CHAPTER II
METAL CHELATION USING POLYMER SUPPORTED LIGANDS: AN OVERVIEW

Synthetic macromolecules have revolutionised various technologies in the present century. The ability of chemistry to design giant molecules or polymers to meet specific needs and then to produce them according to plan has led to an avalanche of new products with qualities that could never be duplicated with natural materials.

Macromolecular metal complexes, both synthetic and natural, have metal complex moieties on their polymer backbone. A variety of solid supports and matrices (both organic and inorganic) have been used for anchoring chelating groups on to them. In the last two decades, the separation of metal ions using chelating ligands bound to polymer supports have gained much attention. Lightly crosslinked polymers are functionalised suitably and appropriate chelating groups are attached to them which can be co-ordinated with various metal ions in solutions. Polymer anchored ligands have the advantage that the heterogeneous (insoluble) nature of the system makes them easy for separation and work up.

2.1 Classification and Formation of Macromolecular Metal Complexes

Macromolecular metal complexes can be classified into three main groups.
Type 1

MMC's with metal ion or metal complex bound on the side chain of an organic polymer or surface of an inorganic high molecular weight compound.

Type 2

MMC's in which the bifunctional or higher functional ligand L and metal ion/metal are part of a polymer chain or network.

Type 3

In this type of MMC's, there is only physical interaction of a metal complex or metal cluster with an organic polymer or inorganic high molecular weight compound.

The general route of type 1 synthesis is usually as follows.

Support → support functionalisation → interaction with MXn → Separation of unbound reagents.

Another possibility uses the polymerisation of vinyl substituted metal complexes (or ligand followed by metallation).

For type 2 MMC's, different possibilities such as reaction of a bifunctional or higher functional ligand L with M Xn or the reaction of a
bifunctional low molecular weight metal complex with another bifunctional reagent, exist.

Preparation of Type 3 MMC's is realised by different methods such as impregnation, coprecipitation, sorption, deposition by evaporation, sublimation and insertion into a structural support dispersion, microencapsulation etc.

2.2. Structural Features of MMC's

Type 1

Three different types of bondings are possible in type I MMC's.

1. Electrostatically bound to a macromolecule.

\[ \begin{array}{c}
\text{---} \\
\downarrow \text{X}^+ \\
\text{M}^{\text{\textsuperscript{\textbullet}}} \\
\end{array} \quad \equiv \quad \begin{array}{c}
\text{---} \\
\uparrow \text{X}^+ \quad \text{M}^{\text{\textsuperscript{\textbullet}}} \\
\end{array} \]

2. Co-ordinately bound to a macromolecule.

\[ \begin{array}{c}
\text{---} \\
\downarrow \text{M} \\
\text{---} \\
\end{array} \quad \equiv \quad \begin{array}{c}
\text{---} \\
\text{---} \\
\text{---} \\
\end{array} \]
3. Covalently bound to a macromolecule.

Fig. 1 Type 1 Metal Ions/Complexes/Chelates Bound to a Chain or the Surface of Organic or Inorganic Macromolecule

Type 2

Two different structural variations are possible with type 2 MMC's

1. Part of a polymer chain or network via the ligand.

Fig. 2 Type 2 Metal Complexes as Part of a Polymer Chain or Network.

2. Part of a polymer chain via metal ion

Type 3

In type 3 MMC's, there is only physical interaction of metal ions/chelates with organic or inorganic macromolecular support.
2.3. General Uses of MMC's

Recently, the area of polymer supported organic reactions\textsuperscript{24, 25} and polymer supported catalysts\textsuperscript{26, 27} has gained renewed interest with the latest developments in solid phase combinatorial chemistry. Majority of the catalysts are efficient since they are less toxic and more stable towards moisture and other contaminants enabling them to be superior over low molecular weight analogues. Apart from this, recovery of the catalyst can be carried out by filtration, with subsequent regeneration. Uses of MMC's as ion-exchange resins\textsuperscript{28}, metal ion separating agents for leached liquors\textsuperscript{29, 30}, spectrophotometric colour developers\textsuperscript{31} etc. are well known. MMC's find applications in controlled drug delivery systems\textsuperscript{32}, non-linear optical activity\textsuperscript{33} and molecular conversions based on multielectron transfer\textsuperscript{34, 35}. 

Fig. 3 Type 3 Metal Ions/Complexes/Chelates Physically Interacting with Organic or Inorganic Macromolecules.
2.4. Different Types of Polymer Supports for MMC's

Both organic and inorganic matrices have been used for anchoring chelating functions\textsuperscript{36,37}. Organic matrices used as supports may be natural or synthetic polymers. Among the naturally occurring polymers, cellulose finds wide applications\textsuperscript{38}. Chitin (N-acetyl D-Glucosamine) is another naturally occurring marine polymer used as support\textsuperscript{39}. Organic synthetic polymers are of two types, condensation and addition polymers. Condensation polymers are high molecular weight crosslinked structures usually formed by an ionic organic reaction from small polyfunctional monomers through removal of small molecules such as water, alcohol or ammonia and forming C-C, C-N, C-O or other bonds\textsuperscript{40}. These condensation polymers can easily undergo hydrolytic cleavage and therefore have poor chemical and mechanical stability\textsuperscript{41}. Addition polymers are formed by free radical polymerisation of mixtures of olefinic and diolefinic compounds\textsuperscript{42}. These polymers contain only C-C bonds in the main chain and therefore resist hydrolytic cleavage and can withstand wide variations of pH over alkaline and acidic ranges and are stable at relatively high temperatures. In this case, functionalisation can be easily achieved and the type and degree of crosslinking can be readily controlled.

2.4.1. Polystyrene(PS) Supports

The most commonly used sorbents are based on styrene-divinyl
benzene copolymers as matrices\textsuperscript{43}. The sorption capacity and selectivity of the sorbents greatly depend on the method of synthesis. Synthesis of polystyrene crosslinked with DVB by suspension polymerisation yields beads with diameters and surface area appropriate for large scale application. By using polystyrene resins with proper crosslink density, optimum swelling behavior for the resin can be achieved.

Usually, crosslinked polystyrene beads of 1 to 15\% degree of crosslinking are employed. Chloromethylated resins (Merrifield resin) prepared from these beads are functionalised by polymer analogous reactions. The use of chloromethylated polystyrenes as supports for preparing chelates and synthetic reagents have increased tremendously since Merrifield demonstrated their use in peptide synthesis\textsuperscript{44,45}.

PS is still one of the most popular polymeric materials used in the synthesis due to its low cost, ready availability, mechanical robustness and facile functionalisation. The polymer is most commonly prepared by copolymerisation with active monomers such as chloromethyl styrene or bromomethyl styrene, thus ensuring an even site distribution of the functionalised sites within the polymer matrix. Various percentages and types of crosslinking agents have been incorporated into the PS resins, the most common being DVB, but other examples include ethyleneglycol dimethacrylate (EGDMA) and tetraethyleneglycol dimethacrylate (TEGDA) to give different properties.
Typical supports used in early studies were 2% crosslinked (microporous or gel type resins) which require solvent swelling for reagents to access internal functional groups\textsuperscript{46}. With PS resins this can sometimes be a problem, especially when protic high polar media such as alcohols and water are necessary, resulting in poor swelling and therefore poor site accessibility. The use of macroporous resins which typically contain greater than 10-15\% levels of crosslinker, can overcome the need to swell the supports in a compatible solvent, due to their permanent pore structure\textsuperscript{47}. The macroporous resins can however sometimes suffer from poor loading capacity and brittleness.

