Polymer-Metal Complexes: A Retrospective Survey
The chemistry and technology of reactive functional polymers is an area which has achieved rapid progress in the recent past. The applications of these functionalised polymers depend largely on the characteristics of the specific active functional groups. The architectural characteristics of the macromolecule influence the behaviour of these functional groups. This interdependence of the polymer microstructure and reactivity of functional groups in functionalised polymers dictates the applications of such systems in a number of areas of functional and technological interest. Organic synthesis using functional polymers, design of polymeric reagents and polymeric catalysts, complexation and separation of metal ions using polymeric ligands, understanding of the specificity of biological reactions of naturally occurring macromolecules, biomimetic chemistry, enzyme immobilization, controlled release formulations, conductive polymers, polymeric surfactants, stabilizers and polymeric liquid crystals are some of the important fields wherein the chemistry of functionalised polymers bears relevance.

Chemical modification is used extensively to modify the properties of polymers for various applications. A functional polymer can be considered as a macromolecule on which reactive functions are attached. These macromolecules are often tailormade to perform specific functions and are sought for these properties rather than the physical properties of the polymers. Thus a functional polymer possesses the combination of the physical properties of the polymer support and the chemical reactivities of the attached functional group.
Polymer science has emerged as an active discipline of material sciences. This field impinges on areas of commodity, engineering and speciality polymers thereby stimulating interest all over the globe in exploiting newer domains. One such branch that has emerged is polymer-metal complexes comprising an organic polymer containing coordinate sites complexed with metals. This is of relatively recent origin and an interdisciplinary approach taking into its frontier areas like chemistry, metallurgy, environmental and material sciences.

A coordination compound may be defined as a compound containing a central atom or ion which are attached with molecules or ions whose number usually exceeds the number corresponding to the oxidation number or valency of the central atom or ion. The chemistry of coordination compounds is at present undergoing rapid development in diverse disciplines. The impetus for progress in this area has resulted from its many biological applications. A large number of metal proteins and other metal complexes of biological importance have been studied. Work on coordination complexes has revealed that heterogeneous systems possess more economical potentials and advantages over homogeneous systems. Polymer-metal complexes belong to the former case. The high molecular weight polymer-metal complexes work as storage houses for solar energy.

Polymer-metal complexes have been of interest to many researchers during the past three decades in the light of their potential applications in diversified fields like organic synthesis, waste water treatment, hydrometallurgy, polymer drug grafts, recovery of trace metal ions,
environmental protection,\textsuperscript{20} and nuclear chemistry.\textsuperscript{21} Besides, they are also used as enzyme models\textsuperscript{22,23} and catalysts.\textsuperscript{24,26}

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

This chapter is a retrospective survey of polymer-metal complexes which throws light upon various areas like synthesis, classification and applications of polymer-metal complexes with special emphasis on their catalytic activity.

\section{2.1 Polymer-metal Complexes: Synthesis and Classification}

Recently there has been growing attention to the molecular function of macromolecular complexes as a new frontier in material systems. A typical example of macromolecular metal complex is illustrated in Figure 2.1. Their synthesis represents an attempt to give inorganic function to an organic polymer.
In macromolecular complexes, physicochemical properties and chemical reactivities of the complex moieties are often strongly affected by interactions with the surrounding polymer matrix. These interactions are weak but significant and act cumulatively and dynamically. They not only construct the macromolecular complexes themselves, but also control their higher-order structure based on a dynamic conjugation between the complex moieties and the polymer matrices. Thus a weak and soft profile in the coordination reactions, a cooperative interactions between the complex moieties and a multiplied or enhanced interactions are observed as characteristic features of the macromolecular complexes.
Polymer-metal complex is formed by the interaction of a polymer containing coordinating groups with metal ions. The polymeric ligand can be obtained by the polymerisation of monomer containing coordinating sites or by the reaction between a polymer and a low molecular weight compound having coordinating ability. The general methods for incorporating active functional groups are classified into four different groups: (i) direct polymerisation or copolymerisation of monomers containing the desired functional groups, (ii) chemical modification of preformed polymer; (iii) functional monomer inhibition into or grafting onto the preformed polymer, followed by polymerisation, and (iv) immobilisation of hydrophobic chelating extractants during polymerisation or post-polymerisation.

### 2.1.1 Pendant complexes

In pendant complexes the metal ion is attached to the ligand function which is appended on the polymer chain. Based on the chelating abilities it is classified as monodentate or polydentate polymer-metal complexes.

**(a) Monodentate pendant complexes**

A monodentate pendant polymer-metal complex is formed when a metal ion or a stable metal complex in which central metal ion is already masked with low molecular weight ligands except for one coordinating site that remains vacant is coordinated to a polymer ligand. Such complexes have a simple structure of the monodentate type as shown in **Scheme 2.1**. Even if the metal ion
or the metal complex has more than two labile ligands it is often possible to form a monodentate complex by selecting appropriate reaction conditions.

\[
\begin{align*}
\text{Scheme 2.1. Monodentate pendant polymer-metal complexes}
\end{align*}
\]

An example of the formation of a pendant monodentate complex is the complexation of cis-{Co(en)$_2$X$_2$}X with poly (4-vinyl pyridine) (1).$^{27}$

\[
\begin{align*}
X = \text{Cl, Br, N}_3 \\
\text{en} = \text{ethylenediamine}
\end{align*}
\]
(b) Polydentate pendant complexes

Polydentate ligands often result in the formation of stable metal complexes with bridged structures. Most of the chelating resins come under this category. Pendant polymer-metal complexes are characterised by their relatively well-defined coordination structure. Structure of the polydentate pendant metal complexes is given in Scheme 2.2.

