CHAPTER I
INTRODUCTION

1.1 POLYMERIC REAGENTS

The idea of using functionalized polymers as carriers for effecting various organic and inorganic synthetic transformations continues to be an active field of investigation ever since the introduction of solid phase synthesis of peptides by R. B. Merrifield in 1963.1,2

The successful use of functional polymers as carriers for attaching synthons by Merrifield, tempted researchers to consider polymers as organic molecules. Since then, polymer chemistry entered into different branches of chemistry so that polymers and polymer bound materials were extensively used as oxidizing agents, reducing agents, catalysts, photosensitizers, ion exchange resins and agriculturally and pharmacologically active agents.3

The chemistry and applications of these functionalized 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 inter dependence of the polymer microstructure and reactivity of functional groups in functionalized polymers dictate the applications of such systems in a number of areas of functional and technological interest.
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The study of the complexation behaviour of polymeric ligands has received increased interest in the various branches of chemistry, chemical technology and biology. Polymeric ligands can be obtained by the polymerization of monomers containing coordinating groups or by the introduction of low molecular weight ligands by polymer analogous reactions. In a polymer metal complex, a complex with a specific structure results since the metal ion is surrounded by a structured polymer chain. The suitability of a polymeric ligand in metal ion separation depends on the nature and structure of the chelating group, kind of metal ion to be separated, molecular architecture of the polymer support and the conditions of complexation.

1.2 POLYMER SUPPORTS

A considerable number of polymeric and inorganic materials have been investigated as support matrices. While many of these are conveniently available from commercial sources, others lend themselves readily to synthesize in the laboratory. Linear and cross linked organic macromolecular species have found wide application in more recent years, the latter in particular being experimentally very attractive because of their ease of filtration and purification. There have also been some attempts to reproduce the elegant synthesis of structurally well defined, polymer supported reagents employing various inorganic supports.
1.2.1 Synthesis of Linear Polymers

Synthetic linear macromolecules fall into two groups, those formed by polycondensation and those made by addition polymerization.

Polycondensation involves the repetition of a simple condensation process to form a long chain species. Very often these are acid catalyzed processes, although the condensation of acid chlorides or isocyanates with amines or alcohols proceed without the aid of catalyst. The mechanism of each reaction step is usually the same as in simple monomeric systems and chain propagations can occur at both ends of these growing macromolecule.

Addition polymerization takes place, in contrast, by a single chain reaction propagated by a reactive intermediate.

\[
\begin{align*}
\text{nCH}_2 & \longrightarrow \text{CH}_2 \text{CH} \text{CH}_2 \text{CH} \ldots \text{CH}_2 \text{R} \\
\text{R} & \\
\text{CH}_2 \text{R} & \longrightarrow \text{R} \text{CH} \text{CH}_2 \text{CH} \ldots \text{CH}_2 \text{R} \\
\text{R} & \\
\text{n} & \\
\text{n} \left( \text{CH}_2 \right)_{m} & \longrightarrow \left[ \left( \text{CH}_2 \right)_{m} \text{X} \right]_{n}
\end{align*}
\]
1.2.2 Preparation of Functionalized Supports

A required functional group can be introduced on to a support in two ways. It can either be incorporated during the synthesis of the support itself or by chemical modification of a non-functionalized polymer support matrix. The introduction of a functional group during polymerization requires an appropriately substituted monomer. A wide variety of vinyl derivative molecules can be obtained from commercial sources and can be polymerized or copolymerized to produce an appropriately functionalized support. One potentially very useful monomer is 4-chloromethyl styrene, which is reported to be made via, direct chloromethylation of either 2-phenyl ethyl bromide\textsuperscript{10} or ethyl benzene\textsuperscript{11} as shown in schemes 1 and 2. The product in each case, however, is a mixture of chloromethyl isomers and overall yields are also low. More satisfactory methods have been developed recently\textsuperscript{12,13} and yield specially the para isomer (Schemes 3 and 4).

![Scheme 1](image)

**Scheme 1**
Scheme 2

Scheme 3
1.2.3 Characterization of Functionalized Supports

The adequate characterization of chemical changes carried out on supports is a major problem associated with 'supported chemistry'. The two most powerful techniques of analysis that are readily applicable are elemental microanalysis and infrared absorption spectroscopy. The former is a much used technique and carbon, hydrogen, halogen, nitrogen, sulphur and phosphorous analysis have been performed widely and routinely.

1.2.4 Interesting Features of Polymer Supported Reagents

Easy separation of the polymer supported species from other species present in the reaction mixture results in the following
advantages. The separation is particularly easy when cross linked polymers is used as it then merely involves filtration.

