CHAPTER 1

INTRODUCTION

The synthesis of functionalized polymers has attained considerable technological interest as reactive materials. Many polymers with definite functional groups are now being synthesized, tested and used. Organic polymers (macromolecules), because of their extreme length give rise to entangled materials with unique properties. They are part of our daily life, and sometime it is remarked, based on their broad applications, that we are living now in the so called “plastic age”. Today, macromolecular chemistry is a subject of world-wide importance in education and research at universities and research institutes, and an extremely important economic factor in different areas of industry. This has stimulated interest, all over the world, exploring new domains in the field of polymer science and technology. One such branch which has emerged is polymer-metal complexes comprising an organic polymer containing co-ordinating sites, complexed with metal ions. Scientifically and practically, a polymer-metal complex overlaps the disciplines of physics, engineering science, medical and materials science.

Chelating polymers are, in general, co-ordinating polymers with covalently bound side chains, which contain one or more multiple donor atoms (Lewis bases) that can form co-ordinate bonds with most of the toxic metal ions (Lewis acids). Due to co-ordination-type interactions, all such chelating polymers offer extremely high selectivity towards commonly encountered M(II) (cations), namely Cu(II), Pb(II), Ni(II), Cd(II), Zn(II) and alkaline-earth (Ca(II), Mg(II)) metal cations. For a longtime, the
co-ordination compounds were considered as a rare and special class but subsequently have become versatile.

Polymers containing metals have emerged as a new generation of material with tremendous potential in fields like superconducting materials, ultra-high strength materials, liquid crystals, biocompatible polymers, organic synthesis, nuclear chemistry, waste water treatment, hydrometallurgy, and polymer drug grafts. Metal chelates play an essential role in the chemistry of living matter viz; chlorophyll’s (Mg(II) complex) and haemoglobin (Fe(II) complex) (Vernon and Seely 1966). A large number of metal proteins and other metal complexes of biological importance have been studied.

Apart from biological field, co-ordination compounds play an essential role in chemical industries. For instance in 1963, the Nobel Prize in chemistry was awarded jointly to K. Zeigler of the Max Plank institute in Germany and G. Natta of the University of Milan in Italy, for developing a new metal complex catalyst containing aluminium and titanium. This catalyst revolutionized in the polymer synthesis.

The progress made in the synthesis of polymers with widely varying properties permits one to obtain macromolecular systems with well defined characteristics. The nature of monomer, the chemical nature, and different experimental conditions of polymerization can be controlled to produce polymers of definite functional morphology and physicochemical characteristics. Work on co-ordination complexes has revealed that heterogeneous systems possess more economical potentials and advantages over homogeneous systems. Polymer-metal complexes belong to the former case. The high molecular weight polymer-metal complexes work as storage houses for solar energy. Efficient chemical conversion in storage of solar energy will be difficult with the homogeneous systems. Molecular design using a heterogeneous system would therefore be important. Fundamental
research on the photoreaction in the micro heterogeneous environment provided by the polymer has been reported (Mathur et al 1980).

Metalloenzyme is a kind of polymer-metal complex present in nature, where metal ions are surrounded by a giant protein molecule of definite three dimensional structures. A typical example of such a metalloenzyme whose structure has been determined is plastocyanin (a kind of blue-copper protein) (Coleman et al 1978). In plastocyanin the copper ion shows a distorted tetrahedral structure and is co-ordinated by methionine’s sulfur atom which is not normal in usual low molecular weight metal complexes. This abnormal co-ordination behaviour and the hydrophobic environment around the copper ion brought by giant protein molecule cause unusual redox behaviour of the copper ion. Generally, the protein in metalloenzyme not only decides the chemical structure, but also causes an allosteric effect through conformational change of its polymer chain. In order to throw light upon the effect on the protein surrounding the metal ion, intensive studies of the structure and catalytic activity of synthetic polymer metal complexes were initiated.

Polymer-metal complexes have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields like, organic synthesis (Samuelson 1963), waste water treatment (Bolto 1980), hydrometallurgy (Vernon 1976), polymer drug grafts (Ramirez and Andrade 1974), recovery of trace metal ions (Coleman 1975) and nuclear chemistry (Schmuckler 1965). In addition, they are also used as models for enzymes (Banazak et al 1965 and Palumbo et al 1978).

A polymer-metal complex is composed of synthetic polymer and metal ions, wherein the metal ions are bound to the polymer ligand by a co-ordinate bond. A polymer ligand contains anchoring sites like nitrogen, oxygen or sulfur obtained either by polymerization of monomer possessing
the co-ordinating site or by a chemical reaction between a polymer and a low molecular weight compound having co-ordinating ability. The synthesis results in an organic polymer with inorganic functions. The metal atoms attached to polymer backbone are bound to exhibit characteristic catalytic behaviour, which are distinctly different from their low molecular weight analog. Indeed, many synthetic polymer-metal complexes have been found to possess high catalytic efficiency, in addition to semi conductivity, heat resistance and biomedical potentials.

### 1.1 CHELATING POLYMER: GENERAL PROPERTIES

The chemistry underlying the use of chelating polymers for the separation and preconcentration of trace elements is reasonably well understood (Kantipuly et al 1990) and progress today is mainly in improving the specificity of the resins and the techniques of application. The analytical applications of chelating polymers depend on many factors. Normally a metal ion exists in sea water/waste water as a hydrated ion or as a complex species in association with various anions, with little or no tendency to transfer to a chelating polymer. To convert a metal ion into an extractable species its charge must be neutralized and some or all of its water of hydration replaced. The nature of the metal species is therefore of fundamental importance in extraction systems. Most significant is the nature of the functional group and/or donor atom capable of forming complexes with the metal ions in solution, and it is logical to classify chelating polymers on the basis. Also, for simplicity, it is desirable to classify chelating polymers according to Figure 1.1. This method of classification is not meant to imply that these systems are mutually exclusive. Indeed, some polymers can belong to more than one class, depending on experimental conditions.
1.1.1 Functional groups

The functional group atoms capable of forming chelate rings usually include oxygen, nitrogen and sulphur. Nitrogen can be present in a primary, secondary or tertiary amine, nitro, nitroso, azo, diazo, nitrile, amide and other groups. Oxygen is usually in the form of phenolic, carboxylic, hydroxyl, ether, phosphoryl and some other groups. Sulphur is in the form of thiol, thioether, thiocarbamate, disulphide groups etc.

These groups can be introduced into the polymer by chemical transformation of the matrix or by the synthesis of sorbents from monomeric ligands. The insertion of suitable specific functional groups into the polymeric matrix makes them capable of reacting with metal ions or metal species under certain favourable conditions, to form chelate rings. The selective concentration and separation of elements from natural water systems depends both on elemental speciation and the chelating properties of the polymer.
1.2 CLASSIFICATION OF POLYMER-METAL COMPLEXES

The polymer-metal complexes may be classified into different groups according to the position occupied by the metal, which is decided by the method of preparation. The methods include complexation between a ligand function anchored on a polymer matrix and metal ion, reaction of a multifunctional ligand with metal ion and polymerization of metal containing monomers.

1.2.1 Pendant metal complexes

A pendant metal complex is one in which the metal ion is attached to the polymer ligand function, which is appended on the polymer chain. Based on the chelating abilities of the ligands, pendant complexes are classified as monodentate or polydentate polymer-metal complexes.

The monodentate pendant polymer-metal complexes are formed from a metal ion or stable metal complex in which the central metal ion is already masked with low molecular weight ligands except for one co-ordinating site that remains vacant. In these complexes, the effects of polymer chains are exhibited clearly and the polymer–metal complexes are often soluble in water or in organic solvents, since it contains few bridged structures which reduce the solubility.

Even if the metal ion or the metal complex has more than two labile ligands, it is often possible to form a monodentate complex by selecting an appropriate reaction condition. When the reaction between the metal ion or metal complex, the probability of the substitution of the second labile ligand of the metal ion would be very less, resulting in a predominantly monodentate type (Kurimura et al 1971).
When the polymer backbone contains multidentate ligands the co-ordination structure of polymer-metal complex can be represented in Scheme-1.

![Scheme-1](image)

Polydentate ligands often results in the formation of stable metal complexes with bridged structure (I) (Pittman et al 1971).

![I](image)

Most of the chelating resins come under this category. These are characterized by their relatively well defined co-ordination structure. Here the effect of the polymer chain is more predominant (Pittman et al 1971).

### 1.2.2 Inter/intra-molecular bridged polymer-metal complexes

When a polymer ligand is mixed directly with metal ion, which generally has four or six co-ordinate bonding sites, the polymer-metal complex formed may be of the intra-polymer chelate type or inter-polymer chelate type as shown in Scheme-2.
The co-ordination structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between inter/intra-molecular bridging. Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer metal complex is sometimes soluble, while inter-polymer metal complex results precipitation of the linear polymer-metal complexes as exemplified by poly(acrylic acid)-Cu(II) complexes (Tsuchida et al 1974).

1.2.3 Complexation of multifunctional ligands with a metal ion

Co-ordination polymers have been used since before restored history, though not recognized as such until recently. For instance, the tanning of leather depends on the co-ordination of metal ions with the proteins which make up the hide. These protein-metal ion complexes resist bacterial attack for weathering which befall non-tanned animal skins. Metals bound to other natural polymers including proteins, affect numerous enzymatic and membrane interactions (Vallee et al 1978).

A low molecular weight compound with multifunctional ligands on both ends of the molecules grows into a linear network polymer. The polymer
chain is composed of co-ordinate bonds and the ligand is the bridging unit as per the following representation (Scheme-3).

Scheme-3

Multifunctional ligands capable of forming this type of co-ordination polymers are classified into linear co-ordinated polymers and network co-ordinated polymers (Parquet).

Linear co-ordinated polymers can be of two types. In one case the polymer chain is composed of bifunctional ligand and metal ions as exemplified by copper complex of poly(thiosemicarbazide) (II) (Tomic and Campbell 1962 and Donaruma et al 1979).

II

In the other case a simple compound or ion can function as a bridging ion giving rise to a polymeric structure, as in the case of copper complex of poly(α-amino acid)s (III and IV) (Palumbo et al 1978).
Parquet polymers are flat, netlike organic macromolecules in which a metal is completely enmeshed. This type of polymer-metal complex is formed by ‘template reaction’ between two functional groups of the ligand induced by their co-ordination to metal ions, resulting in the following chelated type metal complexes (Scheme-4).