![Scheme 2.2. Polydentate pendant polymer-metal complexes](image)

2.1.2 Intra and inter-molecularly bridged complexes

In the case of the complexation of a polymeric ligand with a metal ion, which has four or six coordinating bonding hands, the polymer-metal complex formed may be of the intra-polymer chelate type or inter-polymer chelate type (Scheme 2.3).
Scheme 2.3. (a) Intra-polymer-metal complex; (b) Inter-polymer-metal complex

The coordination structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between the intra and inter-molecular bridging. Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer-metal complex is sometimes soluble, while inter-polymer-metal complex results precipitation of the linear polymer-metal complexes. A typical example of this type of polymer-metal complex is the poly(vinyl alcohol)-Cu(II) complex (2).
2.1.3 Polymerisation of coordinated monomers

Metal complexes of low molecular weight monomers are polymerised to give polymer-metal complexes. There are three basic polymerisation techniques for the preparation of polymer-metal complexes from the corresponding monomer complexes.

(a) Polymerisation of vinyl compounds containing metal complexes

The vinyl monomers which can be polymerised are limited and the polymerisation depends on the electrostatic interaction between the coordinated monomers and the growing radical. This type of polymer-metal complex is characterised by a clear coordination structure. The polymerisation occurs by the radical or ionic initiation to form a polymer of high molecular weight as depicted in Scheme 2.4

![Scheme 2.4. Polymerisation of coordinated vinyl monomers](image)
Some transition metal salts and model complexes act as inhibitors in the polymerisation of vinyl monomers. Thus the polymerisation of 4-vinyl pyridine is strongly inhibited in the presence of Cu(II) or Fe(III).\textsuperscript{29} But Zn(II), Co(II) or Cu(I)-4-vinyl pyridine complexes can be polymerised to form the corresponding poly(4-vinyl pyridine)-metal complexes.\textsuperscript{30} Methacrylate coordinated with ammine-Co(III) complexes to form methacrylato-pentammine-Co(III) perchlorate (3) and cis-dimethacrylatotetramine-Co(III) perchlorate (4).

(b) \textbf{Polycondensation of metal complexes containing free functional groups}

The preparation of polymer-metal complex by condensation is reported by Hartwell and Baier\textsuperscript{31} (Scheme 2.5). Polyesters and polyamides have been synthesised by interfacial polycondensation with aryl acid chlorides.
(c) **Ring opening polymerisation**

The polymer-metal complexes obtained by polycondensation and ring-opening polymerisation are considered as coordination polymers since the polymer chain is composed of coordinate bonds. This involves the polymerisation of a metal complex containing a strained ring which is capable of ring-opening polymerisation as shown in **Scheme 2.6**. An example of this type of polymer-metal complex formation is the polymerisation of beryllium complex of bis-β-carbonyl compound\textsuperscript{32} (**Scheme 2.7**).

![Scheme 2.6. Ring-opening polymerisation of low molecular weight metal complexes](image)

![Scheme 2.7. Ring-opening polymerisation of Beryllium complex of bis-β-carbonyl compound](image)
2.1.4 Polymers formed by the reaction of peripheral functional groups in metal complexes with polymers

This type of polymer-metal complex is formed by the chemical reaction of neutral or functional polymers with peripheral functional groups of metal complexes as shown in Scheme 2.8. These polymer-metal complexes have definite coordination structures. DVB-crosslinked polystyrene and its modified forms and silica are widely used as the insoluble polymer systems. Some examples are given in Scheme 2.9.

![Scheme 2.8. Formation of polymer-metal complex by polymer analogous reactions](image)

![Scheme 2.9. Formation of polystyrene- and silica-supported polymer-metal complexes by polymer analogous reactions](image)
The immobilisation of metal-porphyrin into a polymer-matrix has been achieved by the reaction of peripheral functional groups in the metal-porphyrins with reactive polymers and they have been used as enzyme models.\textsuperscript{34}

### 2.1.5 Coordination polymers

In coordinate polymers, the polymer chain is composed of coordinate bonds and the ligand is the bridging unit as shown in Scheme 2.10. Multidentate ligands capable of forming, this type of coordination polymers are classified into: (i) linear coordinated polymers, and (ii) network coordinated polymers.

\textbf{Scheme 2.10.} Formation of coordination polymers by bridging of ligands by metal ions

(i) **Linear coordinated polymers**

Linear coordinated polymers can be prepared by two methods, from bifunctional ligands and from simple compound or ion as ligands.

(a) **Bifunctional ligands**

Here the polymer chain is composed of bifunctional ligands and metal ions. A typical example for the coordination complex formed between a bifunctional ligand and metal ion is the complex between dithiooxamide and metal ions\textsuperscript{15} (Scheme 2.11).
(b) Simple compound or ion as ligands

A simple compound or ion can function as a bridging ligand giving rise to a polymeric structure. Cupric chloride forms an associated structure in which the chloride occupying as bridging ligands on both the axial and equatorial coordination sites of Cu (II) (5).\textsuperscript{36}

(ii) Network-coordinated polymers

This type of polymer-metal complex is formed by a ‘template reaction’ between two functional groups of the ligands induced by their coordination to metal ion resulting in a chelate type metal complex as depicted in Scheme 2.12.
Poly(metal phthalocyanine)(6) is an example for this type of network-coordinated polymers. It is formed by the reaction of tetracyanobenzene with metal halides catalyzed by urea (Scheme 2.13).

Scheme 2.12 Schematic representation of the formation of network-coordinated polymers

Scheme 2.13 Formation of network-coordinated polymer-metal complex of tetracyanobenzene
2.2 Applications of Polymer-metal Complexes

2.2.1 Natural chelating polymers

A vitally important application of the chelating polymers is the great influence of natural chelate forming polymers on the transport and function of metal ions in the environment. The humic acids and various other polymers in the soil and natural water provide a slow reacting source and sink for many multivalent ions.

