

Studies on Electrical Properties of Semiconducting Chelate Polymers

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Coordination polymers are well-known for their behaviour as semiconductors. The current interest in doping of iodine in chelate polymers is to a great extent due to their possible application in power sources and electrochemical devices. Infact, the conductivity and other properties such as thermoconduction, photoconduction, luminescence etc. are in close connection with their physical and chemical structure¹. The present study deals with electrical properties of chelate polymers of bis-mercaptoacetamide ethylenediamine (BMAED) and iodine-doped chelate polymers of BMAED. The structure of these chelate polymers is described in our previous communication².

Results and discussion

All the samples were subjected to a thermal treatment consisting in some successive heating and coolings over a certain temperature range. This treatment was used to stabilise the structure of the samples, when the temperature dependence of the electrical conductivity becomes reversible. Electrical properties are presented in Tables 1 and 2.

The temperature dependence of the electrical conductivity of the Mn^{II}-BMAED is shown in Fig. 1. At the first heating (Fig. 1, curve A) the electrical conductivity decreases with increasing temperature, then it increases. The decreasing the electrical conductivity is due to the elimination of the adsorbed or absorbed gases or solvent traces present in the polymers. After the first cooling, typical plots for semiconductor materials are obtained. Continuing the series of heating and coolings, plots similar to those of the first cooling are obtained coming nearer to each other so that after 2-3 successive heating and cooling the curves overlap within JICS-6

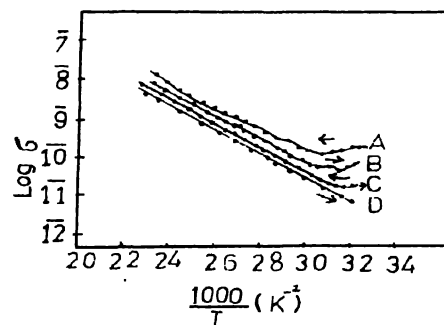


Fig. 1. Effect of thermal treatment on log σ of Mn^{II} chelate polymer : (A) first heating, (B) first cooling, (C) second heating and (D) second cooling.

experimental error (Fig. 1). At this moment, the structure of the samples is stabilised and the temperature dependence of the electrical conductivity becomes reversible. In the electrical conduction domain, the temperature dependence of the electrical conductivity obeys the equation³,

$$\sigma = \sigma_0 \exp(-\Delta E/kT)$$

where, k is the Boltzmann constant, σ_0 the electrical conductivity at temperature $T = \infty$, σ the electrical conductivity at temperature T and ΔE the thermal activation energy of electrical conduction. This reaction has been modified as

$$\log \sigma = \log \sigma_0 + \Delta E / 2.303 KT$$

According to this equation, a plot of log σ vs $1/T$ would be linear with a negative slope. The plots of the temperature dependence of the electrical conductivity for all chelate polymers and iodine doped chelate polymers are shown in Figs. 2 and 3. The values of the electrical conductivity, the values of temperature range

and the thermal activation energy for chelate polymers are listed in Table 2. The activation energies were determined from the high temperature part of the curves, $\log \sigma = F(10^3/T)$. The temperature dependence of the electrical conductivity in pellets of all the chelate polymers is of the same type, but higher values of conductivity have been obtained in iodinated chelate polymers. The plots of $\log \sigma$ vs $10^3/T$ are found to be linear (Figs. 2 and 3) over a wide temperature range which indicates the semiconducting nature of the polychelates⁴.