Scheme-4

Polyphthalocyanato copper(II) (V) and polyporphyrinatocopper(II) (VI) complexes are the most common examples.
Polyphthalocyanato copper(II) complex is formed by the reaction of pyromellitic dianhydride, cupric chloride and urea in the presence of a catalyst at 180°C. The complex varies from green to black in colour and has molecular weights up to 4000. Polyporphyrinato copper(II) complex is formed by the reaction of copper(II) acetylacetonate with tetracyanoethylene at 200°C under vaccum (Sharpe 1976). These polymers are of interest because of their thermal stability, potential electrical properties and similarities to haemoproteins.
1.2.4 Commercial chelating resins

A number of chelating resins containing such functional groups as iminodiacetic acid, amidoxime, aminophosphonic acid, oxine, thiols, pyridine etc., are now commercially available. A classification scheme for reactive polymers and selection of commercial chelating resins along with the details available of their constitution, functional groups and chromophore is given in Table 1.1. The aspect of the commercialization of chelating resins is the development of such compounds for specific use; many such resins have been prepared for different industrial processes, though their details remain hidden in patents. In view of this, the commercial potential of chelating resins must not be underestimated.
# Table 1.1 Details of commercially available chelating resins

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Commercial Name</th>
<th>Active Chelating group</th>
<th>Nature of Chelating group</th>
<th>Donor atoms</th>
<th>Polymer matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IMAC TMR</td>
<td>-SH</td>
<td>Aromatic thiol</td>
<td>$S_x$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>2.</td>
<td>IMAC SYN 101</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>NO$_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>3.</td>
<td>Duolite ES 346</td>
<td>$\text{C}^\text{+}\text{NOH}$</td>
<td>Aminoxime</td>
<td>NO</td>
<td>Polyacrylic (X% DVB)</td>
</tr>
<tr>
<td>4.</td>
<td>Duolite ES 465</td>
<td>-SH</td>
<td>Aromatic thiol</td>
<td>$S_x$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>5.</td>
<td>Duolite ES 466</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>NO$_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>6.</td>
<td>Duolite ES 467</td>
<td>$\text{CH}_2\text{NH}^+\text{CH}_2\text{P}^\text{-}\text{OH}$</td>
<td>Amino phosphonic acid</td>
<td>NO$_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>7.</td>
<td>Dowex A-1</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>NO$_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>8.</td>
<td>Dowex XF-4195</td>
<td>$\text{R}$</td>
<td>Weakly basic groups</td>
<td>N$_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td></td>
<td>Dowex XF-4196</td>
<td>$\text{NH}_2\text{C}^\text{-}\text{H}_2\text{C}^\text{-}$</td>
<td>Weakly basic groups</td>
<td>N$_2$</td>
<td>Polystyrene (X% DVB)</td>
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Table 1.1 (Continued)

<table>
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<tr>
<th>S. No.</th>
<th>Commercial Name</th>
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<th>Nature of Chelating group</th>
<th>Donor atoms</th>
<th>Polymer matrix</th>
</tr>
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<tbody>
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<td>9.</td>
<td>Dowex XFS-43084</td>
<td><img src="image" alt="Chemical structure" /></td>
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<td>10.</td>
<td>Chelex-100</td>
<td><img src="image" alt="Chemical structure" /></td>
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<td>NO$_2$</td>
<td>Diaion CR-10)</td>
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<td>11.</td>
<td>Diaion CR-10</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>Iminodiacetic acid</td>
<td>NO$_2$</td>
<td>Polystyrene</td>
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<td>12.</td>
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<td>13.</td>
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<td><img src="image" alt="Chemical structure" /></td>
<td>Ethylenimine</td>
<td>N$_x$</td>
<td>-</td>
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<td>14.</td>
<td>Misso ALM-525</td>
<td><img src="image" alt="Chemical structure" /></td>
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<td>NS$_2$</td>
<td>-</td>
</tr>
<tr>
<td>S. No.</td>
<td>Commercial Name</td>
<td>Active Chelating group</td>
<td>Nature of Chelating group</td>
<td>Donor atoms</td>
<td>Polymer matrix</td>
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<tr>
<td>15</td>
<td>Ligandex E</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Ethylenediamine triacetic acid</td>
<td>$\text{N}_2\text{O}_4$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>16</td>
<td>Ligandex I</td>
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<td>Iminodiacetic acid</td>
<td>$\text{NO}_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>17</td>
<td>IRC-718 (XE-318)</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>$\text{NO}_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>18</td>
<td>Unicellex UR-50 (also UR-40, UR-30, UR-20 &amp; UR-10)</td>
<td>(o-Hydroxybenzyl iminodiacetic acid)</td>
<td>$\text{NO}_3$</td>
<td>Phenol + formaldehyde</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Wofatit MC 50</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>$\text{NO}_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>20</td>
<td>Permutit S-1005</td>
<td>$\text{CH}_2\text{N}\text{CH}_2\text{CO}_2\text{H}$</td>
<td>Iminodiacetic acid</td>
<td>$\text{NO}_2$</td>
<td>Polystyrene (X% DVB)</td>
</tr>
<tr>
<td>21</td>
<td>Sumichelate Q-10R</td>
<td>$\text{NH}\text{C}\text{S}\text{S}\text{Na}$</td>
<td>Dithiocarbamic acid</td>
<td>$\text{NS}_2$</td>
<td>Polyacrylic acid</td>
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<tr>
<td>S. No.</td>
<td>Commercial Name</td>
<td>Active Chelating group</td>
<td>Nature of Chelating group</td>
<td>Donor atoms</td>
<td>Polymer matrix</td>
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<tr>
<td>22.</td>
<td>Sumichelate CR-2</td>
<td>[Image of active chelating group]</td>
<td>Basic (poly pyridine)</td>
<td>$N_3$</td>
<td>Polyvinylpyridine (20% DVB)</td>
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<td>23.</td>
<td>Spheron Oxine 1000</td>
<td>[Image of active chelating group]</td>
<td>8-Hydroxy-quinoline</td>
<td>NO</td>
<td>Poly(-hydroxyethylmethacrylate-co-ethylenemethacrylate)</td>
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<td>24.</td>
<td>Spheron Salicyl 1000</td>
<td>[Image of active chelating group]</td>
<td>Salicylic acid</td>
<td>$O_2$</td>
<td>Poly(-hydroxyethylmethacrylate-co-ethylenemethacrylate)</td>
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<td>26.</td>
<td>TP-207</td>
<td>[Image of active chelating group]</td>
<td>Iminodiacetic acid</td>
<td>$NO_2$</td>
<td></td>
</tr>
<tr>
<td>S. No.</td>
<td>Commercial Name</td>
<td>Active Chelating group</td>
<td>Nature of Chelating group</td>
<td>Donor atoms</td>
<td>Polymer matrix</td>
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<tr>
<td>27.</td>
<td>Srafion NMRR</td>
<td>$\text{CH}_2\text{S}C\text{NH}$</td>
<td>Isothiouronium</td>
<td>$\text{N}_2\text{S}$</td>
<td>Polystrene (X%DVB)</td>
</tr>
<tr>
<td>28.</td>
<td>Ionac SR-3</td>
<td>$\text{CH}_2\text{S}C\text{NH}$</td>
<td>Isothiouronium</td>
<td>$\text{N}_2\text{S}$</td>
<td>Polystrene (X%DVB)</td>
</tr>
<tr>
<td>29.</td>
<td>Sirorez-Cu</td>
<td>$\text{HO-C}_6\text{H}_4\text{C}-\text{N}-\text{CH}_2$</td>
<td>Phenol-piperazine</td>
<td>NO</td>
<td>-</td>
</tr>
<tr>
<td>30.</td>
<td>Kryptofix 221B (polymer bound)</td>
<td>$\text{H}_2\text{C}-\text{O}$</td>
<td>Cryptand</td>
<td>NO</td>
<td>Polystrene (2%DVB)</td>
</tr>
<tr>
<td>31.</td>
<td>Kryptofix 222B (polymer bound)</td>
<td>$\text{H}_2\text{C}-\text{O}$</td>
<td>Cryptand</td>
<td>NO</td>
<td>Polystrene (2%DVB)</td>
</tr>
</tbody>
</table>
1.2.5 **Criteria for a compound to act as chelating polymer**

Several chelating polymers have been found to be selective for one metal ion or another. A chelating resin consists of two components, i.e., a chelating group and a polymeric matrix. Thus, the properties of both components have to be taken into account when designing and synthesizing a chelating resin. During the early stages of development of chelating polymers, Gregor et al (1952) postulated that a suitable chelating group for incorporation into a polymeric matrix must have the following properties:

i) It should be capable of resin formation, or be capable of substitution into a polymeric matrix.

ii) It should be sufficiently stable to withstand the polymerization or resinification process.

iii) It should be compact enough so that its chelating ability is not hindered by the dense polymeric matrix.

iv) Both arms of a chelate structure should be present on the same monomer unit in proper spatial configuration. Hale (1956) pointed out that chelating polymer, should possess mechanical stability and resistance towards acids and bases used for regeneration of resin. According to Blasius and Brozio (1967), many known chelating agents could lose their selectivity when incorporated into a polymer matrix. Such unsuitable chelating ligands include all those ligands that do not form 1:1 complexes, e.g., anthranilic acid, 8-quinolinol and 1-nitroso-2-naphthol. In view of these facts, long-chain molecules like ethylenediaminediacetic acid also appeared unsuitable, because of the improbability that the chelate configuration occurring in aqueous solution could be
maintained on a cross-linked polymer. The selective behavior of a chelating polymer is based on the different stabilities of the metal complexes formed by a resin at appropriate pH values and the point of maximal efficiency for separation of a given set of metal ions can be established by variation of the pH.

D’Alelio et al (1969) suggested that for an effective chelating polymer the ligating behavior of the chelating group in the polymer matrix should be similar to that of the active group in the monomeric system. He proposed the following strategy for the synthesis of a chelating polymer:

i) Synthesis and characterization of chelating properties of a model compound.

ii) Synthesis and characterization of an oligomer of low molecular weight (dimer, trimer, etc.,) model compound and determination of its chelating properties.

iii) When the results of the second step confirm chelation, a high molecular weight chelating polymer should be synthesized and characterized, and its chelation capacity should be determined.

As pointed out by Nickless and Marshall (1965) the final choice between selective resins is determined by the actual problem under study. They nevertheless gave some requirements for the design of a selective chelating resin. The combination of conditions given in the literature allows one, in principle, to design (and synthesise) a suitable chelating resin with the desired selectivity. According to Hodgkin (1979) the rather poor selectivity of most of the resins originates from the fact that the chelating groups normally anchored onto polymeric matrices are usually strongly chelating,
and not very selective. The inhomogeneous chemical environment inside the resin also has a negative influence on the selectivity. Most early work in this area has neglected these complications, mainly because no methods were available to study the chemical and physical properties of the polymers in sufficient detail. Nowadays, Fourier NMR (\(^1\)H, \(^{13}\)C) and IR spectroscopy allow much better characterization of polymeric chelating resins. Summarizing the preceding discussion, the following essential requirements seem necessary for the synthesis of a chelating polymer:

i) The chelating ligand attached to a solid matrix should possess strong metal-binding properties and selectivity towards certain metal ions. The concept of “soft” and “hard” donors or “a” and “b” class metals can be a useful guide in this regard.

ii) The chelating ligand should preferably be multidentate, permitting formation of a 1:1 chelate with a metal ion, and the chelating ligand should be monofunctional as far as possible. The occurrence of mixed functional groups such as sulfonic, carboxylic or phenolic groups should be avoided in the same resin.

iii) The chelating polymer should possess good swelling properties and compatibility between polymer and the medium (generally aqueous) is essential; this can be regulated by the presence of hydrophilic groups on the polymer and by the extent of cross-linking. A higher degree of cross-linking results in increased mechanical strength, but the swelling properties of polymers are adversely affected.
1.3 SYNTHESIS OF COMPLEXING AND CHELATING RESINS

The synthesis of a chelating resin usually consists in the functionalization of a polymeric matrix which generally consists of an irregular, macromolecular, three-dimensional network of hydrocarbon chains. Functionalization means incorporation of chelating ligands into polymeric matrices. The various methods of polymer modification and synthesizing polymeric reagents have been reviewed (Mathur et al 1980 and Akelah et al 1981 and Heitz 1977) has critically examined the design, scope, and limitations of modified polymers and polymeric reagents. Two important aspects of the synthesis of chelating resins, viz. synthesis of a polymeric matrix and that of a chelating resin, are summarized in the following sections.

1.3.1 Types and synthesis of polymeric matrices

Fundamentally, two types of polymeric matrices can be considered, i.e., inorganic and organic. In spite high mechanical strength, high thermal stability, good ability to withstand pressure and stability both towards organic solvents, Inorganic polymers suffers certain disadvantages like impossibility of a high degree of functionalization, relatively low chelating capacity. Silica is among the most extensively used inorganic support.