(1) Excess and spent reagent can easily be removed from the final reaction mixture, there by simplifying the work up.

(2) If higher reaction yields can be achieved by using an excess of reagent, then an excess reagent can be used without causing separation problems.

(3) Easy recovery of the polymer may make it possible to regenerate and reuse the reagent. This is very important from an economic point of view because polymer supported reagents will generally be more expensive than the analogous non supported reagents. If the reagent can be recycled many times it becomes very similar to a catalyst and it is then worthwhile to prepare complex reagents, which for example, might be used to achieve asymmetric synthesis.

(4) It may be possible to use and to regenerate the reagent using a column of the polymer, rather like ion exchange resins are used.

(5) In favourable cases, the reaction work up will just involve filtration of the polymer from the products in solution. In such circumstances the work up could be automated.

Other advantage comes from the insolubility and involatility of the polymer. Thus, polymer supported reagents are non toxic and odourless. These are important considerations from an environmental point of view.
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Finally, the microenvironment within the vicinity of the polymer chains may differ from that of the corresponding reaction in solution, and that this may lead to interesting rate and specificity effects. One possibility is the microenvironment near the polymer chains is a more favourable medium for the reaction. Another is that the difference in polarity between the polymer and the reaction solvent might cause the substrate to concentrate within the polymer, thereby causing an increase in reaction rate.

1.3 POLYMER METAL COMPLEXES

A polymer metal complex is composed of a synthetic polymer and metal ion. Its synthesis represents an attempt to give an organic polymer with inorganic functions. The ability of a polymer supported ligand to form complexes depends on the nature of the main chain. The matrix effect on ion binding is clearly evident when low molecular ligands and their polymeric analogues are compared as in the case of an iminodiacetic acid ligand supported on polystyrene and polyacrylamide. With increasing polarity of the support, the extent of complexation increases. The metal intakes by polymeric ligands are varied by the incorporation of the cross linking agents which differ in their polarity and flexibility. The replacement of the rigid and hydrophobic DVB cross linking by a flexible and hydrophilic cross linking agents results in increased metal ion intake.
A wide variety of investigations have been carried out on polymeric metal complexes, which include studies of semiconductivity, thermostability, redox reactions, collection of metal ions, biomedical effects and so on. The polymeric metal complexes are classified into the following groups.

Polymer metal complexes, represented by schemes 5 to 9, are defined as complexes composed of a polymer ligand and metal ions in which the metal ions are attached to the polymer ligand by a coordinate bond. Here a polymer ligand is understood to be a polymeric substance that contains coordinating groups or atoms (mainly N, O and S) obtained by polymerization of monomers containing coordinating sites, or by the chemical reaction between a polymer and a low molecular weight compound having coordinating ability. Typical polymer ligands previously reported are listed in Table 1. When a polymer ligand is mixed directly with a metal ion, which generally has four or six coordinating bonding hands, a polymer metal complex is formed. This may be of the intra polymer chelate type (Scheme 5) or of the inter-polymer chelate type (Scheme 6). Complex formation proceeds via scheme 7, where the polymer backbone either contains multi dentate ligands, such as the imino diacetic acid group, or acts as a carrier for low molecular weight multi dentate ligands. Many of the so called chelating resins fit in this scheme. The polymer metal complexes represented by schemes 5 to 7 have chelating structures in their polymer ligands and are
therefore called polymer chelates. The pendant type polymer metal complex (Scheme 8) is formed by the reaction of a polymer ligand with a stable metal complex, the central metal ion of which has already been masked with low molecular weight ligands except for one coordinate site that remains vacant as in metalloporphyrins, cobaltic chelates etc. A polymer metal complex is also obtained by polymerizing a monomeric metal complex (Scheme 9).

Scheme 10 represents coordinate polymers. A low molecular weight compound with multidentate groups on both ends of the molecule grows into a linear polymer with metal ions, and the polymer chain is composed of coordinate binds. The parquet like polymer complexes, poly (metal-phthalocyanine) and poly (metal-tetracyano ethylene), are classified into scheme 11. They are formed by inserting metal ions into planar-net work polymers or by causing a low molecular weight ligand derivative to react with a metal salt and a condensation reagent.

