CHAPTER 1

INTRODUCTION
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Introduction

1.1 General Introduction

The first synthetic reactive polymers of some significance were undoubtedly the ion-exchange resins\(^1\), first prepared as early as 1935\(^2\) from phenol-formaldehyde condensates. These resins were replaced by more suitable styrene-divinyl benzene structures\(^3\), adapted in the early 1950’s, which are still in use today. Despite their great importance, the impact of ion-exchange resins on the specialized field of reactive polymers is overshadowed by Merrifield’s development of the solid-phase method of synthesis in the early 1960’s\(^4\). Since Merrifield pioneered solid phase synthesis back in 1963, work that earned him a Nobel prize, the subject has changed radically. Merrifield’s concept\(^5\)\(^-\)\(^6\) not only revolutionized the field of peptide synthesis for which it has been developed, but also spread quickly to other areas of organic synthesis, catalysts and separation science. Interestingly, the development of numerous new polymeric reagents, catalysts and supports has resulted in a better awareness of the fact that polymers could be designed to have special reactivities. This, in turn has contributed to a new interest in reactive polymers for application in areas not directly related to synthesis, catalysis or separation science.

The element carbon is not particularly abundant but, natural or synthetic macromolecules based on carbon chains fill the world around us. Organic polymers are used as plastics and elastomers, films and fibers in areas as diverse as clothing, car tires, compact discs, packaging materials and prosthesis.

The breadth of synthetic chemistry applied to solid phase synthesis has since widened owing to the emergence of combinatorial
chemistry\textsuperscript{7}, in pharmaceutical\textsuperscript{8} and agrochemical research\textsuperscript{9}. Solid phase oligonucleotide\textsuperscript{10} and carbohydrate chemistries\textsuperscript{11} were established during the 1970's and have received wide spread coverage in the literature. Of late, heterocyclic chemistry has entered a new dimension in being applied to solid phase synthesis\textsuperscript{12}. Interest has focused on creating structurally diverse analogues on resins using multicomponent condensation reactions\textsuperscript{13}. The preparation of small-molecule, drug like compounds on solid-phase has undergone exhaustive study\textsuperscript{14} and specific target molecules for drug discovery programs have been synthesized.

Electro luminescent and integrated optic devices and sensors with exciting new applications has been developed\textsuperscript{15}. The massive growth in the use of organic polymeric materials in the past 50 years can mainly be attributed to the ease of their preparation, light weight nature and unique ease of fabrication. Their ease of preparation is a consequence of not only the advanced state of organic synthesis, which reflects both the intrinsic logic of the subject and the creativity of scientists interested in the area, but is also due to the accessibility of cheap petroleum derived monomers\textsuperscript{16}.

Combinatorial chemistry has emerged as a powerful new technology for chemists to synthesize large numbers of compounds for biological evaluation. It can be described as the preparation, on a solid support of an ensemble of molecules referred to as a 'library'. These libraries are tested as single compounds or as mixtures. They provide an attractive method for the discovery of pharmaceutical lead compounds, with much of the work concentrated on exploring and exploiting the synthesis of heterocycles\textsuperscript{17},\textsuperscript{18}. During the last few years, solid-phase methodology has been rapidly and extensively applied to the preparation of small organic molecules. Polymer-supported reagents have attracted growing interest because they can provide attractive and practical methods for combinatorial chemistry and solid-phase synthesis\textsuperscript{19}.  

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Organic Light Emitting Diodes (OLEDS) has grown in the last decade from a field of nearly purely fundamental research into the commercialisation of devices and displays. Polymeric Light Emitting Diodes (PLEDS) a subset of OLEDs have been extensively studied in recent years due to their promising practical applications. Polymer light emitting diodes are usually constructed in a sandwich structure consisting of an anode, the electroluminescent material and the cathode. The nature of polymer/metal interface is very sensitive to the work function of the metal electrodes. A large number of such polymeric LEDs have been developed. The challenges in PLED development include the discovery of polymers with suitable light emitting efficiencies, colour varieties and lifetime stability.

Besides light-emitting properties, conjugated polymers also demonstrated various interesting electronic and photonic properties, which are comparable to traditional inorganic semiconductors. It has been reported that PPV’s can be used as laser material\textsuperscript{21}, photodiodes\textsuperscript{22} and organic transistors\textsuperscript{23}. Most of the optoelectronic polymers reported to date are based on pure organic conjugated systems, in which different kinds of functional groups are attached\textsuperscript{24}.

Organic polymers are receiving increasing attention as separation media. While the vast majority of separation media used today is based on silica\textsuperscript{25}, organic polymers have the additional advantage as they offer outstanding properties as well as vastly enhanced chemical versatility.

Polymeric coordination reagents are novel type of substances possessing a combination of physical properties of high polymer and the chemical properties of the attached reagent\textsuperscript{26}. Polymeric reagents have been developed over the past decade as an offshoot of a somewhat exotic and esoteric research activity into a fast growing field in applied and specific separation\textsuperscript{27}. Various polymeric reagents for use as separation media have been reported\textsuperscript{28}.
During the last few years there has been a growing interest in temperature-sensitive polymers because they are potential candidates for application as intelligent sensors, separation systems and drug release devices. It has been shown that the temperature-sensitivity of these polymers is connected with their lower critical solution temperature (LCST).

Polymers are now extensively used in optical and electro optical devices because of their several superior properties over inorganic materials, such as transparency, light weight, case of fabrication and possible molecular tailoring through controlled synthesis.

The use of amine-containing polyesters as effective gene-vectors in medical field has been reported. It also finds use as polymeric coating, industrial lubrication and cleaning materials.

The $d^6$ transition metal complexes exhibit characteristic long-lived metal to ligand charge-transfer (MLCT) excited states, which can undergo different photochemical or photo physical process. One of the most promising potentials of these complexes is the conversion of solar radiation into chemical energy. Conjugated polymers incorporated with these complexes, which are able to participate in charge-transport process, have been reported in the literature. Light emitting devices based on ruthenium, rhenium and other transition metal complexes have also been constructed.

The study of biological systems has stimulated the development of composite materials, since the basic units of living organisms responsible for structural complexity of materials has continuously increased in the past decades and a distinct transition from structural materials via functional materials to smart intelligent materials has been observed. These materials are based on a novel concept where the information science is introduced into the material. Today it is one of the challenging tasks to manufacture new multifunctional
materials which possess intelligence at the material level. In the last few years we have observed a migration of interest and activity from the traditional hard materials towards soft areas such as biomaterials, polymer gels and elastomers.

