INTRODUCTION

Research interest in polyazomethines continues owing to their various characteristics such as chelating properties [1,2] thermal stability [3,4], liquid crystal properties as well as intrinsic conductivity [5,6]. A new method of synthesizing polyazomethines was reported i.e. oxidative polycondensation of monomers containing azomethine linkages [7-9]. Phenols and their substituents can be easily polymerized by using oxidants such as NaOCl, H$_2$O$_2$ and O$_2$ which are cheap and easily available. This resulted in the formation of polymeric metal complex compounds having useful properties such as catalytic activity, thermal stability, conductivity and antimicrobial properties [10-13]. Aromatic polymers containing ester and azomethine units are of type of high performance polymers with excellent thermal, physical and mechanical properties [14]. Ester group is believed to increase the electrical conductivity of the copolymers [15].

Opto-electronic properties of series of hole-transport materials based on main-chain triphenylamine based poly(azomethines) exhibited high glass transition temperature (T$_g$ > 250 °C) and displayed outstanding thermal stabilities [16]. Similarly, iodine-doped conjugated aromatic poly(azomethine) derivative, poly (3',4'- dibutyl-L-terthiophene-azomethine-1,4 phenylene-azomethine) revealed electrical conductivities of the order of 10$^{-7}$-10$^{-8}$ S/cm [17]. A variation in the backbone ring (fluorene, carbazole or naphthalene) or donor/acceptor side group on the phenylene ring of thiophene based polyazomethines affected the dihedral angles, thus resulted in the variation of electronic properties (ionization potential, electron affinity and band gap, which is very important for electronic or optoelectronic applications of such materials [18].

A new ferrocene-based poly(azomethine) ester obtained by polycondensation exhibited highly antioxidant (IC$_{50}$ = 2.05 ppm) property and protected the plasmid DNA from damage [19]. A new generation of thermally stable and conducting poly(azomethine) ester revealed a nano-blended morphology for the melt-blended system owing to increased physical interactions (hydrogen bonding and π-π stacking) between the constituent polymers, making it an efficient opto-electronic device [20].

More functional oligophenols may be used to clean toxic heavy metals in industrial waste waters also. In addition, Schiff base compounds have been used for the determination of transition metals in some natural food samples [21]. Therefore, an impetus to synthesize such compounds was developed which has a great importance in analytical, environmental and food chemistry.

EXPERIMENTAL

All the materials were of analytical grade and used as such. Elemental analysis was carried out with standard procedures [22]. The ultraviolet visible spectra were measured by a Perkin
Elmer Lambda UV Chemito Spectroscan UV 2600. The infrared spectra were measured by a Perkin Elmer FT-IR spectrum one (4000-550 cm⁻¹). ¹H and ¹³C NMR spectra (Bruker Avance DPX-400 and 100.6 MHz, respectively) were recorded at 25 °C by using deuterated DMSO as a solvent. TMS was used as internal standard. Thermal data were obtained using Perkin Elmer Diamond Thermal analyzer TGA-4000. Measurements were made between 20-1000 °C (in N₂ atmosphere, rate 10 °C/min). Conductivity was measured on a Keith Conductivity Bridge 305. The pellets were pressed on a hydraulic press developing up to 1687.2 kg/cm². Iodine doping was carried out by exposure of the pellets to iodine vapour at atmospheric pressure and room temperature in a desiccator [23].

**Synthesis of 4-[(pyridine-3-carboimino)]benzene-1,3-diol (4-PCIBD):** 4-[(Pyridine-3-carboimino)]benzene-1,3-diol was prepared by the condensation of 2,4-dihydroxy benzaldehyde (1.38 g, 0.01 mol) with pyridine-3-carboxamide (0.98 g, 0.01 mol) in methanol (25 mL), achieved by heating the solution in microwave conditions. The precipitate was collected, recrystallized from methanol and dried. 

### Results and Discussion

**Solubility:** 4-[(Pyridine-3-carboimino)]benzene-1,3-diol (4-PCIBD) was dark yellow coloured crystalline, completely soluble in methanol, ethanol, acetone, THF, DMF and DMSO, but insoluble in benzene and toluene. Poly-4-[(pyridine-3-carboimino)]benzene-1,3-diol (P-4-PCIBD) is a dark brownish grey powder, soluble in THF, DMF and DMSO, insoluble in ethanol, ethyl acetate, benzene and carbon tetrachloride. Polymer-metal complexes were found to be insoluble in all the organic solvents.

**UV-visible analysis:** UV-visible (methanol and DMSO) of 4-PCIBD revealed K bands and R band of phenol at 205 and 178 nm, respectively. K band of 4-PCIBD (pyridine) and R band of -CH=N- groups at 232 and 351 nm were also visible. However, in case of P-4-PCIBD, K and R bands of phenol were observed at 235 and 355 nm, respectively and at 372 the clear K band of -CH=N group.

**FT-IR analysis:** In the FT-IR spectra of 4-PCIBD and P-4-PCIBD bands of -OH and -CH=N groups were observed at 280 and 350 nm assigned to aromatic C=O and azomethine transitions, respectively. The shifting of CH=N group band from 351 to 372 nm has been assigned for the formation of polymeric conjugated π-system.