The organic matrices used as supports for chelating resins either originate from naturally occurring polymers or from synthetic polymers. Among the naturally occurring polymers used as supports for chelating resins, cellulose has been used extensively. The chemistry of cellulose as a polymeric support, its chelating properties and the use of chelating cellulose for preconcentration of trace elements have been reviewed extensively by Wegscheider and Knapp (1981) and Lieser (1979). Another important naturally-occurring chelating marine polymer is chitin, poly(N-acetyl-D-glucosamine) and its deacetylated derivative, chitosan, which have been
useful for removing heavy metal ions from discharge water. The chelating properties of chitin and chitosan have been studied in detail and review by Muzzarelli (1973, 1976).

Among the synthetic organic matrices, two types of polymers can be considered, viz. condensation and addition polymers, which are extensively used as supports or matrices for chelating polymers. Condensation polymers, nevertheless, continue to be popular as polymeric supports for chelating resins and many important chelating ligands have been synthesized on the basis of condensation polymerization. However, the majority of commercial chelating resins that find wide application possess styrene-divinylbenzene copolymer matrices. The various consequences of the nature of polymeric matrices on the properties of chelating resins have been reviewed (Nielsen et al 1970 and Frechet et al 1977). The more regular a network is built up, the better are the qualitative features the matrix exhibits.

1.3.2 Functionalization and incorporation of chelating ligands into polymeric matrices

The general methods of incorporating active functional groups (in this case chelating ligands) have been summarized by Akelah and Sherrington (1981). According to them, three methods can be distinguished to incorporate active functional groups into polymer chains:

a) direct polymerization and copolymerization of monomers containing the desired functional groups,

b) chemical modification of a preformed polymer,

c) a combination of (a) and (b).

These three methods have been used in one or the other form to synthesize the majority of chelating polymers. The synthesis of polymers
with macrocyclic chelating ligands as pendant or anchor groups has also been discussed by a number of authors (Blasius et al 1980 and Smid 1983). The method involving incorporation of chelating ligands into performed polymers or matrices to synthesize chelating resins is preferred to other methods in view of the fact that the degree of functionalization can be controlled by varying the amount of cross-linking agents and the extent of modification in performed matrices. A large number of such chelating resins have been prepared by attaching a chelating ligand to a performed polymer and the most extensively used preformed polymers have been the copolymers of styrene and divinylbenzene, which are unreactive as such. This material is normally first converted into its chloromethylated derivative and then treated with a chelating ligand to obtain a chelating compounds.

(a) (b) (c)

Scheme - 5
Several methods are available for the preparation of chloromethylating cross-linked polystyrene (Belen’kii et al 1977), but a satisfactory method for chloromethylation consists in treatment of cross-linked polystyrene with chloromethyl methyl ether under Friedel-Crafts reaction conditions (Pepper et al 1953). The conversion of chloromethylated polystyrene (a) into its sulfonium salt (b) is important steps in the synthesis of an iminodiacetic acid chelating resin (c) (Scheme-5); the sulfonium salt is hydrophilic whereas the chloromethylated resin is not and will not react appreciably with the sodium salt of iminodiacetic acid. Alternatively, the problem of hydrophilicity of chloromethylated polystyrene can be solved by partially converting it to a quarternary ammonium salt by treating it with triethyl amine followed by reaction with a chelating group Scheme-6. Using this approach, Melby (1975) synthesized several chelating resins. Several other functionalized derivatives of styrene-divinylbenzene copolymers, such as sulfonated, bromo, lithiated, hydroxyethyl, hydromethyl, phosphinated, thiolated, amino, aldehyde etc., (Frechet et al 1971 and 1979) have also been prepared.
Another approach for synthesizing chelating resin consists in the modification of a polymer through a sequence of reactions on the polymer itself. For instance, the synthesis of iminodiacetic acid resin using styrene-divinylbenzene copolymers as polymeric support can be carried out as depicted in Scheme-7 and Scheme-8. Several poly(hydroxamic acid) resins have also been prepared (Vernon 1982) by this method. The fact that this type of synthesis involves a number of steps is a serious disadvantage because of the possibility of contamination of the end product with by-products and intermediate products due to their incomplete conversion and the inherent problem of their removal.
In recent years, a number of chelating resins have been prepared by the polymerization of a monomeric unit in the presence of a cross-linking agent. This approach of synthesizing a chelating resin can be illustrated by the synthesis of an iminodiacetic acid resin on a polyacrylate as shown in Scheme-9.
Some Cu(II) selective resins containing hydroxyoxime group have also been prepared from substituted phenyl acrylate polymers via the Fries rearrangement using this approach (Walsh et al 1983), depicted in Scheme-10. In this procedure considerable manipulation to optimize the conditions for copolymerization is necessary to obtain a good yield of the chelating resin in satisfactory physical form. However, this method may lead to the formation of a relatively “purer” chelating resin having less contamination with by-products.
Another important method of synthesizing co-ordination polymer is that of polycondensation. Many compounds that form chelates with metal ions can be copolymerized with phenols and aldehydes, to obtain a variety of chelating resins (Nickless and Marshall 1965). For instance, anthranilic acid, anthranilic acid-diacetic acid, m-phenylenediamine diglycine, and m-phenylenediamin tetraacetic acid (Gregor et al 1952 and Pennington et al 1959), among other ligands have been copolymerized with formaldehyde and mono- or polyphenols to synthesize condensation chelating polymers. Many other chelating resins, prepared by a polycondensation method, have been found selective for different metal ions. A quadridentate chelating ligand, N-(o-hydroxybenzyl)iminodiacetic acid, has been copolymerized with phenol and formaldehyde to obtain a new chelating resin (VII), commercially available under the name of Unicellex UR-50 (Nakashima et al 1982).
Efendiev and Kabanov (1982) introduced a new approach based on the “memory” of monomers, to develop highly selective chelating resins. The general principle of their method involves three steps in the preparation of such polymers. In the first step, the linear polymer is treated with a solution of a metal ion to be adsorbed in solution, i.e. under conditions when segments of the macromolecule are still mobile enough. The second step is fixation of the optimum conformation of the macromolecules for ion uptake by cross-linking the metal polymer complex. The final step involves the removal of the template metal ion from the cross-linked sorbent. This approach can be illustrated by the practical example in which the diethyl ester of vinylphosphonic acid (DEVPA) and acrylic acid (AA) have been chosen as the initial monomers to prepare polymer sorbents. For instance, a macromolecular solvent favorably prearranged for the sorption of Cu(II) was obtained by

i) mixing of the linear copolymer with Cu(II) ions in acidic solution under conditions when sorption does not takes place.

ii) Slow titration of the linear copolymer with Cu(II) ammonia solution and isolation of the Cu(II)-copolymer complex precipitate,

iii) Fixation of the optimal conformation for the uptake of Cu(II) ions by cross-linking of the Cu(II)-copolymer complex.

iv) Desorption of Cu(II) ions from the cross-linked sorbent with 1M hydrochloric acid.

1.4 SURVEY OF AVAILABLE CHELATING RESINS

In the following sections, a brief survey of available chelating resins will be presented, classified according to their donor atoms.
1.4.1 **Chelating resins containing nitrogen as the only donor atom**

The number of chelating polymers with nitrogen as the only donor atom has been growing in recent years. Blasius and Brozio (1967) have reviewed the early development of such chelating resins. Gold and Gregor (1959) reported the synthesis of a complexing poly(N-vinylimidazole) (VIII) polymer which contains aromatic nitrogen as the only donor atoms. Chelation was found in the case of Cu(I) and Ag(I). Related systems containing imidazole supported on styrene-divinylbenzene copolymers have also been reported (Drago and Gaul 1979). This complexing resin (IX) can be synthesized from chloromethylated styrene-divinylbenzene copolymers and the sodium or lithium salt of imidazole, using dimethylformamide or tetrahydrofuran as a solvent.

![Chemical structures](image)

**VIII**

**IX**

The reaction product of tetracyanoethylene with copper is a polymer having a phthalocyanine type sheet-like structure complex (X) with nitrogen as the only donor atom.
Polymers containing metallophorphyrin have been studied due their unique electronic structures and optical properties. Monomers and polymers with the structures shown (XI) have been successfully synthesized by Bao et al (1994) and it was observed that the electronic, optical and magnetic properties of these polymers can be tuned by changing different substituents and by incorporating various metal ions into the phorphyrin units.

Various π-conjugated polymers having nitrogen as the chelating ligand with well-defined structure are prepared via organometallic polycondensation reactions (XII and XIII). These polymers are useful materials for electrical and optical devices (Yamamoto 2002)
Diphenylcarbazide and diphenylcarbazone which act as bidentate chelating ligands (Dilworth 1976) have been incorporated into polymeric matrices to obtain chelating resin (XIV) and (XV). A resin (XV) containing diphenylcarbazone as a functional group has been found specific for Hg(II) (Szczepaniak 1965).
Drago et al (1980) described a versatile high-yield synthesis for covalently attaching multidentate chelating ligands to polystyrene matrices. Three polydentate amines, bis(3-aminopropyl)amine, bis(3-aminopropyl)phosphine and diaminopropane have been anchored onto a polystyrene matrix to obtain three new polymer supported multidentate chelating ligands designated by structures such as (XVI), (XVII), respectively. These materials form the basis for the preparation of a wide variety of chelating ligands, e.g., through the Schiff base formation reaction with a variety of aldehydes and ketones.
1.4.2 Chelating resins containing both nitrogen and oxygen as donor atoms

This forms the largest group of chelating resins. The important ligands possessing nitrogen and oxygen as donor atoms include iminodiacetic acids, hydroxamic acids, oximes, hydroxyquinoline derivatives and Schiff bases, which are discussed in this section.

Iminodiacetic acid and its derivatives have been incorporated into a variety of matrices, including both addition and condensation resins. The first resin of this type, containing EDTA as a solid solution within a phenol-formaldehyde condensate, was reported by Klyatshko et al (1951), followed by Blasius and Olbrich (1956), who prepared a condensation chelating polymer from resorcinol, (m-phenylenediaminedinitrilo)tetaacetic acid and formaldehyde. The later resin was found to be useful in the chromatographic separation of Co(II) and Ni(II) and its appears to chelate the metal ions in the manner shown in structure (XVIII). Similarly, anthranilic acid-diacetic acid and m-phenylene-diglycine have also been incorporated into phenol-formaldehyde and resorcinol-formaldehyde condensates (Gregor 1954).

XVIII
Schiff base polymers were prepared by Patel and co-workers (1989) by condensation of bis(bromo salicylaldehyde) with 1,6-diaminohexane, and insoluble chelates of Cu, Ni, Co, Zn and Mn were synthesized (Scheme-11). The authors determined the co-ordination geometry of the chelated metal ions via electronic reflectance spectroscopy and magnetic susceptibility measurements. It was reported that the Cu(II) metal center in the polychelates adopts a square planar geometry, Co(II) ions are tetrahedral, while Mn(II) and Ni(II) have octahedral and distorted octahedral geometry respectively. Thermal analysis indicated that decomposition occurs above 250°C. Not surprisingly, Schiff base polymers containing aliphatic amines are less thermally stable than their counterparts constructed from aromatic amines.