The combination of polymers with nanomaterials displays novel and often enhanced properties compared to the traditional materials. They can open up possibilities for new technological applications. New generation of magnetic elastomers, consisting of small, mainly nano-size, magnetic particles dispersed in a highly elastic polymer matrix\textsuperscript{37}. A novel inorganic semiconductor nano composite (Cu\textsubscript{2}S/CdS/ZnS) were prepared in polymeric networks and characterized\textsuperscript{38}. Polyacrylamide-semiconductor nanocomposites with homogeneously well dispersed semiconductor nanoparticles in the polymer matrices were prepared by a novel \textit{in situ} simultaneous polymerisation hydrolysis technique\textsuperscript{39}.

Recently there has been much interest in developing amphiphilic surface-active compounds, which can be used to influence interfacial interactions between solids, liquids and gases. As reactive molecules, polymerizable surfactants or surf mers are interesting because of their potential molecular diversity and their ability to react with other molecules to form chemical bonds. They can be used in emulsion polymerization to stabilize later particles\textsuperscript{40}. Surfactant monomers and polysoaps with acrylite and acryl amide functionalities were synthesized and used in emulsion polymerisation of styrene evaluated\textsuperscript{41}.

Transition metal complexes derived from polymer bound ligands have generated considerable interest due to their greater thermal stability, resistance to chemical attack, novel structural features and several applications. Polymer-metal complexes have been of interest to many chemists as they realize that it is not only an excellent model for the metallo-enzymes but also leads to development of highly efficient catalysts. Polymer supported catalysts are the most attractive types of polymer-supported species for applications in organic
chemistry, because they provide great ease in separation and recycling of the catalyst and isolation of the product\textsuperscript{42,43}.

1.2 PREPARATION AND CHARACTERISATION OF FUNCTIONALISED POLYMERS:

Research directed towards supporting homogeneous transition metal catalysts on organic polymers has tuned into an area of intense research. Since about 1967, a corresponding growth of interest has occurred in heterogenizing homogeneous catalysts onto solid inorganic supports such as silica, alumina etc. by reaction sequences which preserve the structure of the homogeneous complex. Homogeneous catalysts often have the advantages of giving high selectivity at mild operating conditions and the availability of every molecule of catalysts to reactants. Heterogeneous catalysts such as metal or metal oxide surfaces are frequently less selective, less active, but often very durable and easily separable and can be used in fixed beds in gas-solid and liquid-solid contact reactors. It would be ideal to combine the advantages and simultaneously avoid the disadvantages of each class of catalysts, which might be done by attaching homogeneous catalysts to organic polymers in such a way that the ligand sphere of the metal is essentially unchanged and the attached complex is bathed by solvents and reactants. The resulting heterogenized homogeneous catalyst thus could function mechanistically as if it were in solution but would operate as a separate immobile phase.

Before looking at the synthesis of some functionalized polymers, it is useful to consider the following:

- Choice of the physical form of the functional polymer
- Reactions which are currently available for the preparation of functional polymers
- Means of characterization of polymer-supported species.
1.2.1 Choice of the physical form of the polymer:

Polymers are available as linear chains, which can be dissolved in appropriate solvents, or as cross linked gels or macro reticular resins which are totally insoluble in all solvents; each type possess it’s own distinct advantages and disadvantages. Therefore, in any application of a polymer as a reagent or protecting group, careful consideration must be taken of all the variables involved before choosing the physical form of the polymer in order to maximize the advantages of the polymer system while minimizing any potential problem.

1.2.1.1 Linear polymers:

From a preparative point of view, it can be said that heating of a neat liquid monomer in a suitable solvent and initiator yields a linear polymer.

The advantages associated with the use of linear (soluble) polymers is it’s solubility which include the fact that all the reactions will be carried in solution in a homogeneous medium with equal accessibility to all the functional groups of the polymers.

There are a few applications for which soluble polymers are ideally suited; perhaps the best example in a single step reaction is the use of N-chloro nylons as halogenating reagents\(^4\).

Selective and complete precipitation of the polymer may not be easy and obvious pitfalls exist as low molecular weight species may be insoluble in the precipitation medium. Thus complete removal of impurities from the precipitated polymer may not be achieved. Selection of a suitable solvent for both polymer and reactants often creates problem. Separation of the polymer from low molecular weight contaminants may be laborious or difficult. The techniques micro and ultra filtration used for the same are relatively costly and inconvenient. Another problem with the use of linear polymers is the possibility of side
reactions producing unwanted cross-links during reaction. This would result in the formation of a gel, which may be very difficult to process.

1.2.1.2 Cross-linked polymers:

Cross-linked polymers consists of infinite networks in which the linear chains are interconnected through a cross linking agent. Being insoluble in all solvents, it offers the greatest ease of spherical beads, which do not coalesce when, placed on a suspending solvent. They can be separated from low molecular weight contaminants by simple filtration and washing with various solvents. Polymerization can be either condensation or addition.

Free radical suspension polymerization has proved to be perhaps the most useful technique for synthesizing cross-linked polymer supports, principally because of the extremely convenient physical form of the bead product, which lends itself to further batch wise chemical modifications.

In addition to this standard technique, several recent techniques have been described in order to narrow down the particle size distribution\textsuperscript{45}. Recently a new technique, called Atom Transfer Radical Polymerization (ARTP) is now developed combining the benefits of both free radical and living polymerizations which can be applied to a large variety of monomers to produce polymers with well defined microstructures\textsuperscript{46}. The use of ARTP methodology allows for tailoring of individual block sizes within the copolymers.

Typical radical initiators used for the polymerization reaction are azoisobutryonitrile [Fig 1.1(a)] and benzoyl peroxide [Fig 1.1(b)] both of which cleave readily on heating or irradiation with ultraviolet light and are readily soluble in a wide range of monomers and organic solvents.
Different monomers such as acrylamide, styrene, ethylene glycol can be cross linked with a number of cross linking agents such as N, N’-methylene bis acrylamide, divinyl benzene, ethylene glycol dimethacrylate, tetra ethylene glycol diacrylate to produce cross linked polymers (Scheme 1.1)

Scheme 1.1 Preparation of cross-linked polymers
Cross-linked polymers exhibit considerable differences in properties depending on the degree of cross-linking and method of preparation. Although numerous variations exist, the two types of cross-linked polymer beads, which are most frequently encountered, are gel and macro porous resins.

1.2.1.2.1 Gel-type resins:

Gel type or microporous polymers are generally prepared by suspension polymerization using a vinyl monomer suspended in water in the presence of low amounts of a cross linking agent, typically 0.5-2%. The product obtained in the form of spherical beads in which the cross-linking sites are essentially randomly distributed, can be handled easily handled.

The pore size in a gel polymer is inversely related to the amount of the cross-linking agent used in its preparation; the lower the amount, the larger the pore size. In dry state, the pores of a gel resin are collapsed but on addition of a good solvent, extensive solvation of the polymer chains causes the beads to swell extensively and results in the reappearance of the pores. Here, the polymer chains are very mobile with no well-defined boundaries of the pores. However, as the degree of cross-linking increases, the mobility of the polymer chain is reduced.