The coordination structure of the derived polymer metal complexes also depends on the molecular character and extent of cross linking in the polymer support16,17. The kinetics of metal ion complexation, the adsorption of metal ions and the interaction between the complexed/adsorbed species are also decided by the rigidity of the cross linking agents.18 The thermal decomposition behaviour of the polymer-metal complexes decreases with increasing rigidity of the cross linking agents.19,20 This is because of the
increased strain at the cross linking points. The thermal stabilities of the same metal complex with varying extent of cross link also depend on the extent of cross linking in the polymer support.

(A) Polymer-metal complexes

Scheme 5

(B) Coordinate polymers

Scheme 6

Scheme 7
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Scheme 8

Scheme 9

Scheme 10

(C) Poly(metal-phthalocyanine) type

Scheme 11

L=Coordinating atom or group; M=Metal ion
1.4 POLYMER SUPPORTED LIGANDS AS REAGENTS FOR METAL ION REMOVAL

Polymer supported metal complexes have wide range of applications. Organic synthesis using functional polymers, design of polymeric reagents, 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, conductive polymers, polymeric surfactants, stabilizers, polymeric liquid crystals and ion selective electrodes are some of the important fields where the chemistry of functionalized polymers bear relevance.

Polymer supported metal possess enough flexibility to permit interaction of polymer bound anchoring groups with the metal complex. The practical advantages of attaching insoluble supports are recognized and industrially exploited. High selectivity of chelating sorbents together with advantageous sorption kinetics enable the extraction of trace metals from their complex solutions. They are also used for the separation of metal ions by ion exchange chromatography. The rapid development of functionalized polymers with chelating properties has been due to their inherent advantages over simple ion exchange resins. These advantages include higher metal to polymer bond energies and slower reaction processes between the metal and the polymeric ligand. In addition, the
formation of polymeric chelates with vacant coordination sites on the polymeric ligand has led to the concept of selective separation by ligand exchangers based on the relative magnitudes of the stability constants of the ligand metal systems.

Many methods have been used for controlling pollutants in industrial effluents. Polymer complexes are effective for the removal of toxic metals like Hg(II), Cd(II), Pb(II) and As(III) even in microgram level and find promising applications in applied analysis. Polymeric ligands prepared by condensing formaldehyde with alicyclic or resocyclic acid have been used as selective ion exchange reagent for the extraction of uranyl ion from solution. Attachment of multi dentate ligands to insoluble polymeric supports is a technique commonly utilized for the preparation of selective ion exchange resins, which are capable of separation, and purification of metal ions.

Among the various ligands, amines, dithiocarbamates, iminodiacetic acid, schiff bases and amidoximes are widely used for the collection of heavy metal ions. The specific binding of metal ion by metal ion template cross linked polymers have been reported. If the coordination stereo structure of a polymer metal complex is not destroyed, that polymer will preferentially complex the metal ion which was initially present. In addition to chelating polymers, polymers attached to macrocyclic ethers have been shown to complex metal ions. Recently, three different types of polymeric
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ethers, crown ethers, cryptands and podands have been introduced as new classes of neutral ligands to replace the conventional ion exchangers. The ion chelating properties of these neutral ligands have led to their selective application in extraction or separation of trace metals, isotopes and organic solutes.\textsuperscript{39,40}

Cross linked polystyrene beads carrying aminomethyl phosphonic acid group\textsuperscript{41,42} (i.e., Duolite ES 467) and iminodiacetic acid groups\textsuperscript{43} (i.e., Chelex100) have been demonstrated to be efficient in the removal of trace quantities of metal ions. Due to chelating effects, these are superior to the common ion exchange resins.

Amine ligating polymers react with metal ions and counter anions of the metal cations to form other sphere complexes, and the overall process of complexation is sorption of the metal ions together with their counter anions.\textsuperscript{44}

Chlorosulfonated styrene-DVB (10\%) resin beads were interacted with excess of ethylene diamine to give the corresponding sulfonamide derivative. Upon treatment with 20\% excess of potassium chloroacetate, the amine functional groups on the polymer were carboxymethylated quantitatively. The resulting chelating polymer is an extremely powerful sorbent for Ca(II) and Mg(II) ions.\textsuperscript{45} The cross linked polymer has an EDTA like structure and so, is expected to show strong complexation for transition metal ions.
The multi dentate ligand, imino diacetic acid (IDA) and ethylene diamine tetra acetic acid (EDTA) are known to form extremely stable complexes with Ga(III)\textsuperscript{46} and In(III).\textsuperscript{47} Hence, the chelating resins with these types of functional groups seem promising for the recovery of the metal ions from the leaching solutions.