![Scheme - 11](image)

Polysiloxane-Schiff base copolymer was synthesized by a different strategy (Scheme-12). Cu(II) and Ni(II) salen-diol monomers were first converted to the corresponding alkali metal salt through the addition of NaOH. Subsequent polycondensation with chloromethyl-terminated poly(dimethylsiloxane) afforded the polymers as brown (Cu) and orange (Ni) solids. The polymers were characterized by IR, UV-Vis, and 1H-NMR spectroscopies. TGA indicated that copolymers with longer polysiloxane segment have improved thermal stability. Polysilanes are known to exhibit σ-delocalization and these materials may be semiconducting (Miller and Michl 1989).
Gurnule et al. (2002) synthesized terpolymer resins by the condensation of salicylic acid and melamine with formaldehyde, 4-hydroxy acetophenone and biuret with formaldehyde in the presence of acid catalyst. The chelating properties of this polymer were studied for Cu(II), Ni(II), Co(II), Zn(II) ions. A batch equilibrium method was employed in the study of the selectivity of metal ion uptake involving the measurements of the distribution of the given metal ions between the polymer sample and a solution containing the metal ion. Chelating properties of this resin have also been studied for metal ion uptake over a wide pH range and in media of various ionic strength.

Patel et al. (2004) synthesized acrylic copolymers with different feed ratios of 8-quinoloyl methacrylate with methyl methacrylate by free radical polymerization, and studied the metal ion uptake capacity using different metal ion solutions under different experimental conditions. Due to the presence of pendant ester bound quinolyl group, the copolymers are capable of adsorbing the tested cations from their aqueous solutions.

A chelating phenol-formaldehyde polymer, poly(salicylaldoxime 3,5-diylmethylene) was synthesized and characterized by Ebraheem et al. (1997). The sorption properties of the resin towards various divalent metal ions were studied as a function of pH and contact time. The resin has high selectivity towards Cu(II) ions and showed fast rates of metal ion uptake.
Nakajima and coworkers (2006) studied the mechanism of Cu(II) adsorption by polyvinyl polyacrylate (PVPA) using ESR and magnetic measurements. The ESR spectrum of Cu(II) ion in PVPA are axial type with tetragonally distorted octahedral symmetry. The absorption peaks originated from Cu(II)-Cu(II) dimer was also observed.

Samal et al (1999) synthesized the chelating resin by condensing phenolic Schiff bases derived from 4,4’-diamino diphenyl sulfone and o-hydroxy acetophenone with formaldehyde/furfuraldehyde. The polymeric Schiff bases were found to form complexes readily with transition metal ions [Cu(II) and Ni(II)]. The resins and complexes were characterized by usual analytical method. The effect of contact time, pH, and temperature, the size of the adsorbent and the concentration of the metal ion solution on the metal uptake behaviour of the resins were also studied.

Agarwal et al (2004) synthesized a PVC-based sensor for Nd(III) ions based on chelating inorganic ion-exchange resin [tetracycline-sorbed zirconium(IV) tungstiphosphate TCZWP] as an electro active material. The sensor exhibits a nernstian response for Nd(III) ion over a wide concentration range. The detection limit has been found to be 1x10^{-5}M. The proposed membrane sensor reveals good selectivity for Nd(III) with regard to other trivalent lanthanide metal ions and could be used in the pH range 3-7 as well as in the partially non-aqueous media. The sensor has also been successfully used as an indicator.

Simple methods for the immobilization of 8-hydroxy quinoline on silica have been demonstrated by Luhrmann et al (1985). The suitability of the immobilized quinolinol for trace enrichment has been tested for Cu(II), Ni(II), Co(III), Mn(II), Zn(II), Cd(II), Pt(II), Hg(II), Fe(III), and Cr(III) in the pH range from 4 to 6. The metal uptake capacities were found to range from
0.2 to 0.7 mmole/g and the distribution ratios from $1 \times 10^3$ to $9 \times 10^4$. McLaren et al (1985) have employed 8-hydroxy quinoline immobilized on silica for preconcentration of trace metal ions from sea water samples, with the final determination performed by inductively-coupled argon plasma-mass spectrometry (ICP-MS). The work was extended by using ICP-MS for samples concentrated by chelation with 8-hydroxyquinoline immobilized on silica.

Kaliyappan et al (1999 and 2007) synthesized series of chelating ligands based on 8-hydroxy-5-azo quinoline ligand and investigated their binding properties of divalent metal ions and studied their geometry. The sorption properties of the chelate forming resin towards various divalent metal ions were studied as a function of pH and electrolyte. Elemental analysis of polychelates suggested a metal-ligand ratio of 1:2.

8-hydroxyquinoline terephthalate Ni(II) and Cu(II) complexes were synthesized by Mishra et al (2002). These terephthalates are known in industry for their polymeric heat and chemical resistant and tolerant nature. Besides industrial and biological significance mixed ligand chelates have their theoretical and chemical importance.

Polycondensation method is based on the capacity of some monomeric organic ligands to react with aldehydes forming polymeric sorbents. Some times cross-linking agents (phenol or resorcinol) are used (Scheme-13). In the same way chelating resins based on 8-hydroxyquinoline, iminodiacetic acid, and derivatives of hydroxy acetophenones have been synthesized The property of chelating sorbent to react with metallic ions under certain favorable conditions is determined by the nature of the functional groups and/or donor atom (O,N,S) capable of forming chelate rings(Bilba et al 1998).
Poly(2-hydroxy-4-methacryloyloxy acetophenone semicarbazone), poly(2-hydroxy-4-acryloyloxyacetophenoneoxime) and poly(2-hydroxy-4-methacryloyloxy acetophenoneoxime) were synthesized and complexed with various metal ions. The polymer metal complexes were synthesized by the reaction of the metal acetates with the polymer and characterized (Thamizharasi et al 1999).

Rivas and Seguel (2001) synthesized polychelates of poly(maleic acid) with Cu(II), Ni(II), Co(II), and Zn(II). Elemental analysis, as well as magnetic, spectral and thermal properties in addition to electrical conductivities of the chelates were investigated and possible structures have been assigned to the polychelates.

Bekhir Salih (2002) synthesized a polymer containing 1,4,8,11-tetraaza-cyclotetradecane with acryloyl chloride. The affinity of the polymeric material for transition metal ions was used to characterize the polymeric structure, and to test the adsorption-desorption of the selected ions [Cu(II), Ni(II), Cd(II), Pb(II)] from aqueous media containing different amounts of these metal ions (5-800 ppm) at different pH values (2-8). It was found that the adsorption rates were high and the adsorption equilibrium was reached in about 30min.
1.4.3 Chelating resins containing oxygen as the only donor atom

Several types of ligands containing oxygen as the only donor atom have been incorporated into different types of polymeric matrices. Some of the ligands used for such studies include polyphenols, polycarboxylic acids, 1,3-diketones, phosphonic acids, arsenic acids, polyphenolic carboxylic acids, fluorones, flavones and related compounds.

Compounds containing phenolic groups can easily be converted into polymeric compounds by condensing them with aldehyde, with or without an appropriate phenol, in the presence or absence of a cross-linking agent to obtain a gel-type resin. A chelating resin containing salicylic acid, chemically bound via the side-chain azo groups to hydrophilic glycol methacrylate gels, has been reported by Slovak et al (1976). This resin, which is now commercially available under the trade name of Spheron Salicyl-1000 shows high selectivity for Fe(III) and Al(III) ions above pH 2.5. It has been shown that the enhanced sorption of heavy metals by complex formation is accompanied by non-specific ion exchange arising from dissociation of the carboxyl group of salicylic acid. The sorption capacity for heavy metals was found to exceed 0.35 mmol g⁻¹ and sorption equilibrium was achieved within two min. The chelating properties of salicylic acid-urea-formaldehyde resin (XIX) have also been described (Joshi et al 1982). The copolymer showed higher selectivity for U(VI), Cu(II) and Fe(III) than for Mn(II), Co(II), and Zn(II). The IR spectra of the complexes showed that urea present in the copolymer is not involved in the complexation, and it only improves the stability of the copolymer.
Thamizharasi and Venkata Rami Reddy (1992) prepared oxygen donor ligand poly(2-hydroxy-4-methacryloyloxyacetophenone) and its Cu(II) and Ni(II) complexes. Elemental analysis of polychelates suggested a metal-ligand ratio of 1:2 and all the polychelates were poor electrical conductors.

Poly(2-hydroxy-4-methacryloyloxyacetophenone-formaldehyde) was prepared from a mixture of 2-hydroxy-4-methacryloyloxyacetophenone and 37% formalin solution and then polymerized using benzoylperoxide as free radical initiator. An aqueous solution of Cu(II)/Ni(II) acetate was added drop wise, to get polymer-metal complexes. These complexes found to catalyze the ester hydrolysis and oxidation of phenol and also initiate the polymerization of N-vinylpyrrolidone (XXI) (Kaliyappan et al 1994).
2,5-dihydroxyacetophenone was treated with acryloyl chloride and polymerized to get poly(2-acetyl-4-hydroxyphenyl acrylate). The polymer metal complexes were obtained with the aqueous solution of Cu(II)/Ni(II) with the polymer. The polymer metal complexes were characterized by FT-IR and the results revealed that the ligands are co-ordinated through the oxygen of the keto group and oxygen of the phenolic –OH group with the metal ions. The electronic spectra and magnetic moment of polymer-metal complexes showed an distorted octahedral and square planar structure for Ni(II) and Cu(II) complexes respectively. The X-Ray diffraction studies revealed that the polymers are amorphous and polymer-metal complexes were crystalline. The thermal stability and glass transition temperature of the polymer-metal complexes were found to be higher than that of polymer (Nanjundan et al 2005).

The complexes of Cu(II), Co(II), and Zn(II) with oligosalicylaldehyde were synthesized. Due to the groups of –OH and –CHO in its structure oligosalicylaldehyde has the capability of co-ordination with different metal ions (Mart et al 2004) (XXI).
A series of monomers were prepared by reacting (meth)acryloyl chloride with 2,4-dihydroxy benzophenone, 2,4-dihydroxy benzaldehyde and 2,4-dihydroxy acetophenone. The monomers were polymerized and complexed with Cu(II)/Ni(II) metal ions and characterized (XXII). These polymer-metal complexes initiated the polymerization of N-vinyl pyrrolidone. Cu(II) complexes were found to catalyze the oxidation of cyclohexanol to cyclohexanone in the presence of H₂O₂ (Kaliyappan et al 2003).

R= C₆H₅, CH₃, H.

X= H₂O for Ni(II)

XXII
Bhaduri et al (1982) incorporated acetylacetone into a styrene-divinylbenzene (8%) copolymer by chloromethylation and treatment with acetylacetone in the presence of sodium ethoxide as catalyst in a swelling solvent such as tetrahydrofuran (XXIII). The IR spectra of the modified beads and soluble functionalized derivative of acetylacetone show a medium and high intensity band at 1700cm\(^{-1}\) respectively; this band can be assigned to the \(\nu\text{C}=\text{O}\) vibration of acetylacetone.

\[
\text{XXIII}
\]

Stamberg and Seidl (1962) described the preparation of a condensation chelating polymer incorporating 2,6,7-trihydroxy-9-phenyl-3H-xanthene-3-one (phenylflurone) (XXIV), which is highly selective for germanium. Griesbach and Lieser (1980) synthesized several chelating resins, incorporating 4,5-dihydroxynaphthalindisulfonic acid (XXV), alizarin (XXVI), 1,2,5,8-tetrahydroxyanthrachinon (chinalizarin) (XXVII) and morin (XXVIII) into a polystyrene matrix. The synthetic route involved the nitration of cross-linked polystyrene, followed by reduction, diazotization and coupling with the appropriate ligand. The capacities of these resins are relatively low and lie in the range 0.4 - 0.7 mmol g\(^{-1}\). The flavone resin has been found to be selective for iron (Veruovic 1964).
1.5 APPLICATIONS OF CO-ORDINATION POLYMER AND ITS METAL COMPLEXES

One of the interests in building co-ordination polymers is the creation of new tunable functional materials. This part reviews some examples of how metal-organic frameworks are promising as materials for
applications in catalysis reactions, conductivity, luminescence, NLO or deposition of thin films, liquid crystalline, and magnetism,

1.5.1 Polymer-metal complex catalyzed reactions

Polymer-metal complexes of transition metal ions are efficient catalysts both in homogeneous and heterogeneous reaction and the activity of these complexes varied with the type of ligands, co-ordination sites and metal ions. The catalytic activity of metal complexes has been analyzed critically in various reactions as given below.

