Investigation of Poly-2-[(4-Pyridilmethylene)-Imino] Phenol's Some Properties: Electrical Conductivity, Antimicrobial Activity and Synthesis of Its Metal Complexes

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Abstract: Poly-2-[(4-pyridilmethylene)-imino] phenol-metal complexes were synthesized from the reactions of poly-2-[(4-pyridilmethylene)-imino] phenol with Cu(II), Co(II), Zn(II), Cd(II) and Ni(II) ions. The structures of the synthesized compounds were confirmed by FTIR techniques. The thermal stability of the polymer-metal complexes were measured by thermogravimetric analysis under a nitrogen atmosphere and their antimicrobial activities were tested against *E. coli*, *S. aureus*, *K. pneumoniae*, *M. smegmatis*, *P. aeruginosa*, *B. megaterium* and two fungi namely *K. fragilis* and *R. rubra*. Also, the electrical conductivities of the poly(2-PIP) have been put forward with this study for the first time.

Key words: Oxidative polycondensation, polymer-Schiff base, polymer-chelat complexes, antimicrobial activity and conductivity.

1. Introduction

Polyphenols and their Schiff base derivatives have been used in various fields because of their electron structure properties. They possess useful properties such as paramagnetism, semi conductivity, electrochemical cell and resistance to high energy. Because of these properties they were used for photoresistors [1], graphite materials [2], thermostabilizers [3], semiconducting materials [4] and antistatic materials [5]. In addition, Schiff base substitute polyphenols have antimicrobial activity. Antimicrobial activities of polymer metal complexes were studied by Kaya, et al. [6-8]. Thermal properties of polymer metal complexes were studied by

Khuhawar, et al. [9]. For these reasons, the synthesis of the Schiff base polymer and polymer metal complexes are gaining much interest. In our previous study we investigated the synthesis and characterization of poly(2-PIP) [10].

In the present paper, the synthesis, characterization, antimicrobial and thermal stability studies of poly(2-PIP)-metal complexes were described. Also, electrical conductivity of poly(2-PIP) was investigated.

2. Experiments

2.1 Materials

KOH, H₂SO₄, HCl (37%), ethyl acetate, ethanol, DMF, THF, DMSO, methanol, acetone, chloroform, toluene, n-hexane and Cu(AcO)₂·H₂O, Co(AcO)₂·4H₂O, Zn(AcO)₂·2H₂O, Cd(AcO)₂·2H₂O, Ni(AcO)₂·4H₂O were supplied from Merck (Germany)

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and were used as received. We have already previously prepared poly-2-[(4-pyridylmethylene)-imino] phenol [poly(2-PIP)].

2.2 Physical Measurements

Poly(2-PIP) was wholly characterized by elemental analysis, GPC, FT-IR, UV-vis, ^1H -NMR and ^{13}C -NMR methods as described earlier [10]. The infrared spectra of the metal complexes were measured by a Mattson 1000 FTIR spectrometer. The FTIR spectra were recorded $4,000\text{--}550\text{ cm}^{-1}$. Thermal data of the metal complexes were obtained by using Perkin Elmer Diamond Thermal Analysis. The TG-DTA measurements were made between $20\text{--}1,000\text{ }^\circ\text{C}$ (in N_2 , rate $10\text{ }^\circ\text{C}/\text{min}$).

2.3 Electrical Properties

Conductivity was measured on a Keithley 2400 Electrometer. The pellet was pressed on a hydraulic press developing up to $1,687.2\text{ kg/cm}^2$. Iodine doping was carried out by exposure of the pellet to iodine vapor at atmospheric pressure and room temperature in desiccators [11].

2.4 Synthesis of Poly(2-PIP)-Metal Complexes

A solution of $\text{M}(\text{AcO})_2 \cdot x\text{H}_2\text{O}$ (1.5 mmol) [$\text{Cu}(\text{AcO})_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ and/or $\text{Ni}(\text{AcO})_2 \cdot 4\text{H}_2\text{O}$] in methanol (10 mL) was added to a suspension of poly(2-PIP) (3.0 mmol/unit) in THF (50 mL). The mixture was stirred and heated at $65\text{ }^\circ\text{C}$ for 6 h. The precipitated complexes were filtered and washed with cold methanol/THF, then dried in the oven (Scheme 1).