Epoxidation of alkenes by a highly reusable and efficient PS supported molybdenum carbonyl catalyst was reported by Grivani \textit{et al}. High conversion of a range of alkenes to epoxides was achieved with tert-butyl hydroperoxide\textsuperscript{48}.

\textit{Anilkumar et al} have prepared some isoxazole and pyrazole ligands immobilised on polystyrene matrix for complexing various transition metal ions\textsuperscript{49}. An organic - inorganic ion exchange resin with a styrene support has been reported by Varshney \textit{et al}\textsuperscript{50}. An o-phenylene (diphosphine) pendant group supported on Merrifield resin was synthesised by Gulliver \textit{et al} and the characterisation of some of its metal complexes were done\textsuperscript{51}.
Polystyrene matrix was used for supporting pyridylazo-α-naphthol (PAN) and was used as an ion exchanger by Abdelaal et al. Chloromethylated polystyrene was chemically modified through alkylation of pyridylazo-β-naphthol in the presence of a phase transfer catalyst. The polystyrene supported PAN moiety was detected by FTIR spectroscopic analysis.

Jang has reported the use of polystyrene supported palladium catalyst in the Suzuki coupling of a number of organoboranes with alkenyl bromides, iodo benzene and aryl triflates, with polymer supported catalyst being prepared from Merrifield's resin.

![Diagram of PS Supported Pd Catalyst](attachment:diagram.png)

**Scheme 1. Preparation of PS Supported Pd Catalyst**

Leadbeater has prepared a polystyrene supported ruthenium phosphine complex. The immobilised complex was prepared by stirring RuCl₂(PPh₃)₃ with PS-PPh₂ in dichloromethane. The catalyst has been used for the oxidation of a range of alcohols and hydrocarbons.

Seebach and coworkers have prepared a range of polystyrene immobilised BINOLS (1,1'-bis-2-naphthol) by suspension polymerisation of
suitably functionalised BINOL derivatives with styrene\textsuperscript{55}. These supported BINOLs have been used with success in a wide range of stereoselective, metal-mediated transformations.

Titanium metal complexes of TADDOLs (\(\alpha,\alpha,\alpha',\alpha'\)-tetraaryl-1,3-dioxolane-4-5-dimethanol's) supported on polystyrene were prepared by Burguete and coworkers\textsuperscript{56-58}. These supported TADDOL's have proved to be very efficient catalysts for Diels-Alder reaction.

2.4.2. Poly (methyl methacrylate) (PMMA) Supports

Poly (methyl methacrylate) (PMMA) has been used as a versatile support for anchoring quite a large number of ligands. Copolymers of methyl methacrylate with DVB and EGDMA were prepared and used as macromolecular support for anchoring chelating pyrazoles and isoxazoles. PMMA supports are well-known for their mechanical and thermal stability. The thermal stability of PMMA supports was studied in detail by Varma \textit{et al}\textsuperscript{59}.

The nature of the support has an important role on the complexation behavior of the macromolecular ligand. Tyagi \textit{et al} have made some important studies on the polarity of the supports on which the functional moieties are attached\textsuperscript{60}. Physicochemical studies of methyl methacrylate - acrylonitrile copolymer indicate that the polar character of the surface increases with increase in acrylonitrile content.
Poly (methyl methacrylate) bound dithiazone was used for the extraction of metal ions from aqueous solutions\textsuperscript{61}. The complex formation of Ti(IV), V(V) and Mo(V) with macro ligands containing carbonyl group on PMMA proceeded effectively in non-aqueous medium\textsuperscript{62}. This is mainly due to the hydrophobic nature of the polymer.

2.4.3. Poly (2-hydroxyethyl methacrylate)(PHEMA) Supports

The non-toxic and non-carcinogenic properties of crosslinked micro beads of poly (2-hydroxyethyl methacrylate) (PHEMA) finds wide range of applications for this polymer in biotechnology and biomedical engineering. The material has high biocompatibility. The crosslinked PHEMA is highly polar giving rise to hydrophilic three dimensional network\textsuperscript{63}.

Cukurova \textit{et al} have recently developed a novel suspension polymerisation technique for the preparation of PHEMA particles with desired properties\textsuperscript{64} (i.e. excellent spherical shape, size in the range 2 \(\mu\text{m} \) - 100 \(\mu\text{m}\) in diameter, very narrow size distribution and desired porosity). Since the new method eliminates the use of polymeric stabilisers in the aqueous phase, it is easy to apply and extremely useful for particle preparation for biomedical applications. Some of the biomedical and biotechnological applications necessitate the surface modification of PHEMA by chemical or biological methods \textsuperscript{65, 66}.
Highly crosslinked macroreticular copolymers of 2-hydroxyethyl methacrylate (HEMA) and ethylene dimethacrylate (EDMA) are known under the commercial generic names 'Spheron' (Lachema Brno) and “Separon HEMA” (Laboratory Instrument Works, Prague). They themselves and their derivatives are used as sorbents, carriers of biologically active substances and ion exchangers for various types of chromatography. Poly (2-hydroxyethyl methacrylates) containing primary alcoholic groups are reactive polymers and by chemical transformation of their hydroxy groups, many new polymers with various functional groups can be prepared. The derivatives containing pendant imidazole, primary amino groups and complexon groupings (EDTA and DTPA) were prepared by Kahovec, Jelinkova and Coupeck.

Hydrogels based on a copolymer of HEMA with 2-ethoxyethyl methacrylate (EEMA) were synthesised. The ability to absorb large amounts of moisture by these systems helped in ready passage of oxygen through the membrane made of such materials. This makes them suitable for application in contact lenses. The high water uptake of HEMA containing polymers is due to the high polarity of HEMA compared to EEMA.

![Chemical structures of PHEMA and PEEMA](image)

Fig. 4 Polymers of 2-Hydroxyethyl methacrylate and 2-Ethoxyethyl methacrylate
2.4.4. Poly (glycidyl methacrylate) (PGMA) Supports

Many speciality polymers with epoxy groups and subsequently modified ones can be prepared using glycidyl esters. These acrylic polymers containing epoxy groups have been widely used for various applications such as pressure sensitive adhesives, coatings in contact lenses, dental composites etc. Synthesis and characterisation of copolymers of GMA and acrylic comonomer were also done.

Hradil et al. have prepared a phase transfer catalyst (PTC) immobilised on a macroporous GMA-EDMA resin. This resin is of great importance for mechanistic studies as it provides an environment that is much more polar than that afforded by styrene-divinyl benzene resins.

Complexes of bivalent ions with reaction products of the copolymer of glycidyl methacrylate-ethylene dimethacrylate with 2-hydroxyethyl, ethyl and diethyl amine moieties were reported by E. Kalalova and Z. Radova.

