



Electrical Conducting Behaviour of Newly Synthesised p-Nitrophenol-Resorcinol-Formaldehyde Terpolyligand and its Polychelates

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ABSTRACT

The resin (abbreviated as PNPRF) was derived from acid catalyzed Polycondensation of p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) using 1M HCl at 120-125°C. The chelates of Cr (III), Co (II), Ni (II), and Cu (II) were prepared by using metal salts and PNPRF ligand in DMF medium. The materials were characterised by using elemental analysis, magnetic studies and spectral analysis. In the present paper, electrical conductivity properties of terpolymer and its chelates were studied over a wide range of temperatures. The terpolymer resin and its chelates were found to show semi conducting behaviour. The activation energy of conduction was found to decrease in order $[PNPRF]_n > [Ni-PNPRF]_n > [Co-PNPRF]_n > [Cr-PNPRF]_n > [Cu-PNPRF]_n$.

Keywords: Wilson's law, Electrical conductivity, Terpolymer, Semiconductor, Polychelates.

INTRODUCTION

Terpolymeric resin owing to large applications in electronic devices as sensors, electronic controls, semiconductors and thermally stable insulators, have been open up hopefully new vistas of applicability in the field of electronics. Since terpolymer offer novelty and versatility have been widened up horizon of research and knowledge to materialists incessantly [1]. Electrical conductivity properties of newly synthesised melamine, aniline and formaldehyde terpolymer and its polychelates available in literature [2]. Electrical conductivity studies on Co(II), Cu(II), Ni(II), and Cd(II) complexes of azines reported by Revanasiddappa *et al* [3]. The semiconducting behaviour of polymeric ligand and its coordination polymer have been studied by electrical conductivity measurement at different temperatures [4]. Patel have measured the electrical resistivity of 2,4-dihydroxyacetophenone-urea-formaldehyde polymeric ligand and its polychelates over a wide temperature range [5]. Coordination polymers of Cu(II), Ni(II) with ethylene diaminetetrahalato and tetrathioazalotetrathio flavane were prepared and their electrical conductivity has been studied [6-8]. Various researchers have been studying the application of terpolymer resins of substituted phenols and formaldehyde [9-12]. In our laboratory extensive research work has been carried out on synthesis, characterisation and different properties of various terpolymeric resins [13-18].

Kapse *et al* [19] studied the semiconducting behaviour of the ter-polyligand derived from p-Hydroxyacetophenone, quinhydrone and melamine. Coordination chain polymers of transition metals Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with salen type schiff base and their oxidation catalysis of solid state conductivity lies in the range of 6.06×10^{-12} - 1.09×10^{-6} indicating the semiconducting behaviour reported [20]. Electrical conductivity of metal complexes of α -oximinoacetoacetate-o/p-toluidine thiosemicarbazones (OAPTTS and OAPTTS) with Ni(II), Co(II), Zn(II), Mn(II), Cd(II), Hg(II), and $UO_2(II)$ studied [21]. Electrical conductivity of charge transfer complex of phenothiazine with chloranil and picric acid were recorded [22].

The present communication deals with Electrical conductivity properties of newly synthesised terpolymer resin derived from p-nitrophenol, resorcinol and formaldehyde and its chelates.

MATERIALS AND METHODS

Experimental

All chemicals were AR grade or chemically pure grade-nitrophenol, resorcinol and formaldehyde were procured from Sd fine, India. Triple distilled water was used for all the experiments.

Synthesis of p-nitrophenol-resorcinol-formaldehyde terpoly ligand

A mixture of p-nitrophenol (0.1M), resorcinol (0.2M) and formaldehyde (0.4M) was refluxed in presence of 1M HCl (150ml) in oil bath at 120-125°C for six hours with intermittent shaking. The resinous reddish-brown coloured product so obtained was repeatedly washed with cold distilled water, dried in air and powdered. The product was washed with many times with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove p-nitrophenol-formaldehyde and resorcinol-formaldehyde copolymer which might be produced along with terpolymer. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of 1:1 HCl with constant and rapid stirring in order to avoid the lump formation. The PNPRF resin so obtained was filtered, washed several times with hot distilled water. The yield of terpolymer PNPRF was found to be 73.34%. [Molecular formula of repeating unit: $C_{22}H_{19}NO_7$, Molecular weight of repeating unit: 409].