2.5 Biological Studies

The polymer and its metal complexes were evaluated for both their in-vitro antibacterial activity against *Escherichia coli* ATCC 8739, *Staphylococcus aureus* Cowan 1, *Klebsiella pneumoniae* FMC 5, *Mycobacterium smegmatis* CCM 2067, *Pseudomonas aeruginosa* ATCC 27853, *Bacillus megaterium* DSM 32, and their in-vitro antifungal activity against *Kluyveromyces fragilis* A 230, *Rhodotorula rubra* by the disc diffusion method [12]. All the bacteria mentioned above were incubated in nutrient broth (NB) (Difco) at $37 \pm 0.1\text{ }^\circ\text{C}$ for 24 h, and the yeasts were incubated in sabouraud dextrose broth (SDB) (Difco) at $25 \pm 0.1\text{ }^\circ\text{C}$ for 48 h. The bacteria and yeasts (prepared as above) were injected into petri dishes (9 cm) in the amount of 0.01 cm^3 ($10^5/\text{cm}^3$ for the bacteria and $10^3/\text{cm}^3$ for the fungi), 15 mL of mueller hinton agar (MHA, Oxoid) and sabouraud dextrose agar (SDA) (sterilized in a flask and cooled to $45\text{--}50\text{ }^\circ\text{C}$) were homogenously distributed onto the sterilized petri dishes [13]. All the compounds were injected into empty sterilized antibiotic discs having a diameter of 6 mm (Schleicher & Shüll No. 2668, Germany) in the amount of $25\text{ }\mu\text{L}$. The compounds to be tested were dissolved in DMF to a final concentration of 2,000 ppm and soaked in filter paper. Discs injected with complexes were located on the solid agar medium by pressing slightly. After petri dishes so obtained were placed at $4\text{ }^\circ\text{C}$ for 2 h, plates inoculated with fungi were incubated at $25 \pm 0.1\text{ }^\circ\text{C}$ for 24 h. At the end of the period, inhibition zones formed on the food

Scheme 1 The synthesis route of polymer-metal complexes.

Fig. 1 Electrical conductivity of I₂-doped poly(2-PIP) versus doping time at 25 °C.

medium were evaluated is millimeters [12, 13]. These studies works were performed in triplicate. Gentamicin (Bioanalyse) and Nystatin (Oxoid) were used as standards.

3. Results and Discussion

Poly(2-PIP) were prepared and characterized as described earlier [10]. Poly(2-PIP) has conductivities of 10^{-11} S/cm. When doped with iodine, their conductivities could be increased by about three orders of magnitude (up to 10^{-8} S/cm). Fig. 1 shows the results of poly(2-PIP) doped with iodine at various times at 25 °C. In the doping of poly(2-PIP) with iodine, it was found that the conductivity of poly(2-PIP) first increases greatly with doping time, but then tends to level-off. The maximal (or saturated) conductivity was 1.3×10^{-8} S/cm (Fig. 1). The increasing conductivity could indicate that a charge-transfer complex between

poly(2-PIP) and dopant iodine is continuously formed.

The physical data and solubility test of the complexes were given in Table 1. Solubility of the products was investigated in 12 types of solvents in detail. The products were completely insoluble in some of organic solvents such as ethanol, ethyl acetate, methanol, chloroform, hexane, acetone and toluene, and KOH solutions. The soluble or partly soluble ones were given in Table 1.

In order to better understand the structure of the complexes, the IR spectra of the complexes are given in Fig. 2. The azomethine group (CH=N) vibration of the monomer and its polymer occurs at $1,643\text{--}1,640\text{ cm}^{-1}$ as a strong band [14]. This band was not observed at the same frequency in the spectra of all the complexes. It shifted to a lower frequency region, indicating the coordination of Schiff base through azomethine nitrogen. Conclusive evidence of the banding is also shown by the observation that new bands in the spectra of the coordination compounds appear at $606\text{--}597$ and $588\text{--}415\text{ cm}^{-1}$ range assigned to (M-O) and (M-N) bands stretching vibrations which are not observed in the spectra of the monomer and polymer. The strong band observed at $3,000\text{ cm}^{-1}$ for the complexes can be attributed to the H₂O group vibration [15].

The thermal behaviors of all compounds have been studied using TG and DTA equipments at N₂ medium and thermal analyses results and the curves which belong to these compounds are present in Fig. 3 and Table 2.

The characteristic mass losses related to absorbed

Table 1 The some physical data and solubility results of poly(2-PIP)-metal complexes.