2.2.2 Ion selectivity

The main application of the chelating polymers is based on the high selectivity of the materials for particular ions. There are many mixing or pollution situations in which the precious or toxic ion is a small part of a mixture of many other ions, and if this ion can be recovered specifically, the energy and material requirements of the process can be reduced dramatically. One potentially important example of this technology is in the use of new membrane cells for the electrolysis of brine. The cells use perfluoro sulfonic and perfluoro carboxylic acid ion-selective membrane to separate the two halves of the electrolysis cell. Chelation effects in these membranes strongly hold multivalent ions in the membrane and block the passage of the commercially important monovalent ions. Iminodiacetic acid chelate resins are often used to purify brine before electrolysis to overcome this problem.

A series of new copper-selective amino pyridine Dowex resins were designed for large-scale hydrometallurgical separation of copper from its ores.
Another possible large scale application of chelating resins is in the selective removal of precious metals from sea water. Research projects in a number of uranium deficient countries, eg., Germany, Japan, Russia and U.K. are investigating the recovery of uranium from sea water using chelating resins. These include materials such as amidoximes, poly(hydroxamic acid)s and various other experimental resins. Selective removal of gold from seawater, although the subject of a number of patents, is equally far from reality. However, the use of chelating resins to remove gold from mining solutions of cyanide or chloride salts, and also waste solutions from precious metal manufacturing is more important. Activated carbon or various commercial anion-exchange resins are now used to recover gold from such solutions, but they are very unselective and recover a mixture of metals. Very selective chelating resins with isothiouronium structures are available and can be used to separate the anionic gold complex ions from other non precious metal ions. These resins are the Srafion and Monivex resins.

Commercial chelating resins have mainly been used in analytical applications, especially in the preconcentration of trace elements from solutions so dilute that no analytical determinations are possible. For example, the retention of traces (0.5-4 ppb) of Zn, Cd, Pb and Cu extracted from sea water on a Chelex 100 resin has been studied. The same resin and method were used for the preconcentration of Cu, Zn and Pb from urine. Comprehensive lists of recent analytical reports on chelating resins used in interesting and important ways of concentrate selection and analysis of metal ions in practical situations are available.
Another promising application for chelating resins is in nuclear-medicine applications where very short lived isotopes must be removed quickly and selectively from mother and daughter ions. A recent example is the use of pyrogallol-formaldehyde polymer made for the separation of $^{68}$Ga and $^{68}$Ge ions.\textsuperscript{47}

Chelating polymers have many potential applications for the selective removal and recovery of metal ions from industrial waste solutions.\textsuperscript{48} The selective removal of mercury, using resins with thiol groups is one such application\textsuperscript{49}. Many chelating polymers have been fabricated on a small scale into different forms like membranes and hollow fibres, other than ion-exchange resin in attempts to get more convenient materials for the selective separation of ions in special applications.\textsuperscript{50} H Kasgoz et al. prepared polyacrylamide hydrogels and studied their application in removal of Cu(II) ion.\textsuperscript{51}

2.2.3 Catalytic activity

Catalysts are substances that increase the rate of a reaction without modifying the overall standard free energy change of the reaction. Catalysts function by providing an alternative pathway having a lower energy of activation than the uncatalysed or spontaneous reaction. Consider the spontaneous reaction,

\[
\text{Substrate or reactant } \rightarrow \text{ Product} \\
(S) \rightarrow (P)
\]

In the presence of catalyst (C) the reaction may be schematically represented as

\[
C + S \rightarrow CS \\
CS \rightarrow P + C
\]
Both the elementary reactions will be faster than the spontaneous reaction with respect to the catalyst, the process being cyclic, one can represent the reaction scheme in the form of a catalytic loop or cycle.

Reactions may be catalyzed homogeneously or heterogeneously. In homogeneous catalysis, the catalyst and the reactants are in the same phase whereas in heterogeneous catalysis, these are in different phases. The homogeneous catalysts often have higher substrate selectivity and better reproducibility in the catalysed reaction when compared to heterogeneous catalysts, which are more widely used in industry. Even with these advantages, homogeneous catalysts have not been preferred because their recovery from the reaction mixture is difficult and results in a considerable loss of the catalyst. Heterogeneous catalysts have very good thermal stability and can be easily separated from the reaction mixture. However less drastic conditions are required in the case of homogeneous catalyst.

This problem has been circumvented by an intermediate system that involves the preparation of a homogeneous catalyst in a heterogeneous form. This is achieved by binding the homogeneous catalyst to inorganic carrier materials or organic polymers. Thus when a homogeneous catalyst such as transition metal complex, transition metal or an enzyme is covalently bound or strongly absorbed on a polymer matrix we have a polymer-supported catalyst.
Insoluble supports are preferred because the main purpose of supporting a catalyst is to be able to recover and recycle it with ease.

It is convenient to classify homogeneously catalysed reactions on the basis of the catalytic species involved. Thus we have (1) acid-base catalysis, (2) catalysis by transition metal ions and their complexes, and (3) enzyme catalysis. The present investigation is concerned with catalysis by transition metal ions.

The polymer bound transition metal catalysts have the following advantages:

(i) Homogeneous catalytic activity is retained by transition metal ion on binding to the resin.

(ii) The economy and convenience of heterogeneous catalyst is attained.

(iii) The steric environment of the catalyst is altered and substrate selectivity is increased.