Synthesis of polychelates

Terpolymeric ligand and the respective metals as Cr (III) acetate, Co (II), Ni (II) and Cu (II) nitrates, solutions were prepared in dimethyl formamide separately. Both the solutions were filtered, mixed in hot condition and refluxed on oil bath for 5-6 hrs. The chelates were separated out on addition of saturated solution of sodium acetate. It was then digested for 30 min. to 1 hour on a water bath, filtered; the solid [23-24] washed with DMF and hot distilled water and dried at 60°C.

RESULTS AND DISCUSSION

The prepared PNPRF terpolymer resin and chelates were characterised by using various physical methods viz, elemental, magnetic susceptibility, IR, 1H NMR and UV-Visible. All these data reveals that formation of metal complexes through the donor sites of O-atom [25-27].

Electrical conductivity of PNPRF terpoly ligand and poly chelates

The DC conductivities of PNPRF terpolymer resin and chelates were studied for wide temperature range. The electrical conductivity as a function of temperature of the polymer was studied. The electrical conductance of polymeric materials depends upon incalculable parameters such as porosity, pressure, method of preparation and atmosphere [28-29]. The powdered samples of PNPRF terpolymer resin and chelates were palletised by hydraulic press at pressure of 17lb inch⁻². The surface of pallet were made conducting by applying graphite paste. The diameter and thickness was measured using screw gauge. The solid state conductivity as function of temperature was recorded by two probe method [30].

The plot of $\log \sigma$ versus $1/T$ was found to be linear in the temperature range under study, which indicate that the Wilson's exponential law, $\sigma = \sigma^0 \exp^{(-E_a/kT)}$ was obeyed.

Where,

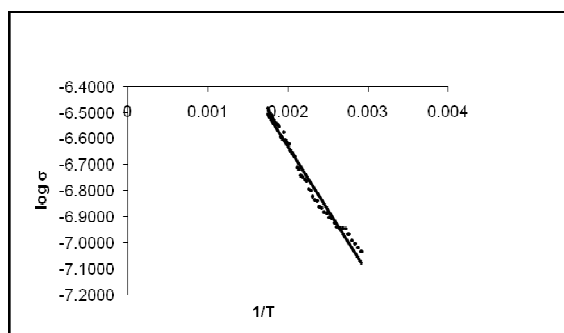
k =Boltzmann constant.

σ =Electrical conductivity at temperature T .

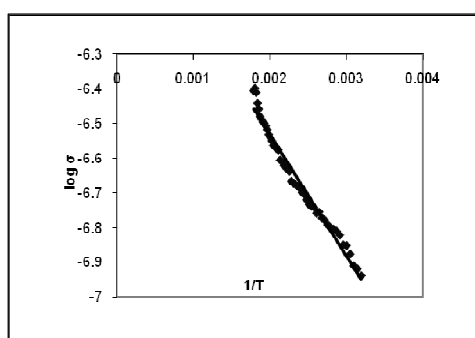
σ^0 = Electrical conductivity at temperature $T \rightarrow \infty$.

E_a =Activation energy of conduction.

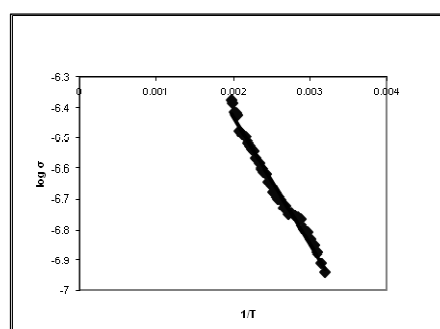
The energy of activation (E_a) of electrical conduction of PNPRF terpolymer resin and chelates, calculated from the slope of the plot. Electrical conductivity plots of PNPRF terpolymer resin and chelates are given in Figure1 (a-e). Electrical conductivity data of PNPRF terpolymer resin and chelates are shown in Table 1.