1.5.1.1 Polymerization initiation reaction

The polymerization reactions are catalyzed with various catalysts and based on experimental observations; the following conditions apply to the efficient use of catalysts in the polymerization of different monomers.

i) Catalyst must have high olefin-insertion ability.

ii) Catalyst must have two available cis-located sites for polymerization.

iii) Catalyst must be stable enough under the usual polymerization conditions.

A series of Schiff base ligands (14a-d) were prepared in good yield (>80%) via an imine condensation process (Scheme-14) (Cameron et al 1999) and used in ethylene polymerization (Cavell et al 2002). The tridentate ligand on treating with Me₃Al in toluene at room temperature produced dimethyl complexes [3,5-But-2-(O)C₆H₂CH=NL] AlMe₂ with elimination of methane (Scheme 15), which on reacting with B(C₆F₅)₃ produced the cationic system (3,5-But-2-(O)C₆H₂CH=NL)-AlMe⁺ able to catalyze the polymerization of ethylene.
Ethylene polymerization with complexes of Ni(II) and Pa(II) produced linear and high-density polyethylenes without molecular chain walking (Gibson et al 2004). These catalysts, residing on an inorganic support, were used in the commercial scale polymerization of ethylene (Kim and coworkers 2003).

The fourth groups of metal complexes (XXIX to XXXIII) of phenoxyimine (PI) were efficient catalysts in the polymerization of ethylene at normal pressure. These complexes showed high activity in the presence of methylaluminiumoxane (MAO) as a co-catalyst. Among these catalysts, the zirconium PI catalyst was exceptionally active (Matsui et al 2001). The complexes (XXIX and XXX) were active at 30 min whereas, complexes (XXXI to XXXIII) showed their activity within a period of 5 min (Table 1.2).
Table 1.2  Polymerization of the ethylene in the presence of PI Catalyst

<table>
<thead>
<tr>
<th>Complex</th>
<th>Complex concentration (μM)</th>
<th>Yield (g)</th>
<th>Activity (kg PE / (mmol cat h))</th>
<th>Mv × 10^4</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>20.0^a</td>
<td>0.18</td>
<td>&lt;0.01</td>
<td>-----</td>
</tr>
<tr>
<td>27</td>
<td>20.0^a</td>
<td>3.44</td>
<td>1.4</td>
<td>Oil^c</td>
</tr>
<tr>
<td>28</td>
<td>20.0^b</td>
<td>1.38</td>
<td>3.3</td>
<td>51</td>
</tr>
<tr>
<td>29</td>
<td>0.08^b</td>
<td>0.87</td>
<td>519.0</td>
<td>1</td>
</tr>
<tr>
<td>30</td>
<td>20.0^b</td>
<td>2.69</td>
<td>6.5</td>
<td>3</td>
</tr>
<tr>
<td>Blank</td>
<td>20.0^b</td>
<td>1.25</td>
<td>3.0</td>
<td>7</td>
</tr>
<tr>
<td>C_{p2}ZrCl_3</td>
<td>02.0^b</td>
<td>1.13</td>
<td>27.0</td>
<td>104</td>
</tr>
</tbody>
</table>

Viscometric Mol. wt. (Mv). Conditions: temperature, 25°C; pressure, 0.1MPa; Solvent, toluene (250 ml); cocatalyst [MAO], 1.25mmol (Al),

^a Polymerization time: 30 min.

^b Polymerization time: 5 min.

^c GPC Mol. wt.

The Fe(II) and Co(II) complexes of pyridine bis(imine) ligands showed significant activity in the polymerization of ethylene. These complexes were also used successfully for copolymerization of ethylene with 1-hexene (Souane et al 2002). The Fe(II) Schiff base complexes showed higher yield and activity than the Co(II) complexes (Table 1.3).
Table 1.3 Ethylene polymerization with iron and cobalt catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Loading (μmol)</th>
<th>Yield (g)</th>
<th>Activity (gmmol⁻¹bar⁻¹h⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1</td>
<td>10</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>9</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>10</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>9</td>
<td>4.9</td>
</tr>
<tr>
<td>Co</td>
<td>2</td>
<td>10</td>
<td>3.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>9</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>10</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>9</td>
<td>1.3</td>
</tr>
</tbody>
</table>

The salicylalidiminato complexes of zirconium were long lived catalysts in ethylene polymerization and promoted radical decomposition in certain cases (Knight et al 2002). Chiral Schiff base complexes were used successfully in the synthesis of crystalline high molecular weight racemic poly(lactic acid) from racemic lactides (Radane et al 2002). These complexes were also used as catalysts in the cyclooligomerization of isoprene and butadiene. The electronic and geometric factors of Schiff base ligands showed pronounced effect on rate of oligomerization.

1.5.1.2 Ring opening polymerization reaction

Recently the ring opening metathesis polymerization (ROMP) (Scheme-16) has become an important tool both in synthesis of fine chemicals and macromolecular chemistry. The catalytic activity of complexes (XXXIV) was tested in ROMP and it was noted that olefin metathesis polymerization involved decooordination and coordination of ‘onearm’ of the bidentate Schiff base ligands (Clercq et al 2003).
Clercq et al. (2002) prepared series of ruthenium Schiff base complexes and tested for their activity in atom transfer radical polymerization (ATRP) in the presence of trimethylsilyldiazomethane (TMSD). These complexes were also active in ring opening metathesis polymerization (ROMP) of norbornene and cyclooctene. The percentage conversion of norbornene and cyclooctene was increased within 100 min and after that the conversion was almost constant. The activity of complexes in ROMP and ATRP was dependent on steric hindrance and electron donating ability of Schiff base ligands.

Electron-donating alkyl substituent groups at one or both meta position on arylaine ring facilitate the ring opening/degradation at lower temperature (Ishida et al. 2001). The salen complexes also showed activity in ring opening oligomerization or polymerization of epoxides. (Scheme-17) (Mark et al. 2000).
Radano et al. (2000) used Al(III) binaphthyl complexes to obtain stereoselective polylactides (Scheme 18). This process has provided an easy way to synthesize stereoselective poly(acetic acid) directly from racemic lactides, unlike other methods, which required enantiopure (R)- and (S)-poly(acetic acid) combination with polylactides. The Al(III) complexes of binaphthyl chiral Schiff base were also used as catalysts in the stereo selective polymerization of lactides in which, catalysts opened meso-lactides preferentially at site B.

**Scheme – 18**

### 1.5.1.3 Oxidation reaction

Chiral Schiff base ligands of -O-N-O- type with transition metal ions i.e., Ti(IV), V(IV), Cu(II) or Zn(II), were used in various asymmetric chemical transformations. The addition of trimethylsilylcyanide to
benzaldehyde in the presence of Ti(IV) ions resulted in trimethylsilyl cyanohydrins in 40-85% enantioselectivity (Scheme 19) (Gama et al 2002).

Schiff base complexes of Cr(III), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) were encapsulated in zeolites and tested for their activity in the oxidation of cyclohexane to cyclohexanol and cyclohexanone (Hueso-Urena et al 2003). The reaction was catalyzed more successfully with Schiff base complexes of Mn(II) ions than other Schiff base complexes.

The conversion of cyclohexane was enhanced from 2.4 to 60% with immobilized metal complexes, which indicated that zeolites-Y acted as cytochrome P-450 oxidation system. The Mn(II) complexes of N,N’-ethylenebis-(salicylidene aminato) salen; N,N’-ethylene bis-(5-chlorosalicylidene aminato)Cl salen; N,N’-ethylene bis-(5-brome-salicylidene aminato)Br salen and N,N’-ethylene bis-(5-nitrosalicyli-2,2-diene aminato) NO salen were encapsulated in zeolites-Y for aerobic oxidation of styrene to benzaldehyde, styrene oxide and phenyl acetaldehyde (Farzaneh et al 1999).

The Co(II) complexes were effective in the oxidation of reactive substrates, such as aldehydes and phenols. The phenoxy radicals were assumed to be responsible for the oxidation of phenols in the presence of Co(II) complexes (Musie et al 2001). These complexes showed high catalytic
activity in the oxidation of phenols in ScCO$_2$ (super critical CO$_2$), which suggested that this high activity of Co(II) salen complex in ScCO$_2$ would expand the range of substrates for oxidation. The oxidation resistant substrates such as hydrocarbons and lignins could be oxidized using these catalysts in ScCO$_2$.

The chitosan supported Co(II) complexes of bis(salicylidene ethylene diamine) catalyzed the oxidation of DOPA in the presence of oxygen and the activity was compared with unsupported monomeric complexes (Hu-D et al 2000). The catalytic activity of Co(II) salen complex in ScCO$_2$ was evaluated for oxidation of phenols in the presence of organic peroxides as oxidant.

The alkyl aryl sulfides were oxidized in an asymmetric fashion using Mn(III) salen complexes with ee of 94%. The oxidation of sulfides was carried out using equimolar amount of iodosylbenzene and 1% of catalyst. Solvents influenced the enantioselectivity of reaction. The Mn(II) salen complexes showed catalytic activity in asymmetric oxidation of silyl ketone acetals with high enantioselectivity (<81%). The yield and enantioselectivity was dependant on the type of oxygen donor, pH of the medium, additives and substitution pattern of the enol substrate (Adam et al 1996). Schiff base ligands prepared with (S)-tert-leucinol and chiral and racemic salicylaldehyde were used in vanadium-catalyzed asymmetric sulfoxidation of thioethers in the presence of hydrogen peroxide (Vetter et al 1998). The enantioselectivity of the product was dependant on the structures of salicylaldehydes.

The dinuclear Ru(II) Schiff base complexes of pyridine 2-carboxaldehyde and diamines were efficient catalyst in epoxidation of alkenes. The ruthenium dinuclear Schiff base complexes (XXXV) also showed activity in ROMP of norbornene and ATRP of methyl methacrylate and styrene (Opstal et al 2003).
1.5.2 Conductivity

Conductivity may be an interesting research topic providing that short inorganic or conjugated organic bridges exist in the metal-organic framework.

Some one-dimensional co-ordination polymers \([\{M(L_{10})(\mu-L_{11})\}\]n built shown on (XXXVI) with or without doping with iodine exhibit conductivities in a range of \(1 \times 10^{-6}\) to \(2 \times 10^{-4}\)Scm\(^{-1}\) (Hanack and coworkers 1988). (Conductivities of metals is \(10^4\) – \(10^5\)Scm\(^{-1}\) and increases with decreasing temperature) the conductivity is due to the interaction between the metal d-orbital and the \(\pi^*\) level of the bridging ligand L\(_{11}\).