The basic copolymer, (GMA-EDMA), was prepared by radical suspension copolymerisation in the presence of an inert phase represented by a mixture of higher alcohols making possible the formation of a macroporous structure. The modified polymers used in the reactions with metal ions were prepared through the reaction of 2-hydroxyethylamine, ethylamine and diethylamine with epoxide group of the copolymer according to the following scheme.
Scheme 2. Preparation of PGMA Bound Ligands

Chettiyar et al. have prepared some semicarbazone Schiff base complexes of transition metal ions anchored on to PGMA-DVB and PGMA-EGDMA supports\textsuperscript{74}.

2.4.5. Polyacrylamide (PA) Supports

Lightly crosslinked polyacrylamide systems have been found to be a high quality support for studying the behaviour of complexes\textsuperscript{75}. The hydrophilic nature of the system facilitates easy metal ion uptake from aqueous solutions. When the polymer is crosslinked, restricted interaction of functional groups can be achieved. A high degree of crosslinking, a low level of functionalisation, low reaction temperature and origin of electronic charges near the polymer backbone tend to encourage the situation mimicking the infinite dilution condition in solutions.
Polyacrylamides with 2-20 mol % crosslinks were prepared by solution polymerisation and glycine functions\textsuperscript{76} were incorporated by transamidation with excess sodium salt of glycine. Metal ion complexation of these glycine functions in varying structural environments were investigated for Fe (III), Co (II), Ni (II) and Cu (II) ions. It has been found that with increasing degree of crosslinking the metal uptake increased upto 8\% crosslinking and decreased further.

\[
\text{CONH}_2 + \text{H}_2\text{N—CH}_2—\text{COO Na} \xrightarrow{100^\circ\text{C}, 20\text{ h}} \text{CONH—CH}_2—\text{COO Na}^+ + \text{H}_2\text{N—CH}_2—\text{COO Na}
\]

Scheme 3. Transamidation of NN’ MBA Crosslinked Polyacrylamide with Sodium salt of Glycine.

Polyacrylamide supported metal complexes were also subjected to enzyme model study\textsuperscript{77}. Kinetics of catalysis and the dependence of various factors of the catalytic reactions on the decomposition of hydrogen peroxide were also studied.

2.4.6. Inorganic Polymeric Supports

The preparation of small metal particles supported on inorganic carriers has been investigated thoroughly and is well documented\textsuperscript{78,79}. 
Generally accepted preparation techniques are ion exchange or impregnation of an inorganic oxide surface (e.g. alumina, silica) with metal salt solutions followed by calcination and subsequent reduction with hydrogen.

Inorganic ion exchangers of single and double salts are being increasingly used for separation of metal ions, because of their stability towards high temperature and radiations. Selectivity towards a particular metal ion by inorganic ion exchangers is one of the most important factors for their development. In order to achieve stable materials with chromatographic properties interest has been generated in organic-inorganic ion exchange materials.

There are many inorganic solids with regular structures that incorporate spaces having molecular dimensions. Sheet silicates (often called clays) like Zeolites are cation exchangers. The spaces between the layers are accessible even to large molecules, the incorporation being referred to as intercalation. Like polymers, the smectites are able to swell and many transition metal complexes have been incorporated between the layers.

The layered silicate hectorite was used as a host for rhodium phosphine complexes.
2.5 Polymer Supports - Structure and Morphology

A large number of organic and inorganic materials have been used as supports in solid phase reactions, many of which are commercially available and others can be synthesised in the laboratory. An ideal support should be mechanically, thermally and chemically inert under conditions of use. They should be easily prepared and functionalised and should be obtained in a good physical form.

The supports can be linear or crosslinked resins. Linear polymer supports have the advantage that the reaction can be carried out in a homogeneous medium and allow rapid unimpeded access of reagents to functional groups on the support. The separation of the support after the reaction is done by addition of a suitable precipitant, by micro or ultrafiltration and in some cases by thermal cycling. A major disadvantage of using linear polymer supports is that they are useful only with solvents in which they dissolve. Furthermore, the separation process is difficult,
relatively time consuming and often inefficient. Nevertheless, a key factor in their use is that the reaction can be monitored, for example, by high resolution solution phase $^1$H and $^{13}$C NMR spectroscopy$^{85}$. The use of linear polymers in reaction and as supports has been well documented$^{86}$.

Crosslinked polymers consisting of linear chains interconnected by crosslinks are insoluble in almost every solvents and are used for organic synthesis. Their use facilitates the reaction to be carried out in a heterogeneous medium and easy separation of the products is possible by simple filtration.

Crosslinked polymers can be prepared by many techniques. Bulk polymerisation consists of polymerisation of the pure monomers with or without initiator in the absence of solvents. Pure high molecular weight polymers are formed. In solution polymerisation technique, polymerisation is carried out in a suitable inert solvent. Here, low molecular weight polymer will be formed due to the action of solvent as chain transfer agent.

Suspension and “popcorn” polymerisations are generally used to obtain robust spherical particles of appropriate size, which facilitates handling of the support and also withstands mechanical agitation. In suspension polymerisation, monomers are dispersed as liquid droplets (dispersed or non-continuous phase) in excess of immiscible water phase (continuous phase) along with initiator and a water soluble organic or
inorganic suspension stabiliser. Polymerisation yields hard glassy polymer particles referred to as ‘beads’, ‘pearls’ or ‘resins’.

Popcorn polymerisation produces white glassy opaque granular material called ‘Popcorn’ or ‘Cauliflower’.

Another type of polymer with three dimensional crosslinked networks, where linear polymer chains are interconnected by a separate chemical reaction following polymerisation called ‘macronet’ polymers are also widely used as supports, although they have poor mechanical strength.

The resin morphology of the support has profound influence on the reaction. Based on resin morphology, polymer supports can be generally classified into (a) gel-type microporous resins (b) macroporous and (c) macroreticular resins. Gel-type resins are generally lightly crosslinked. The resin does not have permanent porosity, but in the presence of a good solvent, the space between the crosslinks is occupied by the solvent and the resin ‘swells’. These spaces are considered as small pores and hence the name microporous. In the presence of good solvents, a gel network with porosity depending on the degree of crosslinking is obtained. Generally, highly swollen gel type resins are soft and compressible.

If suspension polymerisation of styrene-DVB mixture is carried out with an appropriate organic solvent (dilutent or porogen) at an appropriate
level, phase separation of polymer matrix occurs\textsuperscript{95,96}, i.e, each polymer bead is composed of a crosslinked polymer phase and a discrete porogen phase, the latter acting as a template for the permanent porous structure of the resin. The removal of porogen at the end of polymerisation gives resin beads which are hard but opaque and with a rough surface. The polymer matrix is heterogeneous (i.e. non-uniform) with some areas consisting of impenetrable crosslinked polymer chains, while other areas are devoid of polymer. These materials are not swollen in a solvent to allow access to the interior, because they possess a permanent well developed porous structure even in the dry state, whose dimensions can be manipulated during polymerisation. Such materials are called macroprorous resins, the term not intended to convey anything about the size of pores. Miller et al have suggested that, for styrene-DVB resins, criterion of macroporosity is that uptake of cyclohexane by the resin should not be less than 0.1 m\textsuperscript{2}g\textsuperscript{-1} dry polymer\textsuperscript{97}. Recently, Miller has suggested the use of n-heptane instead of cyclohexane\textsuperscript{98}.

