



Electrical conducting behaviour of newly synthesized m-cresol-hexamine-formaldehyde terpolymeric resin and its polychelates

K. M. Khedkar¹, V. V. Hiwase², A. B. Kalambe³ and S. D. Deosarkar⁴

^{1,3}Institute of Science, R. T. Road, Nagpur(MS) INDIA

²Arts, Commerce and Science College, Arvi, Wardha (MS) INDIA

⁴Swami Ramanand Teerth Marathwada University Nanded(MS) INDIA

ABSTRACT

Terpolymeric resin, abbreviated as m-CHF-II was prepared by polycondensation of m-cresol (0.1M), hexamine (0.05M) and formaldehyde (0.15M) in the presence of 1M HCl as catalyst. The polychelates of Ni(II) and Co(II) were prepared. The electrical conductivity of resin and its polychelates was determined by voltage divider method. The activation energy of conduction was found to decrease in order $m\text{-CHF-II} > [\text{Ni(II)}m\text{-CHF-II}]_n > [\text{Co(II)}m\text{-CHF-II}]_n$. The chelation was found to decrease in band gap due to incorporation of metal electrons. The resin and its polychelates were found to obey Wilson's law and hence show semiconducting behaviour. The activation energies of these samples were in range 0.0097 to 0.0280 eV in temperature range 303 to 593K.

Keywords: Terpolymer, Polycondensation, Resin, Electrical conductivity.

INTRODUCTION

In recent years, considerable interest has been shown in the synthesis and study of chelating resins containing ligands with nitrogen, sulphur and oxygen donor atoms on a polymer matrix. Terpolymer chelates containing nitrogen, sulphur and oxygen donor atoms on polymer matrix have ability to donate electron pairs to the transition metal ions forming chelates under suitable conditions known as polymer chelates. Chelations with polymer matrix have received considerable interest in the field of conducting polymer, organometallic chemistry, catalysis and synthetic organic chemistry. Recently it has been reported that the chelate polymers can be used as semiconductors. Polymer metal complexes shows interesting and important characteristics, especially in areas such as semiconductors, high energy material, molecular recognition and heat resistance [1-3]. In fact conductivity depends upon the external condition such as temperature, humidity, pressure, thickness of sample as well as its chemical structure[4,5]. Pal *et al* [6] have reported electrical conductivity of salicylic acid-biuret /dithioamide/dithiobiuret-trioxane terpolymer resin. Masram *et al* [7] reported the synthesis and electrical properties of some resins.

The electrical resistivities of 2-hydroxyaceto-phenoneoxime-thioureatrioxane resin were reported that these polymer ranked as semiconductors [8]. Revanasiddappa *et al* [9] reported electrical conductivity studies on Co (II), Cu (II), Ni (II) and Cd (II) complexes of azines which showing semiconducting behaviour of polymers. Temperature dependence of the electrical conductivity of salicylaldehyde metal chelates was reported by El-Sayed *et. al* [10]. Recently Kushwaha *et al* reported semi conducting behaviour of terpolymer derived from p-Nitrophenol, resorcinol and formaldehyde [11]. Kapse *et al* reported, very recently, semi conducting behaviour of terpolymeric resin derived from p-Hydroxyacetophenone, melamine and quinhydrone [12]. In this connection many co-worker have made attempt to improve the conducting property by changing the composition of monomers by deposition of conducting polymers on the surface terpolymer to satisfy electrical properties [13-15].

In present paper, electrical conducting behaviour of m-CHF-II and its polychelates of Ni(II) and Co(II) are reported with rise in temperature.

EXPERIMENTAL SECTION

Preparation of m-CHF-II

A mixture of m-cresol (0.1 M), hexamine (0.05 M) and formaldehyde (0.15M) with 1M HCl was refluxed over oil bath at 120-125°C for 6 hrs with stirring. The solid product so obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with hot water, dried and powdered. The product was repeatedly washed with hot water to remove unreacted monomers. The air dried product was extracted with ether to remove copolymer which might be present along with the terpolymer. It was dissolved in 1M NaOH and reprecipitated using 1:1 HCl solution. The product, finally, collected by filtration, washed with hot water, dried and kept in vacuum. The yield was found to be 78%

Preparation of polychelates: Metal nitrate and resin was dissolved in minimum quantity of DMF solvent separately in the molar ratio of 1:1 by heating. Both solutions were poured simultaneously in a round bottom flask in cold condition. Then pH range was adjusted between 8 -11 by using 0.01M NaOH. The mixture was then refluxed for 6.00 hrs to obtain chelate polymers. The conditions for preparing chelate polymers of Ni (II) and Co(II) were almost the same but to increase the yield, slightly modified methods were employed for the synthesis of chelate polymers. Synthetic details of samples are given in Table 1.