In some cases co-ordination polymers can have semiconductor behaviour. The three-dimensional polymer \([\{Ag(H_2btc)_2[Ag_2(Hbtc)]\}]n\)
$\text{H}_2\text{btc} = \text{benzene-1,3,5-tricarboxylate}$ (Sun et al 2002) presents weak semi-conductivity (conductivity of $1.06 \times 10^{-6}$ S cm$^{-1}$ and increase of conductivity with temperature) due to the presence short Ag-Ag contacts as the whole structure can be regarded as parallel Ag chains connected by the $\text{H}_2\text{btc}$- and $\text{Hbtc}_2$- ligands. The Ag-Ag contacts, ranging from 2.9626 to 3.2782 Å, are known for giving semi-conductivity properties to the materials.

The semi-conductivity is better for the compound $\text{Ag}_2\text{CA}$ (CA = Cyanuric acid, $\text{C}_3\text{H}_3\text{N}_3\text{O}_3$) being an organic-inorganic hybrid material. It is composed of Ag sheets with the cyanuric acid as linkers between the sheets. The conductivity is furthermore anisotropic in this case, $5 \times 10^{-3}$ S cm$^{-1}$ parallel to the sheets, and $2 \times 10^{-5}$ S cm$^{-1}$ perpendicular to the sheet (Rao et al 2000).

Semi-conductivity was also reported for the compound $\{[\text{Ni}_2(\text{pyrimidine-2-thiolate})]\}_n$ which exhibits two dimensional motifs based on $\text{Ni}_2\text{S}_2$ units spaced out by the ligand molecules (Zhao and coworkers 2001). There are therefore short distances between the metal centers of 3.774Å. Its conductivity is found to be $5\times10^{-3}$ S cm$^{-1}$ at 28°C and increases with temperature. The semi-conductivity provides evidence for nickel and pyridine ring interactions.

Ng and co-workers (1998) synthesized polyazomethines by chemical oxidative polymerization with ferric (III) chloride of novel thiophene- or furan- containing monomers (XXXVII). The conductivities of the undoped polymers were less than $10^{-9}$ S cm$^{-1}$, while those doped with iodine were ranged from $10^{-7}$ to $10^{-6}$ S cm$^{-1}$. The low conductivity values were attributed to the low degree of conjugation in the polymers caused by non-planarity of the polymer chains.
El-shkeil et al (1998) obtained soluble polyazomethines by the condensation of 3,3’-dimethoxy benzidine and 2,6-diamino-3,7-dicyanothiene[2,3-f]-4,8-dihydroxybenzo thiophene with terephthaldehyde and p-diacetylbenzene. The conductivity of the virgin polymers was in the range $10^{-11}$ to $10^{-10}\text{S cm}^{-1}$. On raising the temperature to 80°C, the conductivity increased slightly; and at higher temperatures, the polymers showed semiconducting behavior. The conductivity of polyazomethines doped with I$_2$ and H$_2$SO$_4$ was slightly higher than that of the undoped polymer, at higher temperatures (>80°C), the conductivity of the doped polymer showed an abrupt increase in conductivity from $10^{-11}$ to $10^{-7}\text{S cm}^{-1}$. Polyazomethines synthesized by solution polycondensation of terephthaldehyde with various diamines (XXXVIII) was found to possess conductivity in the range $10^{-12}$ to $10^{-13}\text{S cm}^{-1}$. 
Bhatt and Ray (2001) investigated polyesters containing azomethine linkages (XXXIX). The conductivity of the polymers was in the range $10^{-9}$ to $10^{-14}$ Scm$^{-1}$. Doping of the polymers with silver increased the conductivity many fold (upto 0.1 Scm$^{-1}$)

![XXXIX](image)

Diaz et al (1999) synthesized polyketanils derived from selenophene (XXXX). Electrical properties of the polymers, undoped and doped with iodine, AlCl$_3$, FeCl$_3$, SbF$_5$, were measured at room temperature and atmospheric pressure. No variation in conductivity was observed when AlCl$_3$, or FeCl$_3$ were used as dopants. Iodine, on the other hand, greatly increased the conductivity of all the polymers ($10^{-6}$ Scm$^{-1}$), with SbF$_5$ doping; all the polymers exhibited decreased conductivity.

![XXXX](image)
1.5.3 Luminescence

Luminescent supramolecular architectures have recently attracted much interest because of their potential applications in optoelectronic devices or as fluorescent sensors and probes. Indeed inorganic–organic coordination polymers often afford more stability (thermal- and solvent-resistant) than the pure organic ligands and may affect the emission wavelength of these organic molecules. Determination of the fluorescence is usually made in the solid state and mostly at room temperature. In some cases fluorescence measurements are also made in solution in order to prove the existence of oligomeric fragments (Tong et al 1999). Different phenomena can explain the luminescence observed in related luminescent co-ordination polymers, they would be discussed here.

Sun et al (2002) and Fu coworkers (2002) assigned these emissions in a significant number of examples to ligand-to-metal charge transfer (LMCT), if the luminescence is due to the metal–ligand complex formation. The intense photoluminescence emission of these materials can be used in order to design potential candidates for emitting diode devices. The two compounds \{[\text{Tb}(\text{O}_2\text{CPh})_3(\text{CH}_3\text{OH})(\text{H}_2\text{O})]\}_n and \{[\text{Tb}_2(\text{O}_2\text{CPh})_6(4,4\text{-bipyridine})]\}_n (XXXXIa and b) present strong bright green emission and their emission spectra are almost identical (XXXXIc and d). The emission is due to LMCT processes (Seward et al 2001). Indeed the emission bands of the ligand molecules do not appear in the spectra. Thus, the ligand transfers the excitation energy efficiently to the Tb(III) ions, the four bands corresponding, respectively (from left to right) to the transitions $^5\text{D}_4 \rightarrow ^7\text{F}_6$, $^5\text{D}_4 \rightarrow ^7\text{F}_5$, $^5\text{D}_4 \rightarrow ^7\text{F}_4$ and $^5\text{D}_4 \rightarrow ^7\text{F}_3$. 
In some other cases the fluorescence intensity can be significantly enhanced in the polymeric compound in comparison to the one of the pure organic molecules without change in the emission wavelength (Paul et al. 2004). It is only due to contribution of the organic part, the enhancement coming from the increase in the rigidity of the ligand molecules in the complexes and/or the decrease of the symmetry within the ligand molecules. Sometimes red- or blue-shift is observed due to particular interactions (π-π stacking) or to (de)protonation of the ligand. The emission of the compound \{[Cd(terephthalato)(pyridine)]\}_n occurs at 464 nm while the terephthalato acid emits at 466 nm. But the intensity of the complex emission is 100 times larger than that of the free ligand. The emission is due to intraligand π–π* transitions. The same observation is made with the compound [Cu(PPh₃)(N,N-(2-pyridyl)(4-pyridylmethyl)amine)₁₅]·0.5CHCl₃·ClO₄/n: the free ligand emits at 460 nm whereas the complex emits at 490 nm with an intensity 10
times larger. The weak bathochromic shift is probably due to the increase of aromatic $\pi - \pi$ stacking in the crystalline metal-organic frameworks (Chen et al 2000).

Silver co-ordination polymers display weak luminescence at room temperature. They are known to be greater emitting materials at low temperature, with an enhancement of the emitting intensity and/or a shift of the emission wavelength. In the particular case of co-ordination polymers containing silver–silver contacts, the luminescence properties may be assigned to the short metal–metal contacts. In the series of polymers based on AgX ($X = PF_6^-, ClO_4^-, OTs^-, NO_3^-, BF_4^-)$ and 4,4’-dipyridyldisulfide (4-PDS), only the compound $\{[Ag(4-PDS)]OTs\}_n$ has Ag–Ag interactions. No fluorescence is observed for the co-ordination polymers except for $\{[Ag(4-PDS)]OTs\}_n$. The band at 600 nm is attributed to the Ag–Ag contact (Horikoshi et al 2002).

1.5.4 Non-linear optical properties

For the construction of non-linear optical (NLO) materials, a non-centrosymmetric arrangement in the solid state is required, and this consists in an interesting challenge. These materials should also contain organic ligands with large molecular first hyperpolarizabilities, $\beta$, ideally chromophores with a good electron donor and a good electron acceptor connected through a conjugated bridge. Metal-organic framework building is used to order asymmetric chromophores which are highly dipolar and, due to dipole–dipole repulsions, difficult to align in a non-centrosymmetric way. Some examples of metal-organic frameworks showing frequency conversion (intensity modulation of light: second harmonic generation (SHG) processes) can be found in literature (Huang and co-workers 1999 and Hou et al 2002). The SHG is studied there by the use of the 1064 nm fundamental wavelength of a Nd:YAG laser using the Kurtz–Perry powder method.
Evans and Lin (2002) have outlined strategies to build noncentrosymmetric metal-organic frameworks. They use $p$- or $m$-pyridinecarboxylate linear, rigid and non-symmetric organic ligands as linkers between $d^{10}$ metal ions (Zn(II), Cd(II): tetrahedral or pseudo-tetrahedral) in hydro(solvo)thermal conditions. The building blocks lead to the construction of threedimensional diamondoid networks or two-dimensional frameworks XXXXIIa. Even with weak electron donor/acceptor combinations, it is possible to obtain efficiently NLO properties, as the well chosen complexation can allow a good alignment and cooperation between the molecules. The powder SHG intensity of some compounds is comparable or higher than that of technologically important LiNbO$_3$. Furthermore they get a relatively good thermal resistance and are optically transparent. Huang and co-workers (1999) synthesized a non-centrosymmetric co-ordination polymer including the symmetric 4,4′-bipyridine ligand. The compound $\{[\text{Cd}_2(4,4′\text{-bpy})_2(\text{H}_2\text{O})_3(\text{SO}_4)_2]\cdot 3\text{H}_2\text{O}\}_n$ crystallizes in the non-centrosymmetric space group $C2$. It consists of one-dimensional chains containing two types of Cd centers co-ordinated by $\mu_2$- and $\mu_3$-$\text{SO}_4^{2-}$ anions and water molecules in the equatorial co-ordination sites. The chains are connected together with the bipyridine ligands co-ordinated in the apical sites of the Cd centers XXXXIIb. This compound shows powder SHG intensity. However, a remaining problem in the use of such compounds is their poor stability in the laser light.

![Diagram of XXXXIIa and XXXXIIb](image.png)
Recent interest in polyazomethines has been inspired by the successful synthesis of these materials using chemical vapour deposition CVD (McElvain et al 1998). This process, which forms a polymer by reacting two separate molecules in the vapour phase directly onto a substrate surface, has been shown to be an effective and efficient means of producing Schiff base with long conjugation lengths. McElvain et al (1998) investigated third-order NLO properties of the polyazomethine films prepared by CVD. The third-order susceptibility was $2.8 \times 10^{-11}$ esu for polymer 1 in XXXXIII and $1.8 \times 10^{-11}$ esu for polymer 2, while the off-resonance values were nearly an order of magnitude smaller.

![Polymer structures](image)

**XXXVII**

### 1.5.5 Liquid crystalline properties

Rodlike structure in a molecule, consisting of few aromatic rings bonded directly or by various linkages, is known to induce liquid crystalline (LC) behaviour upon heating or in concentrated solution. Among the various linkages, the imine bond is typical (Sauer et al 2003 and Sudhakar et al 2000). These structures built into polymer chains can promote mesophase formation with changes in temperature (thermotropic LC) or at certain concentrations in a suitable solvent (lytotropic LC). Low-molecular weight liquid crystals and LC polymers have very wide technological applications due to their self-assembly in the mesophase. Nevertheless the search for new materials that show liquid crystalline properties is still an aim of investigations that involves co-ordination polymers. The preparation of thermotropic polyazomethines with moderate melting temperatures has been the goal of several studies.
Pioneering work at DuPont showed that melting temperatures can be effectively reduced either by incorporating lateral substitution or flexible spacers into the polymeric chain, thus favouring the formation of mesophases.