Phosphates and chromates are selectively removed from contaminated water by a new class of sorbent, referred to as a polymeric ligand exchanger (PLE)\textsuperscript{48}. The exchanger bed comprising a styrene-divinyl benzene or poly methacrylate matrix having an electrically neutral chelating functional group with nitrogen or oxygen donor atoms, and a Lewis acid type metal cation, such as Cu, bonded to the chelating functional group in a manner that the positive charges of the metal cation are not neutralized. PLEs are very selective towards phosphates and chromates, chemically stable and amenable to efficient regeneration.

Thus polymeric complexes can be used for the metal ion removal study. Heavy metal ions such as Cu(II), Hg(II), Fe(III), Fe(II), Cr(III), Ni(II), U(IV), etc. can be removed using polymer supported reagents.
1.5 POLYMER SUPPORTED REAGENTS AS ION SELECTIVE ELECTRODE MATERIALS

The need of selective determination of heavy metal ions has increased immensely during last few decades due to growing environmental problems. The ion selective electrodes prepared with suitable polymers are potentially useful to determine the various metal ions in solution. The styrene co-acrylonitrile copolymer (SAN) based electrode has shown an outstanding sensitivity and selectivity for the estimation of copper ions in comparison to the reported ion-selective electrodes. Among the reported electrodes for Cd(II) ions, the cadmium electrode prepared with 3,6-dioxano octane dithiamide has shown a better selectivity over alkali and alkaline earth metal ions but gets poisoned by Cu(II), Pd(II), Pt(II), Ag(I) and Hg(II) ions. The lipophilic 2,2-bipyridine carrier supported PVC based electrode has shown interesting selectivity for Cd(II) over Co(II) and Ni(II) ions. Electrode prepared with styrene acrylonitrile polymer has shown a substantial reduction in anion interference due to highly polar cyano group in the polymer chain, which requires a very small quantity of the anion excluder such as sodium tetraphenyl borate. The cyano copolymer based cadmium ion selective electrodes have better selectivity for Cd(II) ions in the presence of alkali and alkaline earth metal ions.

A novel plastic poly(vinyl chloride) membrane electrode based on pethidine-phosphotungstate ion association as electro active
material for the determination of pethidine hydrochloride in injections and tablets has been developed.\textsuperscript{56} Also a PVC based capric acid membrane electrode for Pb(II) ion has been developed.\textsuperscript{57}

1.6 A BRIEF ACCOUNT OF POLYMER SUPPORTED LIGANDS/COMPLEXES

A close examination of the literature reveals that a number of attempts are reported on the synthesis, characterization and application studies of polymeric ligands/complexes. An account of the selected reports is given as a brief review.

H. A. Goodwin \textit{et. al.} reported some coordination compounds derived from the polymeric schiff base produced by the condensation of triethylene tetramine with 5,5'-methylene bis(salicylaldehyde) and 5,5'-sulfonyl bis(salicylaldehyde) containing sexadentate units, during 1960s.\textsuperscript{58}

The synthesis and thermal stability of bis(8-hydroxy quinoline) schiff base coordination polymers\textsuperscript{59} and that of some ferrocene containing polyazines and polymeric schiff bases\textsuperscript{60} are also reported. Organolithium reagent has been reported for the synthesis of polyfluoro phenyl Co(II) schiff base complexes.\textsuperscript{61}

Polymeric reagents obtained by alkylation of Merrifield resins with diethyl malonate malononitrile or acetyl acetone were reduced by LiAlH\textsubscript{4} to the corresponding 1,3-diamine or diol. The diamine serves as a starting material for condensation reactions leading to
polymeric schiff bases. These materials are potential ligands for transition metals like Cu(II) and Co(II). There is also a report on the use of polymeric schiff base chromium complexes as stationary phases in adsorption gas chromatography to separate the spin isomers of hydrogen and deuterium (but not of a mixture of both isotopes) at ambient temperature with an extremely short retention time. Only paramagnetic complexes having a pseudo-tetrahedral structure were formed on treating ethylene dimethacrylate-glycidyl methacrylate copolymer with H₂NCH₂CH₂NH₂, salicylaldehyde and cobalt or nickel acetate. The effects of the polymer matrix and of the immobility of the bonded schiff bases on the distortion of the coordination sphere of the central ion are discussed. Polycondensation reactions of 5,5'-methylene bis(salicylaldehyde) with alkylenediamines yield polymeric aromatic schiff bases which behave as strong complexing agents towards toxic metals.