Compounds	m.p. (°C)	Yields (%)	Solubility test			
			DMF	THF	DMSO	H ₂ SO ₄
Poly(2-PIP)-Cu	>300	95.7	±	-	±	+
Poly(2-PIP)-Co	>300	97.1	±	-	±	+
Poly(2-PIP)-Zn	>300	95.3	±	-	±	+
Poly(2-PIP)-Cd	>300	84.9	+	-	+	+
Poly(2-PIP)-Ni	>300	97.6	±	-	±	+

Symbols: (+), soluble; (±), partly soluble; (-), insoluble. Abbreviations: m.p., melting points.

Fig. 2 The IR spectra of poly(2-PIP)-metal complexes (a) Cu, (b) Co, (c) Zn, (d) Cd and (e) Ni complexes.

Fig. 3 TGA curves of poly(2-PIP) metal complexes.

Table 2 Thermal values of 2-PIP and poly(2-PIP) metal complexes.

Compounds	Initial (°C) (wt loss)	5% (°C) (wt loss)	50% (°C) (wt loss)	Char residue (%) (at 1,000 °C)
Poly(2-PIP)-Cd	160	263	849	47.0
Poly(2-PIP)-Co	173	286	1,000	50.0
Poly(2-PIP)-Cu	162	252	1,000	50.0
Poly(2-PIP)-Ni	191	264	784	45.0
Poly(2-PIP)-Zn	180	300	1,000	50.0

Table 3 Antimicrobial activity studies of poly(2-PIP) and its metal complexes [diameter of inhibition zone (mm); concentration 2,000 ppm, 25 µL/disc].

Compounds	Bacteria Inhibition zone, mm						Fungi Inhibition zone, mm	
	E. coli	S. aureus	K. pneumoniae	M. smegmatis	P. aeruginosa	B. megaterium	K. fragilis	R. rubra
Poly(2-PIP)	7	7	8	10	8	0	0	8
Poly(2-PIP)-Cu	0	0	0	0	0	10	0	7
Poly(2-PIP)-Co	0	0	0	0	0	0	0	22
Poly(2-PIP)-Zn	0	0	0	0	0	0	0	14
Poly(2-PIP)-Cd	7	7	7	8	0	0	7	16
Poly(2-PIP)-Ni	0	8	7	7	0	0	8	14

water molecules were detected between 50-120 °C for all curves. After this common step all compounds showed a decomposition stage. The 5% mass losses are at the temperature range of 240-300 °C. The final peaks 1,000 °C due to occurrence of the metal oxides structure [16]. The poly(2-PIP)-Zn has the highest decomposition temperature for 5% mass losses.

According to these values, thermal stability of poly(2-PIP) metal-complexes are higher than oligo-N-2-aminopyridinyl salicylaldimine [8], oligo-2-[(pyridine-2-yl-methylene)amino] phenol [17], oligo-4-[(pyridine-3-yl-methylene)amino] phenol [18], oligo-2-[(pyridine-3-yl-methylene)amino] phenol [19].

Fungicidal and bactericidal activities of the Schiff base substitute polymer and its polymer-metal complexes against pathogenic fungi and bacteria are listed in Table 3. The antimicrobial activities of pyridine containing Schiff base substituted oligophenols were examined with *E. coli*, *S. aureus*, *M. smegmatis*, *B. megaterium* [8, 18], and *R. rubra* [19] by other groups; however, they did not demonstrate antimicrobial activity toward *E. coli*, *B. megaterium*, and *R. rubra*. These researchers did find that poly(2-PIP) exhibited considerable antimicrobial behavior for *E. coli*, *B. megaterium* and *R. rubra*. The results indicate the importance of azomethine polymers or oligomers as new biologically active materials.

4. Conclusions

The synthesis of metal complexes of poly-2-[(4-pyridilmethylene)-imino] phenol with Cu(II), Co(II), Zn(II), Cd(II) and Ni(II) were achieved.

The new structures were characterized by FT-IR. Also, antimicrobial activities of the metal complexes against *E. coli*, *S. aureus*, *K. pneumoniae*, *M. smegmatis*, *P. aeruginosa* and two fungi namely *Megaterium* and *R. rubra* were reported. As might be expected the polymer-metal complexes showed thermal stability and graphite material properties. According to electrical conductivity measurement, poly(2-PIP) show a typical semiconductor polymer properties. These properties are important for technological usage.

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