A macroreticular resin is the one produced in a suspension copolymerisation with an appropriate porogen, which is good only for the monomer\textsuperscript{96} and gives rise to phase separation or precipitation of the crosslinked polymer. Scientists from the Rohm and Hass Co. coined the term macroreticular resins for such polymers\textsuperscript{99}.

The development and control of resin morphology is complex and difficult to study. Based on experimental data, pseudophase diagrams
defining resin morphology from the given type and level of porogen and degree of crosslinking, has been developed\textsuperscript{97,98,100}.

2.6. Solvation Behaviour of Polymer Supports

Solvation characteristics of polymer supports play an important part in the reactivity of immobilised species. A polymer dissolves in a solvent when the polymer-polymer interaction is overcome by polymer-solvent interactions. The thermodynamic parameter $\delta$ is used to measure the attractive strength between molecules in a material. A solvent is likely to be 'good' for a polymer (i.e. compatible with the polymer), if they have similar solubility parameters.

For crosslinked polymers which are insoluble in common solvents, due to their three dimensional network, the reactivity of the species bound on the polymer depends largely on the solvation behaviour\textsuperscript{101}. They 'swell' in a 'good' solvent, the extent to which it is inversely related to the degree of crosslinking. The solvent occupies the space between the polymer chains. Swelling can be demonstrated by the 'Shrinking core model' (Figure 6).

Swelling occurs from outside to the interior. Polymer network on the exterior of the resin beads swells first to form an expandable outer layer with a central unswollen core. Slowly, the outer swollen layer expands while the central core shrinks and disappears finally.
Very low levels of crosslinking (<1%) give highly swollen but mechanically weak resins, whereas highly crosslinked networks give mechanically strong resins, which may swell very little even in 'good' solvents.

Solvation behaviour of polymer supports has significant influence on the bound species in the synthesis of biopolymers. This has led to the modification of the original Styrene-DVB support used by Merrifield. Supports that resemble the peptide to be synthesised has been reported. Development of supports, with similar structure as that of the substrate, were initiated.

The design of synthetic polymeric supports like polyacrylamide and poly(vinyl pyridine) resulted in better support-solvent compatibilities. Polyacrylamide resins are more polar than polystyrene and is therefore superior to the latter in peptide synthesis and oligodeoxyribonucleotide synthesis. Many other polymer supports modified to show better solvation behaviour has been reported.
2. 7. Characterisation of Chelating Sorbents and Chelates

Absence of adequate analytical methods to characterise the supported moiety at each step of the reaction, along with the insolubility of polymer supports, presents a big problem in polymer supported reactions. Linear polymer supports can be characterised by usual physio-chemical methods of analysis; but crosslinked polymers, which cannot give a homogeneous solution required for analysis, are more difficult to be characterised. Different methods adopted have their own advantages and disadvantages and are used individually or in tandem.

The methods of characterisation of macromolecular chelates can be broadly grouped into three:

(1) Chemical and Physico- chemical analysis
(2) Spectroscopic methods
(3) Magnetic studies

2.7.1. Chemical and Physico-Chemical Analysis

2.7.1.1. Elemental Analysis

The usual methods of analysis for elements like nitrogen, halogen, sulphur and phosphorus etc. are used to estimate the loss or gain of these elements during a reaction.
2.7.1.2. Metal Estimation

The determination of the metal ion content helps in the prediction of the co-ordination number and stereochemistry of the MMC. This can be estimated by destructive or non-destructive techniques. Usually chemical estimation or atomic absorption techniques are resorted to.

2.7.1.3. Gravimetric Method

This method is used to analyse polymers, which do not degrade under normal conditions, i.e., mostly for crosslinked polymers. The difference in the weight of polymers during the reactions is used to monitor the reactions. Occurrence of unwanted side reactions hamper the efficiency of this method.

2.7.1.4. Titration of Reactive Groups

The acid-base, reducing or oxidising nature of the species bound on the support can be quantitatively estimated by titration with appropriate reagents. Usually the polymer is reacted with excess titrating agent or a suitable reagent followed by back titration.

2.7.2 Spectroscopic Methods

The nature of co-ordination of the functional groups of the resin and
the geometry around the metal ions are studied by spectroscopic methods such as IR, NMR, ESR, XRD, solid state reflectance UV-Vis. etc.

2.7.2.1 Infrared Spectroscopy

Infrared spectroscopy is a good tool in the hands of the chemist to locate and identify the co-ordinating sites. IR spectroscopy has mainly been used qualitatively to determine to what extent a chemical transformation has taken place and also to show the presence of functional groups on polymer supports\textsuperscript{107}. In polymers, the infrared absorption spectrum is often surprisingly simple because of the fact that many of the normal vibrations have almost the same frequency.

The IR absorption by a ligand is usually shifted by complex formation with metal ions\textsuperscript{108, 109}. It is desirable to supplement the observations of infrared absorption. For this purpose, observations in the far infrared region become important. Despite serious experimental difficulties, valuable information is available in this region. The application of Fourier-Transform infrared spectroscopy to polymers has been reviewed by D' Esposito\textsuperscript{110}. Utilisation of lasers as light sources has greatly decreased experimental difficulties in this technique and the method has now become one of the standard tools for polymer analysis.
2.7.2.2. Electron Spin Resonance Spectroscopy (ESR)

ESR technique is one of the foremost techniques that are used for characterising MMC's with paramagnetic ions. ESR gives information on metal ion valence states. Direct proof of the existence of chemical bond between metal ion and ligand can be established\(^\text{111}\). From the values of \(g_{||}\) and \(g_{\perp}\), \(A_{||}\) and \(A_{\perp}\), the covalent character of the metal-ligand bond can be evaluated\(^\text{112}\).

2.7.2.3 Nuclear Magnetic Resonance Spectroscopy

\(^1\text{H}, \ ^{13}\text{C}\) and \(^{19}\text{F}\) NMR spectroscopy have been used in monitoring solid phase reactions\(^\text{113-115}\). However, the application of NMR in the structural analysis of polymers and their complexes are limited due to the low solubility of the sample and broadening of the spectra. \(^{13}\text{C}\) NMR spectra are recorded routinely by pulse techniques and with simultaneous double irradiation of all the proton resonances. This produces a proton decoupled spectrum of singlet signals with one line for each non equivalent carbon atom in the sample\(^\text{116}\). Relaxation rates of carbon nuclei vary widely and the rate predominantly depends on whether or not the carbon atom is attached to hydrogen. Hydrogen provides an efficient relaxation route for the carbon nucleus to lose its excess energy after it has absorbed the strong excitation pulse of radio frequency. Proton decoupling effects an additional increase in
signal intensity, but again this is true only of those carbons which are attached to hydrogen\textsuperscript{117}.