(iv) Polymer bound catalysts can be employed under conditions comparable to those of conventional homogeneous catalysts, i.e. at temperatures below 100°C and at ambient pressure. These catalysts are best considered as “heterogenised-homogeneous” (He-Ho) catalysts.¹

2.2.3.1. Basis of catalytic action

The catalyst-substrate interaction can be considered as some sort of activation of the substrate molecule so as to enable it to react faster. This activation pertains to the electron pairs of a particular bond (X:Y) in the substrate molecule. A catalyst (C) can decrease the electron density in the bonding molecular orbital of X-Y or increase the electron density in the
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antibonding molecular orbital of X-Y. In either case, the bond X-Y is weakened as a result of the catalyst-substrate interaction and thus the reaction requires a lower activation energy. Thus a catalyst functions by lowering the activation energy of the chemical reaction. In order to effect reactions under production conditions, it is necessary for the activation energy (E) to be, as a rule, less than 170 kJ mol\(^{-1}\) of the basic substance. If some products have to be produced profitably, E should be reduced to 40 kJ mol\(^{-1}\). At the same time, some reactions which are important to the national economy occur homogeneously (uncatalysed) only when the activation energy is greater than 200 kJ mol\(^{-1}\). Such reactions include the oxidation of SO\(_2\) and NH\(_3\) to produce H\(_2\)SO\(_4\) and HNO\(_3\) respectively.

For the oxidation of SO\(_2\), the activation energy decreases from 280 kJ mol\(^{-1}\) to 90 kJ mol\(^{-1}\) on a vanadium catalyst and to 70 kJ on a platinum catalyst. When ammonia is oxidised on a platinum catalyst, activation energy is around 34 kJ.

For enzyme catalysed reactions, the activation energy is as a rule, around 30-50 kJ mol\(^{-1}\). When the activation energy diminishes, the reaction order simultaneously decreased. For e.g., the reaction 2SO\(_2\) + O\(_2\) → 2SO\(_3\) is of third order (n = 3) under uncatalysed conditions. Under standard production conditions on a low activity iron oxide catalyst (E = 120-160 kJ mol\(^{-1}\)) n = 2.5; on a more active vanadium catalyst n = 1.8 and on the most active platinum catalyst, the reaction order decreases to n = 1. The reaction order decreases because, in the presence of a catalyst, the reaction proceeds through several elementary stages, whose order may be smaller than that of uncatalysed reactions. From the point view of catalysis, the availability of vacant d-orbitals for \(\sigma\)-bonding and non-bonding orbital for \(\pi\)-bonding, appear to be important. Besides, the ability to
assume a variety of oxidation states and different coordination numbers are also important. The catalysts are believed to ‘activate’ the substrate molecules by enabling them to coordinate to the central metal ion. In order to function as a catalyst, a complex must have vacant coordination site. This coordinative unsaturation can usually be brought about by dissociation of the complex.

**Other modes of activation**

Other modes of activation are oxidative addition, reductive elimination and ligand migration (insertion). Mechanistic schemes proposed for reactions catalysed by transition metal ions involve one or more of these processes. These lead to the formation of intermediates and according to Tolman diamagnetic organometallic or analogous complexes with 16 or 18 electrons around the central metal atom have increased stability and are likely to be the intermediates (16 or 18 electron rule).

(i) **Oxidative addition and reductive elimination**

The term oxidative-addition is used to designate the addition of a molecule XY to transition metal complex in such a way that both the formal oxidation state and the coordination number increase by two units. The reverse reaction in which there is a decrease in both oxidation state and coordination number is called reductive elimination.

\[
\text{L}_4 M^{n+} + XY \rightarrow \text{L}_4 M^{(n+2)+} XY
\]

(d^8) \hspace{2cm} (d^6)

No. of valence electrons (NVE) \(8+8+16\) \hspace{1cm} \(6+12 = 18\)

eg. \(\text{Ir}^1 \text{Cl(CO)}(\text{PPh}_3)_2 + \text{H}_2 \rightarrow \text{Ir}^{111} (\text{H}) (\text{H}) (\text{CO}) (\text{PPh}_3)_2 \text{Cl.}\)
Example for reductive elimination:

\[ \text{Rh}^{111} \text{ClH} (R) (\text{PPh}_3)_3 \rightarrow \text{Rh}^I \text{Cl} (\text{PPh}_3)_3 + \text{RH} \]

(ii) Insertion reaction

The 1° 2 addition of a M-H or M-C (M = transition metal) bonds to unsaturated compounds like olefins can be looked upon as the "insertion" of the olefin in the M-H or M-C bond.

\[ L_n \text{M-H} + \text{X=Y} \rightarrow L_n \text{M-X-Y-H} \]

The insertion reaction in the case of an olefin can be represented as

Insertions are generally concerted processes involving a more or less cyclic transition state involving simultaneous bond breaking and bond making. It should be noticed that the same result can be obtained by the ligand R migrating to the secondary carbon. Hence the term ligand migration is preferably used.

2.2.3.2 Macromolecular effects on catalytic activities of polymer-metal complexes

a) Porosity and surface area

During the past few decades, heterogeneous catalytic processes have been developed to such an extent that they constitute the main process routes to the
bulk of the output of the chemical industry. The pore-size and surface area of the polymers varied with the nature and degree of crosslinking agent. Optimum crosslinked polymeric ligands should have large surface area and average pore-radius. A high porosity allows good flow of solvent and substrate particles into the interior of the polymer matrix and does not hinder the penetration of substrate leading to high activity of polymeric catalyst. Considerable insight has been obtained on the chemical characteristics of catalytically active species and it has been well correlated that the reaction rate increases with the exposed area of the catalytic species. In order to obtain reasonable reaction rates, such area has to be increased to an adequate level per unit volume and this is possible only by making the catalyst highly porous and spreading the active species over the entire surface which would be largely in the interior of the catalyst. Thus the internal areas are accessible to the reactants by diffusion only.

In the case of catalytic reaction taking place in the interior surfaces of a porous catalyst, frequently, gradients in reactant concentration and temperature may be present inside the catalyst making the interpretation of experimental or operational data difficult. The development of a catalyst formulation should therefore take into account not only by the chemical nature and dispersion of the active species but the design of the catalyst should also consider factors such as the average pore-size, the variation in pore-size and adequate mechanical strength.