The chelate polymers of Ni (II) and Co (II) obtained were first washed with several quantity of hot water to remove the insoluble impurity of nitrates. They were dried in vacuum desiccators over calcium chloride

The chelate polymers were found to be insoluble in common organic solvents like benzene, DMF, dioxane, chloroform, carbon tetrachloride and acetone.

Table 1: Synthetic details of Chelate Polymer of m-CHF-II

Proposed composition of polymer	[Ni-m-CHF-II] _n	[Co-m-CHF-II] _n
Solvents	DMF	DMF
Suitable condition	0.01M NaOH	0.01M NaOH
M:L ratio	1:1	1:1
Time of Reflux (hrs.)	6.00	6.00
Temp. (°C)	130-140	130-140
Colour	Light yellow	Reddish brown

Measurement of electrical conductivity: The purified powder sample is crushed with acetone. In order to get fine powder, it was sieved with the help of 300 mesh sieve. The polychelate material was then palletized using a dye (EN24) and hydraulic pressure of 5 tones inch⁻². However the resin sample was palletized by applying pressure of 15 tones inch⁻² without using binder. The pallets so obtained were rubbed on sand paper to remove the impurity on the surface. The surface was cleaned with acetone. The surface of pallet was coated with thin film of graphite paste in order to make it conducting. The pallets were then kept in oven at 60°C for 5 hrs. The continuity of surfaces was checked by multimeter. The electrical conductance of the material was measured by using voltage-divider method. In this method, the DC electric current of known voltage (50V) was supplied by SMPS power supply. A known resistance was joined in circuit in series with sample holder of pallet. A voltage (V₁) across this known resistance (R₁) was recorded as a function of temperature. With the help of total voltage supplied (V_T), known resistance (R₁) and voltage across this resistance (V₁), the resistance offered by pallet of sample was calculated. With the help of resistance, thickness and radius of pallet, the specific conductivity was determined.

Table 2: Elemental Analysis of m-CHF-II

%C Found (Calc.)	%H Found (Calc.)	%N Found (Calc.)	%O Found (Calc.)	empirical formula of repeat unit	Molecular weight of repeating unit
77.69 (77.93)	7.25 (7.14)	4.71 (4.55)	10.35 (10.38)	C ₂₀ H ₂₂ NO ₂	308

RESULTS AND DISCUSSION

Elemental Analysis: The terpolymeric resin was analyzed for carbon, hydrogen, nitrogen and oxygen content. The elemental analysis was carried out at Sophisticated Analytical Instrumental Facility (SAIF) Punjab University, Chandigarh. The elemental analysis of resin is incorporated in Table 2.

UV-VIS spectrum: The UV-VIS spectrum of m-CHF-II resin was recorded by instrument Shimadzu UV-VIS-NIR spectrophotometer Model No.1601. The spectrum so obtained is shown in fig. 1. The peak at 284.5 nm was assigned to $n-\pi^*$ transition due to phenolic group. Absorption at 252.6 nm was assigned to $\pi-\pi^*$ due to aromatic ring. The absorption at 230.86 nm was assigned to $n-\sigma^*$ which support to ether linkage in structure of resin [16-18] in fig. 4.

