CHAPTER II

POLYMERIC LIGANDS AND METAL COMPLEXES: AN OVERVIEW

1. Historical background

The idea of using complexing resins originated with the observation of Erlenmeyer and Dahn\(^1\) that a mixture of various cations could be chromatographed on a column of powdered 8-hydroxyquinoline, the suggestion of Meinhardt\(^2\) that complexing agent could be fixed on a supporting solid and Griessbach's\(^3\) concept of ion exchange as a function of pH. The work of Kennedy et al. is a milestone in the development of specific and ion selective resins.\(^4\) In the late fifties a chelating resin with iminodiacetic acid as a functional group anchored onto a polystyrene matrix was reported.\(^5\) The synthesis, and successful application of this resin prompted systematic research in the area of chelating resins and introduced the concept of solid phase synthesis.\(^6\) From a study of the various complexing sorbents it has been found that the introduction of complexing groups into the polymeric matrix imparts the ability to interact with elements via coordination bonds.\(^7\) A large number of chelating ligands such as amino carboxylic acids, hydroxamic acids, oximes, pyridine, carboxylic acids, hydrazides, arsionic acids, phosphonic
acids, dithiocarbamates, thiols, Schiff bases, crown ethers, and cryptands have been incorporated into a variety of both organic\textsuperscript{8,9} and inorganic polymeric matrices.\textsuperscript{10,11} A number of biologically active compounds such as haemins\textsuperscript{12,13} desferrioxamine B\textsuperscript{14,15} and porphyrins\textsuperscript{16} have also been grafted on different types of polymeric supports and their chelating properties have been studied. The polymeric ligands derived from the modification of chloromethylated styrene divinylbenzene copolymers with iminodiacetic acid remain the most popular and thoroughly studied class of commercial resins.\textsuperscript{17,18}

A polymeric ligand or chelating resin consists essentially of two components: a ligand functionality and a polymer matrix. The properties of both these components have to be taken into account when designing and synthesising a polymer supported ligand. According to Gregor\textsuperscript{19} et al. a suitable ligand function for incorporation into a polymer matrix should have the following properties: i) it should be capable of easy incorporation into a polymer matrix; ii) it should be sufficiently stable to withstand the polymerisation 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. Mechanical stability and resistance
towards acids and bases used for regeneration of the resin are also desired features of a ligand function for polymer complex formation. Blasius and Brozio found that many ligand functions lose their selectivity when incorporated into a polymer matrix. So the functional configuration occurring in aqueous solution should be maintained after incorporation on a crosslinked polymer also. D'Alelio suggested that for an effective chelating polymer the ligating behaviour of the chelating group in the polymer matrix should be similar to that of the active group in the monomeric system.

2. Macromolecular effects on complexation

The problem of complex formation with macromolecular ligands overlaps areas of various allied sciences with the prospect of production, investigation and utilization of compounds exhibiting unusual behaviour due to their macromolecular character. The reactivity of the complexing groups is determined by the covalent bonding of separate ligands in a macromolecular unit. Polymeric ligands cause steric, electrostatic, hydrophobic, configurational and cooperative effects upon the complex formation as well as upon the catalytic activities of the resulting polymer metal complex, accelerating the catalytic activities or giving specificities to it.
In low molecular weight complexes all the ligand molecules possess the same structure and consequently exhibit the same properties provided the substance is properly purified. But in spite of the very different synthetic routes leading to the macromolecular compounds and of the differences in characteristics of the functional groups on the chain, as well as in the structure and conformation of the main polymeric chain carrying these groups, these systems exhibit similar features characteristic of macromolecular ligands. These derive from the polyfunctional nature of macromolecular complexing agents.

The ability of macroligands to form complex depends to a certain degree on the nature of the main chain: Whether it is a polymeric alkane or polyaromatic compound produced via polymerisation of corresponding monomers or otherwise contains heteroatoms representing polycondensation polymers. Polymeric iminoacetic acids with functional groups occurring on different polymeric matrices may serve as examples.\textsuperscript{23-25} The complexing power of macromolecular ligands also depends on the arrangement of functional groups relative to the main chain. The shorter the distance between them, lower the efficiency of complex formation because of steric hindrance. As illustrated by complexes of vinylpyridine series such as
poly-4-vinylpyridine, poly-2-vinylpyridine and poly-5-vinylpyridine. The complexing power of the resin varies substantially even though the nature, basicity and concentration of these are very similar. Studies on complex formation with low-molecular weight analogues, vinylpyridines do not indicate any such variation.

The complexing characteristics of insoluble polymeric systems are also strongly influenced by the extent of crosslinking in the ligand. Soldadze and coworkers report the colouration of copper complexes with polyvinyl pyridines to change from blue to deep green on increasing the extent of crosslinking from 4 to 16. To judge from the colour evidence, a conversion of planar coordination centre into tetrahedral one occurs. This change in stereochemistry results from an increase in steric hindrance to complex formation with a macromolecule, which is also known with low-molecular weight coordination compounds.

