CHAPTER - I

INTRODUCTION

INTRODUCTION

Polymers represent a very important contribution of chemistry to the well being of mankind. Our daily lives would be very much poorer without this important class of materials. Polymers present an unique combination of properties and therefore find applications in almost every walk of life ranging from general purpose applications, engineering applications, elastomers and synthetic fibres. They can be super tough,rigid as well as flexible , transparent as well as opaque and can allow selective permeation or act as a barrier. They can be relatively easily processed into a variety of articles of everyday life.The range of useful properties of polymers can be further increased by modifying their structure during synthesis and processing. Properties like strength, ease of fabrication and environmental resistance can be "built-in" to the polymer simultaneously. This ability to tailor the material properties enables researchers to prepare polymers for almost any usual or unusual applications.(1,2)

1.1 Polymer Supports in Syntheses and Separations

The use of polymers as a support to anchor various reagents, catalysts and ligands is one of the important areas of polymer applications. Earlier work in this field has been reviewed by Hodge et al.(3) and Mathur et al.(4).

Since then there has been a rapid increase in the variety of uses to which specifically chemically modified polymers have been put. Most of these can be placed in the generic class of polymer supported species. Polymer immobilised drugs(5), biocides(6,7) (herbicides, insecticides, antifoulants, fungicides, molluscicides, rodenticides, nematicides and algicides), insect repellents and attractants (8) (pheremones), fertilizers, food antioxidants, sweeteners, sunscreens(7) have all been investigated. The techniques employed involve simple physical encapsulation or specific chemical attachment. In some cases polymers are designed to degrade in a controlled manner to release the species.

1.2 Polymer Supported Catalysts and Reagents

The use of polymer supports dates back to 1935 as ion exchange resins and coloumn packing for chromatography(9). Since the discovery of solid phase peptide synthesis by Merrifield (10,11), various reagents, catalysts and other reactive species have been anchored onto polymer supports.

Homogeneous catalysts have the advantage of giving high selectivity at relatively mild reaction conditions. Furthermore, every molecule of the catalytic complex is accessible and participates in catalyzing the reaction in contrast to the heterogeneous catalysts where only surface atoms or molecules may participate. Heterogeneous catalysts, such as metal or metal oxide surfaces, are often less active and less selective, however, they are often very durable and they are readily separated from the reactants and products. It would be desirable to combine the advantages, and simultaneously leave out the disadvantages of each class of catalysts. This has been achieved by anchoring homogeneous catalysts onto organic polymers. The polymer supported catalysts exhibit chemical properties of the anchored reactive species and physical properties of the polymer support.

The main advantage of using polymer supported catalysts, reagents, is the ease in separating the species from the reaction medium after the reaction is completed. There are certain requirements a polymer should meet to be useful as a support. It should be chemically inert under the conditions of use.It should possess good mechanical and thermal stability. Also, it must provide the correct microenvironment which includes a proper balance of hydrophilicity, hydrophobicity, the correct polarity, etc. The most commonly used polymer support is polystyrene crosslinked with divinylbenzene.

Polymer supports used can be placed into three main types (12). The first one is highly crosslinked resin bead called macroreticular or macroporous resins. Polystyrene crosslinked with 20-60% divinylbenzene prepared by emulsion polymerization technique and in presence of volatile solvent belong to this class of resin supports. The high extent of crosslinking hinders diffusion into the core of the beads. Common ion exchange resins are examples of this class. Resins which are in swellable microporous bead form make second type of resin supports. In this case diffusion of solvent and soluble species into the core of polymer beads is possible, and the resins are swelled before use. The degree of crosslinking is low which allows swelling of the beads and diffusion into core of beads. An example of this type of resin is polystyrene crosslinked with 1 - 2 % divinylbenzene. In many cases there is no sharp distinction between macroporous and microporous resins. The third class of support resin include linear soluble polymers. In this case separation is achieved by precipitating the polymer by adding a nonsolvent.

Polystyrene is the most commonly used support. Other supports used are polymers derived from acenaphthalene(13), 2-vinylthiophene(14), alkylmethacrylates (15,16), N,N-dimethylacrylamide or N,N-dimethylmethacrylamide.

In biological environments, that is, in affinity chromatography most widely used polymer supports are acrylics. These include polyacrylamide (Bio-Gel P), Trisacryl and hydroxyalkyl methacrylates. Among natural polymers dextran cellulose, agarose, etc crosslinked with epichlorohydrin have been used. Polymer supported catalysts/ reagents have been the subject of many review articles (3,4,12,17).

