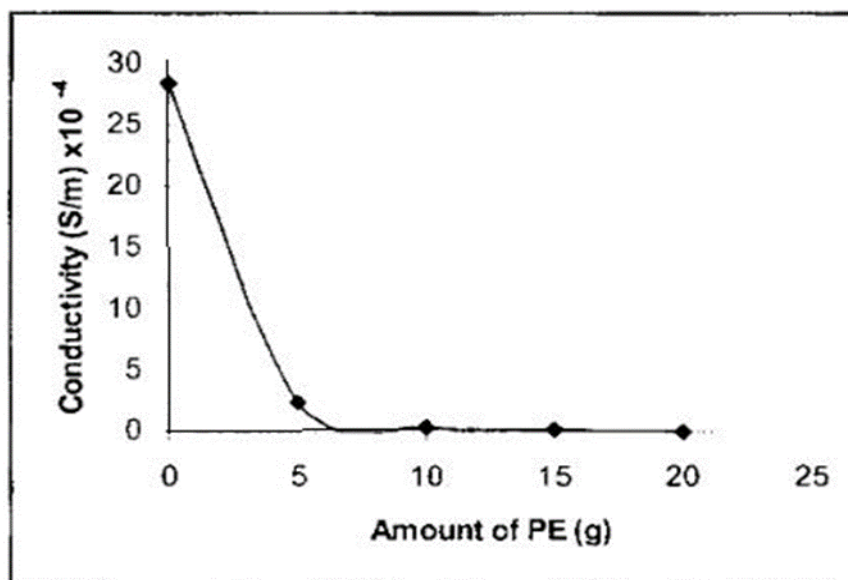**Fig. 12: D.C. Conductivity of the conducting polymer/polyethylene blends doped with HClO$_4$**

Fig. 13: D.C. Conductivity of the conducting polymer/polyethylene blends doped with HCI

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

TGA (Thermogravimetric Analysis): In the thermogravimetric analysis of the sample (fig.10), there was about 10% weight toss at 300^0C and about 20% weight loss at 400^0C 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.

D.C. Conductivity: The D.C. conductivity of the blends decreased with increase in the amount of polyethylene as given in figures 11- 13. It was because polyethylene is an insulator and the presence of polyethylene in the composite prevented the free movement of electrons through the conducting polymer chain.

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 perchloric acid doped samples was more than that of other doped samples. This may be due to the attachment of ions to the N atom of the polymer using the lone pair of electrons. Oxidation of the polymer chain takes place and the electron transfer occurs between the polymer chain and through the polymer chain. Conductivity of the 1_2 doped samples was lower than that of samples doped with HCI and $HClO_4$. It may be due to the fact that the binding force between iodine and polymer chain was very low. $HClO_4$ was found to be the better doping agent. It was because the size of ClO_4^- counter ion is large compared to Cl^- ion and so the ions were more

tightly attached to the polymer chain. Hence the removal of the dopant was not occurring readily. The stability of the $HClO_4$ dopant was also evident from the IR spectra. The intensity of the absorption band due to $HClO_4$ was more while that of HCI was very weak.

Conclusion

1. The conducting polymer poly(p-phenylenediazomethine) was synthesized by the condensation polymerization of glyoxal and p-phenylene diamine and was characterized by IR spectra, GPC and TGA.
2. The D.C. conductivity of the undoped conducting polymer blends was lower than the D.C. conductivity of the conducting polymer.
3. The D.C. conductivity of the undoped polymer blends decreased with increase in the amount of polyethylene.
4. The D.C. conductivity of the conducting polymer blends increased on doping with HCI, $HC1O_4$ and iodine.
5. The D.C. conductivity of all blends of conducting polymer with polyethylene doped with HCI, $HC1O_4$ and iodine decreased with increase in the amount of polyethylene.

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