Adell et al (2003) synthesized a series of semiflexible homo- and co-polyazomethines based on hydroxyl functionalized mesogenic cores and aliphatic spacers, as shown in XXXXIV. Thermal and mesomorphic behaviours were investigated by optical microscopy and differential scanning calorimetry (DSC). Polyazomethines, except homopolymers synthesized from 4-methyl-1,3-phenylenediamine, exhibited nematic mesophase formation during heating. From polyazomethines containing a para-substituted diamine e.g. 2-methyl-1,4-phenylenediamine and an aliphatic chain with two CH$_2$ groups (polymer P2 in XXXXIV), a melting temperature at 333°C, close to decomposition, was observed and no mesophase was found. However, as the spacer length increases the transition temperature decreases and the formation of mesophases is more likely. Polymer P6 exhibited two endothermic points at 229 and 259°C, while the one with ten methylene groups (P10) showed only one melting point at 175°C. Both homopolyazomethines (P6 and P10) developed nematic textures. Due to the presence of hydroxyl groups the polyazomethines formed metal complexes with Zn, Ni, V and Fe, which, in the range of 1.08-1-75 metal atoms per hundred repeat units, caused crosslinking of the macromolecules (XXXXIV). However, this did not influence the nematic mesophase isotropization temperature, while the melting points of the complexed polymers decreased only slightly.
Liquid crystalline mesophases can be also formed by polymers with mesogenic moieties bonded to main chains as side groups. Such polymers are sometimes called comblike LC polymers. (Cano et al 1999) prepared mesogenic, azomethine monomers terminated with methacrylic or vinyl ether groups (see XXXXV) and polymerized them using thermal and photoinitiation methods. These monomers and their metal complexes exhibited mesogenic behavior forming, in most cases, a variety of smectic mesophases. Photopolymerization was carried out in the presence of photoinitiator (Irgacure 784-DS) and at temperatures at which the monomers formed smectic or nematic mesophases. Mono- and di-acrylates were found to have the same textures as the initial monomers.
Though many azomethine oligomers form liquid crystalline mesophases, in some cases this behavior can be induced by hydrogen bond formation with substances having an H-bond donor. This phenomenon was described by Pucci et al (2004) who studied the azomethines and their Ni-complexes having structures shown in XXXXVI. Neither ligands nor their complexes with nickel ion exhibited formation of a liquid crystalline mesophase; however, addition of 4-decyloxybenzoic acid, which was able to form a hydrogen bond with the pyridyl moiety of the azomethine, caused the adducts to behave as liquid crystalline moieties. The 1:2 adduct of compound 1 with the acid exhibited a monotropic nematic phase while the same mesophase was enantiotropic for the 1:1 aggregate. For 1:2 adducts of Ni complexes and the aromatic acid, crystal-to-crystal and crystal-to-smectic C transitions took place during heating.

XXXVII

To conclude this part, the progress in liquid crystalline co-ordination polymers is continuing in order to develop functionalized and performance materials that can be applied to information and communication technologies.

1.5.6 Magnetism

Co-ordination polymers strategy is furthermore employed for the design of molecular-based magnets. Indeed antiferromagnetism,
ferrimagnetism and ferromagnetism are co-operative phenomena of the magnetic spins within a solid. They require an interaction or coupling between the spins of the paramagnetic centres. The building of metal-organic frameworks allows the choice of the coupling parameters.

The magnetic co-ordination polymer has to own a residual permanent magnetization at zero-field for an as high as possible $T_c$ (critical temperature). Its structure should allow parallel coupling of the spins (↑↑↑↑, ferromagnetism) or an antiparallel coupling of inequal spins (↑↓↑↓, ferrimagnetism) of neighbouring paramagnetic spin carriers, so that a non-zero spin of the bulk material results. Some antiparallel couplings of spins (↑↓↑↓, antiferromagnetism) are found in numerous examples as the state of low-spin multiplicity is often more stable than the state of high-spin multiplicity.

An efficient coupling in magnetic materials can occur through open shell organic ligands. Materials with oxo, cyano or azido bridges show a strong coupling between the metal centres and their unpaired electrons. As example, the review of Batten and Murray (2003) focuses on the correlation between structures and magnetic properties of coordination polymers containing dicyanamide and tricyanomethanide.

Noro et al (2005) found out the magnetic behavior for co-ordination polymers built up with carboxylate group containing ligand. Mixed metal (Cu(II), Mn(II) or Fe(II)) two-dimensional co-ordination polymers exhibit ferromagnetism due to the one dimensional repeating motif (–M–O–C–O–Cu–O–C–O–M–) (XXXXVII). With the use of such ligands, metal-carboxylate subunits are often formed reinforcing the framework stability and the coupling. Moulton et al (2002) present a scarce example of ferromagnetic co-ordination polymer ($\{[\text{Cu}_2(\text{pyridine})_2(\text{bdc})_2]\}_n$) even at room temperature.
Examples of magnetic co-ordination polymers with polytopic nitrogen-based ligands exist but are much rarer. For instance, the complex \{[\text{Fe}_2(\text{trans}-4,4'-\text{azopyridine})_4(\text{NCS})_4]\cdot \text{EtOH}\}_n \) presents a temperature dependant magnetic moment due to spincrossover behaviour. The long ligands avoid or lower the coupling between the metal centres. The complexes \{[\text{Cu}(\text{L}_{12})(\text{H}_2\text{O})(\text{SO}_4)]\cdot 2\text{H}_2\text{O}\}_n \) and \{[\text{Co}(\text{L}_{12})(\text{NCS})_2]\cdot 2,5\text{H}_2\text{O}\}_n \) \( (\text{L}_{12} = 2,5\text{bis}(4\text{-pyridyl})-1,3,4\text{-thiadiazole}) \) show very weak antiferromagnetic coupling (Huang et al 2004).

Wen et al (2005) synthesized mixed ligands co-ordination polymer, which can well illustrate the magnetic behaviour of metal-organic frameworks. The complex \{[\text{Cu}(\text{N}_3)_2(\text{1-R})-6,6\text{-dimethyl-5,7-methano-2-(2-pyridinyl)-4,5,6,7- tetrahydroquinoline})\}_n \) presents weak antiferromagnetic interactions between the Cu(II) ions through the azide bridge.

In order to allow efficient magnetic coupling, metal ions should be bridged by small ligands allowing short metal–metal contacts. Low-dimensional polymer networks can lead to a final magnetisation within the polymer structure if ferro- or ferrimagnetism can be achieved. Kagomé-
lattices in which spin frustration (inhibition of long-range antiferromagnetic coupling) occurs due to the linking of triangular moieties in two dimensions, are one possibility to realize such a material Perry et al (2004). In order to avoid anti-ferromagnetic coupling between chains or sheets, further magnetic interaction has to be considered in all three dimensions.

1.5.7 Metal-containing macromolecules in biological systems

1.5.7.1 Metal complexes in living systems

The range of metals used by biological systems is very large, reaching from the alkaline to the transition metals (Berthon 1995 and Reedijk 1993). They play an essential role in living systems, both in growth and metabolism. Some metals such as Na, K, Ca, Mg, Fe, and Zn are necessary in gram quantities. Other trace elements such as Cu, Mn, Mo, Co, V, W, and Ni are essential beneficial nutrients at low levels but metabolic poisons at high levels. Some metal ions such as Pb, Cd are called ‘detrimental metal ions’ because they are toxic and impair the regular course at life functions at all concentrations.

Metal ions such as Ca, Mg, Na, K, and Mn exhibit more ionic or co-ordinative interactions whereas Pt, Hg, Cd, and Pb are going more for the covalent bonds, and Ni, Cu, Zn have to be considered as intermediates. In biological systems metal ions can coordinate to a variety of biomolecules such as (Table 1.2):
Table 1.4 Important bio-ligand groups and their co-ordination to metals in natural systems

<table>
<thead>
<tr>
<th>Ligand group</th>
<th>Metal</th>
<th>Substance in which detect or proven</th>
</tr>
</thead>
<tbody>
<tr>
<td>=O</td>
<td>Fe</td>
<td>P-450 enzymes</td>
</tr>
<tr>
<td>-OH</td>
<td>Fe, Zn</td>
<td>Carbonic anhydrase</td>
</tr>
<tr>
<td>H₂O</td>
<td>Fe, Zn, Ca</td>
<td>Many proteins; additional ligands</td>
</tr>
<tr>
<td>O₂/O₂⁻</td>
<td>Fe, Cu</td>
<td>Hemoglobin, hemocyanin, hemerythrin</td>
</tr>
<tr>
<td>O₂⁻</td>
<td>Cu, Fe</td>
<td>Superoxide dismutase</td>
</tr>
<tr>
<td>-OOH</td>
<td>Fe</td>
<td>Hemerythrin</td>
</tr>
<tr>
<td>Tyrosine</td>
<td>Fe</td>
<td>Oxidases</td>
</tr>
<tr>
<td>Glutamase (and Asp)</td>
<td>Fe</td>
<td>Hemerythrin, ribonucleotide reductase</td>
</tr>
<tr>
<td>OPO₂R</td>
<td>Ca, Mg</td>
<td>Nucleic acids; ATP</td>
</tr>
<tr>
<td>NO₃⁻, SO₃²⁻</td>
<td>Mo</td>
<td>Several reductases</td>
</tr>
<tr>
<td>-Cl⁻</td>
<td>Mn</td>
<td>Mn Cluster in photosynthesis</td>
</tr>
<tr>
<td>-S²⁻</td>
<td>Fe, Mo</td>
<td>Ferrodoxin; nitorgenase</td>
</tr>
<tr>
<td>-SR- (cysteine)</td>
<td>Fe, Cu</td>
<td>Ferrodoxin, plastocyanin, P-450, azurins</td>
</tr>
<tr>
<td>Imidazole</td>
<td>Cu, Zn, Fe, Mn</td>
<td>Plastocyanin, insulin</td>
</tr>
<tr>
<td>Me-S-R (methionine)</td>
<td>Cu, Fe</td>
<td>Plastocyanin, cytochromes, azurins</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>Co</td>
<td>Vitamin B-12</td>
</tr>
<tr>
<td>(N&lt;)- (peptide)</td>
<td>Cu</td>
<td>Albumin</td>
</tr>
<tr>
<td>Tetrapyrroles</td>
<td>Fe, Co, Ni, Mg</td>
<td>Prosthetic groups, hemoglobin</td>
</tr>
<tr>
<td>CO</td>
<td>Fe</td>
<td>Toxic for myoglobin; cytochrome oxidase</td>
</tr>
<tr>
<td>(CH₂-R⁻)</td>
<td>Co</td>
<td>Vitamin B-12</td>
</tr>
</tbody>
</table>

- proteins at the (C=O)- or (N–H)-bonds and especially, at N, O, S-donor atoms of side chains;
- nucleic acids at basic N-donor atoms or at phosphate groups;
- carbohydrates and lipids at (C-O)- and (P-O)-groups;
- In solid bones, teeth, kidney stones.

Metal or metal compound clusters are found, for example, in the respiratory chain (Fe–S clusters) or in the photosynthesis apparatus (Mn clusters).
1.5.7.2 Metal complexes at natural polymer

A bridge between natural and artificial macromolecular metal complexes is the interaction of metal ions/complexes with peptides/proteins (Severin 1998), nucleic acids/DNA (Chen et al 1996), enzymes (Ryabov 1991), steroids (Jaouen et al 1993), carbohydrates (Krawielitzki et al 1997). Biometal-organic chemistry concentrates on such complexes. The reason for the increasing interest in this field lays in medical applications of metal complexes (Guo et al 1999) (cancer, photodynamic therapy of cancerimmuno-assays, fluorescence markers, enantioselective catalysis, template orientated synthesis of peptides) as exemplarily shown below.