Covalently bound polymeric cobalt chelates from divinylsalenes and their dioxygen binding and catalytic activity was studied by Woehrle D. et al. Polymeric coordination compounds with electronic semiconducting properties and biological activity are prepared by treating metal salts with polydentate ligands obtained by condensation of aromatic dialdehydes with \( \beta \)-hydroxy-\( \alpha \), \( \gamma \)-diamines. Template synthesis of a polymer schiff base Co(II) complex and formation of a specific cavity for chiral amino acid was reported by Fuji Yuki et al. The efficiency of polymeric schiff base
complexes as solid phases for the chromatographic separation of low molecular weight gases was tested. Woehrle et. al, synthesized some polymeric Schiff base chelates which are used as the effective heterogeneous catalyst for the valence isomerization of quadricyclane to norbornadiene.

Three types of the novel polymer ligands in which 6,8,15,17-tetramethyl-dibenzo-5,9,14,18-tetraaza-cyclo-tetradecene was present in an integral part of the polymer back bone were prepared. Among the polymer ligands, one which contained a triethylene glycol bis (p-phenylene) group as a linkage group was an excellent extractant for Cu(II).

Polymer bound 2,2'-dipyridylamine has been prepared. Like naphthyridine and bipyridine, this ligand can be easily bound to the polymer support. Studies on these complexes revealed that polymer bound dipyridylamine ligand has an important application in quantitative and qualitative removal of metal ions like Fe$^{3+}$ in organic media.

A review with seven references on the ESR study of the dissociation and ligation of polymeric Cu(II) and VO(II) complexes was reported by Jezierska Julia et. al. Perm selective thin membranes useful for separation of gas mixtures were prepared from polymer bound Schiff base complexes. Synthesis, characterization and catalytic properties of mono nuclear and dinuclear complexes of UO$_2$(II), Cu(II) and Ni(II) with
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Compartmental schiff bases derived from 2,6-diformyl-4-chlorophenol and polyamines was reported by Guerriero et. al. Coordination structure and magnetic property of poly(pyridylenemethylidene )nitriloirons was studied by Nishide et. al. The counter anion species and spacer length of the polymers affected the coordination structure and magnetism.

Deodrant polymers containing schiff base metal complexes was reported by Osawa Yasuko et. al. Osaka Gas Co. Ltd prepared magnetic iron-schiff base polymer chelate compounds. Synthesis and characterization of new polymer supported chelating resins obtained by the condensation of cross linked chloromethylated polystyrene with schiff bases from salicylaldehyde-4-amino-3-hydroxy naphthalene-1-sulfonic acid, salicylaldehyde-anthranilic acid, 3-formyl salicylic acid-o-aminophenol, 3-formyl salicylic acid-o-hydroxy benzyamine were reported. Synthesis and characterization of new redox polymers based on copper containing units and evidence for the participation of copper in the electron transfer mechanism was reported by Audebert et. al. Study of metalloorganic schiff base polymers showing anomalous magnetic behaviour was conducted by Garcia Joaquin et. al.

A room temperature organic ferro magnet of schiff base polymer synthesized by reacting 2,6-pyridine dicarboxaldehyde-hexamethylene diamine copolymer with Fe(II) sulfate was reported. A partially oxidized copper complex of bis (salicylidine)
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Ethylenediamine which possess conductivity and electro chromic properties is reported. Different hydroxy-functionalized polyazomethines have been modified by complexation using paramagnetic Cu(II) ions. Coordination polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with poly schiff base derived from 5,5’-methylenecis(3-nitrosalicylaldehyde) and 1,3-diaminopropane have been synthesized and characterized. The electronic properties of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) polychelates of 4,4’-dihydroxy-3,3’-diacetyl-biphenyl-butanedione dihydrazone (DDBBD) and 4,4’-dihydroxy-3,3’-diacetyl biphenyl mercapto diaminotriazine (DDBMT) have been studied in their pellet form. There is also another patent on polyazomethine complexes and method for making optical devices and other materials there with.

Synthesis and characterization of polymer supported Cu(II), Ni(II), Fe(III), Zn(II), Cd(II), Zn(IV), Mo(V and VI) and U(VI) complexes of polystyrene supported schiff base derived from 3-formylsalicylic acid and o-aminophenol have been reported. New poly chelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) were synthesized from schiff base derived from 4, 4’-dihydroxy-3, 3’-diacetyl-biphenyl and 1,5-diamino naphthalene and were characterized. New compartmental macroacyclic and macrocyclic schiff bases were prepared by reaction of the formyl precursors 2,3-dihydroxybenzaldehyde, 3-methoxy-2- hydroxybenzaldehyde and 2,6-diformyl-4-chlorophenol with 1,2-diaminoethane, 1,3-
diaminopropane and the polyethylene oxydiamines $\text{H}_2\text{N}(\text{CH}_2)_2\text{[O(CH}_2\text{)]_n}\text{NH}_2$ ($n = 1,2,3$) in the presence of a templating ion. In these ligands the shape of one or both compartments has progressively been enlarged and the denticity increased to link up to four metal ions into the coordination moiety. These ligands react with Cu(II), Ni(II) or lanthanide(III) salts to form mono nuclear, homo and hetero trinuclear or homo tetranuclear complexes.