The efficiency of complex formation involving macromolecular ligands is influenced not only by the characteristics of the functional groups but also by their distribution along the polyligand chain. If the functional groups occur at every monomeric unit they cause steric hindrance. The efficiency of complex formation may be
increased by using copolymers in which functional groups are not present on all the monomeric units. Thus polymethacryloylacetone, polyvinylacetonylketone or polyvinylacetooacetate while binding Ni(II) ions utilise far below the total number of complexing groups. These occur at every monomeric unit and cause steric hindrance. With polyketoesters all the complexing groups bind metal ions such as copper. In such cases functional groups are separated by several methylene units instead of being situated at every carbon atom in the chain. Gregor et al. reported the Cu-complex formation of poly(methacrylic acid) (PMA) resins crosslinked with 1% or 9% DVB. The formation constants of the Cu complexes with these resins were smaller than that of the noncrosslinked PMA. Here rigidity of the polymer chain was considered to hinder chelate formation. Dingman et al. studied the adsorption of metal ions on poly(ethyleneimine) (PEI) resins crosslinked with toluene diisocyanate. The amount of metal ions adsorbed decreases with the degree of crosslinking but the crosslinked PEI resins bind metal ions with high efficiency and exhibit selective binding ability.

The rigidity or flexibility of the polymer backbone affects the complexing efficiency of polymeric ligands. The complexing groups in a macromolecular ligand exist in
conformations different from that required by the preferred stereochemistry of a given metal ion. Functional groups are usually statistically distributed over a macromolecule so that both the more favourable conformations and less favourable will occur. Hence the formation of a given spatial structure required by the electronic configuration of an ion $M^{n+}$ is followed by a conformational change in the ligand so that it may assume an appropriate orientation. Since the coordination bond energy remains constant for a given metal ligand pair the stability of polymeric complexes is proportional to the flexibility of a macromolecule and to the set of conformations it can generate.

3. Types of ligands

a) Polymer supported amino ligands

Amino functions are well known complexing ligands. They can be introduced into a polymeric system by extending simple organic reactions. Polymers containing polyamine functional groups form an important class of such ligands. Several groups$^{31-33}$ have studied the modification of synthetic resins with polyamines such as ethylenediamine, diethylenetriamine and triethylene tetramine. Blasius and Bock$^{31}$ and Szabadka$^{32}$ studied the
reaction of crosslinked chloromethylated polystyrene with several polyethylene-polyamines and suggested that these polyamines are linked to the matrix by one or more bridges by the amination reaction, depending upon their length. These reactions appeared to proceed in a fashion depicted in scheme II.1 for amination of chloromethylated polystyrene with ethylenediamine.

![Chemical structure](image)

Scheme II.1. Amination of chloromethyl polystyrene with polyamines.32

Two products, monoaminated polystyrene and diaminated polystyrene were obtained.32 Shambu et al.33 studied the reaction of several polyethylene-polyamines with chloromethylated popcorn polystyrene resins in pyridine
medium. It was observed that the rate of chloride displacement decreased with increasing molecular weight of the amine and higher degree of resin chloromethylation while the event of multiple attachment to the polymer matrix increased. The additional crosslinking as a result of multiple attachment caused the polyamine to swell to a lesser extent in pyridine and water. The capacity of the resin containing ethylenediamine with respect to its adsorption of Cu(II) ions from dilute solutions increases with increasing amounts of ethylenediamine. With diethylenetriamine the capacity remains unchanged while with triethylenetetramine the capacity decreases. The complexation and protonation of chelating ion exchange resins containing ethylenediamine functional groups have also been studied and the apparent stability constants of Cu(II), Co(II), Ni(II), Zn(II) and Cd(II) complexes have been determined. It has been observed that with the exception of Zn–Cd pair ethylenediamine resins can be used very advantageously for the separation of the metal ions. These chelating resins containing polyethylenepolyamine functional groups have been used as precursors for the preparation of iminodiacetic-type resins by carboxymethylation. Leyden and coworkers have used N-β-aminoethyl-γ-aminopropyltrimethoxysilane and γ-aminopropyltrimethoxysilane to immobilize diamino functional groups and these materials have been used for
x-ray spectrometry techniques. Chelating resins obtained by anchoring diethylenetriamine onto chloromethylated polystyrene contain up to 3.02 mmole ligating groups per gram of the resin. Several partially crosslinked polyamine polymers have been synthesised for the removal of metal ions from waste water.

The preparation of various crosslinked amino polymeric systems and the effects of crosslinks on the extent of functionalisation have been extensively studied. The complexation of the supported amino functions was investigated towards Cu(II), Co(II), Ni(II), Zn(II) and Hg(II) ions. The general trend in complexation was in the order Hg(II) > Cu(II) > Zn(II) > Ni(II) > Co(II). The kinetics of complexation was found to be first order and the free energy of interaction between the complexed species depends on the nature of the polymer backbone. The metal ions can be adsorbed and desorbed any number of times without considerable reduction in functionality. The swelling of the resin decreases on complexation with metal ions which is suggested to be due to the additional crosslinking. It was also observed that if the optimum conformation of the coordination sphere of a metal ion is not destroyed, this resin would prefer the particular metal ion which was initially present. This is because the 'pocket' left by
the initial metal ion, may not be fit for other metal ions or the configuration of the decomplexed resin is more suited for the original metal ion. This assumption was further supported by the rapid complexation of Cu(II) ions by the Cu(II) desorbed resin. During recycling, if the resin was subjected to vigorous stirring, the 'memory' of the polymeric amino ligand or the pockets fitted for the specific metal ion was disturbed and this would lead to reduced metal intake. This observation is similar to the adjustment of macromolecular chains of enzymes to the tertiary structure optimum for the sorption of corresponding substrates.\textsuperscript{45,46}

