CHAPTER VI

CONCLUSION
In view of the enormous potentialities of chelate polymers, the present work has been deliberately planned in which attention has been paid towards the synthetic, structural, thermal and semiconducting studies of some of the polymers of the metal ions of first transition series as described in the chapter II, III, IV and V.

In the present investigation chelate polymers of Co (II), Ni (II), Cu (II) and Zn (II) with Schiff base ligands BHMADP, BHCADP, BHMAB, BHCAB, BHMAP, BHCAP, BMHADB, BHCADB, BHMADM and BHCADM have been synthesised. All the ligands used are characterised on the basis of the elemental analysis, IR and NMR studies. Structure of these Schiff bases are given in Chapter II. All these Schiff bases under present investigation do not melt but decompose above 285 °C. On the basis of IR, NMR and insolubility in common organic solvents, intramolecular hydrogen bonding has been suggested.

Several methods have been employed for the characterization to reduce the ambiguity of information in individual technique by making use of the different physico chemical methods. The results of these studies have been discussed in chapter II to V, and offer a consistent view of polymeric nature. The analytical data presented in chapter II suggest molar ratio as 1:1 expected for
linear polymers. General compositions calculated on the basis of elemental and thermal studies are cited in chapter II. Chelate polymers are highly insoluble in water and almost all organic solvents indicative of their polymeric nature.

**Stereochemistry:**

On the basis of physico-chemical studies carried out in chapter III with the help of electronic spectra, IR spectra and magnetic studies the following two stereochemical patterns could be suggested to the chelate polymers in the present investigation.

1) Variation of stereochemistry as a function of metal ion in a series of chelate polymers of constant ligand.

2) Variation of stereochemistry as a function of ligand structure in a series of chelate polymers with the same metal ion.

Stereochemical patterns are summarised in Table 6.1. While concluding the stereochemistry as a function of metal ion it may be seen from the Table 6.1 that the stereochemistry of co-ordination polymers changes when we go from Co (II) to Zn (II) metal ions. Therefore, it may be concluded that with constant ligand, the stereochemistry of polychelates changes with the change in metal ions. This change in stereochemistry with the change in metal ions can be attributed to metal characteristic.\(^2\text{--}^4\)

Examination of the Table 6.1 (vertical row) reveals that with constant metal ion the stereochemistry of polychelates appears to be dependent on the ligand characteristics and chelate polymers of same metal with different ligand shows different stereochemistry. This different stereochemistry can be interpreted in terms of different crystal field stabilization energies.\(^5\)
Structure:

On the basis of elemental analysis, electronic, IR spectral, magnetic and thermal studies various possible structures (I, II, III) have been tried for the chelate polymers in the present study. The structure which agreed mostly with appropriate findings (III) have been taken as the approximate one while proposing the structure, size of the ligand, steric consideration and chelating behaviour of the ligand towards the metal ions. On the basis of the views presented in chapter I, linear chain unit structure (III) is proposed for the polymers in the present work.

[Structure I reveals pure chelate formation and suggest that Schiff's bases are polydentate. However on the basis of its highly insoluble nature, high thermal stability and other physico-chemical observations presented in this thesis are not aggregable to structure I. Therefore structure (I) is discarded. Likewise structure II which is depicted suggest M-M interaction which may cause magnetic anomaly. However, magnetic moment values recorded in the present study are not of anomalous nature. Hence structure (II) is also discarded.]

The tentative structure which can be suggested are given in fig. 6.1-6.8. These structures may not be taken as confirmed but as most probable tentative one due to their high insolubility.

1) Co (II) chelate polymers:

On the basis of various structural studies i.e. elemental analysis, magnetic susceptibility, electronic spectra, IR and thermal studies the six coordinated octahedral structure have been suggested for Co (II) chelate polymers with BHMADP, BHCADP, BHMAB, BHCAB, BHMAP, BHCAP, BHMADB,
BHCADB. Thermal studies in this case do confirm the presence of two water molecules. This is also supported by IR studies (fig 6.1). While four co-ordinated tetrahedral structure have been suggested to Co (II) BHMADM and Co (II) BHCADM (fig. 6.2).