In the thermal study, weight-losses of Mn^{II} and Cu^{II} polychelates at around 154° are 4.10% and 4.40% respectively. The weight-losses correspond to one crystal water mole per repeating unit of polychelates. The Co^{II} and Ni^{II} chelates show weight-losses around 160 – 220° to 8.0% and 9.02% corresponding to two coordi-

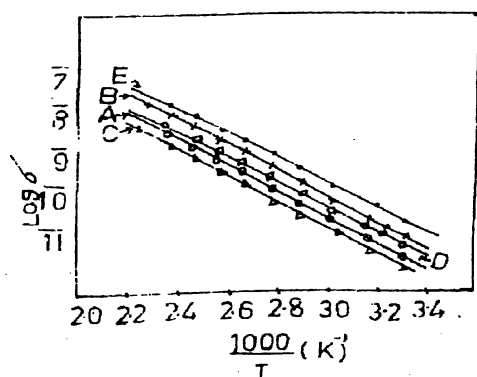


Fig. 2. Temperature dependence of $\log \delta$ of chelate polymers : (A) Mn^{II} , (B) Co^{II} , (C) Ni^{II} , (D) Cu^{II} and (E) Zn^{II} .

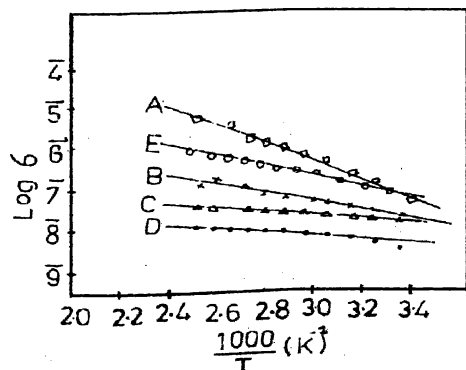


Fig. 3. Temperature dependence of $\log \delta$ of iodinated chelate polymers : (A) Mn^{II} , (B) Co^{II} , (C) Ni^{II} , (D) Cu^{II} and (E) Zn^{II} .

TABLE 1 – ELECTRICAL CONDUCTIVITY DATA FOR IODINATED CHELATE POLYMERS

Polymer	Time of iodine vapour exposure h	Cond. (302 K) $\Omega^{-1}\text{cm}^{-1}$	ΔE eV
Mn-BMAED	0	4.28×10^{-11}	0.623
	8	5.24×10^{-10}	0.602
	16	6.52×10^{-9}	0.505
	24	5.67×10^{-8}	0.457
Co-BMAED	0	8.19×10^{-11}	0.659
	8	6.82×10^{-10}	0.530
	16	4.79×10^{-9}	0.401
	24	1.97×10^{-8}	0.210
Ni-BMAED	0	3.25×10^{-11}	0.671
	8	5.28×10^{-10}	0.492
	16	2.78×10^{-9}	0.289
	24	1.93×10^{-8}	0.124
Cu-BMAED	0	1.79×10^{-11}	0.592
	8	2.07×10^{-10}	0.398
	16	7.75×10^{-10}	0.310
	24	3.24×10^{-9}	0.129
Zn-BMAED	0	6.43×10^{-10}	0.595
	8	9.68×10^{-10}	0.502
	16	1.52×10^{-9}	0.314
	24	8.31×10^{-8}	0.261

ated water moles. The observed weight-loss is a little higher than that required in this region and this may be due to some other chain degradation reactions involved in pyrolysis of the chelates⁵. In case of the Zn^{II} polychelate there is gradual mass-loss above 250° . From the procedural decomposition temperatures, the order of thermal stability of the polychelates is found to be $\text{Ni}^{\text{II}} > \text{Mn}^{\text{II}} > \text{Cu}^{\text{II}} > \text{Co}^{\text{II}} > \text{Zn}^{\text{II}}$.