Microporous supports are less fragile, require less care in handling, react faster in the functionalization and application reactions and possess higher loading capacities.

Gel polymers are usually found to be slightly less reactive than linear polymers due to diffusion of the reagent within resin pores. The reaction yields can be affected by the degree of cross-linking, with lower yields observed for highly cross-linked resins.
These facts suggest that resins with very low degree of cross-linking would be the most suitable as increased swelling would result in higher accessibility through enhanced diffusion properties. However, if the cross-linking density is very low, the gels will become difficult to handle, and under some conditions may be degraded to produce soluble linear fragments.

1.2.1.2.2 Macroporous or macroreticular resins:

These are also prepared by suspension polymerization, using higher amounts of the cross-linking agent and a solvent. This results in the formation of tiny, highly cross-linked polymer particles surrounded by solvent droplets containing some dissolved monomer and cross-linking agent. As the reaction proceeds, the particles grow and incorporate some monomer depleted solvent droplets which will become the pores of the final resin beads. When the solvent is removed once the polymerization has been completed, the pores may collapse partially such that the initial macro porous structure is restored when placed again in a good solvent. The description of macro porous resin, is of course simplified as the density of cross-links is far from being uniform throughout and the beads therefore is a hard, fairly unreactive core of low porosity.

Mechanical stability about the pores is obtained through extensive cross-linking. Their dimensional stability makes them ideally suited for column applications where better solvent flow rates can be achieved, than gel polymers. The main advantage of macro porous resins is their large interior surface area within large pores, which allows easy access of the reagents. This large surface area is essential for reactivity as the highly cross-linked beads do not swell appreciably and reactions are carried out on to a monolayer. Due to same reason, reactions of these resins are often carried out in a variety of solvents without appreciable changes in reaction rates.
Disadvantages may include a lower reactivity in numerous instances, lower capacity and poor mechanical stability of the beads, which tend to break up when handled repeatedly, with formation of fine particles, which are extremely difficult to work with. Also, static electricity often makes handling of dry beads a difficult and frustrating operation.

1.3 PREPARATION OF THE FUNCTIONAL POLYMERS:

Two approaches exist for the preparation of functional polymers namely

(1) polymerization or co-polymerization of monomers, which carry the desired functionality

(2) chemical modification of pre-formed polymers.

1.3.1 Polymerization of functional monomers:

A route to reactive functional polymers is the polymerization or co-polymerization of monomer, which contain the desired functionality. The number of reactive ends in the polymer chain can be reduced by the addition of the co-monomer. Insoluble resins are obtained in the presence of small amounts of a cross-linking difunctional co-monomer. The polymerization of a functional monomer will be advantageous for a system if synthesis of the required monomer can be accomplished in high yield and purity resulting in a polymer of the required mechanical strength with good thermal and chemical resistance.

Supported imidazole, pyridine and morpholine species can be synthesized from monomers such as 4-vinyl imidazole, 4-vinyl pyridine and N-acryloyl morpholine respectively. Chloromethyl polystyrene resin can be prepared by polymerization of vinyl benzyl chloride. Tartrate polyesters for use in epoxidation have been prepared by condensation polymerization of tartaric acid and polyethylene glycol. However, problems may arise due to differences in reactivities of various monomers.
1.3.2 Chemical modification of pre-formed polymers:

This approach has been widely used in the preparation of polymeric reagents and protecting groups. The chemical modification approach seems to be simple and straightforward and every solid phase chemist rightfully expects a polymer containing aromatic rings to be easily modified by an electrophilic aromatic substitution reaction.

The functionalization of a polymer may be more advantageous for a particular system due to the availability of the appropriate polymer and the ease of accomplishing the required functionalization reaction in high yield with a minimum of side reactions.

1.3.2.1 Chemical modification of polystyrene:

Most of the work involving functional polymers has been carried out on cross-linked polystyrene resins. This choice is by no means coincidental as polystyrene meets many of the requirements of a solid support, a fact that was recognized very early by Merrifield in his pioneering work on solid phase peptide synthesis.

By far the most commonly employed polymer supports prepared by suspension polymerization are styrene-DVB copolymer resins, and the majority of the preparations are in the literature.

The resin beads first used by Merrifield and still widely used today, is a gel-type polymer made from cross-linked polystyrene. The internal molecular structure of polystyrene where X could be any suitable functionality generally derived from chloromethyl group is shown in Fig 1.2
Chemical reactions for the introduction of functional groups in polymer and the functional groups conversion in polymers are also dependant on the nature of the polymer backbone, molecular character, the extent of cross-linking, pore size, pore volume of the polymer particles and the separation of functional groups from the polymer supports.\textsuperscript{51}

The main advantages of polystyrene resins are the following:

- very pure polystyrene resins in bead form with good mechanical stability and well defined physical characteristics are available commercially
- the aliphatic backbone of the polymer is unreactive and thus the polymer is not overly susceptible to degradative chain scission.
- the aromatic rings are very reactive and can be functionalized easily, for example by electrophilic substitution reaction.

Three versatile intermediates are mainly used in the preparation of new polystyrene supports or reagents; chloromethylated polystyrene, ring-brominated or ring-lithiated polystyrene.
The former resin, often referred to as Merrifield resin, has been used extensively both as support as in peptide synthesis and as a precursor to numerous other functional polymers. Its versatility due to the ease with which its chlorine atoms can be replaced in nucleophilic substitutions; is applied in a large number of reactions. The scope of the reaction has been recently enlarged through the use of phase transfer catalysis to afford several otherwise difficultly accessible resins. The reactions of malononitrile with chloromethylated polystyrene proceeds smoothly under phase transfer conditions with little side reactions.

One of the most important reactions in the functionalization of cross linked polystyrene is its chloromethylation, by Friedel-Crafts reaction, using chloromethyl methyl ether and stannic chloride, since the chloromethyl group provides a reaction handle on the polymer and subsequently be transferred into numerous other functional groups. (Scheme 1.2)

\[ \text{Scheme 1.2 Reactions of chloromethylated polystyrene} \]

X= -CHO₂-NO₂
Ring -brominated polystyrene is also very versatile intermediate in the preparation of other polystyrene resins. It is achieved by using bromine / CCl₄ in presence of catalytic amounts of thallium (III) salt, FeCl₃ or other catalysts and in all cases bromination seems to occur exclusively in the para position. The degree of functionalization can be controlled accurately by regulating the amount of bromine available for the reaction.

Lithiation of aromatic rings of polystyrene can be achieved directly using n-butyl lithium-TMEDA complex in cyclohexane or indirectly by bromination followed by reaction with n-butyl lithium in benzene. The second method is advantageous when a good control of the degree and position of lithiation is required and when high loadings are required. Lithiated polystyrene is a useful intermediate in the preparation of numerous other nucleophiles containing thiophenol phenol reactive groups (Scheme 1.3).
1.3.2.2 Chemical modification of other polymers:

Numerous attempts at using polymers other than polystyrene have been made; most of them have met with limited success for reasons such as lack of reactivity, degradation of the polymer chain or unsuitable physical properties of the finished polymer.