Two types of poly(azomethines) containing repeating pairs of a tri-dentate ligand and an oligo-dimethylsiloxane in the backbone were synthesized and complexed with cobalt ion. The resulting polymer complex membranes showed good oxygen perm selectivity at 1 atm pressure difference. The complexes function as oxygen carrier. Four new schiff base polymers and their Cu(II) and Ni(II) chelates were prepared and characterized. An attempt was done to develop and characterize new air separation membrane materials based upon polymers with tetradeionate schiff base. Two new conjugated poly schiff bases ($\text{PP}_P\text{P}$ and $\text{PP}_M\text{P}$) were synthesized by polycondensation of p-phenylene diamine or m-phenylene diamine with 2,6-pyridine dicarboxaldehyde.

Coordination polymers of Co(II), Ni(II), Cu(II), Mn(II) and Zn(II) with poly schiff base derived from 5,5'-methylene bis(3-nitro salicylaldehyde) and 1,4-diamino butane were prepared and characterized. EPR parameters and polarized light micrographs of three polyazomethines bearing OH groups and containing the
paramagnetic centres Cu(II), VO(II) or Fe(III) were reported. Mesogenic and thermal properties were studied and discussed with respect to metal complexation.

A new hydroxy functionalized liquid crystalline polyazomethine has been synthesized by solution polycondensation of a dialdehyde and a diamine. Studies on the liquid crystal properties reveal its nematic mesomorphic behaviour. Poly schiff bases incorporating dicyano vinyl groups in the main chain were prepared by the solution polymerization of p-bis[1-(4-formylphenoxy)-2, 2-dicyanovinyl] benzene (I) and terephthaldehyde (TA) with 4-aminophenyylether (ODA). A magnetically active organometallic iron-schiff base polymer, was synthesized by polymerizing 2,6-diacetyl pyridine with diamino hexane, followed by treatment of the obtained polyazomethine with FeSO₄.

Patel et. al. synthesized and characterized chelate polymers of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with a schiff base of 5, 5-methylene-bis(3,3'-dinitrosalicylaldehyde) with 1,6-hexanediame. There is also a report on the application of polyazomethines in organic electroluminescence devices. Polychelates of Mn(II), Fe(II), Co(II), Ni(II) and Cu(II) with schiff base copolymer derived from 4,4'-dihydroxy-3,3'-diacetylbbiphenyl and 2,3-butanedionedihydrazone have been prepared by Aswar et. al. Cross linked polymeric materials have been synthesized by Cu(II) complexation of a semiflexible main-chain liquid crystalline polyazomethine.
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Coordination polymers of Cu(II), Ni(II) and Zn(II) containing schiff base derived from terephthaldehyde and thiocarbohydrazide were synthesized and characterized by Zabin Sami et al.\textsuperscript{104} A number of semiflexible liquid crystalline polyazomethines were synthesized by condensation of dialdehyde monomers (1,10-bis[(4-formyl-3-hydroxyphenyl)oxy]decane or 1,10-bis[(4-formyl-phenyl)-oxy]decane) with diamines (2-methyl-1,4-phenylenediamine or 3,3'-dimethoxybenzidines).\textsuperscript{105} Twelve new poly(etherazomethines) with linear structures were prepared by a conventional procedure by reacting six different diamines with two different bisaldehydes containing ether linkages in the back bone.\textsuperscript{106} Polynuclear manganese complexes of 2,5-dihydroxyterephthaldehyde(dhterH\textsubscript{2}) and its schiff base polymer ligand (PdhterenH\textsubscript{2}), [MnII(dhter)]\textsubscript{n}, [MnIIIn (Pdhteren)] and [MnIIIn (Pdhteren) (OAC)\textsubscript{n}] were synthesized and characterized.\textsuperscript{107} Catalytic epoxidation of olefins with hydrogen peroxide was studied using the above manganese complexes under heterogenized homogeneous reaction conditions in the presence of a base. A polymer bound schiff base manganese complex prepared from polystyrene bound salicylaldehyde and phenylalanine is found to be a good catalyst for the oxidation of cyclohexene, linear aliphatic olefins and styrene by oxygen.\textsuperscript{108} A styrene-divinylbenzene copolymer with (5\% and 15\% cross linking) containing palladium (II) diaminopropane complexes were found to be active catalyst for hydrogenation.\textsuperscript{109} A schiff base activated glycine supported on a soluble polymer(poly(ethylene glycol) was readily alkylated with a
wide variety of electrophiles in the presence of a carbonate base in acetonitrile. The presence of the polymer provided a phase transfer catalysis environment which accelerated the reaction.

