CHAPTER 1

INTRODUCTION

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1.1. Polymer Supports

Polymer supports have been widely used as reagents, substrates and catalysts for many reaction systems. Both organic and inorganic polymer supports are extensively used for carrying out reactions more conveniently at controlled rates. Certain inorganic polymer supports are found to have electrical, optical and thermal properties. Functionalized polymers are highly versatile to open an excellent area of research.

A functionalized polymer contains a functional group that is able to perform a chemical transformation. The chemical activity of the polymer support depends greatly on structural factors and on the chemical nature of the functional group. The polymer support should be porous to allow the access of the reagent and the solvent and it should be with sufficient mechanical, chemical and thermal stability. Polystyrene, PMMA, PVC, PAN, poly acrylic acids, polysulfones, PEG, poly vinyl acetate, cellulose and silica are some among them. Polystyrene cross linked with 1-2% divinyl benzene satisfies the requirement for a good polymer support as reagent and substrate. It is microporous and microreticular. It is highly swollen in solvents like DMF, THF, dichloromethane etc. It allows the access of the reagent and solvent. They are less fragile and require less care in handling, react faster in functionalization and application reactions and they possess higher loading capacities.

Highly cross linked polystyrene provide rigid structures. So they are useful as ion-exchange resins which can be easily removed from a reaction system. A poly ion in the form of a membrane exposed to an electrolyte will allow the counter ion to pass through it and it will retain a barrier to the complementary ion.

The pioneering work on polymer substrate technology in solid phase polypeptide synthesis developed by R. B. Merrifield was one of the greatest achievements. It is very useful in confirming the structure of naturally
occuring bio-macromolecules and it is a source for bio-macromolecules which showed more desirable biological activity. Since then investigations on polymer supports is progressing.

Polymer catalysts are of many advantages. They are less toxic, easy to handle and more resistant to atmospheric contaminants. Further the removal of the catalyst is also very simple. Sulphonated polystyrene, super acids like nafion\(^3\) are also good catalysts. Polymer phase transfer catalysts act as the meeting place for two immiscible reactants.

Polymer supported drugs are of potential advantages when compared with the low molecular weight drug. They can be employed where a sustained and delayed action of drug is required. Immobilized enzymes are prepared of polymeric supports which are found to have increased stability to pH and temperature.

Polymeric photosensitizers are prepared from benzophenone and polystyrene\(^4\). Polymer supported bio-membranes are a promising approach for the development of biosensor devices\(^5\). Ion-exchange membranes are perm selective. Thus polymer supported membranes can be used as ion selective electrodes. The hydrophilicity of moderately ionic polymers leads to another type of membrane application called reverse osmosis.

Now polymer supported reactive chemistry is being developed and exploited at an amazing rate and it seems to join the routine world of synthesis and to become a methodology\(^7\).

1.2. Polymer Supports as Ligands

Polymers are used as efficient complexing agents. The wide variety of ligands include amines, schiff bases, dithiocarbammates, iminodiacetic acid,
amidoximes, thiosemicarbazones etc. for the complexation of metal ions. Recently there observed a growing interest in the use of functionalized polymers for the preparation of metal complexes for various applications. More polar and flexible cross linking agents are found to enhance the metal ion intake of the polymer supported ligand. Thus the extend of complexation depends on the hydrophilicity of the polymer support. DVB cross linked polystyrene supports are insoluble and they can be easily separated from the reaction system and products of high purity are obtained. Highly cross linked resins are more brittle, hard and more impervious. Functional groups in the immediate vicinity of cross links are prone to steric hindrances from chelating with the metal ions. Among the various chelating groups, iminodiacetic acid supported on styrene divinyl benzene matrix forms a large group with N and O as donor atoms.

Polymer support containing 8-hydroxy quinoline units are useful for the complexation of metal ions like Ni$^{2+}$, Co$^{2+}$ and Cu$^{2+}$. Here the complexation is through N and O atoms. The metal can be separated from the polymer by changing the pH. There are polymers containing chiral groups for resolving racemic mixtures into enantiomers where one of the enantiomers is complexed more strongly than the other and thus separation is achieved. Macrocyclic crown ethers like 18-crown-6 and cryptands are useful for binding metal ions because of their high degree of selectivity for specific metal ions.