It is observed that, in general, complex formation with metal ions leads to shifts, splitting or broadening of the peaks due to ligand molecules. In the absence of anion effects, a downward shift is expected due to increased electronegativity of the donor atom of the ligand\textsuperscript{118}. $^{13}$C NMR technique has been used to study the structure of crosslinked polymers in a number of cases.

Demura \textit{et al} used $^{13}$C NMR to determine the tacticity of poly(methyl methacrylate) (PMMA), and poly (ethyl methacrylate) (PEMA)\textsuperscript{119}. The $^{13}$C NMR relaxation parameters, spin-lattice relaxation time ($T_1$) and nuclear overhauser effect (NOE) were determined. The application of $^{13}$C NMR to the examination of polymers in the solid state by magic angle spinning (MAS) technique is opening up new and sometimes different structural information about polymers because it is examining them in their natural states. Herring \textit{et al} have studied the amorphous and crystalline samples of poly (aryl-ether-ether-ketone) (PEEK) and poly (p-phenylene sulphide) (PPS) by both $^{13}$C high resolution cross-polarisation and magic angle spinning (CP/MAS) and wideline proton NMR spectroscopy\textsuperscript{120}. The CP/MAS spectrum of the amorphous PEEK sample displays much broader signals than does the crystalline sample.
2.7.2.4 UV-Vis Spectroscopy

Electronic spectra of metal complexes are generally used to study the geometry around the metal ions in the complex \(^{121, 122}\). The number and position of the bands give an idea of the geometry of the polymer complex. However the use is limited because of the low solubility of the polymer complexes in common solvents. Nevertheless, the diffuse reflectance spectra of complexes are successfully used to find their geometries.

2.7.2.5 Electron Spectroscopy for Chemical Analysis (ESCA)

This is also known as X-ray photoelectron spectroscopy and is a non-destructive analytical tool which gives information regarding the chemical nature of the surface. Local chemical concentration on the surface of polymer fibers can be studied. Traces of elements present on the polymer surface can also be determined. Thus ESCA is an excellent tool for the study of polymer surfaces, diffusion controlled reactions etc. which help the characterisation of polymers \(^{123}\). The surface structure of PHEMA beads prepared by special suspension polymerisation were characterised by ESCA by Cukurova \textit{et al} \(^{124}\).

2.7.2.6 Matrix Assisted Laser Desorption/Ionisation Mass Spectrometry (MALDI-MS)

Application of mass spectrometry (MS) to the analysis of polymers appear to have been somewhat limited. Recent developments in ionisation techniques and instrumentation has drastically changed this picture\(^{125-128}\).
In order to obtain structural information of polymers, thermal, hydrolytic and radiative methods can be employed to degrade macromolecules to low molecular weight compounds which are susceptible to MS analysis by volatilisation or desorption.

In this non-linear spectroscopic method, organic materials adhering to a surface is volatilised by a short laser pulse. Many molecules can be vapourised or desorbed in this way without pyrolysis or surface reaction. The surface with the adsorbed molecule is placed near the surface of a supersonic jet of helium. About 1% of desorbed species is cooled from the initial temperature of nearly 1000K to the neighbourhood of 10K by supersonic expansion. At such a low temperature, most of the vibrational and rotational structure which broadens room temperature spectra collapses. Narrow spectral features remaining can be compared to those seen in supersonic experiment at large concentration. The resulting molecular ion is then resolved by a mass spectrograph.

High molecular weight organic molecules fragment in a characteristic way and thus can be identified by optical and mass spectra. Trace quantities of complex organic molecules can be detected by resonant ionisation spectrometer. MALDI-MS experiments show high sensitivity and selectivity which is an innovation of resonant ionisation mass spectrometry. Employing optimum laser power, the molecular weight information of polydisperse PMMA was obtained.
2.7.2.7 Fast Atom Bombardment Mass Spectrometry (FAB-MS)

Fast Atom Bombardment Mass Spectrometry (FAB-MS) has been used to investigate the structure of synthetic polymers\textsuperscript{126}. The technique has been applied to the study of sequences in synthetic polymers. Georgio \textit{et al}\textsuperscript{31} has employed FAB-MS to identify the oligomers formed in the partial methanolysis followed by HPLC fractionation of poly (β- hydroxy butyrate) (PHB) and poly(β-hydroxy butyrate-co-hydroxy valerate) (PHB-PHV). The FAB-MS spectra yield all the information that would be expected from the knowledge of the co-polymer structure and of the degradation method used.

2.7.2.8 Pyrolysis Gas Chromatography-Mass Spectrometry

Pyrolysis Gas Chromatography (PGC) has been established in recent years as an effective analytical technique for exploring polymeric samples\textsuperscript{132}. It has proved to be a powerful tool for the study of various structural aspects such as monomeric composition, determination of sequence of distribution, kinetic parameters, branching and H-T and T-T linkages in various polymers\textsuperscript{133}. Apart from being complementary to various spectral techniques such as NMR and IR, it overcomes the problem of finding suitable solvents for dissolving polymers\textsuperscript{134}. In conjunction with mass spectrometry(MS), PGC has gained new dimension in the study of the pyrolytic mechanism from the analysis of pyrolyzates \textsuperscript{135}. 
2.7.3. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements play a prime role in the characterisation of polymer anchored metal complexes. Magnetic moment values give an insight into the geometry of the molecule and is a clear indication of the metal bond in the complex\(^{136}\). Magnetic susceptibility measurements coupled with Mossbauer parameters were used to establish the nature of ion exchange resins in several cases\(^{137, 138}\).

2.8 Nature of Ligand Functions

The chemistry of macromolecular metal complexes is a new field connecting polymer and metal complex chemistries. The use of polymers as supports for chelates and catalysts as well as synthetic reagents have grown tremendously\(^{139, 140}\).

Polymer metal complexes are defined as complexes composed of a polymer ligand and metal ion in which the metal ions are attached to the polymer ligand by a co-ordinate bond. A polymer ligand is understood to be a polymeric substance that contains co-ordinating groups or atoms (mainly N, O and S) obtained by polymerisation of monomers containing co-ordinating sites or by chemical reaction between a polymer and a low molecular weight compound having co-ordinating ability. When a polymer chelating ligand is equilibrated with a metal ion a polymer metal chelate is formed.
Various types of ligands have been incorporated into polymer matrices which are capable of sorbing metal ions from solutions. The most commonly used groups are iminodiacetic acid, amidoxime, amines, phosphoric acid, oxine, thiazoles, pyrazoles, pyridines, isoxazoles, diketones and Schiff bases\textsuperscript{141}. These chelating groups contain donor atoms like nitrogen, oxygen or sulphur. Nitrogen is present in the form of primary, secondary or tertiary amino group, nitro, nitroso, azo, diazo, nitrile, amide, Schiff base and other heterocyclic groups. Oxygen is usually in the form of phenol, carboxyl, ketone, aldehyde groups etc. Sulphur is in the form of thiol, thioester, thiocarbamates, thiosemicarbazones etc.

2.8.1 Ligands Containing Nitrogen as the Only Donor Atom

A number of chelating resins with nitrogen as the only donor atom have been synthesised in recent years.