Electro oxidative polymerization of schiff base of 1,8-diaminonaphthalene and 3-acetylthiophene. The electrodes so obtained were stable chemically and electrochemically both in aqueous solutions and in mixtures containing methanol, making them excellent candidate for sensing and/or electrocatalytic applications. The preparation and electrochemical characteristics of electrodes modified by cobalt complexes of N, N'-bis(salicylidene)-ethane-1,2-diamine were described. A cobalt salen polymer film modified electrode has strong electrocatalytic effects for the oxidation of ascorbic acid.

New metal containing epoxy polymers were prepared from diglycidyl ether of bisphenol A and tetradentate schiff base metal complexes. A novel poly schiff base sulphide polymer was synthesized by nucleophilic displacement polymerization of N, N'-bis(p-chlorobenzyldiene)4,4'-diaminodiphenyl ether with sodium sulphide in anhydrous condition. There is also a report on the synthesis and properties of polymeric schiff bases of the antibiotic spiramycin.

Polychelates of 4, 4'-bis(N-phenylsalicylaldimine-5) azobiphenyl with some transition metal ions were studied by Aswale et al. Interaction of local anaesthetic drug richlocain with linear polyacrylic
acid and cross linked sodium polyacrylate, linear and cross linked acrylic acid schiff base copolymers has been investigated.\textsuperscript{117} Similarly manganese bis (salicylidenediaminopropane) thiocyanato dimer polymer has been synthesized and its structure and magnetic properties were studied.\textsuperscript{118} Catalytic epoxidation of olefins with molecular oxygen was studied in the presence of a sacrificial aldehyde using polynuclear manganese complexes of ligands, 2,5-dihydroxyterephthalaldehyde and its schiff bases.\textsuperscript{119} The Mn(II) schiff base complex with nitrogen coordinating environment is found to be more stable and effective epoxidation catalyst than the oxygen bound complex.

In order to investigate the selective antiproliferative effects shown by 2-(6-hydroxynaphthyl)-b-D-xylopyranoside, the fourteen possible D-xylopyranosidic compounds were synthesized on solid support.\textsuperscript{120} An amino methylated polystyrene resin was converted into an acid chloride resin and then esterified using dihydroxynaphthalene. The free hydroxy group was then xylosylated under BF\textsubscript{3} x OEt\textsubscript{2} mediated conditions. The xyloside was deprotected and simultaneously cleaved off the resin using NaOMe/MeOH. Final purification using reverse phase HPLC gave the pure xylosides in 6–42 \% yield with virtually no formation of a xyloside. Cross linking of diglycidyl ether of bisphenol A (DGEBA) with tetradentate and hexadentate schiff base metal complexes of transition metals and maleic anhydride (MA) was investigated.\textsuperscript{121} The cross linking reaction is proposed to proceed through a complex mechanism.
A schiff base complex of Zn(II) as a neutral carrier for highly selective PVC membrane sensors for the sulfate ion was developed. Novel polymeric membrane (PME) and coated graphite (CGE) sulfate-selective electrodes based on a recently synthesized schiff base complex of Zn(II) were prepared. The electrodes reveal a Nernstian behaviour over wide $SO_4^{2-}$ ion concentration ranges ($5.0 \times 10^{-5}-1.0 \times 10^{-1}$ mol dm$^{-3}$ for PME and $1.0 \times 10^{-7}-1.0 \times 10^{-1}$ mol dm$^{-3}$ for CGE) and very low detection limits ($2.8 \times 10^{-5}$ mol dm$^{-3}$ for PME and $8.5 \times 10^{-8}$ mol dm$^{-3}$ for CGE). The electrodes were used as an indicator electrode in the potentiometric titration of sulfate and barium ions and in the determination of iron in ferrous sulfate tablets. The electrochemical formation of films of poly [M (salen)] (M = Ni or Pd, $H_2$salen = N,N'-ethylenebis (salicylideneiminine)) and their halo and methoxy derivatives along with their spectroscopic characteristics in the UV and visible spectrum regions were studied. The spectroscopic characteristics of these polymer complexes in oxidized and reduced forms were recorded at wavelengths of 300-900 nm, after depositing the polymer layer on optically transparent electrode. Cyclic voltammograms are discussed for these polymer complexes on platinum in acetonitrile containing tetrabutylammonium perchlorate.