1.2.1. Functionalization of Polymers

A functionalized polymer can be prepared by different methods. The monomer containing the desired functional group can be polymerized or copolymerized to get a functionalized polymer. Polymerization of p-vinyl benzyl chloride gives chloromethylated polystyrene. Poly[4(5)vinyl imidazole], synthesized by the polymerization of the monomer, is used as a catalyst. A wide range of functionalized polystyrenes are prepared by electrophilic and nucleophilic substitutions with suitable reagents. Chloromethyl and lithio
derivatives are the most useful among them. Lithio derivative of polystyrene can be easily converted to polystyrene containing OH, COOH, B(OH)₂, RSnCl₂ and PΦ₂ groups. Chloromethylated polystyrene on treatment with an amine or ammonia gives amino methylated polystyrene. Amino methylated polystyrene on treatment with chloroacetic acid gives the iminodiacetic acid derivative. Another type of functional polymer is telechelic polymer which contains functional groups such as OH or COOH at each end. They are useful for synthesizing block copolymers by step polymerization.
If a polymer supported ligand possess an ordered structure, the complex formed will also be of definite geometry. Parameters like surface area, apparent density and pore structure of the polymer matrix are found to have profound influence on complexation. The efficiency of complexation also depends on the arrangement of functional groups in the polymer support. The swelling

Polystyrene iminodiacetic acid

1.3. Polymeric Metal Complexes
characteristics of the polymer matrix also depends on the flexibility of the cross linking agent. The kinetics of metal ion complexation, adsorption of metal ions and the interaction between complexed and adsorbed species are also affected by the rigidity of the cross linking agent.

A cross linked polymeric ligand forms a stable metal complex than a linear polymer and it shows definite selectivity for metal ions due to its characteristic structure. But highly cross linked resins are macroporous and macro reticular and the complexes formed from them are unstable. These macroporous structures are found to be efficient ion-exchange resins. Cross linked polystyrene functionalized with quaternary ammonium groups are anion exchange resins and that functionalized with sulphonic, carboxylic, phenolic etc. groups are cation exchange resins.

The iminodiacetic acid supported on polystyrene forms compact 1:1 complexes with copper, iron and other heavy metals and it is highly selective [Chelex 100]. An important application of chelating resins is ligand exchange chromatography. An ion-exchanger containing a complexing metal ion like Cu$^{2+}$ or Ni$^{2+}$ can be used as a solid sorbent. The successful application of ligand exchange depends on keeping the complexing metal ion in the resin. The potential ligands like amines, amino acids, polyhydric alcohols etc are sorbed from solutions on the basis of the stabilities of ligand-metal complexes.

Various transition metals including Rh, Pt, Pd, Co and Ti bound to polymer supports have been used as catalysts in hydrogenation, hydroformylation and hydrosilation reactions. The incorporation of metal atoms in to a polymer is found to improve its electrical conductivity. Poly[ferrocenylene] polymer on oxidation with I$_3^-$ shows a tremendous increase in conductivity.
When a polymer supported ligand is treated with a metal ion, a polymeric metal complex is formed. Here the co-ordinating site may be the functional group containing atoms like O,N,S etc. or the co-ordinating group is incorporated by a reaction with a small molecular weight substance. Thus the metal ion will form co-ordinate bonds with the ligand moiety of the same polymer chain or it will form complex with the chelating sites of two adjacent polymer chains [Scheme 1].

When the polymer support contains multi-dentate ligands, chelate complexes will be formed [Scheme 2]. Recently there has been considerable activity in bringing phthalocyanine moiety into polymer structures. Dehydration of the phthalocyanine diols at high temperature gives phthalocyanine polymers. [Scheme 3]
Scheme 3

Here the coordinating group may be amino group of amino methylated poly styrene (a), nitrogen of a polymer supported heterocyclic base (b), polymer anchored schiff bases (c), poly methyl acrylic acids (d), phosphonic acid groups in a polymer matrix (e), polymer supported dithiocarbammates(f), polymer anchored sulphonamides (g), iminodiacetic acids (h), etc.
1.4. Polymer Supported Ligands for the Removal of Metal Ions