1.3 Polymer Supported Ligands

The ligand is covalently linked to the polymer molecule. These polymers are also termed as chelate forming polymers.The most common example of this class of polymers are the ion exchange resins. There are variations in the attachment of multidentate ligands to the polymer network (18). The multifunctional ligands may be attached at one point (a), as is the general.case with ion exchange resins,or at two or more positions in the network(b). The polymer support may be linear with pendant ligands forming either intramolecular chelating groups (c), or intermolecular chelating groups (d). In some cases the chelate may be a constituent of polymer backbone.

In this case monomeric or oligomeric ligands are bridged by forming complex with metal ions(e).Another type includes low molecular weight ligands entrapped in the network structure of inert polymers(f). In other words, the chelating ligands are not covalently linked to the polymer. The latter two groups of materials, though related to, can not be considered as chelate forming polymers from the strict sense of the definition. All these materials are schematically depicted in Fig.1.1

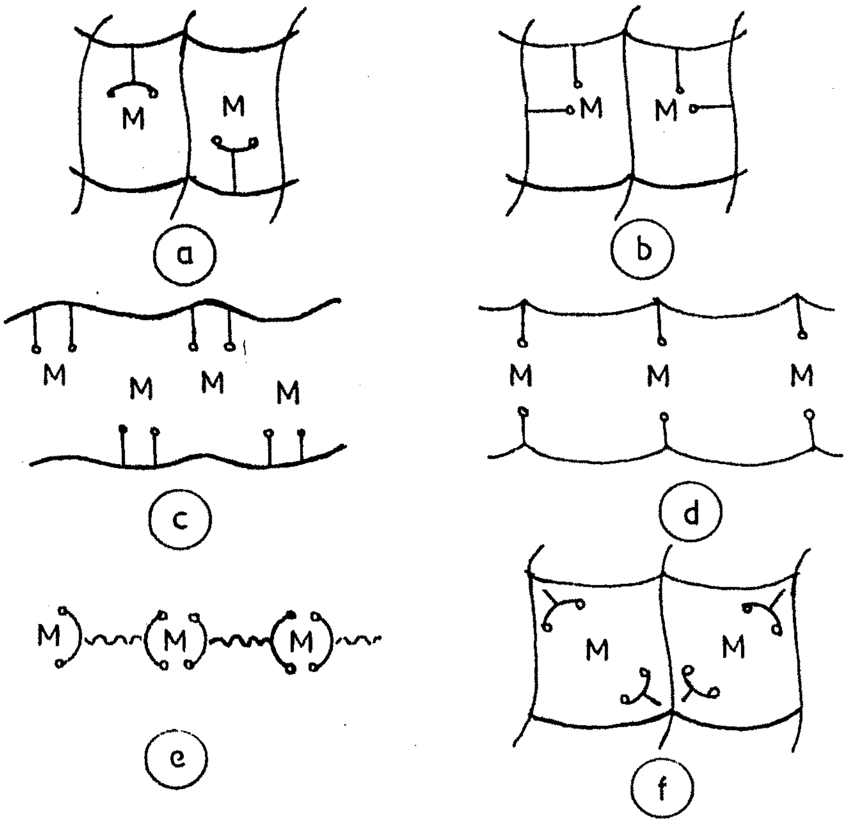


Fig.1 : Chelate Forming Polymers (Ref. 18)

The principal commercial interest in the chelate forming polymers has been in the selective removal and recovery of multivalent metal ions from aqueous solutions. Much higher ion selectivities have been obtained than with conventional ion exchange resins, and the metal ions are generally much more strongly retained. More recently, polymer chelation of monovalent ions (using crown complexes) and multivalent anions has been accomplished. Some of these polymer complexes find applications as ion-selective electrodes and ion exchange membranes.

A successful polymeric ligand should meet the following requirements (19), (i) distinctly characterised metal binding group, (ii) a well characterised polymer with large macroporosity and / or good swelling in polar solvents, (iii) good chemical stability of metal binding groups and matrix, (iv) good mechanical and thermal stability, (v) good reversible complexation/elution steps, and (vi) good rates of metal binding and release.

Most polymeric materials only partially fulfill these requirements. Organic and inorganic matrices differ remarkably in chemical, mechanical, and thermal stability. Chemical stability depends much on polymerization method, polymer tacticity, chelating group distribution and mode of attachment of the ligand to the polymer. Aromatic polymers show higher chemical stability. Polymer supports commonly used are outlined in Section 1.2.