A polystyrene based resin which contains methyl aminoglucitol was developed by Schilde\textit{ et al.} The resin was found to be capable of removing stannate, germanate, tellurite, molybdate and tungstate from brines\textsuperscript{142}.

An 1-(2-amino ethyl) piperazine resin (Fig-7) was synthesized from the reaction of 1-(2-amino ethyl) piperazine with poly (vinyl benzylchloride). The resin was then examined for its affinity for precious metal ions\textsuperscript{143}. 
Poly (glycidyl methacrylate) resins were modified with pyrazole, imidazole and 1,2,4-triazole (Fig. 8). All three resins selectively removed Cu(II) from a solution containing Cu(II), Cd(II), Co(II), Ni(II), and Zn(II) at pH > 2.5.

Several polymeric ion exchange resins composed basically of crosslinked (divinyl benzene or any other suitable crosslinking agent) recurring units of substituted imidazoles and 2-aminomethylpyridine have been reported (Fig. 9) which are capable of being utilised to separate copper, nickel and cobalt from each other and also from other metals in solution.\textsuperscript{145,146}
Some ion exchange resins containing pyridyl imidazole and pyridyl imidazoline (Fig.10) groups anchored onto macroporous styrene-divinyl benzene copolymers have also been evaluated for their ion-selective properties and found useful for the separation of copper and iron mixtures.

A group of new chelating resins, incorporating 2-picolyamine in a polystyrene matrix has been described as selective sorbents for separation of
non-ferrous transition metal ions such as copper and nickel from acidic hydrometallurgical leach liquors where polystyrene-iminodiacetic acid type resins are not applicable\cite{148}.

Two commercial chelating resins, Dowex XF-4194 and Dowex XF-4196 possessing N-alkylated picolylamine functional groups offer many interesting possibilities in the extractive metallurgy of copper, nickel and cobalt. Their selectivity for copper and nickel over iron and most other cations in acid solution and their ability to be regenerated with sulfuric acid or ammonia solutions make them useful in a number of hydrometallurgical applications\cite{149}.

2.8.2 Ligands Containing Nitrogen and Oxygen as Donor Atoms

Chelating resins containing nitrogen, and oxygen as donor atoms form the largest class of chelating resins. The important ligands possessing nitrogen and oxygen as donor atoms include iminodiacetic acids, hydroxamic acids, oximes, hydroxy quinoline derivatives and Schiff bases.

Balasubramanian et al\ have synthesised two macromolecular metal chelates, poly(2-hydroxy-4-acryloxy acetophenone oxime) and poly (2-hydroxy-4-methacryloxy acetophenoneoxime)\cite{150}, containing Copper (II) and Nickel (II). The polymer chelates were charcterised by IR, NMR spectral data, thermal, magnetic and conductivity studies. It was found that the
Copper (II) chelates were planar and Nickel (II) chelates were likely to possess a distorted planar geometry.

Raja et al have reported the supported polymer chelates of 7,7'-[1,4-N,N'-dimethyleneepiperazinylene]-8-quinolinol (DMPQ) with Cu$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Mn$^{2+}$ and Cd$^{2+}$ 151. The chelates have a 1:1 metal : ligand stoichiometry.

Preparation of polymer chelates of epoxy based polyesters containing oxine as pendant groups were reported by Shah et al 152. Ram et al have described the synthesis of some polystyrene supported Mn(II) Schiff base complexes. The catalytic activity of the supported metal complexes were studied in the epoxidation of norbornene and cis-cyclooctene using tert-butylhydroperoxide(TBHP) as the terminal oxidant 153.

Cagnola et al have prepared supported complexes of Rh, Ru, Pd and Ni with tridecyl amine and chloride as ligands and tested as heterogeneous catalyst for hydrogenation of cyclohexene 154.

A versatile chelating ion exchange resin (Fig. 11) has been prepared by copolymerising N-(O-hydroxybenzyl)iminodiaceticacid with phenol and formaldehyde 155,156. This resin is now commercially available under the name Unicellex UR50.
A chelating ion exchange resin incorporating N-\((p\text{-hydroxybenzyl})\) iminodiacetic acid has also been prepared (Fig. 12) and its ion-selective properties have been compared with Unicellex UR 50 and Dowex A-1\textsuperscript{155,156}.

Cellulose powder with a low content of hydroxamic acid groups has been prepared from a starting material of carboxy cellulose\textsuperscript{157} (Fig. 13).
2.8.3. Chelating Ligands 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. The ligands mainly used were polyphenols, polycarboxylic acids, 1,3-diketones, phosphonic acids, arsonic acids, polyphenolic carboxylic acids, flavones and related compounds.\textsuperscript{158-166}

Polyphenols and polycarboxylic acids bearing chelating ion exchange resins are important members of this class.\textsuperscript{167} Compounds containing phenolic groups can be easily converted into polymeric compounds by condensing them with formaldehyde (or any other aldehyde, with or without an appropriate phenol in the presence or absence of a crosslinking agent to obtain a gel-type resin. The resins obtained from pyrogallol\textsuperscript{168,169}, salicylic acid\textsuperscript{170,171}, resorcinol\textsuperscript{172}, 2,3,4-trihydroxy benzoic acid,\textsuperscript{173} 2,4-dihydroxy benzaldehyde and 2'-4'-dihydroxy acetophenone by this
procedure have been described in literature. The resins obtained from salicylic acid and formaldehyde were first described by Davies et al. Warshawsky and Khanna have prepared a catechol derivative of polystyrene (Fig. 14) by a Friedel-Crafts reaction. This catechol derivative can be used as an intermediate for the preparation of new chelating ion exchange resins.

![Fig. 14 Polystyrene Resin with Catechol Groups](image)

Several cation exchangers (Fig. 15) with improved selectivity have been prepared by treating chloromethylated styrene-divinyl benzene copolymers with sodium malonic acid monoester followed by hydrolysis.

![Fig. 15 Polystyrene Resin with Dicarboxilic Acid Groups](image)
2.8.4 Chelating Ligands Containing Sulphur as the Donor Atom

Polythiostyrene was the first class of sulphur containing chelating ligands to be prepared and studied\textsuperscript{177}. The crosslinked polythiomethyl styrene was found to take up mercury quantitatively, when a solution of mercuric nitrate was allowed to pass through a column of this resin. An improved synthesis of this resin containing thiomethyl groups attached to polystyrene rings and involving three phase systems and the use of a phase transfer catalyst has been developed\textsuperscript{178}. The resin with thiomethyl group is specific for mercury whereas the resins of polythiostyrene selectively bind Fe(II), Co(II) and Ni(II)\textsuperscript{179}.

Kurimura \textit{et al} have recently synthesised poly(4-vinyl benzylamine-N, N-diacetate) costyrene sulphonate (P-SS) and their acid dissociation constants were determined\textsuperscript{180}. The formation constants of (P-SS) M\textsuperscript{2+} (M=Co, Ni, Cu) chelates have been determined by spectrophotometry. The results obtained in the polymer system are largely explained in terms of a powerful microheterogeneous field effect of the anionic polyelectrolyte chain.