b) Polymer supported amino acids

Complexation behaviour of almost all amino acids have been studied throughly.\textsuperscript{47} They form stable complexes with the transition metal cations. Amino acids very often act as potential biogenic ligands.\textsuperscript{48} They serve as bidentate ligands but in the case of trifunctional amino acids they can display polydentate character. For example histidine shows tridentate function via the amino groups, the carboxyl group and the imidazole moiety.

The significance of metal ions in biological systems is obvious. The function of many enzymes is metal ion-
Reactions between metal ions and proteins or nucleic acids offer examples of macromolecular ligand character influencing complex formation in the case of naturally occurring complexes. When isolated from biological objects, nucleic acids incorporate certain amounts of one or a number of metals. Walker and Vallee report samples of DNA and RNA to contain metal ions like chromium, nickel, iron, manganese and zinc. Metals coordinately bound to nucleic acids are difficult to remove even with strong complexing agents as ethylenediaminetetraacetic acid and 8-hydroxyquinoline. Metal ions account for the binding of nucleic acids to protein; they are essential for the structure and function of nucleoproteins; they influence protein synthesis and hereditary information transfer. Fe ions play a role in DNA functioning; these ions participate in the formation of bonds between separate chains and provide control of the denaturation process. Sigel and McCormick studied the discriminating behaviour of metal ions and ligands with regard to their biological significance. During the past two decades considerable progress in understanding the role of metal ions in biological processes has been achieved from the discovery and purification of a large number of metalloproteins and from efforts to ascertain their function in catalysis and electron transport.
Attempts to resolve racemic compounds by ligand exchange chromatography have been made in a few cases with polymer supported \(\alpha\)-amino acids. Davankov et al. have prepared metal complexes of asymmetric sorbents obtained by reacting chloromethylated polystyrene with \(\alpha\)-amino acids\(^{66-68}\) (Structure II.1).

\[\text{Structure II.1. L-Proline incorporated polystyrene}\]

These studies indicated that the most satisfactory chromatographic resolution of \(\alpha\)-amino acid racemates was possible using Cu complexes of L-proline or L-hydroxy proline stationary ligands.\(^{69,70}\) Vesa et al. prepared Cu(II) complexes of poly(styrylsulphonyl-L-phenylalanine)\(^{71}\) (Scheme II.2). Synder et al. reported the preparation of styrene-DVB copolymers containing the
Scheme II.2. Preparation of poly(styrylsulphonyl-L-phenylalanine)

complex N-carboxymethyl-L-valine copper(II) (Scheme II.3 & II.4) and found that partial resolution of several amino acids was possible with this resin. 72 Petit and Jozefonviez studied polymer-supported amino acids and their Cu(II) complexes starting from chloromethyl-polystyrene and chlorosulphonated polystyrene. 73 Akelah and Sherrington prepared DVB-crosslinked polystyrene supported L-proline for the synthesis of chirally modified sodium borohydride reducing agents. 74 Gokak et al. reported the preparation and characterisation of some polymer-anchored chelated metal complexes supported on PS-DVB copolymer and their catalytic activity in the decomposition of hydrogen peroxide and in the hydrogenation of 1-octene 75 (Scheme II.5).
Scheme II.3. Incorporation of N-carboxymethyl L-valine into chloromethylstyrene-DVB copolymer through dimethyl sulphonium salt.

Scheme II.4. Incorporation of N-carboxymethyl-L-valine into chloromethylstyrene-DVB copolymer by iodomethylation.
Scheme II.5. Incorporation of glycine into crosslinked chloromethyl polystyrene and complexation with Co(II) ions

Morcellet et al. investigated amino acids supported on polymethacrylate backbone. They prepared poly(N-methacryloyl-L-alanine) (PNMA) (Structure II.2) and investigated the interaction of Cu(II). PNMA is a water
soluble polyacid which interacts with Cu(II) in a manner similar to poly(acrylic acid) and poly(methacrylic acid). The presence of an amide group in the side chain offers a second binding site for copper in this case. The PNMA:Cu system was studied by potentiometry, conductometry, visible and UV spectroscopy and circular dichroism (CD). The model molecule N-isobutyroyl-L-alanine (NIBA) was also analogously studied. The interaction between PNMA and copper occurred in three steps beginning with the formation of a complex in which only the carboxylate groups are involved (Structure II.3).
On further increase of the pH, the deprotonation of the side chain amide nitrogen and/or water bound to copper occurs and leads to the formation of two other complexes (Structures II.4 and II.5).

Structure II.4. Copper complex of poly(N-methacryloyl-L-alanine) at pH 7.2

Structure II.5. Copper complex of poly(N-methacryloyl-L-alanine) at pH 10.