A large number of chelating ligands capable of interacting with ions in solution are known and attempts have been made to incorporate a vast number of them into polymer networks. Recent reviews cover many of the newer examples (22, 23) and a book covers the earlier literature(24). Among the many ligands introduced into polymer networks, 8-hydroxyquinoline is one of the best known (18). Hundreds of examples of experimenatal polymers that have been produced incorporating this ligand by a variety of pathways have been reported. However, probably due to the bulky aromatic structure that may hinder ion interaction when incorporated into polymer network, or the fact that ligand reacts in different ways, the chelating resins produced have been rather variable and not particularly useful. The most commonly employed ligand in commercial chelating resins is iminodiacetic acid (25). Other ligands used include hydroxamic acids, oxamines, Schiff bases, and the great variety of sulfur ligands used in heavy metal chelation of ions such as mercury and lead (18). Some of the commercial chelating resins are listed in Table 1.1.

1.3.1 Synthesis of Chelating Polymers

There are several techniques commonly employed in preparing polymers containing chelating groups. Various forms of polymers such as crosslinked resins, films, membranes, fibres, etc can be obtained.These techniques can be classified into two categories,

(i) modification of a preformed polymer which may be of addition type, condensation type or natural polymers, and

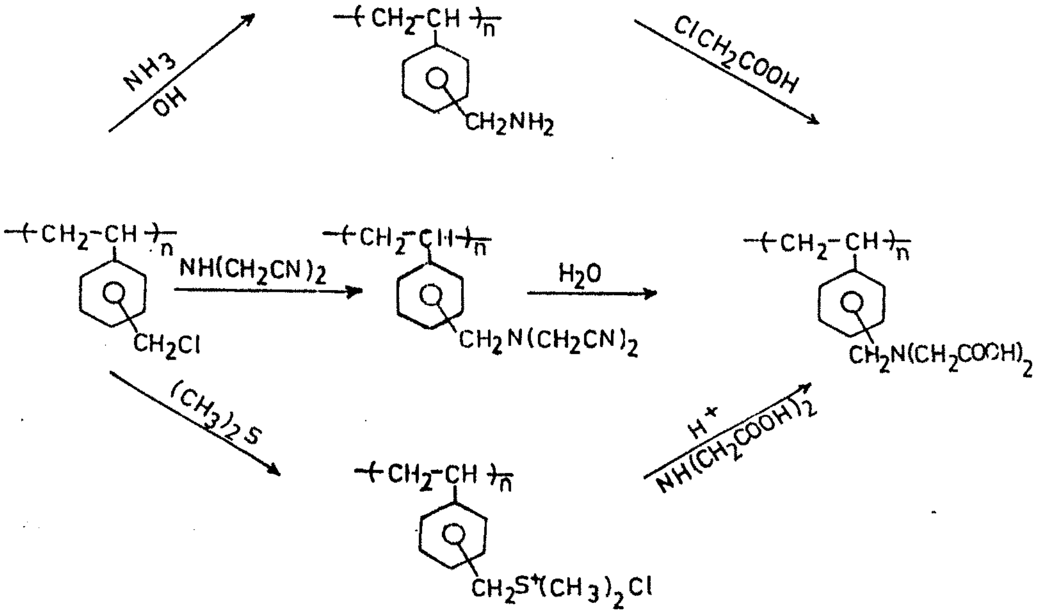
Table 1.1 Some Commercial Chelating Resins (Ref. 18)

Active Structure	Manufacturer	Trade names	Special metal selectivity
iminodiacetic acid	Duolite International	Duolite ES-466	
	Dow Chemical	Dowex A - 1	
	Mitsubishi	Diaion CR - 10	
	Rohm & Haas	Amberlite IRC-718	
	Unitica	Unicellex UR - 10	
	Bio-Rad	Chelex 100	
	Veb Chemie Kombriat Bitterfeld,GDR.	Wofatit CM-50	
	Bayer	Lewatit TP - 207	
isothiouronium	Ayalon	Srafion NMRR	Au,Pt metals at low pH
	Sybron-Chemical Division	Ionac SR-3	
amino	Duolite Inernational	Duolite ES-467	Pb,Cu,Zn
phosphoric carbamate	Sumitomo	Sumichelate MC-90	Ca,Mg
	Nippon Soda	Nisso ALM-525	Hg,Cd,Zn, Pb,Cu
Pyridine types	Sumitomo	Sumichelate CR-2	Mo,Au
	Dow Chemical	Dowex XF-4195 Dowex XF-4196	Cu,Ni,Fe
Polyamine	Mitsubishi	Diaion CR-40 Diaion CR-20	Cu
thiol	Akzochemie	IMAC-TMR	Hg
	Duolite International	Duolite ES-465	
phosphoric acid	Duolite International	Duolite C- 63 Duolite C- 65	
amidoxime	Duolite International	Duolite ES- 346	U

(ii) polymerization of vinyl monomers containing chelating groups. In few cases chelating resins have been obtained by polymerization of condensation , monomers containing chelating groups.