Fatma \textit{et al} have prepared a thionein modified PHEMA membrane which was used for the removal of Cd(II) ions from human plasma\textsuperscript{181}. Cd(II) ions could be repeatedly be adsorbed and desorbed with the novel metallopeptide affinity PHEMA membranes without noticeable loss in their Cd(II) adsorption capacity. Susuki \textit{et al} have studied three different
poly (methacrylic acid-co-styrene sulfonic acid) bound cis Co(III)(en)$_2$(OH)$_2$L species having different degrees of copolymerisation and varying amounts of Co(III)$^{182}$.

2.9 Further Applications of Polymer Metal Complexes

The applications of polymer metal complexes are wide and varied. They include preconcentration and separation of metal ions, catalysis, use as electronic gadgets, transport phenomena and separation of small molecules, photoinduced electron transport, photoconductivity, photovoltaic and nonlinear optical (NLO) devices.

2.9.1 Preconcentration and Separation of Metal Ions

Certain chelate-forming ligands have been extensively studied by Kantipuly et al.$^{83}$ Such ligands are characterised by the presence of reactive functional groups of O, N, S and P in the matrix capable of co-ordinating to different metal ions and hence used for the preconcentration and separation of trace metal ions. Bayer condensed o-aminophenol and glyoxal and obtained glyoxal-bis-2 hydroxyanil in a polymer matrix and this substance showed high affinity for Cu$^{2+}$, U$^{4+}$, and Ni$^{2+}$ ions.$^{184}$

Metal ion specific polymers have received much attention as a medium to prepare support materials for metal ion separation easily and inexpensively.
The synthesis of crosslinked polymeric ligands for the separation of specific metal ions is based on the 'memory' of the three dimensional crosslinked polymeric matrix. The various physicochemical characteristics of crosslinked polymer matrix, like the nature and extent of crosslinking and microenvironment of the ligand functions attached to polymer are the important factors affecting the specific and selective concentration of metal ions.

Diphenyl carbazide and diphenyl carbazone which act as bidentate chelating ligands have been incorporated into polymeric matrices to obtain chelating ion exchange resins (Fig.16 and 17). A resin containing diphenyl carbazone group has been found specific for mercury (II). Dore et al treated a chloromethylated styrene-divinyl benzene copolymer with diphenyl carbazide in refluxing dioxane to obtain a chelating ion exchange resin. This resin was proved to be specific for chromium(VI).

![Fig. 16](image1.png)

![Fig. 17](image2.png)

Chelating Resins with Diphenylcarbazide and Diphenylcarbazone Pendant Groups
2.9.2. Electronic Processes and Gadgets Using Macromolecular Metal Complexes

Since Wright reported that polyoxyethylene (POE) dissolved in inorganic salt solutions showed considerable ionic conductivity at ambient temperatures\(^1\), the development of ion conductive macromolecules (solid macromolecular electrolytes) have greatly increased. Eventhough we have at present more conducting MMC's than that of Wright, if the ionic conductivity can be increased 10 fold higher, many advantages of macromolecular materials such as light weight, thin film formation, flexibility etc. would lead to new types of electrochemical devices and batteries. The study on the (POE/inorganic salt) composite systems started with the analysis of structures of complex crystalline materials. The normally atactic POP (Fig.18) complexes are completely amorphous and show ionic conductivity of approximately \(10^{-6}\) S/cm which is ten fold higher than that for crystalline POE system\(^2\).

\[
\text{CH}_3\bigl(\text{CH}_2\text{CHO})^n\bigr
\]

\[1.0 \times 10^{-4}\ \text{S/cm (LiClO}_4, 25^\circ\text{C)}\]

Fig.18 Solid Macromolecular Electrolyte with POP Complexes

2.9.3 Catalysis Using Macromolecular Metal Complexes

The use of MMC's in heterogeneous catalysis has tremendous commercial potential. The important features of macromolecule-metal complexes as polymer bound catalysts are greater selectivity, recoverability,
good facility for treatment and especially appearance of novel catalytic activities.

Recent interest in the development of environmentally benign synthesis has evoked a renewed interest in developing polymer bound metal catalysts and reagents for organic synthesis that maintain high activity and selectivity (192-194). Catalysts and reagents immobilised upon a range of insoluble supports have been utilised and reported since the late 1960's (195). The immobilisation of transition metals on polymer supports offers a number of advantages over solution phase chemistry. In an ideal case, the supported complexes can be recovered from reaction mixtures by simple filtration, they also do not contaminate the product solution, they can be recycled, and they can help increase in selectivity. Such immobilisation also enables the use of high concentration of reagents to drive reactions to completion. Another advantage is due to the unique microenvironment created for the reactants within the polymer support. Supported catalysts have also been used for rapid production of compound libraries (196, 197). Ravindranathan et al have anchored l-valine to crosslinked polystyrene and its Cu(II) complexes were prepared. The polymer supported Cu(II) complexes were found to be versatile and recyclable catalysts for the oxidation of benzyl alchol, cyclohexanol and styrene (198).

The development of polymer supported catalysts can be considered to be an advancement for attaining one of the major goals of
'green chemistry' to facilitate efficient recovery of the catalyst from the reaction products, thereby reducing inorganic waste.

Macromolecular heterogeneous catalysts are effectively used in asymmetric reactions. The asymmetric heterogeneous catalytic reduction of carbonyl bonds by hydrogen transfer reduction or hydrogenation by means of molecular hydrogen as well as the asymmetric allylic substitution of allylic acetates were reported by Marc Lemaire et al. These polymers were either a Merrifield resin with a chiral pendant ligand or a chiral main chain polymer with ureas, thioureas or a diphosphine as pendant groups.

Styring et al. have described the synthesis of a Salen type Pd(II) complex supported on to a Merrifield type resin. The supported complex is an effective recyclable heterogeneous catalyst for the Suzuki cross-coupling reaction with out the use of phospheine ligands. Leaching of the metal into solution from the supported catalyst proved negligible.

There are a large number of reports on resin supported Jacobsen's alkene epoxidation catalysts. Sherrington et al. reported some resin supported alkene epoxidation catalysts. Polystyrene and poly (methyl methacrylate) based resin supported Jacobsen's chiral Mn salen complexes were prepared and were used as enantioselective catalysts in the epoxidation of 1, 2-dihydranaphthalene, indene, 1-phenyl cyclohex-1-ene and 1-phenyl-3,4-dihydronaphthalene using m-chloro perbenzoic acid as the oxidant and 4-methyl morpholine N-oxide as the co-oxidant.
Mirkhani et al reported the preparation of supported tetra(4-pyridyl)porphyrinato manganese(III) in one step by a quaternisation reaction and was found to be an efficient catalyst for alkene epoxidation and alkane hydroxylation by sodium peridate. The catalyst showed high selectivity in epoxidation of stilbenes and R(+)-limonene$^{202}$.