UV visible spectroscopy and circular dichroism studies indicated that the formation of the complex involves only the carboxylate group at low pH (4.5) (Structure II.3). The deprotonation of one amide nitrogen at pH 7.2 leads to the formation of an optically active chelate ring (Structure II.4) and at higher pH another proton is neutralised with formation of an optically
inactive complex (Structure II.5). Spectroscopic study of the complexes of poly(N-methacryloyl-L-asparagine) with palladium and copper were also reported. In the case of poly(N-methacryloyl-L-lysine)-Cu(II) complex, the existence of CuL and CuL₂ species were indicated. No deprotonation of amide group occurs. The CuL₂ complex is predominant even at low pH and low ligand/metal ratio. This is attributed to the high local concentration of the ligand in the vicinity of the polymer chain. The catalytic properties of the complexes resulting from the interaction of copper(II) and polymer supported aspartic acid have been investigated. Comparison with the results obtained in the case of the analogous complexes derived from the polymer of glutamic acid support the assumption that additional interactions with the β-COOH side chain are present in the aspartic complexes.

4. Physicochemical characterisation of polymer metal complexes

The kind and microenvironment of the coordinating site, the nature and the structure of the macromolecular metal complex, the effectiveness of the chelating groups and their use for analytical purposes can be assigned by physicochemical methods based on spectral, magnetic and optical properties. The complexation reaction of a
polymeric ligand with metal ions and the structure of the resulting polymer metal complex are usually studied by IR, NMR, ESR, X-ray, ORD and CD analyses. Usual chemical methods of analysis applied to low molecular weight species have been found to be satisfactory with linear polymers. But with crosslinked polymers such methods which require solubilisation of the samples cannot be applied.

As in the case of the low molecular species, the elemental analysis is widely used for the qualitative and quantitative determination of elements such as nitrogen sulphur, phosphorous, and halogens which are introduced or lost during the reaction, provided no side reaction has occurred. The percentage of carbon, hydrogen and nitrogen are estimated by CHN analysis. The metal content can be accurately estimated by atomic absorption spectroscopy. The usual gravimetric experiment is not conducted for the metal estimation since the metal content in the polymer complex is very small. The conventional proton NMR has not been commonly used for structural analysis of polymer complex because the complexation of polymer ligand with metal ions brings about broadening of the spectrum. IR spectroscopy is adopted based on the KBr pellet method. For the electronic spectral studies, the reflectance spectra and the solid state spectra with nujol mull are possible.
a) Infrared spectroscopy

The most useful and simple physical method for determining the functional groups on polymers and the formation of complexes with metal ions is the IR spectroscopy. It also provides an excellent method to locate the coordination or bonding sites in the metal complexes of chelating resins.\(^{82-84}\) The IR analysis can be carried out with solid samples which is the key point necessary for the analytical study involving a crosslinked polymer, where there is the solubilisation problem.

The IR absorptions of a ligand are usually shifted by complex formation with metal ions. The splitting or shift in the characteristic absorption peak is a clear indication of complexation. The NH stretching frequency of Cu(II) complex is lower than their corresponding amino ligands.\(^ {85}\) Upon coordination the N-H bond is weakened and so the stretching frequency is lowered. Such observations are reported in the case of Cu(II) ion complexed to crosslinked polyacrylamide supported amine. Metal coordination prevents hydrogen bonding and the NH stretching absorption exhibits shouldering. The intensity of this shouldering increases with the metal content (Figure II.1).\(^ {86}\)
Figure II.1. Infrared NH$_2$ absorptions of resins crosslinked with 8 mole% of NN MBA; (a) acrylamide, (b) aminopoly(acrylamide), (c) aminopoly(acrylamide) complexed with minimum Cu(II), (d) aminopoly(acrylamide) completely complexed with Cu(II).

Kurimura et al.$^{87}$ studied the effect of complexation on IR absorption of pyridine based monomers and polymers. Complexation of pyridine and PVP with Co(III) shifts the $\gamma$ C=C or $\gamma$C=N band to a higher wavenumber. The peaks due to $\delta$ CH of PVP also shifts to higher wave number in the Co(III) complexes. The absorption peak at 1600 cm$^{-1}$ in the PVP complexes shows the presence of uncoordinated PVP units. Roda et al. also reported similar shifts in IR absorption of PVP on complexation with RhCl$_3$. $^{88}$
IR spectroscopy is also used to assign the coordinating site if a polymer contains more than one ligand functionality. Thus in the complex of Cu(II) with vinylamine/vinylalcohol copolymer it was concluded from the relative absorbances ($\nu_{\text{Cu-O}}/\nu_{\text{OH}}$) of the IR spectrum that the Cu(II) ion is coordinated exclusively with nitrogen atoms of the copolymer.\textsuperscript{89}

The coordination structure of the Cu(II) complex of poly(0-isophthaloylisophthalamide oxime) was studied by comparing its IR spectrum with that of the model compound 0,0'-dibenzoylisophthalamide oxime.\textsuperscript{90} The IR spectrum of the model compound shows strong amide absorption bands at 3250 ($\nu_{\text{NH}_2}$), 1730 (carbonyl) and 1280 cm$^{-1}$ as well as band characteristic of $\nu$ C=N at 1630 cm$^{-1}$. Its chelate formation was confirmed by the disappearance or by a marked decrease in the amide band intensity and by the formation of new bands at 1560, 1430 and 1340 cm$^{-1}$. It was concluded from these results that both the carbonyl and amide groups, take part in the chelation reaction with Cu(II) ion. The IR absorption pattern of the polymer complex indicates the same coordination structure as the model compounds.