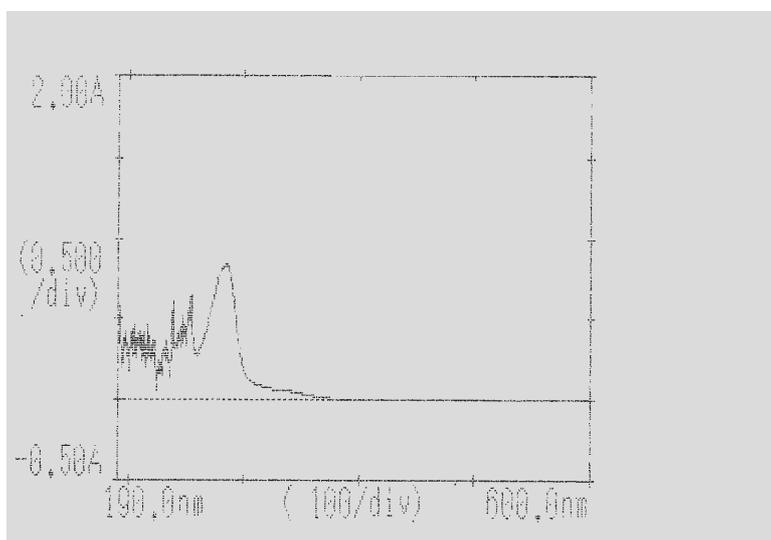


Fig. 1: UV-VIS spectra of m-CHF-II

FTIR and NMR data of m-CHF-II: The IR spectra (fig. 2) of m-CHF-II terpolymeric resin was carried out at Pharmacy Department, Mahatma Jyotiba Phule Campus, R. T. M. Nagpur University and NMR spectra (fig. 3) of m-CHF-II resin was carried out at Sophisticated Analytical Instrumental Facility(SAIF) Punjab University, Chandigarh which is presented in Table 3.