2) Ni (II) chelate polymers:

The experimental data of elemental analysis, magnetic susceptibility, electronic, IR and thermal studies, six co-ordinated octahedral structure for Ni (II) BHCADB, Ni (II) BHCADM and distorted octahedral structure for Ni (II) chelate polymers with BHMAB, BCHAB, BHMAP, BHCAP and BHMADM have been suggested as shown in fig. 6.3. Similarly four co-ordinated square planer structure have been suggested for Ni (II) BHMADP, Ni (II) BHCADP and Ni (II) BHMABD. (fig. 6.4)

3) Cu (II) chelate polymers:

Chelate polymers of Cu (II) with BHCADP, BHMAB, BCHAB, BHMADB, BHCADB, BHMADM and BHCADM may be represented by the structure as shown in (fig. 6.5) for fix co-ordinated distorted octahedral stereochemistry. The nature of water molecules present in these polymers has been elucidated on the basis of thermal studies. While Cu (II) BHMADP, Cu (II) BHMAP and Cu (II) BHCAP polychelates are four co-ordinated square planar (fig. 6.6). These structures are supported by elemental analysis, magnetic and spectral studies.

4) Zn (II) chelate polymers:

The probable structures of Zn (II) chelate polymers with BHMADP, BHCADP, BHMADB, BHCADB, BHMADM and BHCADM described in preceding chapters on the basis of structural studies have been suggested as four co-
ordinated tetrahedral (fig. 6.8). While Zn (II) BHMAB, Zn (II) BHCAB, Zn (II) BHMAP and Zn (II) BHCAP have six co-ordinated octahedral stereochemistry (fig. 6.7).

In all the chelate polymers, IR studies reveal that the bonding takes place through Oxygen and Nitrogen atom only.

Thermal Studies:

Thermogravimetric studies were undertaken to observe the decomposition pattern of the chelate polymers as described in chapter IV. Initial weight loss upto 110 - 210 ºC indicates the presence of water molecules and their nature as water of hydration or co-ordination. The introduction of different groups may cause difference in decomposition temperature and so also in thermal stability. Thermal patterns have been used to evaluate the kinetic parameters of the chelate polymers.

In the present case of studies, thermogravimetric analysis shows that, all chelate polymers follows similar decomposition pattern which is further suppilimented by comparable thermodynamic parameters. The values of ΔS for the chelate polymers are negative which indicate that the activated complex has a more ordered structure than reactants and that the reactions are slower than normal.

The examination so far conducted of the decomposition pattern of the chelate polymers prompts one to conclude that the first step of decomposition after loss of water molecules is faster as compared to the second step decomposition. This is indicative of the fact that some part of the chelate ligand may be decomposed first, whereas intact species of the chelate polymer
decompose at a second stage. Finally the TG curve in all chelate polymers attains a constant level after 580 - 600 °C leaving a residue of metal oxides.

Kinetic parameters calculated by both 1) Freeman - Carroll and 2) Sharp - Wentworth methods, are in harmony with each other. Further, various thermodynamic parameters have been calculated by using the data of the Freeman - Carroll method. The values of the thermodynamic parameters for all the chelate polymers are found nearly same for each chelate polymers. The similarity of the thermodynamic parameters for polychelates indicate that the basic steps involved are similar in the thermal degradation of chelate polymers.