Manecke has successfully modified poly (vinyl alcohol) by reaction with polyfunctional acetals\textsuperscript{53}, but the low capacity of the polymers and their solubility properties make them only suitable for a very limited number of applications.

1.3.3 Role of solvents:

The role of a solvent in the application of a functionalized resin is complex. Ideally, it should interact with the polymer matrix to optimize the diffusional mobility of reagent molecules. It should have the correct solvating characteristics to aid any chemical transformations being carried out. It should not limit the reaction conditions which are to be applied, for example the temperature. And in the case of bound photosensitizers, for example it should encourage translucence and not opacity. Naturally it is difficult to satisfy all of these criteria simultaneously, and the selection of a solvent is often a compromise. There has been a number of attempts to quantify the interaction of solvents with a polymer support matrix, and the nitroxide spin–labelling experiments have achieved this with respect to the local motions of the polymer backbone and the associated side chain substituents\textsuperscript{54}.

1.3.4 Isolation of reactive sites:

An extremely attractive potential feature of polymer-supported species would be the ability of the polymer to effectively isolate the reactive sites from one another during reaction. This would be a convenient alternative to the high
dilution conditions, which are used in solution to prevent interaction of reactive ends. Unfortunately however the polymer chains of lightly cross linked resins have a high mobility and, as a result, reaction involving interactions of sites are found to occur quite frequently and to various extents with polymer supported species.

In general, it can be said that while true site isolation is extremely difficult to achieve on a lightly cross linked polymer, interactions of reactive sites can be reduced and even almost eliminated through an appropriate choice of polymer morphology, degree of functionalization, reactions and reaction conditions.

Another critically important factor is the rate of intra polymeric reactions. This rate is not limited primarily by diffusion, as would be the case in classic systems, but by the restricted conformational motion of the cross-linked polymer chains. Although results vary with reaction conditions, it is found that such intrapolymeric reactions are relatively slow.$^{55}$

Thus it can be expected that if a reaction involving a polymer-bound reactant and a species in a solution is much faster than the motions of the polymer chains which would bring two polymer-bound sites in close proximity, apparent site isolation can be achieved in a way which would not normally be obtained in solution.

In general, when designing a synthesis, which involves a polymer-supported moiety, the following factors, which have a direct influence on the extent of site-site interactions, should be considered.

- Degree of cross-linking of the support in general, a higher degree of cross-linking means lower mobility of the polymer chains and lower interactions of the site.
- Degree of functionalization of the polymer in general, low degree of functionalization results in fewer site interactions.
- Nature of the solvent swelling affects the mobility of the polymer chains; the polarity of the solvent may also have an influence.
- Reaction condition and relative concentration of the reactants
- Rate of reaction being contemplated Vs rate of movement of the polymer chains
- Presence of charges on the polymer may render the support more rigid and thus may decrease the frequency of intersite reactions

Other factors will vary from reaction to reaction.

Some typical polymeric ligands are given in fig 1.3.

<table>
<thead>
<tr>
<th>Co-ordinating group</th>
<th>Structure of repeating group</th>
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<tbody>
<tr>
<td>Heterocyclic nitrogen</td>
<td><img src="image1" alt="Structure" /></td>
</tr>
<tr>
<td>Amine, Imine</td>
<td><img src="image2" alt="Structure" /></td>
</tr>
<tr>
<td>Schiff base</td>
<td><img src="image3" alt="Structure" /></td>
</tr>
<tr>
<td>Carboxyl,Ketone</td>
<td><img src="image4" alt="Structure" /></td>
</tr>
<tr>
<td>Amino carboxyl</td>
<td><img src="image5" alt="Structure" /></td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td><img src="image6" alt="Structure" /></td>
</tr>
<tr>
<td>Phosphine</td>
<td><img src="image7" alt="Structure" /></td>
</tr>
<tr>
<td>Thiol</td>
<td><img src="image8" alt="Structure" /></td>
</tr>
</tbody>
</table>

Fig 1.3 some typical polymeric ligands
1.4 APPLICATIONS OF CROSS-LINKED FUNCTIONALIZED POLYMERS:

Functionalised polymers found use as reagents, substrates and catalysts. They possess many practical advantages compared to their small molecule analogs. Being insoluble, they can be separated from the other components of a reaction system by filtration. Reactions with functional polymers are sometimes advantageously carried out in a manner similar to column chromatography. The polymeric species is packed in a column and the small molecule species poured through the column. Being easily recoverable, they can be economically used in large excess to achieve high yields in a reaction. Reactive, toxic, or malodorous small molecules, reagents, substrates or catalysts can be handled much more safely and easily in the form of the corresponding polymers.

1.4.1 Polymeric reagents:

A wide range of polymer reagents has been studied\(^\text{56}\). The epoxidation of alkenes by a polymer peracid illustrates the use of polymer reagent\(^\text{57}\) (Scheme 1.4)

![Scheme 1.4 Function of a polymer peracid as a reagent](image-url)
An important application of polymer-supported ligands is the selective separation of metal ions and the efforts in the recovery of metal ions from aqueous solutions using polymeric chelating agents are steadily increasing\textsuperscript{58}. Several applications of functional polymers for achieving chemical separations have been described. Ion-complexing polymers allow the removal of ions from solution for analytical or preparative purposes. Polymers containing the 8-hydroxyquinoline unit (Fig 1.4) are useful for chelating nickel, cobalt and copper ions.

![Fig 1.4](image)

A variety of polymers containing chiral groups are useful for resolving racemic mixtures into the individual enantiomers\textsuperscript{59}. Copper (II) complex of (Fig 1.5) resolves racemates of aminoacids\textsuperscript{60}.

![Fig 1.5](image)

Chelating resins containing ligands such as dithiocarbamate, pyridine, imidinoacetic acid, oxine are widely used in the separation of metal
Polymers containing macrocyclic ligands such as crown ether [Fig 1.6 (a)] or cryptand [Fig 1.6 (b)] bind and separate various cations.\(^\text{62}\)

![Fig 1.6 (a)](image1)

![Fig 1.6 (b)](image2)

Polymer drugs are of interest since they offer a number of potential advantages. A polymer drug can be synthesized by the covalent binding of a drug to a polymer or the synthesis and copolymerization of a monomer containing the drug moiety. Other polymeric reagents of interest include polymer antioxidants, flame-retardants and UV stabilizers as additives to polymers\(^\text{63}\) and agricultural chemicals such as polymer herbicides, fertilizers and insecticides\(^\text{64}\).