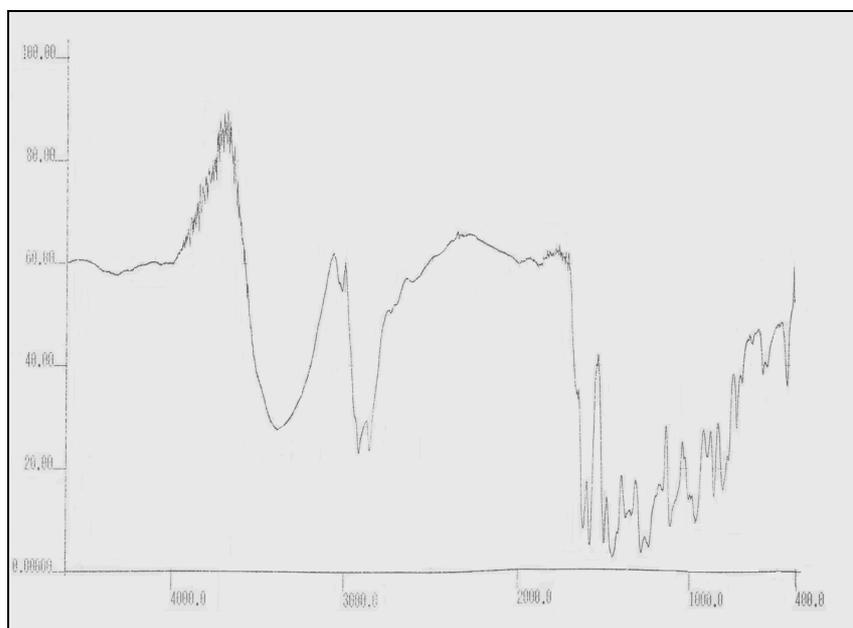


Fig. 2: IR spectra of m-CHF-II resin

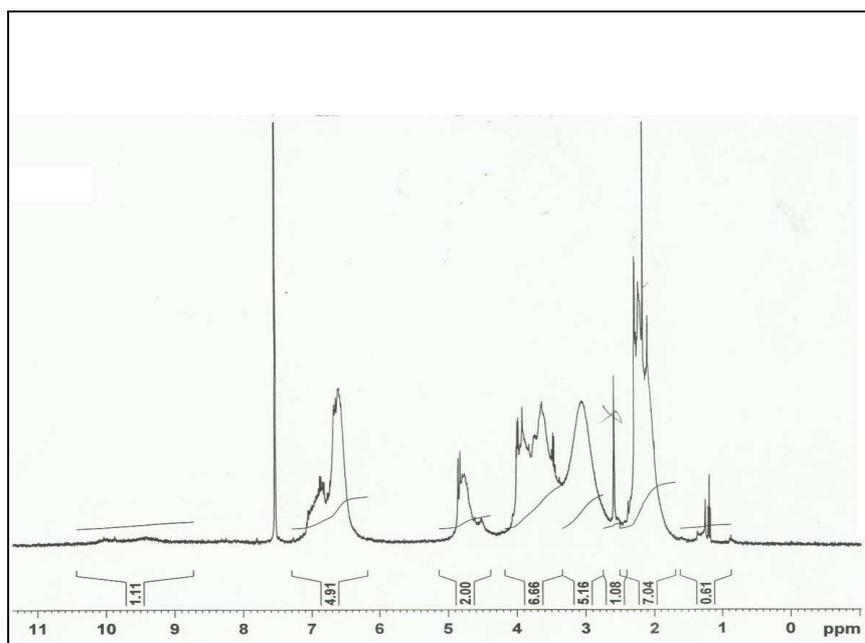


Fig. 3: NMR spectra of m-CHF-II resin

Table 3: IR and NMR spectra of m-CHF-II resin [19-25].

IR (wave number in cm^{-1})	Nature of fragment assigned	NMR □ in ppm	Nature of fragment assigned
3600-3700 broad	phenolic -OH	7.0 to 8.0	Aromatic proton. (Ar-H)
2800-2950	C-H stretching in -CH ₂ and -CH ₃ groups.	2.3	Ar-CH ₃ moiety
1480(m), 1430(m) and 588(m)	aromatic ring	2.7	Ar-CH ₂ proton
1280 and 1282	-CH ₂ -NH-CH ₂ moiety	4.1-4.7	Ar-OH phenolic
1190-1195	Tetra-substituted aromatic ring	2.0 to 3.2	-NH- bridges
1020, 1018 and 825-850	C-N-C deformation.		
1143	C-O-C (cyclic ether)		

According to data obtained in physicochemical methods, the tentative structure of terpolymeric resin was assigned as shown in fig. 4.

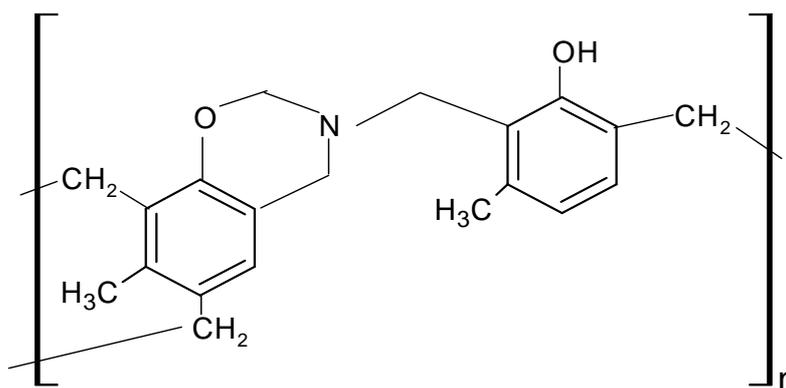


Fig. 4: Tentative structure of m-CHF-II

Electrical Conductivity: The resistance of terpolymeric resin as a function of temperature was calculated by indirect method known as voltage divider method. In this method, a constant source of 50 V DC was supplied into circuit where in sample holder and known resistance were connected in series. The digital voltmeter was connected to record voltage (V_1) across known resistance (R_1). The resistance of the pallet at a given temperature is given by

$$R_2 = \frac{R_1 (V_T - V_1)}{V_1} \quad \text{-----1}$$

Where, R_2 = Resistance offered by sample, R_1 = known resistance, V_T =Total voltage supplied in circuit, V_1 = voltage across known resistance.

Resistivity ρ was calculated using relation

$$\rho = \frac{R_2 A}{T} \dots\dots 2$$

Where, ρ = Resistivity in Ω cm, A = Surface area of pallet and T = Thickness of pallet in cm.

The conductivity measurements were made over wide range of temperature. The electrical conductivity (σ) varies exponentially with absolute temperature accordingly to well known equation,

$$\sigma = \sigma^0 \cdot \exp^{-E_a / kT} \dots\dots 3$$

Where, σ =electrical conductivity at temperature T , σ^0 =Electrical conductivity at $T \rightarrow \infty$, E_a = Activation energy of electrical conductance and k = Boltzmann constant

The above equation (3) has been modified as [26]

$$\log \sigma = \log \sigma^0 + \left(-\frac{E_a}{2.303kT} \right) \dots\dots 4$$

The electrical conductivity plots of terpolymeric resin and its polychelates of Ni (II) and Co (II) are shown in figure 5.