The characteristics of the pore structure also influence greatly the response of catalysts to poisons. In general, poisons are chemical constituents which are very strongly absorbed by the active catalytic surface. Certain catalytic
transformations are associated with consecutive reactions or side reactions and a catalyst with high selectivity is essential to minimise undesired products. In the hydrogenation of butadiene to butane, and the oxidation of o-xylene to anhydride, further degradative reactions can occur on the primary product, which is the desired one. However, the diffusion limitation during regeneration can be minimised by having macro-micro combinations of pore-sizes. Such a catalyst will have a network of larger sized pores which have a lower active surface but facilitate rapid diffusion of the gas inside catalytic part as well as a network of smaller sized pores of much shorter dimensions which incorporate the bulk of the active catalytic species.

b) Nature of polymer support and extent of crosslinking

The performance of a catalyst is influenced by the chemical and physical properties of the polymer support. Heterogenation of homogeneous catalysts by attaching them to polymers leads to improved stability and selectivity since the catalysts produced combine the advantages of the heterogeneous and homogeneous catalysts. A crosslinked polymeric ligand often forms a stable metal complex than a linear polymer and it shows a definite selectivity for metal ions due to its characteristic structure.

The complexation behaviour of ligand function supported on polymer is generally different from the corresponding low molecular weight analogue. This variation is dependent on the polymer matrix to which the ligand function is attached. Complexing groups in a macromolecular ligand may adopt conformation different from that required by the preferred stereochemistry of a
given metal ion. Functional groups are strategically distributed over a macromolecule so that both the more favourable and the less favourable conformation will occur. The characteristic factors like matrix structure, matrix configuration, matrix nature, spacer between the crosslinked matrix and the ligand function and extent of crosslinking has a significant effect on complexation. S. Varghese et al studied the role of hydrophobicity on the structure of polymer-metal complexes. The amount of metal complexed and the structure of the metal complex were influenced by the length of the pendant chain i.e., hydrophobicity. The complexation characteristics of insoluble macromolecules are strongly influenced by the nature and extent of crosslinking in the polymer ligand. A high degree of crosslinking results in a low degree of metal ion intake and a lower stability of the resulting metal complex by making the polymer chain more rigid. In the case of poly(4-vinyl pyridine)-Cu complexes with increasing divinyl benzene content, conversion of planar coordination centres to tetrahedral ones occurs. The change in stereostructure results from an increase in steric hindrance to complex formation with a polymeric ligand.

c) Spacer effects

The complexing ability of macromolecular ligand depends upon the arrangement of functional groups relative to the main chain. The shorter the distance between them, the lower the efficiency of complex formation because of steric hindrance. By introducing a spacer to polymer matrix the less reactive functional groups can make more reactive resulting in high catalytic activity.
Functional groups directly attached to the backbone chain of high polymers are often less reactive than if these groups were not attached to a polymer. This reduced reactivity is caused by steric hindrance or by the fact that all or part of the polymer chains interferes with the reactivity of the individual functional group. It has been observed that the reactivity of the functional groups could be considerably increased if the active site is effectively separated from the macromolecular matrix. Cases of increased reactivity are reported where the functional groups are separated from the polymer backbone by a flexible spacer arm. Spacer groups could be designed to be flexible or stiff, a most important capability to design macromolecular architecture by modern polymer synthesis. The commonly used spacers are hexamethylene diamine, polyethylene glycol and α, ω-dibromoalkane. DVB-crosslinked polystyrene-supported analogue of t-butyl hypochlorite containing a trimethylene spacer between the polymer matrix and the t-butyl function oxidises alcohols to carbonyl compounds in higher yields. The oxidising efficiency of this reagent was found to be significantly greater than those of the reagents containing only one spacer and no spacer between the reagent function and the polymer support. If the functional groups initially present in the polymer are not sufficiently isolated, the spacers may become doubly coupled with the polymer and is effectively lost. Such reactions have been used to study site isolation.

d) Swelling and solvation of the macromolecular matrix

Resin swellability in a given solvent is a multifaceted property reflecting the chemical structure of the polymer backbone, degree of crosslinking and the
architecture of the polymer matrix. The extent of swelling decreases markedly as the percentage of crosslinking increases. The dependence of swellability in crosslink density is understood in terms of interchain linkages formed during the matrix formation. The higher the frequency of bridges between the chains, the smaller the conformation freedom of the chain segments in the matrix and thus the swellability of the resin reduced in any given solvent. Some other factors, which complicate the swelling characteristics in crosslinked matrices are the efficiency of crosslink formation, chain entanglement, the length of the polymer chains and the presence of interchain aromatic interactions. Another factor which depends on the swelling parameter is the nature and proportion of the monomer to diluent ratio used during its matrix formation. The higher the percentage of the monomer diluent, the larger the bulk expanded volume of the resin, but different diluent affect polymer swelling to different extent.

One more practically important aspect of resin swellability is the chemical structure of the polymer backbone, which control the pattern of polymer-solvent compatibility i.e. the relative measure of polymer swelling in different solvents. Several reports in the literature were confirmed such aspect of structure property relationship by swellability data.

Microporous, low crosslinked, gel type supports are the most popular and overwhelmingly used support for polymeric reagents and catalysts. The gel supports swell in the reaction solvents in order to build up and expand their polymeric network. The reactive groups are located along the polymeric strains that form the network. The swelling processes expose these reactive sites and makes them accessible to the reactants. Another practically important aspect of
resin swellability is the pattern of polymer-solvent compatibility i.e., the relative measure of polymer swelling in different solvents. Polymer-solvent compatibility is determined by the chemical structure of the polymer backbone.