**Electrical Behaviour:**

The D.C. conductivities of chelate polymers of Co (II), Ni (II), Cu (II) and Zn (II) with the Schiff base ligand used in the present study in their pellet form are reported. Chelate polymers show semiconducting nature in the 300 - 500 K range of temperature. The electrical conductivity of all these polychelates varied in the range of the order $10^6$ to $10^{11}$ ohm cm$^{-1}$, which is in consistance with observation made by many workers. Moreover, plots of log $\sigma$ Vs ($10^3 / T$) show two distinct region in most of the cases. The two distinct region of plot in lower and higher temperature side is indicative of the extrinsic and intrinsic behaviour of polychelates $^{10,11}$.

**General Remarks:**

It is neither scientifically desirable nor rationally appropriate to draw too many generalization regarding stereochemistry and structure of the chelate polymers on the basis of the study undertaken in the present investigation.
The formation of co-ordination polymers is always questionable unless and until its degree of polymerization is not assigned. But the methods known so far, for the determination of molecular weight of polymer requires some solubility of the product in some solvent. In the present case it was, however, not possible to determine the molecular weight and hence degree of polymerization because the products are highly insoluble in almost all organic solvents. Even their suspension could not be obtained. The extreme insolubility of these products give an indirect proof of the polymeric nature of the product.

To conclude, it may be mentioned that the present study is a part of a group study on chelate polymers being undertaken in these laboratories to develop some chelate polymers having the properties such as thermal stability, semiconductivity, catalysis, plasticity and fabricability for their wide range applications.

Summing up, it may be pointed out that the physico-chemical methods employed in the present studies are capable of providing valid information on the nature of the chelate polymers and to some extent, their co-ordination sphere. It must be however, mentioned here that the stereochemistry, structure and nature suggested for the chelate polymers in the present investigation are tentative and require further confirmation.

Judging from the results obtained in the present work and of those reported earlier the fact has to be emphasised that much studies have been left to be done in the field of chelate polymers. Though not possible, many a goals are yet to be achieved. As such further work on this line is in progress in various laboratories. The present thesis thus forms a part of a collective endeavour that
may in due course of time, break new grounds in co-ordination polymer chemistry.

**TABLE 6.1**  
**Proposed Stereochemistry of Chelate Polymers**

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Co (II)</th>
<th>Ni (II)</th>
<th>Cu (II)</th>
<th>Zn (II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BHMADP</td>
<td>Oh</td>
<td>Sp</td>
<td>Sp</td>
<td>Td</td>
</tr>
<tr>
<td>BHCADP</td>
<td>Oh</td>
<td>Sp</td>
<td>D4h</td>
<td>Td</td>
</tr>
<tr>
<td>BHMAB</td>
<td>Oh</td>
<td>D4h</td>
<td>D4h</td>
<td>Oh</td>
</tr>
<tr>
<td>BHCAB</td>
<td>Oh</td>
<td>D4h</td>
<td>D4h</td>
<td>Oh</td>
</tr>
<tr>
<td>BHMAP</td>
<td>Oh</td>
<td>D4h</td>
<td>Sp</td>
<td>Oh</td>
</tr>
<tr>
<td>BHCAP</td>
<td>Oh</td>
<td>D4h</td>
<td>Sp</td>
<td>Oh</td>
</tr>
<tr>
<td>BHMADB</td>
<td>Oh</td>
<td>Sp</td>
<td>D4h</td>
<td>Td</td>
</tr>
<tr>
<td>BHCADB</td>
<td>Oh</td>
<td>Oh</td>
<td>D4h</td>
<td>Td</td>
</tr>
<tr>
<td>BHMADM</td>
<td>Td</td>
<td>D4h</td>
<td>D4h</td>
<td>Td</td>
</tr>
<tr>
<td>BHCADM</td>
<td>Td</td>
<td>Oh</td>
<td>D4h</td>
<td>Td</td>
</tr>
</tbody>
</table>

where:

Oh - Octahedral, Td - Tetrahedral,
Sp - Square planar, D4h - Distorted octahedral.
Where, $R$ can be $\text{CH}_3$, $\text{Cl}$, $-\{\text{CH}_2\}_j$, etc.