### 1.4.2 Polymeric substrates:

A polymer substrate is an appropriate polymer support to which a substrate is covalently bonded. When the substrate is treated with a low molecular-weight reagent, chemical reaction occurs to yield the desired product on the polymer support, which cleave to get the free desired product. One of the most important applications of polymer substrate technique is the solid-phase synthesis of polypeptides developed by Merrifield\(^\text{5}\), for which he received the 1984 Nobel prize in chemistry.

### 1.4.3 Polymeric catalysts:

Being easier to handle, less toxic and more stable towards moisture and atmospheric contaminants, polymeric catalysts are widely used over
the low molecular weight catalysts. Sulfonated polystyrene has been used to catalyze a variety of acid-catalyzed reactions, including acetal and ketal formation, esterification, hydrolysis of amides and esters, aliphatic and aromatic alkylation, hydration of alkynes and alcohols and synthesis of bisphenol-A from phenol and acetone. Poly (acrylic acid) and the hydrochloride of poly (4-vinyl pyridine) have also been used as polymer acid catalysts.

1.5 POLYMER METAL COMPLEXES

A polymer metal complex is a co-ordination complex between a ligand function anchored on a polymer matrix and a metal ion, in which the metal atom is attached to the polymeric ligand by a coordinate bond. Plastocyanine, a metalloenzyme is a polymer-metal complex present in nature. The polymeric ligand, on complexation, possesses specific structure and unique property, since the metal ion is surrounded by a structured polymer chain.

1.5.1 Approaches for the preparation of polymer metal complexes:

Covalent attachment of the salen complex would offer a more robust system for recycle and separations. To accomplish this goal, covalent attachment of salen complexes onto a polymer support could be performed by either of two methods

(i) by polymerization or copolymerization of monomers that contain the preformed complex and polymerizable moieties
(ii) by chemical modification of accessible functional groups on a preformed polymer

A few studies have used the first methodology to incorporate a homogeneous salen ligand with pendant vinyl groups covalently into a polymerized matrix. A problem with this strategy is the formation of inaccessible catalytic sites within the polymer.
The second one, based on surface modification strategies to produce covalently attached salen complexes on a polymer (Scheme 1.5) possesses many advantages.

Scheme 1.5 A route to synthesize covalently attached salen complexes

In this approach, the first building block for the salen complex is attached via a covalent bond to pendant chloromethyl groups on the surface of a commercially available polymer resin particle. The addition of successive organic building blocks is repeated in a stepwise manner to produce the desired salen complex on the polymer surface. This solid-phase synthesis of the salen complex allows easy separation of the salen intermediates from the various reagents needed for each step. This method of synthesis is similar to the solid-phase peptide synthesis by Merrifield but the completed salen ligand is not cleaved from the surface, as the final product is the supported complex.

The principal advantage of this methodology is that it allows the ligand to be synthesized in a sterically unhindered manner. For successful stage
wise construction of the salen complex, the sites for reaction must be readily accessible by the organic building blocks that produce the ligand. Because of this requirement, these surface sites should also be accessible to the metal being loaded.

**Complexation of polymeric ligand with metal ion:**

This type of polymer–metal complex is formed by the reaction of polymer containing coordinating groups with metal ions.

Usually the reaction of a polymeric ligand with a metal ion or a stable metal complex in which one of the coordination sites remains vacant results in various coordination structures such as
1. Pendant complexes
2. Inter and Intra molecular bridged complexes

Pendant complexes:
Here the metal ion is attached to ligand function, which is appended on the polymer chain (Scheme 1.6) Based on the ligands chelating ability, they may be monodentate or polydentate.

![Scheme 1.6 Formation of pendant complexes](image-url)
A monodentate pendant complex is formed when a metal ion or a stable metal complex in which the central metal ion is already masked with low molecular weight ligands except a single vacant coordination site. They possess simple structures and are often soluble. An example for the formation of monodentate pendant complex is the complexation of cis- \([\text{Co (en)}_2 X_2]\) X with poly [4- vinyl pyridine]\(^{68}\) shown in fig 1.7.

![Fig 1.7](image1)

Polydentate pendant complexes are formed when the polymer backbone contains multidentate ligands (Scheme 1.7). They possess relatively well-defined coordinated structures.

![Scheme 1.7 Formation of polydentate pendant complexes](image2)
Inter and intra molecular bridged complexes:

When a polymeric ligand having four or six coordination reacts with a metal ion, inter or intra polymer chelation takes place (Scheme 1.8). It’s often difficult to distinguish these two bridging types.

Scheme 1.8 Formation of intra and inter bridged complexes

A typical example of this type of polymer–metal complex is the poly (vinyl alcohol)-Cu (11) complex (Fig 1.8)

Fig 1.8
Reaction of peripheral functional groups in metal complexes with polymers:

When functional polymers react with peripheral functional groups of the metal complexes, polymer–metal complexes with definite coordinate structures are formed (Scheme 1.9).

\[
\begin{align*}
\text{Y} \quad \text{Y} \quad \text{Y} &+ \quad \text{M} \quad \xrightarrow{-XY} \quad \text{M} \quad \text{Y} \quad \text{M} \\
\text{Scheme 1.9 Reaction of peripheral functional groups of complexes and polymers}
\end{align*}
\]

DVB-cross linked polystyrene and its modified forms form complexes like wise (Fig 1.9).

\[
\begin{align*}
\text{CH}_2\text{Cl} &+ \quad \text{M} \quad \xrightarrow{\text{COOH}} \\
\text{CH}_2\text{O} &- \quad \text{M} \\
\text{Fig 1.9 Chelation of cross-linked polystyrene}
\end{align*}
\]

1.5.2 Macromolecular effects on complexation:

The complexation behaviour of a ligand supported on a polymer is different from the corresponding low molecular weight analogs. In addition to the changes caused due to the variation of functional groups in the ligand, the variation also depends on the polymer to which the ligand is attached.

1.5.2.1 Effects due to cross-linking:

(a) Degree of cross-linking:

The complexing nature of a polymeric ligand is highly influenced by the degree of cross-linking. Degree of functionalization, solvation of bound
species, diffusion of soluble reagents onto the polymer matrix are all influenced by the degree of cross-linking, which in turn affects the extent of complexation. With increase in cross-link density, rigidity of the polymer backbone increases resulting in a lower degree of functionalization. This results in a low metal intake and low mechanical stability of the resulting metal complex. The dependance of the extent of DVB cross-linking on complexation of the dithiocarbamate resins derived from ethylenediamino methyl polystyrene with 1-20 mole % of DVB cross links were investigated with different metal ions. It was found that, the extent of complexation decreases with increase in cross-link density\textsuperscript{72}. The swelling of the complexed resins is lower than that of the uncomplexed resins and it decreases with increase in cross-linking. The complexation reaction becomes heterogeneous\textsuperscript{73} for the highly cross-linked resins since they are insoluble and non-swellable.