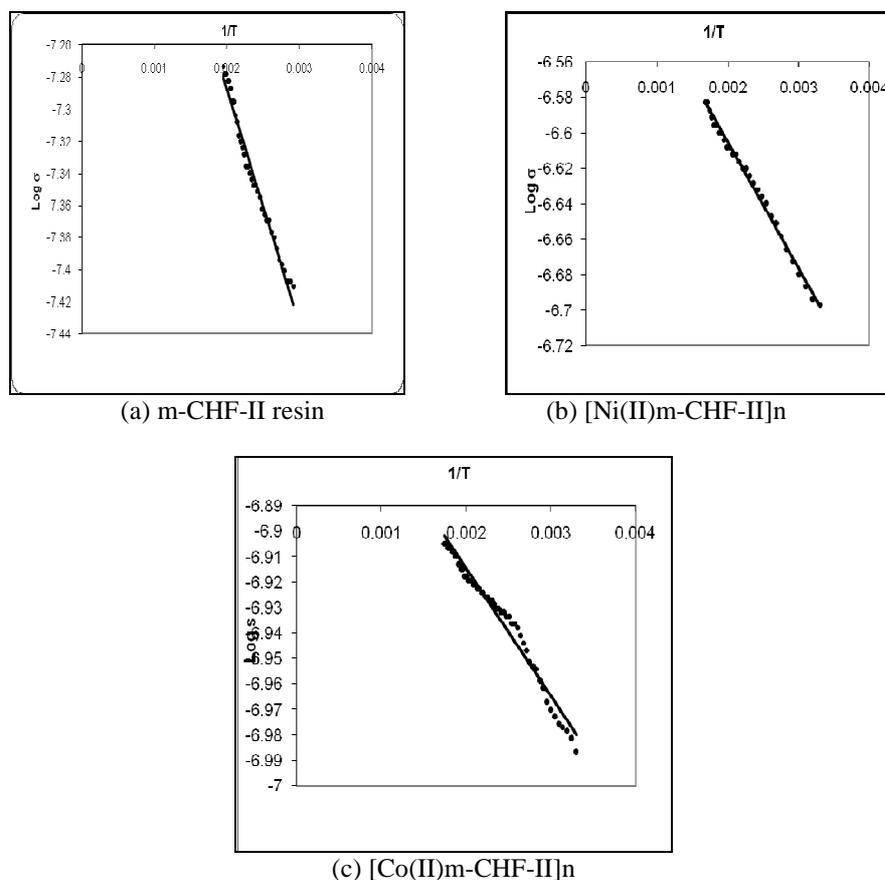


Fig. 5: Wilson plots of m-CHF-II terpolymeric resin and its polychelates

Plots of $\log \sigma$ versus $1/T$ were found to be linear with negative slope. It can be seen from the plots (fig.5 a,b,c) of terpolymer and its polychelates that there is a consistent increase in electrical conductivity with rise in temperature. These trend is a characteristics of semiconducting materials [27-29].

The activation energy evaluated by above methods are shown in Table 4.

Table 4: Activation energy of m-CHF-II terpolymeric resin and its polychelates:

Terpolymeric ligand/Polychelates	Temperature Range(K)	Activation energy (kJ mole ⁻¹)	Activation energy (eV)
m-CHF-II	303-573	2.80	0.0280
[Ni(II)m-CHF-II] _n	303-573	1.35	0.0136
[Co(II)m-CHF-II] _n	303-573	0.96	0.0097

CONCLUSION

From all above observation it is concluded that the activation energy values of m-CHF-II terpolymer and its polychelates found in the range 0.0097eV to 0.0280eV. The activation energy of conduction is decreased with incorporation of metal to which tend to fascilate conduction in polymeric matrix. The values of activation energy suggest that the resin and its Ni (II) and Co (II) polychelates may be ranked as semiconductors in temperature range 303-573 K.

Acknowledgement

Authors are grateful to Dr. M. T. Bharambe, Director, Institute of Science, Nagpur and Dr. R. H. Limsay, Head, department of chemistry for providing available facilities.