A novel inorganic-organic hybrid membrane for oxygen/nitrogen separation containing a Co(II) schiff base complex as oxygen carrier using poly(N-vinylpyrrolidone) as mediator. A
series of porous silica supported metal Schiff base complexes was prepared and characterized. Thus, treatment of amino functionalized porous silica gave Schiff bases, which were further complexed with metal ions. Catalytic properties for oxidation of olefins in the presence of molecular oxygen were investigated. The major products of the aerobic oxidation without reductant were epoxy compounds. The influence of reaction temperature and additives for epoxidation was studied. The selectivity and the conversion of epoxidation varied with reaction time, different additives and different catalysts. Three polymer-Fe(II) complexes were synthesized from Fe(II) and poly(Schiff base)s. The poly(Schiff base)s were prepared from 2,2'-diamino-4,4'-bithiazole (DABT) with phthalaldehyde, 5,5'-methylene-bis(salicylaldehyde) (MBSA) and terephthalaldehyde, respectively, and characterized by IR, XPS, NMR and ESR spectroscopy. The magnetic behavior of these polymer-Fe(II) complexes was examined as a function of magnetic field strength and temperature (5-300 K), respectively. The hysteresis loops were also studied. Based on these results, several novel ferromagnets were obtained.

A photoacoustic study of the thermal diffusivity of some polymer supported halogenobenzimidazole complexes of Co(II), and Cu(II) was carried out by Raman S. Sankara et al. Synthesis and magnetic properties of a polymeric nitrido-chromium(IV) complex with a tetradeutate Schiff base ligand has been reported by Tsuchimoto Masanobu et al. New complexes derived from
polymeric N-N'-o-phenylene diaminebis(cinnamaldehyde) with Cu(II), Co(II), Ni(II), Zn(II), UO$_2$(II) and Pd(II) were prepared and characterized. A series of new polystyrene-anchored coordination complexes has been synthesised by the reaction of metal complex/metal salt with the chelating resin containing the Schiff base derived from o-hydroxybenzylamine and 3-formylsalicylic acid. Some Schiff base Co(II) chelates like ethylenebis [(2-hydroxy-3-methoxy-5-methylphenyl) methylideneiminato] cobalt (II) were coordinatively anchored onto poly(4-vinylpyridine-co-styrene) in diglyme solution and the dioxygen-affinity of the resulting polymeric complexes were measured in situ. A new bidentate oxygen-nitrogen donor Schiff base supported on polystyrene matrix has been synthesised by the reaction of amino methylated polystyrene and salicylaldehyde. The chelating resin reacts with Ni(II), Co(II), Cu(II), Fe(III), Zn(II), Mo(VI) and U(VI) and were characterized. There is also a paper which is a review of the metal complex forming coordination polymers.

1.7 SCOPE OF THE PRESENT INVESTIGATION

As the application of polymeric complexes is enormous, there exists a continuing interest in the synthesis and characterization of these complexes. The use of polymers as supports for metal complexes has grown tremendously since Merrifield demonstrated the applications of polystyrene resins in peptide synthesis.
Chapter 1

The development of new methods for purification of water from spent process and effluent streams and recovery of valuable metals from industrial waste is of major concern in research field. Also development of ion-selective electrodes is highly important in that they can give very good results in metal analysis, without much interference. In considering these facts the following objectives were listed and completed as part of the present investigation.

1. Synthesis and characterization of polymer supported Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and U(VI) complexes of Schiff bases derived by
   - Condensing amino methylated polystyrene with vanillin.
   - Condensing amino methylated polystyrene with 2-nitro benzaldehyde.
   - Condensing amino methylated polystyrene with veratraldehyde.

2. Metal ion removal studies using
   - Schiff base of amino methylated polystyrene with salicylaldehyde.
   - Schiff base of amino methylated polystyrene with 2-nitro benzaldehyde.
   - Schiff base of amino methylated polystyrene with vanillin.

3. Preparation of chloride ion selective electrode using the Schiff base cobalt complex of the Schiff base of amino methylated polystyrene with salicylaldehyde.

The above mentioned studies have been incorporated in the thesis.