2.2.3.3 Types of reactions catalysed by polymer-anchored catalysts

a) Oxidative reactions

Oxidative reactions of organic compounds with molecular oxygen take place with high efficiency and selectivity in the presence of Werner-type metal complexes used as catalysts.

Metal complexes catalyse oxidation of compounds having mobile hydrogens, such as ascorbic acid, hydroquinone, phenols and amines, in the presence of molecular oxygen. In this reaction a substrate coordinates to the metal catalyst, and then the substrate is one electron oxidized by the metal ion with higher valency

\[ 2AH_2 + O_2 \rightarrow \text{M}^+ \rightarrow 2A + 2H_2O \]

The first example of catalysis by a polymer-metal complex was reported by Lautsch et al.\(^{40}\)

Polymer-metal complexes often exhibit high catalytic efficiency in the decomposition of \(H_2O_2\), poly(\(\beta\)-diketone)--Cu(II),\(^{61}\) poly(acetylhydroxamic acid)--Cu(II),\(^{62}\) various poly(\(\alpha\)-amino acid)--Cu(II),\(^{63}\) and poly(4-vinylpyridine)--Co(II).\(^{64}\) Hojo et al. employed Cu(II) poly(vinylalcohol)\(^{65}\) as the catalyst for the decomposition of \(H_2O_2\) and reported that the relation between the initial rate and
initial concentration of $\text{H}_2\text{O}_2$ varied in accordance with the rate expression of Michaelis-Menten type.

Lei and Wang reported the selective oxidation of ethylbenzene, $n$-propylbenzene and $n$-butyl benzene catalysed by organic polymer-supported Ru(II) complexes under oxygen or air in the absence of solvent in heterogeneous phase. The reaction afforded the corresponding ketone and alcohol in good yield. The catalytic selectivity of total ketone and alcohol ranged from 98 to 100% with the different ruthenium polymer-bound 2,2'-bipyridine complexes.

Kaliyappan and Kannan synthesized the poly (2-hydroxy-4-acryloyloxy benzaldehyde)-Cu(II)/Ni(II) complexes and used as the catalyst for the oxidation of cyclohexanol to cyclohexanone with higher conversion. Polymer-metal complexes of glycine function supported on NNMBA-crosslinked polyacrylamides were prepared and their catalytic activity in the decomposition of $\text{H}_2\text{O}_2$ was studied. The extent of catalysis varies with the degree of NNMBA crosslinking.

b) Hydrogenation reactions

A very high catalytic activity was observed for the hydrogenation of olefins catalysed by poly(acrylic acid)-Rh(II) complexes in homogenous solution. The catalyst effected preferential reduction of the olefinic bond in case of substrates having additional functional groups such as diallylether, allylaldehyde and cyclohexene-1-one. In addition greater substrate selectivity and sensitivity to the size of the alkene was also observed in the above reduction.
Grubbs and Kroll reported the rate of hydrogenation of olefins with a polymer-supported Rh(I) catalyst. The rate was 6.25 times greater for cyclohexene than that for cyclooctene. The substrate selectivity was attributed to the restriction of the substrate entering the pores of the ligand beads and indicated that the reaction mainly takes place inside the resin particles.

Card et al. reported poly(styryl)bipyridine Pd(II) acetate to be useful catalyst for the hydrogenation of alkenes and alkynes. More substituted or sterically bulky groups got reduced rapidly than the less hindered olefins. In the case of alkynes, preferential reduction to alkenes in good yield without isomerization was achieved by stopping the reaction after the consumption of one equivalent of hydrogen.

Nayak et al. prepared a polymer-supported Pd(II) species by means of an oxidative addition reaction between Pd(PPh₃)₄ and chloromethylated crosslinked polystyrene and employed it for the reduction of alkenes and alkynes under mild conditions. The high recycling efficiency of the catalyst and solvent effects on the reaction rates were also investigated.

Bis-benzonitrile dichloropalladium(II) was supported on two copolymers containing carboxyl and bipyridyl groups and employed as catalyst for hydrogenation of olefins under mild conditions. The coordination environment and the nature of the metal species on the polymer were studied. Based on environmental evidence it was proposed that polymer-palladium complexes initially contain palladium ions with chloride ion bridges, which are cleaved in activation. The catalyst was found to be active towards the hydrogenation of olefins under ambient conditions. The kinetic and mechanistic aspects of the
hydrogenation of styrene and acrylonitrile and the recycling capacity data have been reported.

Palladium acetate anchored on to a copolymer support containing carboxyl and pyridyl groups was found to be highly selective for the hydrogenation of dienes and alkynes. In the case of disubstituted alkynes, cis-alkynes were formed predominantly. The loss of metal due to leaching was very small under the conditions employed. M.H. Liu and W.Y. Yu prepared and characterised polymer stabilized ruthenium-platinum and ruthenium-palladium bimetallic colloids and studied their catalytic properties for hydrogenation of o-chloro nitrobenzene.

c) Hydroformylation

Polymer-supported catalysts have been used for hydroformylation reactions, the reaction sequence involving addition of an aldehyde group to the terminal or the internal carbon atom of an alkene. The ratio of the two aldehydes formed was dependent on the catalyst used. For example in the case of the two homogeneous catalysts, Rh(acac)(CO)$_2$ and Rh(acac)(CO)PPh$_3$, the ratios of normal to branched chain aldehydes were found to be 1.2:1 and 2.9:1 respectively.