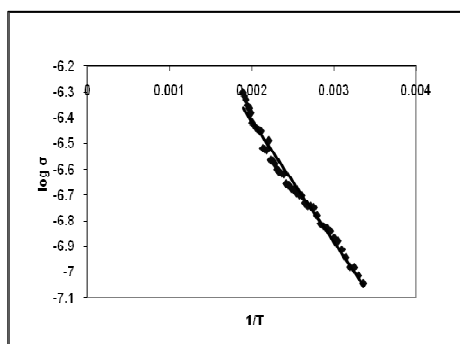
(a)



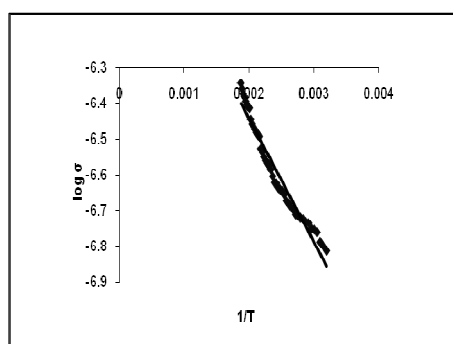
(b)



(c)



(d)



(e)

Figure 1. Wilson plot of a. [PNPRF]_n, b. [Cr-PNPRF]_n, c. [Co-PNPRF]_n, d. [Ni-PNPRF]_n, e. [Cu-PNPRF]_n

Table 1. Electrical conductivity data of PNPRF Terpolyligand and polychelates

Terpolymer Resin/Chelates	Temperature Range(K)	Activation energy (kJ mole ⁻¹)	Activation energy (eV) x 10 ²³	Electrical Conductivity σ x 10 ⁻⁶ (Ω cm) ⁻¹
[PNPRF] _n	343-573	4.089	15.37	0.0926-0.3294
[Ni-PNPRF] _n	313-528	3.970	14.92	0.1049-0.4988
[Co-PNPRF] _n	313-508	3.481	13.08	0.1148-0.4221
[Cr-PNPRF] _n	313-558	2.920	10.98	0.1153-0.3913
[Cu-PNPRF] _n	313-533	2.876	10.81	0.1543-0.4537

CONCLUSION

From the results of temperature dependence of electrical conductivity of PNPRF terpolymer resin and its chelates following conclusions can be drawn.

- 1) At 343 K, PNPRF terpolymer has an electrical conductivity $0.0926 \times 10^{-6} (\Omega \text{ cm})^{-1}$.
- 2) The electrical conductivities of chelates of PNPRF terpolymer resin lies in the range $0.1049 \times 10^{-6} (\Omega \text{ cm})^{-1}$ to $0.1543 \times 10^{-6} (\Omega \text{ cm})^{-1}$.
- 3) The plots of $\log \sigma$ versus $1/T$ are found to be linear [figure 1(a-e)] over a wide range of temperature, indicating semiconducting behaviour of terpolymer resin and chelates.
- 4) Activation energy values of PNPRF terpolymer resin and their chelates lies in the range of $10.81 \times 10^{23} \text{ eV}$ to $15.37 \times 10^{23} \text{ eV}$ (Table 1).
- 5) The activation energy of conduction is in order $[\text{PNPRF}]_n > [\text{Ni-PNPRF}]_n > [\text{Co-PNPRF}]_n > [\text{Cr-PNPRF}]_n > [\text{Cu-PNPRF}]_n$. This shows that chelation enhance conducting ability of resin, may be attributed to increase in electron density and ionizing tendency due to incorporation of different metals.

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