(b) Nature of cross-linking agent:

The metal ion intake depends on the nature of cross-linking also\textsuperscript{72}. The complexing ability of a polymeric ligand depends on the hydrophilic nature of the macromolecular support. The swelling of the complexed resins depends on the flexibility of the cross-linking agent. In some cases, the incorporation of cross-linking agent decreases the hydrophilic nature thereby making the active sites more amenable to substrates and solvents.

1.5.2.2 Effect of spacer groups:

The complexing ability of polymeric ligands depends highly on the arrangement of functional groups with respect to the main chain\textsuperscript{74}. The shorter the distance between them, the lower is the efficiency of complex formation due to steric hindrance. The presence of a spacer group between the polymer matrix and the ligand function influences the complexation with the metal ion\textsuperscript{75}.  

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The iron chelating ability of hydroxamic acid polymers were studied as a function of the atomic chain spacing separating neighboring hydroxamic acid units and it was found that the chelating ability and the stability increases on increasing the number of spacer groups\textsuperscript{76}. There are also cases where metal ion intake is less even though the ligand is at a longer distance from the cross linked matrix which may be due to decreased concentration of ligand functions by cross-linking during functionalization and due to reduced selectivity\textsuperscript{77}.

When the metal complex is separated from the backbone by a saturated spacer, there is no direct electronic interaction between the parts and any interaction is mainly steric. In contrast, when the polymer is functionalized through a conjugated spacer, the complex is in direct electronic communication with the \(\pi\)-conjugated backbone and the interaction between the two subunits of the material modifies their properties\textsuperscript{78}.

1.5.2.3 Micro environmental effects:

Several micro environmental factors like the presence of functional groups in the vicinity, precise stereochemistry and the hydrophilic-hydrophobic balance of the polymer matrix also affects the overall selectivity and specificity of complexation\textsuperscript{79}. The giant polymer ligand cause steric, cooperative, electrostatic, configurational and hydrophobic effects on the reactivities of the polymer-metal complexes\textsuperscript{80}.

The stability of the polymer–metal complex depends to some extent on the large polymer backbone since it sterically influences the coordination. When the coordinating groups on the side chain rotate free from the rigid polymer backbone the coordination of the metal ion occurs without much strain.
The polarity of the polymer backbone may influence the reactivity of the functional groups attached to it and the structure of polymer backbone imparts size and substrate selectivity\textsuperscript{81}.

1.5.3 Site-site interaction and site isolation:

Functional groups in cross-linked polymer supports are capable of interacting each other. Crucial factors in site-site interaction are the degree of cross-linking of the support, spacer group capacity, distribution of functional groups, loading employed and the nature of the solvent used.

In the case of cross-linked polymeric supports, there has been considerable interest in those systems carrying functional groups, capable of interacting with each other or when subsequently chemically modified. The use of more highly cross-linked resins seems to be an ideal method of improving site isolation and indeed macroreticular species has provided more successful isolation\textsuperscript{82}.

In practice, loadings up to approximately 5 per cent (of aromatic group) that is 0.5 mmol per gram of resin, have been employed successfully in syntheses requiring effective site isolation\textsuperscript{83}.

With sufficiently light loadings, local backbone motions and side-chain torsions and rotations alone would not be sufficient to bring about site-site interaction of widely spaced groups.

An improvement in the rigidity of lightly cross-linked resins also appears to aid site isolation. This can be achieved perhaps somewhat fortuitously by the generation of ionic groups in an essentially hydrophobic support\textsuperscript{84}. Clustering of charges appears to give some rigidity in the resin, enhancing the isolation of groups.
The nature of solvent also influences the long-range flexibility of resins. Good swelling solvents appear to enhance site-site interaction thereby affecting the general course of the desired reaction, whereas poor ones aid site isolation\textsuperscript{85}. In the case of lightly cross-linked supports (~2 per cent) carrying carboxylic acid groups\textsuperscript{86}, significant anhydride formation is possible in methylene chloride solvent even when the loading on the resin is reduced to ~0.5 per cent of aromatic groups (Fig 1.10)

\begin{center}
\includegraphics[width=0.8\textwidth]{fig1.10.png}
\end{center}

\textbf{Fig 1.10}

\textbf{1.6 ANALYSES AND CHARACTERIZATION OF POLYMER-METAL COMPLEXES:}

With linear soluble macromolecular supports, the range of analyses that can be applied is more or less the same as applicable to small molecule chemistry. But with insoluble cross-linked resins, such methods, which require solubilization of samples, cannot be applied.

\textbf{1.6.1 Analytical methods:}

Simple methods of chemical analysis and qualitative chemical tests, such as Beilstien and Lassaigne test for the presence of particular elements (halogens, nitrogen, sulphur) are of use in the identification of an unknown polymer. Combustion analysis for qualitative determination of elemental composition can be used to confirm the purity of a homopolymer and to determine the average chemical composition of a copolymer for which the
repeating units are known. Quantitative determination of the end groups can be carried out using titrimetric methods, providing sufficient time for the penetration of the aqueous reagent to carry out back titration. The complexed metal ions are estimated using volumetric, gravimetric or spectrophotometric methods and the amount of metal ion is expressed usually as milli equivalence per gram of the resin. An idea of the geometry of the polymer metal complexes can be had by measuring the magnetic properties. The usefulness of these analyses however restricted by their inability to give structural information.

1.6.2 Characterization:

Spectroscopic methods are by far the most powerful tool for this purpose and in addition to giving overall structural information, they enable molecular microstructure, repeat unit sequence distributions and structural defects to be determined. The structure and nature of functional groups in a polymeric ligand and its coordination and geometry around the metal ions are studied using spectroscopic methods such as IR, NMR, UV-VIS, ESR and X-ray analysis. Thermal methods such as TG, DTA have been used to study the decomposition behavior and SEM analysis for the surface pattern of the resins and their complexes.

Infrared Spectroscopy:

Infrared spectroscopy is a vital qualitative probe for following the course of reactions, particularly those involving organic macromolecular supports. IR spectroscopy has mainly been used qualitatively to determine the extent to which a chemical transformation has taken place by the disappearance of the absorption band of the converting functional group and appearance of absorption bands due to new groups. IR absorptions of a ligand are usually shifted by complex formation with metal ions. When a polymer ligand has more than two kinds of ligands capable of coordination, it is possible to decide from IR
absorptions which group participates in the coordination. When interpreting IR spectra due attention must be taken of the cross-link ratio of the support, since in the case of polystyrene resins prepared with large quantities of commercial divinyl benzene, a significant proportion of aromatic groups are already disubstituted in the unfunctionalized resin. IR spectroscopy also finds application in the characterization of branched polymers and copolymers, monitoring reactions through the appearance or loss of an absorption and measurement of orientation by use of polarized IR radiation. Fourier transform IR has been extensively used for the study of cross-linked polymers and their metal complexes\textsuperscript{87}.