Stable metal complexes can be employed as markers for biochemical and biological systems in immuno-assays, radiographic and electron microscopic investigations of active centers and use as radio pharmaceuticals. Essential is a covalent stable linkage. One simple possibility is the functionalization of peptides and proteins by acylation of, e.g., lysine side chains using succinimyl esters. Modification of this reactive unit with transition metal complexes such as cyclopentadienyl complexes, sandwich complexes or alkinyl clusters leads to the activated carboxylic acid derivatives which can be isolated and reacted with the free amino group of lysine units in peptides and proteins. Fourier-transform-infrared spectroscopy (FT-IR) at 1900–2100cm\(^{-1}\) allows the detection of the bonded carbonyl complexes down to a detection limit of the picomol region. The carbonyl-metalloimmunoassay (CMIA) has the advantage that no radioactive compounds are necessary and by use of different metal organic markers several immuno assays can be carried out simultaneously. Other possibilities are reviewed in (Severin 1998).

The chemotherapy of cancer with cytotoxic drugs is one of the major approaches. Most cytotoxic anticancer drugs are only antiproliferative which means that the process of cell division is interrupted. cis-
Diaminedichloroplatinum(II) (nicknamed cisplatin) is used today routinely against testicular and ovarian cancer. In order to develop new more selective and active anticancer drugs based on platinum, the interaction of the active model compound cisplatin with DNA is important. Structural data have shown that the binding of cisplatin to DNA occurs preferentially at the N7 position of adjacent guanines (Chen et al 1996 and Krawielitzki et al 1997). This binding leads to local denaturation of DNA, inhibits the replication process and kills the tumor cells. Because cisplatin possesses two reactive Cl-groups, intrastrand and interstrand crosslinking can occur.

Reedijk (1996) investigated several ruthenium complexes in the interaction with proteins, cytochromes and nucleic acids. The reason is to use these Ru-complexes as luminescence sensors (e.g. optical O₂ sensor), to trigger electron transfer and photoinduced electron transfer in proteins and DNA. For example, electrogenerated chemoluminescence (ECL) of Ru(phen)₃²⁺ (phen: 1,10-phenanthroline) can be used to detect the presence of double-stranded DNA. Ru(phen)₃²⁺ binds strongly to double-stranded DNA, and minimal binding is observed in the presence of single-stranded DNA. If a given single-stranded DNA sequence is immobilized on an electrode, treatment with a suitable target DNA may generate double-stranded DNA which allows the binding of the Ru-complex and by electrode reactions the detection of ECL.
1.6 CHARACTERISATION OF FUNCTIONALISED POLYMERS AND THEIR METAL COMPLEXES

Spectroscopic methods commonly employed by organic chemists in structural determination, have proved useful in the case of functionalized polymers and their metal complexes. This technique includes IR, NMR and diffuse reflectance spectroscopy.

In addition elemental analysis, viscosity, gel permeation chromatography, magnetic moments, thermogravimetry, differential scanning calorimetry and X-ray diffraction studies come handy, in characterization.

1.6.1 Infrared spectroscopy

The formation of polymer-metal complexes can be followed from their characteristic absorption bands in infrared spectrum. The IR absorptions by a ligand are shifted after complex formation with metal ions.

The absorption peak at 1600 cm\(^{-1}\) due to \(\nu_{\text{C=C}}\) or \(\nu_{\text{C=N}}\) of polyvinyl pyridine (PVP) shifted to a higher wave number by about 20 cm\(^{-1}\) in the case of \(\text{cis(Co(en)}_2\text{PVPCl)}\text{Cl}_2\). When compared to pyridine, the peaks due to \(\nu_{\text{C=C}}\), \(\nu_{\text{CH}}\) (out of plane) and \(\nu_{\text{CH}}\) (in plane) in PVP also shifted to higher wave numbers by 9-11, 2-5 and 6-7 cm\(^{-1}\) respectively in the Co(III) complexes (Kurimura et al 1971). Absorption in the C-O stretching region (2000 cm\(^{-1}\)), for example, provided a good indication of metal carbonyls, whereas that in the far infrared region (<400 cm\(^{-1}\)) allowed characterization of metal-metal or metal-ligands band (Zundel 1969). Biswas and Mukharjee (1995) reported manifestation of the metal-oxygen vibration in the region 301-370 cm\(^{-1}\) for the condensate from Cu(II)-1,10-phenonthroline and trimellite/pyromellite dianhydride.
1.6.2 Nuclear magnetic resonance spectroscopy

$^1$H-NMR is one of the investigative tools for structural identification of functionalized polymers. The success of this application depends primarily on the measurements of chemical shifts and percentage of hydrogen distribution. The development in Fourier transform instrumentation has accelerated data acquisition and improved characterization. However, it has not been often used for insoluble polymer supported metal complexes.

1.6.3 Electron paramagnetic resonance spectroscopy

The electron paramagnetic resonance (EPR) spectra reflect the co-ordination structure of polymer-metal complexes. The interaction between the spin of the metal ion and the co-ordinated ligand and its “g” value dictates the EPR spectrum in such cases. Tsuchida and Nishide (1977) reported the EPR spectral curves of poly(4-vinylpyridine)-Cu(II) complex which is partially quaternized with ethylbromide.

EPR absorptions can be used to derive information about the bonding between metal ion and the ligand. Covalent character of a bond becomes more pronounced when the parameters $g_{||}$ and $g_{\perp}$ decrease and when $A_{||}$ and $A_{\perp}$ increase. Since, the most selective of these parameters is $g_{||}$, the variation in $g_{||}$ is the best indication of the covalent character. Information about the movements of the polymer ligands surrounding the central metal ion in an aqueous solution can also be obtained from EPR spectra (Hoek and Reedijk 1979).

1.6.4 Elemental analysis

Although carbon and hydrogen analysis are often carried out routinely, this technique is most useful when an element such as nitrogen,
halogen, sulphur, phosphorous and metal ions is gained or lost in the reaction. It is noteworthy that some metal ions can be readily quantified by titrimetric methods (Jaffery et al 1994).

1.6.5 Viscometry

Viscometry is a useful technique for determining the polymer molecular weight. The viscosity of the polymer solution is considerably high compared to that of the pure solvent.

1.6.6 Gel permeation chromatography

Gel permeation chromatography (GPC) has been used as a technique in the evaluation of molecular weight of the polymers. It is a special type of liquid-solid elution chromatography which is based on the effective permeation of solute molecules into rigid gel particles. The large molecules are unable to penetrate deep into the void spaces in the gel and hence get eluted them first. Therefore, elution volumes are proportional to the molecular weights of the polymer. This technique is rapid, convenient and provides more reliable and reproducible results.

1.6.7 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique which follows the weight changes of a material as a function of temperature. Alternatively weight loss can be measured as a function of time at constant temperature. Application of thermogravimetry analysis in polymer-metal complexes include comparisons of the relative thermal stability, the percentage of absorbed or crystal water, metal oxides content, studies of degradation kinetics, direct quantitative analysis of various copolymer metal complexes and oxidation stability.
1.6.8 **Differential scanning calorimetry**

Differential scanning calorimetry (DSC) is a technique of nonequilibrium calorimetry in which the heat flow by maintaining a thermal balance between the reference and sample by changing the current passing through the heaters under two chambers. For instance the heating of the sample and reference proceed at predetermined rate until the heat is emitted or consumed by the sample. If an endothermic occurrence takes place the temperature of the sample will be less than that of the reference. The DSC measurements provide heat of transmission, heat of reaction, percentage incorporation of substance and rate of crystallization or melting.

1.6.9 **Magnetic moment studies**

The paramagnetism or diamagnetism of polymer-metal complexes is determined by magnetic studies. Paliwal and Kharat (1989) observed Zn(II) complex of β,β’-(2-hydroxy-5-methyl benzoyl)-p-divinylbenzene to be diamagnetic in nature, whereas Cu(II), Ni(II),Fe(II) and Co(II) complexes paramagnetic. Cu(II), Ni(II), Co(II), and oxovanadium(IV) complexes of 2,4-dihydroxybenzaldehyde oxime-formaldehyde copolymer were found to be paramagnetic in nature (Patel and Patel 1990).

1.6.10 **X-ray diffraction**

X-ray powder diffraction is an important technique used in the study of polymer-metal complexes. It is used to identify the phase, check the purity, find out crystallinity and calculate unit cell parameters (Rudolf et al 1986)
1.7 SCOPE AND OBJECTIVES

Polymer science, over the years has stimulated interest all over the globe because of polymers making an impact as commodity, engineering and speciality materials. As a consequence of exploitation of newer domains, many diversifications have been accomplished. Among them, polymer-metal complexes studies have emerged as noteworthy. This field is interdisciplinary, finding applications in diversified fields viz, organic synthesis, waste water treatment, hydrometallurgy, polymer drug grafts, recovery of trace metals, nuclear chemistry and models for metalloenzymes. Since it is a heterogeneous system it has among others, the advantages of easy separation of products and lack of corrosiveness.

Even though it is of relatively recent origin, the literature survey indicates voluminous work turned out by researchers all over the globe. Taking into consideration, the pre-eminent importance assumed and potentiality as futuristic material, the present investigation was taken up, which deals with synthesis, characterization and application studies on poly(acrylate)s containing hydrazone ligands with nitrogen and hydroxyl functions derived from 2,4-dihydroxy carbonyl compounds and their divalent metal complexes.

The objectives are:

1. Synthesis of new functionalized monomers:
   - 2-hydroxy-4-methacryloyloxy benzophenone hydrazone
   - 2-hydroxy-4-methacryloyloxy benzophenone hydrazone
   - 2-hydroxy-4-acryloyloxy acetophenone hydrazone
   - 2-hydroxy-4-methacryloyloxy acetophenone hydrazone
   - 2-hydroxy-4-acryloyloxy benzaldehyde hydrazone
   - 2-hydroxy-4-methacryloyloxy benzaldehyde hydrazone
2. Polymerization of functionalized monomers by free radical polymerization.

3. Synthesis of polymers:
   - Poly(2-hydroxy-4-acryloyloxy benzophenone hydrazone)
   - Poly(2-hydroxy-4-methacryloyloxy benzophenone hydrazone)
   - Poly(2-hydroxy-4-methacryloyloxy acetophenone hydrazone)
   - Poly(2-hydroxy-4-acryloyloxy acetophenone hydrazone)
   - Poly(2-hydroxy-4-methacryloyloxy benzaldehyde hydrazone)
   - Poly(2-hydroxy-4-acryloyloxy benzaldehyde hydrazone)

4. Synthesis of formaldehyde resins
   - Poly(2,4-dihydroxy benzophenone hydrazone-formaldehyde)
   - Poly(2,4-dihydroxy acetophenone hydrazone-formaldehyde)
   - Poly(2,4-dihydroxy benzaldehyde hydrazone-formaldehyde)

5. Complexation of polymers with Cu(II)/Ni(II) ions in DMF medium.

6. Characterization of polymers by solubility, viscosity, GPC, elemental analysis, FT-IR, $^1$H-NMR, TGA, and DSC.

7. Characterization of polymer-metal complexes by elemental analysis, FT-IR, TGA and DSC, EPR, XRD, magnetic moment, and conductivity measurements.

8. Application oriented studies viz metal uptake studies at different pH, different electrolyte concentration, different contact time, oxidation, hydrolysis, polymerization initiation and recyclability of the polymers under acidic conditions.