The strength of the coordinate bond in a polymer ligand and that in the corresponding monomer ligand was
compared. The peaks of νCo-N shift by about 3-8 cm⁻¹ to a lower wave number in the PVP-Co(III) complexes. It was suggested that the coordinate bond between Co(III) and pyridine unit in PVP is weaker than that in the monomer species. Thus the metal-ligand vibrations have been studied by far-infrared spectroscopy. Fourier-transform infrared spectroscopy has also been used to investigate crosslinked polymers and their metal complexes.

b) Electronic spectroscopy

The UV-visible spectroscopy can be used to find out the electronic transitions of a polymer metal complex and to assign its geometrical structure. The diffused reflectance electronic spectra provides an accurate and simple method for determining the geometry around the transition metal ions in polymer-metal complexes. 1,4-Dibromobutane crosslinked poly(4-vinylpyridine)-Cu(II) complexes were subjected to electronic spectroscopic studies. It was observed that the d-d absorption maxima of the DBQP-Cu chelates were red-shifted from 660nm towards 700nm with increasing crosslink density which could be caused by the relatively weak ligand field introduced by the crosslinking. Morcellet et al. studied the change in the coordination sites of poly(N-
methacryloyl-L-Alanine)-Cu(II) complex with change in pH. Increase of pH resulted in a decrease of the wavelength of the d-d transition of copper. For the first step when pH was 4-8 the wavelength ($\lambda_{\text{max}}$ 770-750 nm) was intermediate between the values expected for a coordination to two carboxylate groups ($\lambda_{\text{max}}$ 750 nm) and a coordination to one carboxylate group and one amide nitrogen ($\lambda_{\text{max}}$ 700 nm). Beyond pH 8 a further decrease of $\lambda_{\text{max}}$ was observed down to a value ($\lambda_{\text{max}}$ 670 nm) but higher than that expected for a 2N complex.

Syamal et al. carried out the characterisation of polystyrene supported schiff bases derived from salicylaldehyde and anthranilic acid and their Cu(II), Co(II), Ni(II) and Fe(II) complexes by reflectance spectra. Cohen et al. followed the complexation of Dowex 50, Dowex 1, Dowex A-1 and Amberlite IR-50 with Cu(II) metal ions and the structure of complexes was studied with IR, electronic and electron spin resonance spectroscopy.

c) Electron spin resonance spectroscopy

ESR spectroscopy is being increasingly used to study the coordination structure. The interaction between the spin of the central metal ion and the coordinated ligand
decides the absorption pattern and its \( v \) values. ESR spectra of Cu(I) complexes are widely investigated since the Cu(I) chelates are ESR active. Tsuchida et al. followed the formation of Cu(Pyridine), and PVP-Cu complexes by the ESR spectroscopy.\(^{103}\) The ESR spectrum of pyridine-Cu complex changes with ligand ratio corresponding to the stepwise formation of the Cu(pyridine), complex. The ESR spectrum of PVP-Cu system shows that the completely coordinated Cu(I) complex is already formed at the lower ligand ratio. This suggests that the PVP-Cu chelate is formed in a one-step reaction. They have also studied the ESR spectrum of DBQP-Cu system (Dibromobutane crosslinked PVP-Cu complex) for various extents of crosslinking\(^{104}\) (Figure II.2). The ESR spectrum of lightly crosslinked system was similar to that of the monomers.

\[ g_1 \]

\[ g_2 \]

\[ g_3 \]

\[ g = 2.0026 \]

*Figure II.2. ESR spectra of Cu(II) complex of partially quarternized PVP*
As the crosslinking increased the parallel orientation was shifted to higher magnetic field region and the anisotropy disappeared. The spectra (1)-(3) are typical patterns for the square planar Cu(II) complex, and the parameters for them are $g_\parallel = 2.3$, $g_\perp = 2.1$ and $A_n = 150 \pm 10\text{G}$. These values are in agreement with those of the monomeric Cu(Py)$_4$ complex. In spectra (4) and (5) the signal due to the parallel orientation is shifted to higher magnetic field. The square planar complex was distorted to a tetrahedral structure as the crosslinking increased. Kalalova et al. studied the ESR spectrum of methacrylate-ethylene dimethacrylate Cu complex which was found to be square planar similar to that of tetramine Cu(II) complex. The ESR spectra also give information about the movements of the polymer ligand surrounding the central metal ion in an aqueous solution. This is evident from the asymmetrical ESR spectrum of Cu(II) complexes of poly(1-vinylimidazole) at 293 K and the symmetrical spectrum of Cu(II) complex of imidazole at this temperature.