A well-known, efficient method of alkene epoxidation in solution is by employing ‘Mukaiyama’ procedure in which an unfunctionalised alkene is epoxidised very efficiently using a transition metal β-diketone complex as the catalyst, molecular oxygen as the oxidant and an aliphatic aldehyde as co-reactant. Nolte et al have reported the aerobic oxidation of alkenes like limonene with Nickel (II) acetylacetone bound to polybenzimidazole as Mukaiyama catalyst with an aldehyde as the co-reactant$^{203}$. Rates of reaction and yields of epoxide were higher with this system than with dissolved Ni(II) acetyl acetone under otherwise identical conditions. The polymer bound catalyst was recovered from the reaction mixture but some loss of activity was observed upon reuse of the catalyst due to leaching of the metal complexes.

A number of reports of the synthesis of polymer supported phosphine-linked chromium arene complexes and their use, both as linkers and catalysts are found in literature. Rigby and coworkers have prepared some phosphine supported chromium arenes by photolysis of arene-tricarbonyl complex with cyclooctene followed by thermal
replacement of cyclooctene with the ligand of choice. With simple arenes such as benzene and toluene the PS-p-CH$_2$PPh$_2$ supported chromium arene was formed easily and the resulting complexes have been used as catalysts for effecting cycloaddition reactions.

Metalloporphyrins have found use as catalysts in a range of reactions, often showing high regio and enantioselectivity. There have been a number of reports of immobilised metalloporphyrins. Using a pyridinium chloride support prepared from Merrifields resin and pyridine, Kuriakose and co-workers have immobilised a cobalt porphyrin complex. The supported complex was used as catalyst for the oxidation of dithiocarbamates to their corresponding disulfides.

The synthesis and reactivity of transition metal metalloocene complex has attracted much interest particularly with their wide catalytic applications in processes such as hydrogenation, hydroformylation and olefin polymerisation. There have been a number of reports of polystyrene supported cyclopentadiene metal complexes, the majority being used as heterogeneous single site catalysts for olefin polymerisation. A polymer supported cyclooctadiene nickel complex, Cp Ni(cod) prepared by Sbrana and co-workers was found to be an active catalyst for olefin polymerisation, the selectivity of the processes being dramatically different from that of the homogeneous analogue, the former giving high density polyethylene, the latter giving lower oligomer.
Asymmetric Diels-Alder reactions using chiral catalysts have been extensively studied and a number of highly efficient solution phase catalysts have been reported. Significant effort has also been applied to the immobilisation of these catalysts on a variety of supports. Itsuno used the copolymerisation methodology for the preparation of a number of PS-bound chiral oxaborolidinone catalysts and the model Diels-Alder cycloaddition between methacrolein and cyclopentadiene was investigated.

Leadbeater has reported the preparation of a resin bound cobalt phosphine complex by agitating commercially available diphenyl phosphino-PS with a solution of CoCl₂(PPh₃)₂ in dichloromethane.

![Scheme 4. Preparation of PS Supported Phosphine-Cobalt Complex.](image)

The PS supported phosphine-cobalt complex was used as a catalyst in the oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds using tert-butyl hydroperoxide as the oxidant.

Ley and co-workers have used a polystrene immobilised tetra-n-propyl ammonium perruthenate (PS-TPAP) for oxidation of primary and secondary alcohols.
Hassanein and co workers have recently prepared some cobalt (II) phthalocyanintetrasulphonate supported on poly-N-alkyl-4-vinylpyridinium/montmorillonite intercalates for the oxidation of 2-mercaptoethanol

2.9.4 Significance and Survey of Polymer Anchored Schiff base Complexes

Among the macromolecular metal complexes, those of polymer anchored Schiff bases are important due to several reasons. They manifest novel structural features and have unusual magnetic properties. The metal chelates derived from low molecular weight Schiff bases were known for over 150 years. In addition to nitrogen, they possess at least one functional group. On complexation with a metal ion a five or six membered ring is formed.

Reddy and co-workers have prepared a series of polymer supported Schiff base cobalt complexes by the reaction of Co(II)-SALEN and other variations thereof with chelating resin containing vinyl pyridine. The polymer chelates were characterised by UV and IR spectra and cyclic voltametry. Sherly et al. have synthesised some polystyrene anchored Schiff base chelates. Multifunctional polystyrene resins bearing Schiff base functionality along with free amino or aldehyde groups were prepared and complexed with Cu(II), Ni(II), Co(II) and Fe(III).
By using chiral Schiff base ligands (Mn(III)-salen complexes) as catalysts and a mono oxygen source (e.g. iodosyl benzene, aqueous sodium hypochlorite, etc) as the oxidant, Jacobsen and co-workers, as well as Katsuki and co-workers have independently reported asymmetric epoxidation of unfunctionalised olefins with high enantiomeric excess\textsuperscript{217,218}.

Polymer supported Schiff base cobaltous palmitate was prepared and used as oxidation catalyst by Anil Kumar et al\textsuperscript{19}. Macroporous crosslinked beads of styrene-divinyl benzene copolymer have been prepared with Schiff base active sites on them. Cobalt palmitate was chelated with the PS supported Schiff base. The oxidation of cyclohexene was carried out using this catalyst with different promoters. Cyclohexane and cyclohexanol were obtained as products with the former in larger concentration.

A number of cases of catalysis by polymer immobilised Schiff base chelates in the decomposition of hydrogen peroxide were reported. Recently Gupta et al have prepared an N,N'-bis(3-allyl salicylidene) o-phenylene diamine cobalt(II) Schiff base chelate anchored onto polystyrene crosslinked with divinyl benzene\textsuperscript{220}. The catalytic activity of the polymer supported N,N'-BSPDA Cobalt(II) complex for the decomposition of hydrogen peroxide was evaluated under different experimental conditions and its catalytic activity was compared with unsupported analogue.
Maeda et al have described the preparation of some Oxovanadium(IV)-Schiff base complexes supported on a Merrifield resin and their use as catalyst in oxidation of methyl phenyl sulphide.\textsuperscript{221}

\textbf{2.9.5 Relevance of the Present Study}

Polymer supported metal complexes find wide application in different fields of science and technology. The most important application involves the recovery of rare metal ions from solution and the removal of heavy metal ions from effluents. Thus these metal sorbing ligands are widely used in hydrometallurgy and pollution control. The catalytic activity of polymer immobilised metal complex has attained considerable interest.

Thus there is further need to develop highly selective chelating ion exchangers with high capacity, favourable kinetics and reasonable mechanical strength and chemical stability. The research work in the area of macromolecular metal chelates has also to be focussed on developing and screening supported metal catalysts with increased activity and selectivity. The task of developing superior chelating ion exchangers and supported catalysts remains difficult but the results described in this review are encouraging for further research.

In view of the numerous applications of polymer supported metal complexes, we have undertaken a project for the synthesis and
characterisation of polymer supported Schiff base chelates. Polymer supported Schiff base ligands containing N and O as the donor atoms forms a special class. These types of ligands possess a high selectivity over a range of pH. Polymer supported Schiff base chelates find numerous applications in heterogeneous catalysis too. The unlimitedly expanding applications of polymer bound Schiff base complexes in the field of pollution control, analytical chemistry and heterogeneous catalysis and their novel structural features has prompted us to explore some of such possibilities. The results of the investigations carried out in this respect are presented in the subsequent chapters.