\[
\begin{align*}
R\text{-CH}=CH_2 + CO + H_2 &\rightarrow R\text{-CH}_2\text{-CH}_2\text{-CHO} \\
R\text{-CH}=CH_2 + CO + H_2 &\rightarrow R\text{-CH-CH}_3 \\
\end{align*}
\]

or

\[
\begin{align*}
R\text{-CH}=CH_2 + CO + H_2 &\rightarrow R\text{-CH-CH}_3 \\
\end{align*}
\]
When these catalysts were bound to the polymer matrix, the ratio further changed. Thus, when Rh(acac)(CO)$_2$ was equilibrated with a phosphenated polymer (CO)$_2$ poly(styrene), poly(vinylchloride) or silica, normal and branched aldehydes were formed in the ratio of 2:2.5:1. The increase in the ratio was an indication of displacement of C=O by a polymeric phosphine ligand. Changing the amount of cis-trans-bound catalyst also influenced the ratio of normal to branched product.

van Dyke et al. reported Rh(I) phosphine complexes attached to the poly (methylsiloxanes) catalyst which were active in the hydroformylation of 1-hexene to heptaldehyde or isoheptaldehyde. Extensive degradation of the catalyst occurred during the reaction.

Polymer-supported chiral phosphine-containing catalysts for the preparation of chiral products, especially by hydroformylation was reported. By exchanging a transition metal onto the crosslinked polymer support, a catalyst was obtained giving chiral products in high enantiomeric excess.

Pan et al. synthesized polystyrene and polystyrene-divinylbenzene containing up to 32% divinylbenzene and PtO$_2$ was exchanged onto the polymer supports. Hydroformylation reactions of $\alpha$-olefins were investigated in the presence of SnCl$_2$. This polymeric catalyst displayed high selectivity to the linear aldehyde (95%) and high activity.

Polyaluminazanes, polytitanozenes and polystanazanes and their complexes with Rh or with Co-Ru were prepared and used for the hydroformylation of 1-heptene. All of the Ru-complexes could not tolerate
higher reaction temperature, when higher selectivity is wanted, except for the polyaluminazane-Rh complex. But the Co and Ru bimetallic complex of polyaluminazane could catalyse the hydroformylation of 1-heptene at a higher temperature without any decrease in the catalytic activity and with a selectivity of ~70% for the branched aldehyde.

d) Hydrosilylation

Capaka et al. reported that the polymer-supported Rh and Pt complexes catalyse the hydrosilylation reaction. The rate of hydrosilylation reaction decreased as the electron withdrawing substituent groups was substituted in the alkene molecule. Although hydrosilylation with triethoxysilane proceeded uniformly with all supported catalysts, complexes that were good catalysts for hydrosilylation with Et₃SiH were poor catalysts for the reaction with Cl₃SiH and vice versa. The reaction conditions for hydrosilylation using a polymeric catalyst were mild and comparable to those with homogeneous catalysts such as chloroplatinic acid.

Kinetic and catalytic studies were carried out to evaluate the role of polymeric organosilicon support of rhodium phosphine catalysts for hydrosilylation of C=C bonds. All kinetic data showed that modification of Wilkinson’s complex by polysiloxyalkylphosphine (insoluble) and silylalkylphosphine (soluble) ligand essentially had no effect on the kinetic parameters and mechanism of the hydrosilylation of 1-hexene.
Heterogenous poly(9-10-anthralenevinylene)-Pt complex was prepared.\textsuperscript{83} Hydrosilylation of CH$_2$=CHCH$_2$OPh with (EtO)$_2$SiH in the presence of the catalyst gave 81\% PhO(CH$_2$)$_3$Si(OEt)$_3$.

Michalska and Ostazewski synthesized a series of polyamides\textsuperscript{84} having different numbers of methylene groups in their repeating units by interfacial polycondensation of terephthaloyl chloride with piperazine and aliphatic diamines, H$_2$N(CH$_2$)$_n$NH$_2$ (n = 2, 6, 10). The materials, with high thermal stability, were used for the immobilization of Rh and Pt complexes. The bound catalysts exhibited high activity in hydrosilylation of 1-hexane. The activities of the Rh complexes were dependent on the structure of the polyamide support, decreasing with increasing distance between the amide groups and closely paralleled the changes in the degree of crystallinity of the polymers. Repeated use of the polymers bearing Rh complexes showed the bond between the metal and polyamide to be fairly stable.

Xiao \textit{et al.} prepared a silica-supported poly(ω-diphenylphosphino undecylsiloxane)platinum complex.\textsuperscript{85} The addition of trimethoxysilane to 1-hexene in the presence of the complex catalyst yielded 80-90\% of hexyltrimethoxysilane. Measurement of the rates of the reaction with various substrates indicated the following order: hexene > styrene > dodecene > allylglycidyl ether. Platinum complex could be easily recovered by filtration after the reaction and repeatedly used with same activity.
c) **Polymerisation initiation**

Tsuchida and Nishide used Cu/Mn poly(4-vinylpyridine) complexes as initiator for the preparation of phenolic polymers. The rate of the reaction, yield and molecular weight of the polymer were high. The polymerization of \( N \)-vinylpyrrolidone initiated by poly(2-hydroxy-4-methacryloyloxybenzaldehyde) Cu(II)/Ni(II) complexes are reported.

Tetrahydrofuran was polymerized in the presence of sebacoyl chloride and AgClO\(_4\), terminated with primary amine, treated with sodium naphthalene and used to initiate the copolymerization of methyl methacrylate, styrene and acrylonitrile. A thermoplastic elastomeric methyl methacrylate-tetrahydrofuran block copolymer was prepared which had tensile strength 157 kgc^{-2}.  