ESR absorptions can be used for providing direct proof of a chemical bond between the metal ion and the ligand. The $g_\parallel$ is the most sensitive function for indicating the covalency; the values are 2.3 or more for ionic compounds and less than 2.3 for covalent
compounds. Covalent character of a bond increases with decreasing value for \( g_m \). The ESR spectrum of DVB-crosslinked polyacrylamide amine-Cu(II) complex and NNMBA-crosslinked polyacrylamide amine-Cu(II) complex indicates a decrease of \( g_m \) as the ligand concentration is increased.

**d) Magnetic moment studies**

The Guoy method has been successfully applied to the magnetic susceptibility measurements of Cu(II) complex of Schiff base ligands by Kuska et al. The magnetic moments of Cu complexes fall in the range of 1.78-2.06 BM which is consistent with the value expected for a d\(^9\) electron configuration. Ni complexes were found to be diamagnetic with planar structure.

Yusuff et al. have followed magnetic susceptibility measurements of Co(II) complexes of polymer bound Schiff bases. All the complexes showed negative magnetic susceptibility values due to the low concentration of cobalt and the very large diamagnetic susceptibility of the polymer part. The approximate molecular weight and empirical formula of the repeating complex unit containing one cobalt atom were derived from the analytical data. The diamagnetic corrections based on the empirical formula
were also calculated. When these values were used for the calculation of magnetic moment, $\mu_{\text{eff}}$ values around 2.1 BM were obtained, which indicate a low spin state for the Co(II) ion in those complexes.

It is generally found that the Co(III) complexes ($d^6$) are low spin diamagnetic; but several octahedral complexes of Co(III) which are of low spin type show small positive susceptibilities.\textsuperscript{111} A large number of binuclear complexes of Co(III) are found to be paramagnetic with magnetic moment values around the spin only value for one unpaired electron (1.73 BM) at room temperature. Thus the magnetic moment values help to some extent in predicting the structure of the complexes of macromolecular ligands and the spin state of the metal ion from which the valence can be calculated.\textsuperscript{112-114}

5. Application of polymer metal complexes

a) Separation of metal ions and organic molecules

Polymeric ligands in the form of insoluble resins or films have been used for the removal of toxic metals from water and for collection of trace precious metals from sea water which help clean up of the environment and saving of energy. Adsorption of metal ions has been studied in detail.\textsuperscript{17,115}
The selective adsorption of metal ions was attained by making use of the dependencies of the stability of the metal complex upon the nature and structure of the ligands, kind of metal ions to be separated, molecular architecture of the polymer support and the conditions of complexation. The experimental variables of complexation like time, temperature and pH may be adjusted effectively for the selective adsorption of a particular metal ion. A small difference of the stability constant of the complex between the polymeric ligand and metal ion enables the selective adsorption of metal ion by the polymer. Although it is possible to adsorb some definite metal ion from a mixture, it is not possible to adsorb any desired metal ion selectively. Among the various ligands, amines, dithiocarbamates, iminodiacetic acids, schiff bases, and amidoximes are widely used for the collection of heavy metal ions.115-119

In the development of chelating resins for metal ion separation, the variation in matrix structure significantly affects ion diffusion and ion selectivities. The variation in reaction conditions and the influence of the resin performance have gained much attention. In the suspension copolymerisation of DVB and acrylamide and subsequent aminolysis of the polymer with hydroxylamine to yield the amidoxime resin the parameters of the polymer
matrix like apparent density, pore volume and surface area and average radius, change with the polarity of the solvent used for polymerisation. It is easier to obtain consistent control over pore structure by choosing slightly polar aromatic solvent toluene and varying the concentration of the solvent in the reaction mixture. The pore structure can also be controlled by changing the crosslinking agent DVB. Optimum polymeric resins for this purpose should have large surface area and average pore radius.

The ability of the polymer supported ligand to form complexes depends on the nature of the main chain. The matrix effect on ion binding is clearly evident when low molecular ligands and their polymeric analogues are compared as in the case of iminodiacetic acid ligand supported on polystyrene and polyacrylamide. With increasing polarity of the support the extent of complexation increases. The metal intakes by polymeric ligands are varied by the incorporation of the crosslinking agents which differ in their polarity and flexibility. The replacement of the rigid and hydrophobic DVB crosslinking by a flexible and hydrophilic crosslinking agent results in increased metal ion intake.
The selectivity of metal ion adsorption is pH-dependent. The metal ion adsorption ability of a chelating resin versus pH is illustrated in figure II.3. When pH range is set at 1 to 2, Hg and Cu ions are taken up by the resin, but Zn and Cd ions are not adsorbed. The variation of binding ability with pH is schematically illustrated in figure II.3b. By adjusting the binding ability i.e., by changing the ordinate value for the respective metal ion species selective binding can be accomplished as depicted in figure II.3c.