An important application of functionalized polymers is metal ion removal for analytical, preparative and for industrial purposes. The wide variety of these ligands include polymer supported 8-Hydroxy quinoline, iminodiacetic acid, thiosemicarbazones, functionalized polystyrenes, schiff bases on polymer supports etc. The high selectivity of these resins for heavy metals enables the
removal and analysis of traces of these metal ions in solution even in the presence of large amounts of sodium and potassium due to the high stability of these complexes. These complexes are separated and upon changing the pH the ligand will be regenerated and it can be recycled. So this method can be employed for the treatment of industrial waste. Macrocyclic ethers are also used to separate metal ions and they are also highly selective. It is observed that the copper desorbed amino resins showed specificity to copper ions in the presence of other metal ions like cobalt, nickel and zinc. This reveals the fixing of stereo structure of copper complex. Recently chelating resins are used as ion-exchangers instead of the conventional type. The affinity of a particular metal ion for a certain chelating resin depend mainly on the nature of the chelating group. The selective behaviour of the resin is mainly due to the stabilities of metal complexes arising from the high binding energy of these resins. Recent investigations led to the remediation of ground water contamination by heavy metal ions by selective ion exchange methods. Many super fast polymeric sorbents with multifunctionalities for the removal of various types of ions have been developed.

1.5. Polymer Supports as Ion Selective Electrodes

Ion selective membranes emerged as a potential tool for monitoring our environment with world wide applications of pollution control, water quality management, food quality control, medical diagnosis and hygiene control, soil and fertilizer analysis, industrial production control, waste water management etc. Polymer membrane electrodes are of various ion-exchange materials in an inert matrix such as PVC, polyethylene, silicone rubber, teflon etc. Synthetic membranes can be tailored for the transport of specific ions among other ions of the same charge. This method enables the qualitative and quantitative analysis of electrolytes from very low concentrations. The potential developed at the surface of a membrane is proportional to the concentration of the specific ion.
Ion selective electrodes can also be employed to ions which are not measurable potentiometrically.

The liquid membrane ion-selective electrode produced in 1967 provided a means for determining the activity of Ca$^{2+}$ ions in solution. A significant advancement in this field was the discovery of a calcium sensor membrane in which the organic liquid of the liquid membrane was immobilized on to PVC to produce a polymer film. This contained about 70% of the plasticizer, 30% of PVC and 1% of the ionophore. Later on sensors for ions like Mg$^{2+}$, Na$^+$, K$^+$, Ba$^{2+}$, NO$_3^-$, NH$_4^+$, Cu$^{2+}$, Cd$^{2+}$, Eu$^{2+}$ etc have been developed. Other polymers like polystyrene, PMMA, polyamides, polyimides, etc are also used as the support. Although the development of ISE occurred rapidly in the past three decades, promising investigations are still going on.

1.6. A Brief Review on Applications of Polymer Supports, Polymer Supported Ligands and Complexes

The literature of polymer supported chemistry is enriched with the innovative investigations of the past three decades. Metal ions dissolved in polyhydric alcohols impregnated in the pores on the surface of polymer supports are found to be useful for the separation of saturated hydrocarbon from unsaturated ones.

Polymer supported quaternary ammonium salts, polymeric phosphonium etc. salts are found to be good phase transfer catalysts. It was found that the solubility properties of substrates, ligands and catalysts can be controlled by the usage of polymer supports.

Synthesis and structural characterization of Ni$^{2+}$ and Co$^{2+}$ complexes with polymer supported linear bis(catechol) amide ligand was carried out by Marilyn et al. Thus it was found that polymer supported sulfonated catechol amide ligands could be employed for the selective metal ion removal from aqueous...
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Investigations on the competitive complexations of Ag$^+$, Hg$^{2+}$ and Cu$^{2+}$ using N-sulfonyl ethylene bis(dithiocarbamate) ligand on macroporous polystyrene support showed that the overall selectivity is Hg$^{2+}$ > Ag$^{2+}$ > Cu$^{2+}$ > Pb$^{2+}$ > Cd$^{2+}$ > Fe$^{3+}$ > Al$^{3+}$. A novel biodegradable carboxy functional lactose copolymer showed high complexing activity for metal ions like Cr$^{3+}$ and Fe$^{3+}$.

Ion-exchange membranes are modern applications of poly-ions. Insoluble poly-electrolytes in the form of water swellable beads with macroporous structure give access to ion-exchange sites. Amberlite IR-120, Dowex SBR etc are widely used as ion-exchange resins. Studies on ion-exchange equilibria using cation exchanger Amberlite-120 showed that it is more selective for Cu$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ than for Mg$^{2+}$.