Conclusion : The results reveal the following conclusions. (i) The simple chelate polymers at room temperature have an electrical conductivity in the range $(1.78\text{--}8.90) \times 10^{-10} \Omega^{-1}\text{cm}^{-1}$. The electrical conductivity of iodinated chelate polymers lies in the range 1.84×10^{-8} to $3.60 \times 10^{-9} \Omega^{-1}\text{cm}^{-1}$ at room temperature. (ii) The electrical conductivity of chelate polymers at room temperature decreases in the order : $\text{Zn} > \text{Cu} > \text{Co} > \text{Mn} > \text{Ni}$, which is in good agreement with

TABLE 2 - ELECTRICAL PROPERTIES OF CHELATE POLYMERS

Polymer	Elec. cond. $\Omega^{-1} \text{ cm}^{-1}$	T K	ΔT K	ΔE eV
Mn-BMAED	5.10×10^{-11} 4.018×10^{-8}	302	302-426	0.634
Mn-BMAED Iodinated	4.870×10^{-8} 2.710×10^{-5}	302 404	302-404	0.397
Co-BMAED	8.900×10^{-11} 1.780×10^{-7}	302 428	302-428	0.642
Co-BMAED Iodinated	1.905×10^{-8} 2.038×10^{-7}	302 371	302-371	0.241
Ni-BMAED	3.038×10^{-11} 4.168×10^{-8}	302 424	302-424	0.614
Ni-BMAED Iodinated	1.846×10^{-8} 3.671×10^{-8}	302 397	302-397	0.163
Cu-BMAED	1.789×10^{-10} 9.923×10^{-8}	302 424	302-426	0.52
Cu-BMAED Iodinated	3.601×10^{-9} 1.275×10^{-8}	302 398	302-398	0.120
Zn-BMAED	6.116×10^{-10} 3.013×10^{-7}	302 424	302-424	0.543
Zn-BMAED Iodinated	8.310×10^{-8} 8.520×10^{-7}	302 405	302-405	0.238

the order suggested by Ghosh *et al.*⁶. The electrical conductivity of iodine doped chelate polymers at room temperature decreases in the order : Zn > Mn > Co > Ni > Cu. (iii) The thermal activation energies of electrical conduction of simple polymers lie in the range 0.542–0.642 eV. The values of activation energies is in harmony with the values suggested by other worker⁷. The thermal activation energies of iodine doped polymers lie in the range 0.120–0.397 eV. (iv) All iodinated polymers show a maximum electrical conductivity after exposure of powdered polymers to iodine vapour for 24 h. Longer exposure to iodine vapour does not show any significant effect on electrical conductivity.

The electrical conductivity increases significantly due to iodine doping. The large increases in electrical

conductivity due to iodine doping can be interpreted in terms of oxidation of the metal chelate ring by iodine which leads to creating some holes in the polymer domain and hence the increase in conductivity, thus redox the reaction, the reduction of iodine the polyiodide ions¹⁻⁹. The large decrease in the activation energy after iodination of the polymers indicates a decrease in the band gap. Thus a large increase in conductivity of iodinated polymers may be attributed to a decrease in the band gap¹⁰

Experimental

The chelate polymers of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} with BMAED were prepared by interfacial polycondensation as described earlier in DMF media². All

the polychelates in the form of coloured powders were found to be insoluble in common organic solvents.

Iodine doping in chelate polymers was carried out by the reported method⁹. For doping, finely powdered chelate polymers were spread in a petry dish and kept in an iodine-saturated chamber. Depending upon the time of iodine exposure, a wide range of dopant stoichiometries was achieved (Table 1). The iodinated polymers were found indefinitely stable in air and iodine could be driven off by prolonged heating above 120°.

The DC conductivity was measured in the temperature range 297–450 K using a BPL-India million megohmmeter Rm-160-Mk IIIA and universal bridge TF-2700. The instrument could read and measure upto 10 to 10⁶ M Ω and 0.1 to 10 M Ω respectively, and test voltage varied from 50 to 500 V, the accuracy being $\pm 5\%$. Pellets (1.2 cm in dia \times 0.25–0.30 cm thickness) were prepared by pressing finely powdered samples at 10 t/cm². On both sides of the pellets a thin layer of colloidal graphite in acetone was applied and dried at room temperature under vacuum for 6–7 h. The pellet sample was put in a specially fabricated cell and resistance was calculated. The TG analysis were recorded on a Perkin-Elmer thermal analyser with heating rate 10°/min in air.

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