### Table 1: Elemental Analysis Data and Yield of Ligand, Polymer and Polymer-metal Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Metal</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-PCIBD</td>
<td>Dark yellow</td>
<td>4.46</td>
<td></td>
<td>1.15</td>
<td>–</td>
<td>68</td>
</tr>
<tr>
<td>P-4-PCIBD</td>
<td>Dark brownish</td>
<td>64.73</td>
<td>3.73</td>
<td>6.11</td>
<td>–</td>
<td>65</td>
</tr>
<tr>
<td>P-4-PCIBD-Pb</td>
<td>Brown</td>
<td>34.80</td>
<td>2.00</td>
<td>6.24</td>
<td>46.22</td>
<td>52</td>
</tr>
<tr>
<td>P-4-PCIBD-Mg</td>
<td>Yellowish</td>
<td>58.80</td>
<td>3.39</td>
<td>10.55</td>
<td>9.15</td>
<td>65</td>
</tr>
<tr>
<td>P-4-PCIBD-Ca</td>
<td>Dark yellow</td>
<td>55.50</td>
<td>3.20</td>
<td>9.96</td>
<td>14.25</td>
<td>60</td>
</tr>
<tr>
<td>P-4-PCIBD-Zn</td>
<td>Greyish black</td>
<td>50.91</td>
<td>2.93</td>
<td>9.13</td>
<td>21.33</td>
<td>52</td>
</tr>
</tbody>
</table>

### Table 2: FT-IR (cm⁻¹) Data of 4-PCIBD, P-4-PCIBD and Its Metal Complexes

<table>
<thead>
<tr>
<th>Compounds</th>
<th>ν(–OH)</th>
<th>ν(–Ar-C-H)</th>
<th>ν(–CH=N)</th>
<th>ν(–C=C)</th>
<th>ν(–C=O)</th>
<th>ν(M-O)</th>
<th>ν(M-N)</th>
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<tbody>
<tr>
<td>4-PCIBD</td>
<td>3254</td>
<td>3050</td>
<td>1625</td>
<td>1589</td>
<td>1215</td>
<td>553</td>
<td>672</td>
</tr>
<tr>
<td>P-4-PCIBD</td>
<td>3158</td>
<td>3020</td>
<td>1605</td>
<td>1580</td>
<td>1195</td>
<td>550</td>
<td>670</td>
</tr>
<tr>
<td>P-4-PCIBD-Pb</td>
<td>3230</td>
<td>3025</td>
<td>1616</td>
<td>1570</td>
<td>1206</td>
<td>551</td>
<td>671</td>
</tr>
<tr>
<td>P-4-PCIBD-Mg</td>
<td>3258</td>
<td>3080</td>
<td>1630</td>
<td>1580</td>
<td>1214</td>
<td>557</td>
<td>677</td>
</tr>
<tr>
<td>P-4-PCIBD-Ca</td>
<td>3260</td>
<td>3030</td>
<td>1615</td>
<td>1568</td>
<td>1207</td>
<td>555</td>
<td>675</td>
</tr>
<tr>
<td>P-4-PCIBD-Zn</td>
<td>3272</td>
<td>3015</td>
<td>1610</td>
<td>1560</td>
<td>1202</td>
<td>552</td>
<td>673</td>
</tr>
<tr>
<td>P-4-PCIBD-Cd</td>
<td>3250</td>
<td>3045</td>
<td>1628</td>
<td>1575</td>
<td>1220</td>
<td>556</td>
<td>671</td>
</tr>
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</table>
**NMR analysis:** In $^1$H NMR, the signals of phenolic -OH and -CH=N groups 4-PCIBD and P-4-PCIBD were obtained at 13.50 & 9.30 ppm and 11.55 & 9.94 ppm, respectively. Cross-linking in the polymeric structure is expected in those cases where *ortho* and *para*-positions in the corresponding monomeric structure are unsubstituted.

**Thermogravimetric analysis:** TGA curves and data of monomer, polymer, and polymer-metal complex compounds are shown in Fig. 1. The onset temperature, 50 and 58% weight loss of 4-PCIBD and P-4-PCIBD was determined, respectively. In TGA curve of P-4-PCIBD, a weight loss of 14.5% in the 50-150 °C was assigned to the removal of absorbed water. Because of long conjugated band systems, polymer demonstrated higher resistance against high temperature than monomer.

P-4-PCIBD-Zn complex demonstrated higher thermal stability as compared to other polymer-metal complex because of smaller size. The high thermal stability of polymer-metal complex compounds indicate the formation of metal-oxygen valence and metal-nitrogen coordination bond between polymer-metal ions. Presence of water can be seen in the polymeric metal complex curves showing between 5 and 20 wt. % losses in 50-200 °C range and corresponding to the loss of water (50-150 °C).

**Electrical properties of polymer and polymer-metal complexes:** Polymer P-4-PCIBD and its metal complexes have conductivities in the range $10^{-11}$-$10^{-3}$ S/cm. When doped with iodine, the conductivity increased in magnitude ($10^{-3}$ S/cm). Little difference in doping effect for the polymer and its metal complexes at various times at 25 °C was observed. In doping of polymer with iodine, it was observed that the conductivity of polymer and its metal complexes first increases greatly with doping time, but then tends to level off. The highest conductivities in the range $10^{-11}$-$10^{-3}$ S/cm). When doped with iodine molecule, this has been also suggested in various literature [27,28].

**Microbial activity:** The polymer and its metal complexes were dissolved in 50 mg/mL of acetone. Incubation was done for 24 h at 37 °C and inhibition zone around each disc was measured. It is found that polymer P-4-PCIBD exhibited no microbial activity whereas the metal coordinated complexes revealed significant activities against *B. subtilis* (Fig. 3).

**REFERENCES**