Figure II.3. Adsorption of metal ions on iminodiacetic acid resin (a) and schematic representation of adsorption behaviour of polymers (b), (c).
Polystyrene supported polyamine

\[
\text{R} \quad \begin{array}{c}
\text{CH}_2\text{(N-CH}_2\text{-CH}_2\text{)}_n
\end{array}
\]

adsorbed metal ions at pH 6 selectively in the order Hg(II) > Cu(II) > Cd(II) > Ca(II).\textsuperscript{124} Nishide and Tsuchida\textsuperscript{104} reported that the crosslinked polymeric ligand forms a stable complex with metal ions than a noncrosslinked polymer and that it shows selectivities for metal ions due to its rigid network structure. The adsorption of metal ions is influenced by the nature and extent of crosslinking. The dependencies on the crosslink density are different with each metal. A higher degree of crosslinking results in a lower degree of metal ion adsorption and in a lower stability of the resulting metal complex. Increased crosslinking brings about a structural strain in the resulting metal complex by making the polymer chain more rigid. In the complexation of polyacrylamide supported amines and dithiocarbamates with DVB, NNMB and TTEGDA crosslinks, the complexation characteristics vary with the molecular character and extent of crosslinking in the polymer matrix.\textsuperscript{125-128} The hydrophilic TTEGDA-crosslinked system has higher complexing ability than the NNMB-and DVB-crosslinked systems. The coordination structure of the derived polymer-metal complexes also depends on the molecular
character and extent of crosslinking in the polymer support. The kinetics of metal ion complexation, the adsorption of metal ions, and the interaction between the complexed/adsorbed species are also decided by the rigidity of the crosslinking agents.

The complexed resins can be recycled several times. The copper-desorbed amino resins showed specificity to copper ions in the presence of other metal ions like cobalt, nickel, and zinc. The copper desorbed resins have pockets specially fitted for copper ions than other metal ions. The specific binding of metal ion by metal ion template crosslinked polymers have been reported. When a metal complex of PVP is crosslinked with 1,4-dibromobutane and then the metal ions are removed by washing with dilute acid the remaining metal free resins show selectivity to adsorb the same metal ions. The crosslinked template resins prepared from Cu²⁺ and Zn²⁺ complexes adsorb the corresponding metal ions with considerable selectivity.

The crown ethers bind metal ions selectively and the selectivity is dependant on the number and chemical structure of the ring member as well as the steric requirements of the ring. Basius et al. prepared resins containing crown ether structure which show selectivity.
for $K^+$ adsorption. Polystyrene supported cyclic polyamines showed selectivity for Cu(II) adsorption. Shimizu et al. prepared chelating polymers in the form of films from the copolymer of 3-vinyl-1,4-butyrolactone and of acrylonitrile and they transported alkaline metals actively. Cellulose-bound β-hydroxyazo compound adsorbs uranyl ions selectively.

The polymer metal complexes can be used for adsorption of coordinating organic molecules which can be isolated and separated from a mixture (Scheme II.6).

\[
\begin{align*}
\text{organic molecules(S)} & \xrightarrow{L - M} \text{L - M - S} \\
\end{align*}
\]

L - M : polymer metal complex,
S : organic molecule.

Porath et al. separated the components of Human blood serum by passing through a column packed with the complex of Zn(II) and Cu(II) with carboxymethylaminated agarose. Such coordination reactions of polymer metal complexes can be used for the isolation of amino acids and amines.
b) Catalytic activity of polymer metal complexes

Polymer metal complexes are used as immobilized catalysts in oxidation, hydrogenation, hydroformylation, decomposition of $\text{H}_2\text{O}_2$, initiation of radical polymerisation, asymmetric synthesis and optical resolution based on specificities of the polymeric ligand molecule. In polymer supported transition metal catalysts the desired metal complex is generally attached to the functionalised polymer by equilibration of the polymer with a metal complex having similar or weak ligands.\textsuperscript{138-140} The mode of attachment depends on the amount of the crosslinking in the polymer. The nature of the support, nature of the metal complex, degree of crosslinking, and the nature of the solvent optimize the polymeric catalyst for a particular reaction.\textsuperscript{141,142} The main characteristics of the catalyst resulting from the polymeric structure are the insolubility, increased activity, stability and selectivity since the polymeric catalyst combines the advantages of both heterogeneous and homogeneous catalysts. The performance of a catalyst is influenced by the chemical and physical properties of the support. The distribution and accessibility of the active sites control the activity of the catalyst. The use of the ion exchange resins as acidic/basic catalysts has been reported for a wide range of organic reactions.\textsuperscript{143}
The oxidation of ascorbic acid and p-hydroquinone were catalysed by poly(L-histidine)-Cu(II) complex. Quaternized PVP-Cu(II) complex catalysed oxidation of ascorbic acid. Cu(II) complexes of poly(1-vinyl imidazole), vinylamine-vinylacetamide copolymer and polyethyleneimine, catalyse oxidation of hydroquinone.

DVB-crosslinked polystyrene supported diphenylphosphate complexes of Rh, Ru, and Ni carbonyls are active hydrogenation catalysts. Allum et al. reported that the acetylacetonato Rh complex of diphenylphosphinated poly(chloromethylated styrene) catalysed the hydrogenation of 1-hexene and cyclodimerisation of butadiene. Polymer-metal complexes catalyse hydroformylation reaction. The diphenylphosphinated PS-Rh complex exhibit isomer selectivity during the hydroformylation of 1-pentene.