Anionic polymerization of acrylamide was initiated with poly(ethyleneoxide)-di-sodium salt in several solvents at various temperatures. The Michael type addition of alkoxide anion of the poly(ethyleneoxide)-di-sodium salt to acrylamide proceeded exclusively via a H-transfer mechanism. The polymerization at a relatively low temperature in a polar solvent resulted in the formation of long and short chain branchings at nitrogen atmosphere in the amide group. On polymerization at a higher temperature in a non-polar solvent, the branching structure was greatly reduced and almost linear poly(\( \beta \)-alanine) was obtained. Natural products such as cellulose and soluble starch were found to initiate the polymerisation of MMA in aqueous solution in presence of Cu(II) ions, probably through the complex formation of Cu(II) with the natural polymer.
Water soluble poly(vinylphosphate)–Cu(II) complex\(^92\) was active as a free radical initiator for the polymerization of styrene in the presence of carbon tetrachloride. The maximum conversion was observed at neutral pH.

Acrylic acid-styrene copolymer-supported Nd showed high catalytic activity and stereospecificity for butadiene polymerization. The cis-1,4 content of poly(butadiene) was 98.7%. The system was also used for isoprene polymerization to give poly(isoprene) with 95% cis-1,4 content.\(^93,37\)

f) Hydrolysis

The catalytic hydrolysis of oligophosphates by poly(L-lysine)–Cu(II) complexes has been reported. The PLL–Cu(II) complex showed strong catalytic activity and attacked pentaphosphate exclusively thus producing orthophosphate as the main product. This result was explained by the chelate structure of PLL–Cu(II).\(^94\)

Kaliyappan et al. reported the good catalytic hydrolysis of ethyl acetate by poly(2-hydroxy-4-(meth)acryloyloxy) benzophenone.\(^95,96\) Nozawa et al. found that poly(L-lysine)–Cu(II) complex exerted a symmetrically selective catalysis of the hydrolysis of phenyl alanine ester, whereas Cu(II) ions and bis(bipyridyl)Cu(II) had no catalytic activity.\(^97\) The improved stability of the intermediate PLL–Cu(II) complex with the D-ester was considered responsible for the catalytic activity.

Breslow and Overman attached the Ni(II) complex to cyclohexamylose (7), which formed a hydrophobic cavity and studied the hydrolysis of
*p*-nitrophenyl acetate.\textsuperscript{98} The reaction was accelerated by a factor of about $10^3$ over the uncatalyzed system, the increased reactivity being the result of binding of the substrate in hydrophobic cavity.

![Structure](image_url)

(7)

The hydrolysis of *p*-nitrophenyl acetate over catalysts such as poly(vinylimidazole) and poly(*N*-methylimidazole) was studied. The activation parameters indicated a second order reaction with high catalytic activity, attributed to the synergetic action of the polymer groups. An acetylation-deacetylation mechanism on the reactive site was proposed.\textsuperscript{99}

Gomez \textit{et al.} studied the hydrolysis of *p*-nitrophenyl acetate spectrophotometrically in ethanol-water at 26°C and pH 8 in the absence and presence of poly(4-vinylimidazole) and Cu(II).\textsuperscript{100} First order kinetics in *p*-nitrophenyl acetate was observed.\textsuperscript{101} The rate was increased by addition of $\approx 10^6$ M Cu(II).

An efficient method for ester hydrolysis on the surface of silica gel catalysed by iridium triiodide under microwave irradiation was investigated by Ranu \textit{et al.}\textsuperscript{101} Enantioselective ester hydrolysis catalysed by imprinted polymers
was studied by Sellergren et al. The hydrolysis of \( N-t \)-butoxy carbonyl phenyl alanine-\( p \)-nitrophenyl ester was used for this study. A theoretical study on the catalytic effect of water in basic hydrolysis of methyl acetate was done by F. Haeffner et al.

Siegfried et al. studied the kinetics and mechanism of the Cu(II) induced hydrolysis of nitrile groups in the side chain of tetraazamacro cycles. The mechanism of the hydrolysis proceeds by an intramolecular attack of a coordinated \(-\text{OH}\) on to the nitrile group in a five or six center transition state.

Nucleophiles such as imidazole, pyridine and hydroxyl amine are known to be powerful catalysts of ester hydrolysis. An extensive study of polymeric analogues of these compounds has shown that they too act as effective esterolytic catalysts. Polymeric imidazole catalysts and the copolymers of \( N \)-vinylimidazole and acrylic acid have been found to be effective esterolytic catalysts for the hydrolysis of \( p \)-nitrophenyl acetate. The carbonyl groups in this polymer can bind a positively charged substrate (A). Thus the catalytic esterolytic activity of such a polymer for the positively charged (A), the neutral (B) and the negatively charged (C) is in the order.

\[
\begin{align*}
\text{(A)} & : \quad \text{O} & - \text{C} & - \text{CH}_3 \\
\text{(B)} & : \quad \text{O}_2\text{N} & - \text{C} & - \text{CH}_3 \\
\text{(C)} & : \quad \text{HOOC} & - \text{O} & - \text{C} & - \text{CH}_3
\end{align*}
\]
Nonionic (hydrophobic) association of the polymeric catalyst-substrate has also been shown to increase the catalytic activity. Thus the rate of hydrolysis of 3-nitro-4-acyloxy benzoic acid (D) by polyvinyl imidazole, increases with increasing bulk of acyloxy group.

\[ \text{HOOC-} \begin{array}{c} \text{O}_2\text{N} \\ \text{O} \end{array} \begin{array}{c} \text{O-} \\ \text{C-(CH}_2)_n\text{CH}_3 \end{array} \]

\(n = 1, 6, 11, 17\)

It was observed that the deacylation step of the intermediate polymeric acylimidazole is rate determining. Since the acylated polymer becomes more hydrophobic, because of the extra group attached to the polymer, apolar associations increase with the chain length of the acyl group and hence increase the catalytic activity. After getting inspirations from these and such other observations, we tried the catalytic activity of the metal complexes of newly prepared 4-20 mol\% NN MBA-crosslinked polyacrylic acids and AA-NVP copolymers in the hydrolysis of \(p\)-nitrophenyl acetate.