Applications of poly (4-styrene sulfonate) liquid binding layer for measurement of Cu$^{2+}$ and Cd$^{2+}$ with the diffusive gradients in thin film technique showed that poly styrene sulfonate behaved like a cation exchanger. CO$_2$ fixation has been achieved by Cu(II) complexes of a tetrapyridinophane aza receptor. Polymer supported Ru(II) complexes are used as metal ion sensors. A new type of organotin chloride supported on highly porous cross linked polystyrene showed good activity and stability towards dehalogenation and radical cyclization. The effect of synthetic conditions on the formation of copper complexes with polyethylene grafted polyacrylic acid was investigated by Pomogailo et al.

Microgels prepared of cross linked polystyrene are used as supports for organic synthesis. Recently a polymer support based on poly ethylene glycol with high loading capacities has been developed. A novel polymer support based on glycerol with cross linked polystyrene has been developed for polypeptide synthesis. The support has unique characteristics as the functionality
hydroxyl group in the cross linker is introduced into the support in the polymerization stage itself. The utility of the resin was tested by the synthesis of a 19 residue peptide and it was compared with the Merrifield resin.28

Chiral bisoxazolines supported on modified polyethylene glycol is used as ligands in some asymmetric transformations under homogeneous conditions.29 They are also used for the enantio-selective synthesis when supported is used in combination with Cu(II) salts. Polysulfones containing pendant aldehyde groups have potential uses as reactive polymer supports to bind enzymes and ligands.30 Poly tetrahydrofuran cross linked polystyrene is employed for solid phase organic synthesis. When poly tetrahydrofuran was incorporated in polystyrene the overall polarity increased and the resin swelled to a greater extent than polystyrene –divinyl benzene matrix. It also enables the easier isolation of products.31 Polymeric aldehyde may also be used to bond inorganic species to the matrix. A novel method for the recovery of precious metal ions from strongly acidic solutions was developed with the polymer supported o-phenylene diammine hydrochloride ligand.32 The transport characteristics of polyglycol liquid membranes are made use for removing organics from aqueous solutions.33 A highly effective water soluble polymer supported catalyst, polyethylene glycol bound ligand is used for two phase asymmetric hydrogenation.34 When the complexation was carried out on polymer supported dibenzo-18-Crown-6, peculiarities were observed for complexes K2PdCl4 and K2PtCl4.35 Enantio pure poly [glycidyl methacrylate co-ethylene glycol dimethacrylate] is found to be a new material for catalytic asymmetric hydrogen transfer reduction.36

Microgels supported on polystyrene have good solubility in organic solvents and they can be precipitated by methanol. They can be used as scavengers to remove the unreacted isocyanate. Microgel supported sodium borohydride is used as a reducing agent.37 Functionalized polymer support was
prepared by the copolymerization of styrene and acryloyl chloride and it is used as an electrophilic scavenger which reacted readily with N, O, S and C nucleophiles. Scavenging ability was demonstrated by the removal of benzyl amine from aqueous solution at room temperature. Polymer supported calix[4] arenes are used for sensing and for the conversion of NO$_2$/NO$_4$. Photo oxygenation was carried out successfully with polystyrene supported tetraphenyl or tetratolyl porphyrin sensitizers. It is highly swollen in organic solvents and so it is irradiated under air using allylic alcohol. Hydrogel characteristics of electron beam immobilized poly[vinyl-pyrollidone] film on PET support were characterized by ellipsometry, XPES and Atomic force microscopy. These studies showed that cross linked layers swell in aqueous solution by a factor 7. Electron beam cross linking of pre adsorbed hydrophilic polymers permits a durable fixation of a swellable polymer network on polymer support.

Palladium(II) complexes supported on silica-poly vinyl pyridine are also reported as hydrogenation catalysts. Polymer supported Rhodium(I) 2,2'$^'$ bipyridine complex is also found to catalyze hydrogenation reactions. Zupan and Segatin found that bromination of organic compounds can be done conveniently by polymer supported bromine complexes. Polystyrene supported phosphonotungstic complexes are used for epoxidation reactions. Synthesis and characterization of transition metal complexes of 2,2'$^'$ bis imidazole supported on polycarbonates was reported by Collier and Cho. Schiff base complexes of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) were prepared on Urea-Formaldehyde polymer support. Oxidation of 2,6 xylenol is catalyzed by polymer supported Cu(II) complexes.