Nuclear Magnetic Resonance Spectroscopy:

NMR spectroscopy offers much greater scope than IR spectroscopy for elucidating detailed features of molecular microstructure. This is especially true of $^{13}$C NMR, which nowadays is by far the most important technique for structural characterization of polymers. The relative abundance of a given nucleus type in the functional groups compared to the same nucleus contained as an intrinsic part of the support matrix and inhomogenities arising from the insoluble nature of the cross linked resins limits the use of this method. Complex formation with metal ions generally leads to splitting, shifting or broadening of peaks arising from ligand molecule. Especially in the absence of anion effects, a downfield shift is expected due to increased electronegativity of the donor atoms of the ligand. However, $^{13}$C NMR can be used for the analysis of highly swollen, lightly cross linked polymers and magic-angle spinning (MAS) methods, widely used for obtaining high resolution spectra, can be used to extend this to more rigid materials\textsuperscript{88}. $^{13}$C and $^1$H NMR of resins with the multivalent metal atoms has been used to determine the sites of metal coordination on the polymer\textsuperscript{89}. $^{19}$F NMR and single pulse excitation (SPE) $^{13}$C NMR analysis\textsuperscript{90} are also used in monitoring solid-phase reactions. In solid state NMR, the dipole-dipole interactions from neighboring magnetic dipoles influence the spectra.
Another important application is the study of chain dynamics by monitoring the magnetic relaxation behavior of the excited nuclei.

Ultraviolet-Visible spectroscopy:

The ability of an organic compound to absorb UV radiation depends upon its electronic structure. The idea of the geometry around the metal ions in a polymer complex can be had from its electronic spectra. UV and visible light absorption spectroscopy can be used to identify chromophores (benzene rings, carbonyl groups) and to determine the lengths of sequences of conjugated multiple bonds in polymers. Additionally, fluorescence and phosphorescence techniques are important in studies of polymer photophysics.

Electron Spin Resonance spectroscopy:

ESR absorptions arise from different alignments, in an applied magnetic field, of the magnetic moments resulting from the spin of unpaired electrons. The ESR spectrum of a polymer-metal complex reflects its coordination structure, the interaction between the spin of the central metal ion and the coordinated ligand deciding the absorption pattern and its ‘g’ value. ESR absorptions can be used as a method providing direct proof of a chemical bond between metal ion and ligand. Covalent character of a bond becomes more pronounced when the parameters $g_{\perp}$ and $g_{\parallel}$ decrease and when $A_{\perp}$ and $A_{\parallel}$ increase. Since the most sensitive of these parameters is $g_{\perp}$, the variation in $g_{\perp}$ is the best indication of the covalent character. ESR spectra also give information about the movements of the polymer ligand surrounding the central metal ion in an aqueous solution.

Thermal studies:

Thermogravimetry (TG) is the technique in which the mass of the sample is continuously recorded as a function of time or temperature. In the case
of polymers, thermal analysis can be used to study the enthalpy changes, response of the system to temperature including polymerization, degradation and chemical changes. In differential thermogravimetry (DTG), the first derivative of TG curve, that is the first derivative of the mass change of the sample as a function of temperature and time is plotted. DTG curves are useful when analyzing overlapping decompositions. Thermal studies can be used to study the stability mechanisms of decompositions and the kinetic parameters such as energy of activation and entropy of activation.

Scanning Electron Microscopy:

The resin morphology can be studied by Scanning Electron Microscopy (SEM). The resin size, shape, surface porosity and the defects of the sample can be furnished from electron micrographs.

1.7 APPLICATION OF POLYMERIC METAL COMPLEXES:

Polymeric –metal complexes have remarkably specific structures, in which an enormous polymer chain surrounds the central metal ions. They show interesting and important characteristics, especially catalytic activities different from the corresponding ordinary metal complexes of low molecular weight. They are used in the separation of metal ion\(^{92}\), and find potential application in many important systems such as polymer-coated electrode, solar energy conversion, and chemical sensors\(^{93}\). The main attraction of the polymeric metal complexes is that they can be regenerated by separation from the reaction mixture by simple or selective filtration and thus can be reused.

1.7.1 Polymer metal catalysts:

The field of polymer –metal complexes as catalysts in organic synthesis has remained active ever since the first example of catalysis by a
polymer-metal complex reported by Lautsh et al. The organic polymer support can induce specific control over the catalytic and the complexing ability of the ligands depending upon the structural variants in and around the macromolecular matrix.

The attachment of soluble, homogeneous catalysts to polymer supports has been the subject of considerable recent research activity. When compared with their counterparts, the catalytic process of the polymer supports was found to depend on the bead & pore size, catalyst distribution, number and structure of pores, concentration and kind of attached ligands, degree of cross linking, swelling properties of the polymer and solvent and the changes in the rate and product distribution.

In a polymer-metal complex, the insoluble polymer support provides a specific catalytic site and acts as an effective matrix for the formation of active centers, which is entirely different from the corresponding monomeric analogue.

The catalytic cycle of a metal complex-catalyzed reaction can be schematically represented in scheme 1.10

![Scheme 1.10 Catalytic cycle of metal complex catalyzed reaction](image)

The substrate coordinates to the metal catalyst producing an intermediate mixed complex in the first step. The substrate then gets activated by the metal ion in the next step. Activated substrate gets dissociated from the intermediate complex and the complex catalyst after completing its function is regenerated to the original
catalyst. The catalytic action of a metal ion depends substantially on the nature of the ligands in the intermediate mixed complex.

There are many advantages of using polymer-metal complexes as catalysts over low molecular weight analogues. Decrease in catalytic efficiency due to aggregation and insolubilisation and catalytic poisoning are the main problems in using the latter whereas in the former case these problems are reduced to much extent due to the rigidity and the protection of catalytic site by the polymer matrix. Thus the polymer-supported catalyst has the advantage of maintaining its catalytic activity over a wide range of concentrations, selectivity of which arises from the steric hindrance and the chemical environment of the polymer matrix\textsuperscript{96}.

In 1960, polymer anchored catalysts were developed for hydrogenation and hydroformylation reactions\textsuperscript{97}. Collmann and co-workers were the first to point out the commercial advantages of polymer-anchored catalysts\textsuperscript{98}. Polymer-supported catalysts have utilized anion exchange\textsuperscript{99}, cation exchange\textsuperscript{100}, and chelating ion exchange resins\textsuperscript{101}, the majority being macroporous polystyrene-based resin.

Transition metal polymer catalysts have been studied in hydrogenation, hydroformylation and hydrosilation reactions\textsuperscript{102, 103}.

1.7.1.1 Decomposition of hydrogen peroxide:

The decomposition of hydrogen peroxide is often employed as a standard reaction to determine the catalytic activity of a metal complex\textsuperscript{104}. Even though, many metal complexes are known to have catalytic activity in the decomposition of hydrogen peroxide, reports on the use of polymer bound complexes towards the reaction are scanty \textsuperscript{105}. The catalytic activity studies of five coordinate polymer bound cobalt (II) Schiff base complexes towards the decomposition of hydrogen peroxide were reported\textsuperscript{106}. 