REFERENCES

- [1] P K Rahangdale , W B Gurnule ,L J Paliwal and R B Kharat , *Synth. React. Inorg. Met. Org. Chem.*, **2003**, 33(7), 187-205.
- [2] G Yang , H G Zhu ,B H Liang and X M Chen , *J. Chem. Soc., Dalton Trans.*, **2001**, 580-585.
- [3] Kimura Hajime, Murata Youchi, Motsumoto Akihiro Hasegawa Kiichi, Ohtsuka Keido and Fulkuda Akinori, *J. Appl. Polym. Sci.*, **1999**, 74(9),2266-2273.
- [4] Gautmann and O. L.E. Lyons, *Org. Semiconductor*. John Willey. New York. **1967**.
- [5] H P Singh and D Gupta . *Ind.J. Pure & Appl. Physc.*, **1986**, 24, 444-447.
- [6] T K Pal and R B Kharat , *J.Indian Chem. Soc.*,**1989**, 28A, 55-85.
- [7] D T Masram ,K P Kariya and N S Bhave , *E Polymers*, **2007**, 75.
- [8] H B Pancholi and M J Patel, *Indian Chem. Soc.*, **1998**, 75, 86-87.
- [9] M Ravanasiddappa ,S Khasim ,S C Raghavendra ,C Basavaraja , T Suresh and S D Angadi , *E-J. Chem.*, **2008**, 5(4), 797-801 .
- [10]B A El Sayed , M M El-Desoky , S M Shaaban ,M B Sayed , *Journal of Material in Electronics*, **1992**, 3,124-126.
- [11] A. D. Kushwaha, V. V. Hiwase and A. B. Kalambe, *Der Pharma Chemica*, **2012**, 4(1), 557-667.
- [12] S. K. Kapse, V. V. Hiwase and A. B. Kalambe, *J. Chem. Pharm. Res.*, **2012**, 4(3), 1734-1739.
- [13] E Matveena ,R J Carracossa, M Palomino and J Parkhutik., *Appl.Polym. Sci.*, **2004**, 94, 1752-1758.
- [14] S S Umare, A D Borkar , M C Gupta, *Bull. Mater. Sci.*,**2000**, 23(3),235-239.
- [15] A E Job,P S Hermann, D O Vaz and J Mattoso, *J Appl. Polym. Sci.*,**2001**, 79, 1220-1229.
- [16] P P Hankare ,S R Naravane,V M Bhuse and S D Delekar , *Indian J. Chem.*, **2004**, 43A, 2578-2581.
- [17] S M Roy ,H D Juneja and K N Munshi , *Synth React Inorg. Met- Org. Chem.*, **2001**, 31(9), 1611-1621.
- [18] H N Sheikh,A S Husain,M Sharma ,B L Kalostra , *Indian J. Chem.*, **2004**, 43A, 562-565.
- [19] P S Kalsi , *Spectroscopy of Organic Compounds 6th Edn*. New Age International Publishers **2004**, 9-20.
- [20] J R Dyer,*Application of Absorption Spectroscopy of Organic Compounds*, 2nd Ed., New Delhi, **1972**, 33-37.
- [21] R M Silverstein and F X Webster , *Spect. Identification of Org. Compd*. 6th edn. John Willey New York **1998**, 144.
- [22] R M Silverstein, G C Bassler, *Spectrometric Identification of Organic Compounds, 2nd Edn*. John Wiley and Sons Inc., New York, **1967**, 80-67.
- [23] I J Ballamy , *The IR Spectroscopy of Complex Molecules*; John Wiley and Sons. Inc., **1958**, 42-60.
- [24] L D Field , S Sternell and J R Kalman , *Org. Struct from spectra*, John Willey and Sons, New York, 2nd Edn. **1969**, 29.
- [25] R T Morrison and R N Boyd, *Org. Chem. 6th Edn. Prentice Hall India Pvt. Ltd.*, **2004**,710.
- [26] I E Katon , *Org semiconducting Polym.*Marcel Decker, Inc. New York,**1968**.

- [27] R N Singru ,*Der Pharma Chemica*, **2011**, 3(5), 123-127.
[28] L Pardeshi ,A Rasheed and R A Bhobe , *J. Ind. Chem. Soc.*, **1999**, 57,388.
[29] D T Masram, *E- journal of chemistry*, **2009**, 6(3), 830-834.