The synthesis of polystyrene supported resin containing schiff bases derived from salicylaldehyde and triethylene tetramine and its complexes of Cu(II), Ni(II), Co(II), Fe(III), Zn(II), Cd(II), Mo(VI), and U(VI) were reported by Symal and Singh. Polymer supported chromium peroxide complex is
found to be very effective for the selective oxidation of alcohols. Enantioselective parallel synthesis was carried out using polymer supported chiral Co[salen] complexes. Polystyrene supported thiosemicarbazone complexes of Cu(II), Ni(II), Fe(III), and Co(II) are found to be very effective catalysts for the decomposition of H₂O₂ and in the epoxidation of cyclohexene and styrene. The study also revealed the dependence of reaction rate on the degree of cross linking.

Silica supported chitosan-palladium complex is reported as an efficient catalyst for the asymmetric hydrogenation of ketones. Polymer supported Fe(III) complex is a good catalyst for the coupling reaction between acyl chloride and Grignard reagent. Polymer supported bis oxazoline copper complexes are used as catalysts in cyclopropanation reactions. Metal nano particles on functionalized polymer supports are also found to be efficient catalysts. A novel hydrazine linker resin is employed for the solid phase synthesis of α-branched primary amines. Spectacular achievements in catalytic asymmetric epoxidation of olefins have been reported using chiral and recyclable Mn(III) [Salen] complexes. The catalytic activity of shiff base complex of Fe(III) on polystyrene was reported by Antony et al. A novel silica-poly glycol supported bimetallic palladium based catalyst is found to be effective for the dechlorination of aromatic chlorides.

An interesting feature of a polystyrene supported oxo rhenium complex is that it is a catalyst for alcohol oxidation with DMSO and for the de-oxygenation of epoxides to alkenes with triphenyl phosphate. Polybenzimidazole supported [Rh (cod)Cl]₂ complex is an effective catalyst for the preparation of substituted polyacetylenes which are widely used in non linear optics. A new homogeneous catalyst of poly[N-vinyl-pyrollidone] CuCl₂ complex is employed for the oxidative carbonylation of methanol to dimethyl carbonate. Saladino et al have found that polymer supported methyl rhenium tri-oxide and hydrogen...
peroxide are very effective for the selective oxidation of phenol and anisole derivatives to quinones. Polyethylene glycol supported Cu(II) triaza cyclononane is found to be an efficient, recoverable and recyclable catalyst for the cleavage of phospho diester. Silica supported poly α-amino propyl silane complexes of Cu(II), Ni(II), and Co(II) are efficient catalysts for Heck vinylation reactions. Investigations carried out on metal complexation with functionalized polymer supports revealed that it is an adsorption/complexation phenomena. Studies on the catalase like activity of polystyrene supported Schiff base metal complexes showed the dependence of activity on the nature and degree of cross linking and the metal uptake is found to be in the order Cu(II) > Co(II) > Ni(II) >Fe(III) . Catalytic activity is found to be high for polymer supports having a lower degree of cross linking. Polymer supported Cu(II) complexes are very effective for C—N and C—O cross coupling reactions with aryl boronic acids. Surface functionalized polyethylene and polypropylene are found to be good humidity sensors.

1.7. Scope of the Present Investigation

Polymer supports have become inevitable as they have been employed successfully and efficiently as reagents, catalysts and substrates. An important application of polymer supports is the separation of trace metals and toxic metal ions from impure water by complexation. Super fast sorbents of ions of multiple functionalities are recent developments.

Polymer supported metal complexes are also found to be highly versatile. Many of them are used as catalysts for the synthesis of organic compounds of industrial and scientific importance. Preparation of potable water, desalination of water and recovery of metal ions including precious metals are new achievements. Development of perm selective membranes and their applicability as ion-selective electrodes are promising achievements. So the present
investigations have been carried out on this expanding area of polymer supported metal complexes. The objectives of the work are the following

1. Synthesis and characterization of polymer supported complexes of Cu(II), Ni(II), Fe(III), Co(II), Mn(II) and Zn(II) with schiff bases obtained by
   - Condensing amino methylated polystyrene with 4-hydroxy benzaldehyde
   - Condensing amino methylated polystyrene with p-dimethyl amino benzaldehyde
   - Condensing amino methylated polystyrene with 3-nitro benzaldehyde

2. Metal ion removal studies using
   - Schiff base of amino methylated polystyrene with 4-hydroxy benzaldehyde
   - Schiff base of amino methylated polystyrene with p-dimethyl amino benzaldehyde

3. Preparation of Cupric ion selective potentiometric sensor using the complex of Cu(II) with the schiff base obtained by the condensation of amino methylated polystyrene with p-dimethyl amino benzaldehyde

The above mentioned studies have been incorporated in the thesis