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The decomposition of hydrogen peroxide has been found to be a suitable model to study the efficiency of polymer-metal catalysts and poly (β-ketone)Cu\textsuperscript{107}, poly (β-keto ester)Cu\textsuperscript{108}, poly (methacrylic acid )Fe\textsuperscript{109}, poly(4-vinyl pyridine)Cu\textsuperscript{110} are a few examples of this category.

1.7.1.2 Epoxidation of alkenes:

The development of viable, polymer-supported catalysts for laboratory and industrial oxidation reactions has received scientific interest\textsuperscript{111}. An important example of such a process is the industrial manufacture of propylene oxide, which is carried out by the liquid–phase epoxidation of propylene with an alkyl hydroperoxide as oxygen source, catalysed by a homogeneous Mo (VI)\textsuperscript{112} or a heterogeneous titanium/silica catalyst\textsuperscript{113}.

By preparing of the salen complex using the stepwise methodology, the sites for reaction must be readily accessible by the organic building blocks that produce the ligand. Because of this requirement, these surface sites should also be accessible to the metal being loaded, as well as the olefins and oxidant involved in the epoxidation reactions. This degree of accessibility is particularly important for enantioselective catalysts, such as the salen complex, as the approach paths to the metal center are vital in establishing stereoselectivity\textsuperscript{114}. The accessibility should also yield a higher percentage of reactive centers for catalysis than do immobilization strategies based on copolymerization using reactive monomers of the salen complex. Therefore the ability to control the asymmetry of the catalyst and the placement of substituents by the solid–phase route allow a greater ability to modify the electronic and steric properties of the chiral catalyst and allow examination of their on the reactivity and selectivity of this catalyst class\textsuperscript{115}. This ability may offer the potential to examine the mechanism of oxygen transfer from the catalyst to olefin, particularly the approach path of the olefins to the coordinated metal center.
Therefore, this systematic approach also provides a versatile method for immobilizing complexes that are not easily produced by homogeneous methods.

Catalytic enantioselective epoxidation of unfunctionalized olefins is an appealing strategy for the synthesis of important optically organic compounds. Amongst various catalysts developed for this purpose, chiral metalloporphyrins and chiral Mn (III)-Schiff base (salen) complexes are noteworthy.

Chiral Mn (III) salen complexes are particularly interesting because unlike porphyrin systems, they can be synthesized more expeditiously and are amenable to structural tuning.

The first report of the design of a polymeric asymmetric metal complex for the use as a recyclable catalyst for enantioselective epoxidation of unfunctionalized olefins was reported by De et al. They reported the application of cross-linked polymer bound manganese Schiff base (Fig 1.11) for the catalytic epoxidation of olefins with iodosyl benzene as the terminal oxidant.

The rates of epoxidation using these polymeric catalysts were found to be relatively slow compared to that of the corresponding homogeneous system.
To enhance the usefulness of this class of chiral catalysts by making them recyclable retaining the catalytic activity, modified polymeric analogs of the same system were reported latter\textsuperscript{121} (Fig 1.12)

![Fig 1.12](image1.png)

A group of supported Mo (IV) epoxidation catalysts in which imidazole containing polymers (Fig 1.13) have been used as supports were reported by Miller \textit{et al.}\textsuperscript{122}. Such polymers containing the imidazole group were particularly active and unlike the other species, did not require preactivation to induce high activity, and they appear to be monometallic species whereas the other polymeric ligands yield oxybridge bimetallic species.

![Fig 1.13(a)](image2.png) ![Fig 1.13(b)](image3.png)

Du \textit{et al.} synthesized new linear polymeric Mn (III) Schiff base complexes (Fig 1.14) in different molar ratios of polystyrene and under homogeneous condition, used as a catalyst in acetonitrile for selective epoxidation of unfunctionalized olefins at room temperature with iodosyl benzene as the terminal oxidant\textsuperscript{123}. The results show that the efficacy of
epoxidation using the polymeric catalysts was comparable with the monomolecular analogs.

Angelino et al. constructed covalently attached salen manganese complexes within the DVB-cross linked polystyrene support (Fig 1.15) for use in the asymmetric epoxidation of olefins. With this system the asymmetric catalytic epoxidation of 1,2-dihydronaphthalene, styrene and cis-β-methyl styrene proceeded with moderate enantioselectivities.

Cross linked polystyrene supported Schiff base complexes (Fig 1.16) of various transition metal ions were found to be very effective as heterogeneous catalysts and the catalytic activity was found to be low at low cross-link density.
Reger et al. reported the most effective (salen) Mn asymmetric epoxidation catalysts (Fig 1.17) that have been attached to gel-type resin, to date, which may have practical applications in high-throughput organic chemistry\textsuperscript{126}. The extent to which any effective polymer-bound catalysts can be recycled for repeated use and a comparison between soluble and insoluble matrices to determine the influence of nature of cross-linking on reactivity was carried out.

Soluble polymer-supported ruthenium porphyrin catalysts exhibiting high reactivity, selectivity and stability in epoxidation were reported by Zhang et al.\textsuperscript{127}.

1.8 SCOPe AND OBJECTIVES:

Polymer supported metal complexes find unlimited applications in metal ion separation, preconcentration and recovery of trace metal ions, water and waste water treatment, pollution control, catalysis and polymer drug grafts.
Owing to the manifestation of novel structural features, unusual magnetic properties and the relevance to biological processes, the study of coordination compounds of polymer based heterocyclic compounds is getting increased interest. The main objective of our work was to prepare polymeric isoxazole and pyrazole ligands with good complexing and catalytic activity.

Very often, under the adopted reaction conditions, an undesirable drop of yield accompanies catalysts with active sites directly bound to chiral groups. Thus there is a need for the synthesis of catalysts with active sites far apart from the chiral centers that is, chiral groups assembled in a chemically stable macromolecular backbone.

Keeping this in mind, an effort has been made to synthesize, characterize and to study the catalytic activity of DVB and EGDMA cross linked polystyrene supported isoxazoles and pyrazoles by introducing a spacer group in between the polymer backbone and the ligand functionality. The complexation and catalytic activity efficiency of the ligand on increasing the chain length in addition to various other factors were studied. The details of the work have been presented in four chapters:

Chapter 2- synthesis, functionalization, complexation and characterization of DVB and EGDMA cross-linked polystyrene supported isoxazoles.

Chapter 3- synthesis, functionalization, complexation and characterization of DVB and EGDMA cross-linked polystyrene supported pyrazoles.

Chapter 4 - catalytic studies of isoxazole and pyrazole complexes in hydrogen peroxide decomposition and epoxidation reaction.

Chapter 5- Summary and conclusion.
1.9 REFERENCES:


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