The polymer metal complexes show much higher catalytic activity in the decomposition of H₂O₂. The decomposition of H₂O₂ can be selected as a catalyst model rather than a catalyst of practical use. The catalytic activity of Fe(III)-triethylenetetramine complex was found to be 10⁷ times higher than that of ferric aquoions in the decomposition of H₂O₂. The O₂H⁻ ion coordinates to the Fe(III) ion as a bidentate ligand resulting in a cleavage of the 0-0 bond with the evolution of oxygen (Scheme II.7).
Polyhydroxamic acid-Cu(II) complex showed higher catalytic activity than the monomeric analogue. The high catalytic activity of this polymer metal complex was ascribed to the weak coordination bonds between the polymer ligand and metal ions. A high molecular weight of polymer ligand gave higher activity.

Initiation of radical polymerisation was catalysed by polymer metal complexes. Nylon-Cu(II) complex system initiated radical polymerisation of methylemethacrylate in the presence of CCl$_4$ and H$_2$O.

Polymeric ligands provide asymmetric structures due to steric hindrance and bring about asymmetric reaction.
Examples of such reactions are reported by Hatano et al. They have succeeded in carrying out an asymmetrically selective oxidation of 3,4 dihydroxyphenylalanine (DOPA) by poly(L-lysine)-Cu(II) complex. D-DOPA was found to be oxidized by the PLL-Cu(II) complex more rapidly than L-DOPA. Such an asymmetric oxidation was ascribed to the asymmetrically selective interaction of DOPA with PLL-Cu(II) complex. The combination of two or more asymmetric cupric complex units held on the -α-helical structure of PLL was considered to cause the asymmetric synthesis.

c) Other important applications of polymer-metal complexes

Metal ions chelated to preformed polymers can produce marked property changes, especially when the metal ion is bound directly to the polymer backbone. Several metal chelate polymers show superior properties than their organic counterparts in certain applications, although properties such as thermal stability are polymer and metal ion dependant. A good example of improved thermal stability is provided by the zinc chelate of poly(terephthaloyloxyalamic bis-amidrazone). This metal chelate polymer and many others are good fire retardants. Brittleness and intractability are the two properties often associated with metal containing polymers.
solar energy conversion, utilization of polymers or macromolecular assemblies has begun to attract much attention. Two main processes in solar energy conversion are photoinduced charge separation carrying within very short excitation times, and the reactions of the separated charges at catalysts or electrodes to give either products or electricity. In these processes, unidirectional transportation of the charges has to be realised in order to prevent energy consuming back reactions. It is almost impossible to achieve such an anisotropic electron flow in a homogeneous solution system where all the components and intermediates can react at random. For this reason the utilisation of heterogeneous reaction system provided by polymers or molecular assemblies has become the centre of interest. Metal complexes are the most promising candidates for the photoreaction centres and catalysts in solar energy conversion systems. Photosynthesis by green plants in nature is a typical example of photochemical solar energy conversion. In this reaction a highly ordered arrangement of the components as donor-chlorophyll-acceptor brings about photoinduced charge separation with almost 100% efficiency. Polymers can provide micro and macroheterogeneous reaction fields for the photoinduced charge separation, electron relay and catalysts. Tris(2,2'-bipyridine) Ruthenium(II) complex is attracting
much attention since it is suitable as photoreaction centre of water photolysis. It absorbs visible light ($\lambda_{\text{max}}$ 450nm) and its ground and excited states are fitted to the redox reaction of water (Structure II.6).

$$\begin{array}{c}
\text{Ru}^{2+} \\
\text{2(CIO}_4^-) \\
\end{array}$$

$R = -C_{13}H_{37}$ (octadecanyl)

or $-C_{27}H_{47}$ (dihydrocholesteryl)

Structure II.6. Tris (2,2' bipyridine) Ruthenium(II) complex.

Polymer pendant Ru(bpy)$_3^{2+}$ was prepared from polystyrene containing 2,2'-bipyridine groups. The monomeric complex Ru(bpy)$_3^{2+}$ is very soluble in H$_2$O but insoluble in benzene or chloroform but the copolymer complex prepared from styrene was insoluble in water and soluble in benzene or chloroform. This specific solubility of the complex was useful for utilizing it as a solid phase or membrane in water.
The polymer metal complex is used as sensor for mechanochemical system in which chemical energy is converted into some mechanical change. The shrinkage of muscles in vivo is an example of the effect of metal ion complexation where Ca\(^{2+}\) ion have been proposed to participate in the shrinkage by forming a mixed complex with myosin-ATP complex and with F- actin ADP complex. Hogo et al. reported\(^{171}\) that the mechanochemical behaviour of cupric ions was superior to one induced by pH change. Kuhn et al.\(^{172}\) observed the elongation of the PVA filament when Cu\(^{2+}\)-complex in aqueous solution is dissociated by reducing the Cu\(^{2+}\) ion to the Cu\(^{+}\) ion. The oxidation of Cu\(^{+}\) to Cu\(^{2+}\) again causes the complex formation and the shrinkage of the filament.