1.3.1.1 Modification of Preformed Polymers

The chemical modification of preformed polymer is a more popular technique of obtaining chelating resin than the polymerization of vinyl monomers containing chelating groups. The most widely used polymer for this purpose is chloromethylated polystyrene crosslinked with divinylbenzene (DVB) (18,26,27). The synthesis of the iminodiacetic acid resins is given below as an example. At least three different synthetic routes have been followed (28—30) in the past and many recent modifications have been attempted.



Scheme 1 : Different routes for the synthesis of iminodiacetic acid resin (Ref. 18).

The reactions are, however, not as straight forward as indicated above. This has been evidenced by the fact that the above three routes yield three different types of resins with quite different properties.

Many other nucleophiles such as those nitrogen and sulfur- containing compounds and metal salts of organic reagents have been reacted with chloromethylated polystyrene(31). Because of the ease of the reaction, most of the well known cyclic and acyclic polyamines have been anchored on the polymer support(26). Halogenation, nitration,sulfonation, and phosphochlorination, besides above mentioned chloromethylation, have been employed as the first step, followed by comparatively mild reactions that lead to the introduction of the more complex chelating groups (22).

Addition polymers other than polystyrene have also been used as polymer supports. Polyacrylonitrile and polyacrylates crosslinked with DVB are preferred because of the ease of chemical modification. A ß-diketone resin has been prepared by the controlled oxidation of poly(vinylalcohol)(32), and a series of chelating polymers have been obtained from glycidylmethacrylate copolymers by reactions with polyamines such as ethylenediamine (33).

The main advantage of chemically modifying preformed polymers is that they are readily available in desired physical forms such as macroreticular or microporous beads with large surface areas or in other forms such as films, membranes, fibres, etc. Further more these polymers have reasonably good chemical, thermal and mechanical stability. The chemistry of their manufacture and that involved in the initial substitution is well understood as some of the resins are in use commercially. The drawbacks of the polymer modification route involve the lack of reproducibility and uniform structure because the reactions are carried out in heterogeneous medium. The synthesis of chelating polymers generally requires a multistep process and, since chelating polymers are produced primarily for ion selectivity, reactions that produce only one type of structure are needed; however, these reactions are very difficult to design(18).

The reliability of chemical modification reaction can be improved remarkably by carrying out these reactions before the linear polymer is crosslinked. However, the reactions that take place easily on soluble monomeric analogues can be very different from those in the related soluble polymers. Many experimental chelating resins have been made by this technique using the same type of reactions as those used for crosslinked resins.

Chelating polymers also have been obtained by the chemical modification of condensation polymers, for example, phenol formaldehyde polymers. In such cases it is difficult to establish the detail structure of the polymer.

Naturally occuring polymers also make an attractive substrate for chemical modifications to obtain chelating polymers. Large quantities of waste lignin, chitin, (poly-N-acetyl-D-glucosamine), cellulose and starch polymers are available and have been modified in many ways to yield chelating resins selective for almost every type of metal(34). Because of the low cost of the starting materials, such polymers have been proposed for selective removal of precious metals from sea water.

Though high selectivity has been claimed for the natural polymers based chelating resins, it is very difficult to establish the detailed structure of these materials because of the complex structure of the starting materials (18). A number of commercially available cellulose resins with selective chelating ability is also known (18).

1.3.1.2 Polymerization of Vinyl Monomers Containing Chelating Groups.

The advantage of this technique to obtain chelating polymers over the previously described method is that it avoids carrying out reactions in heterogeneous medium. Monomers with complicated structures containing chelating groups can be readily synthesized and easily purified as against their polymeric analogues. Thus, uncommon chelating polymers have been synthesized using this route, including those with the metal already present in the monomer. Monomers containing reactive ß-diketone groups also have been synthesized, polymerized and the products well characterized (18,35).

The limitations of this method include the difficulty in obtaining high molecular weight polymers. This is because of the inhibitive effect of the polar chelating groups present in the monomer. Another drawback is the inability to obtain the chelating polymers in the desired physical form.Both these problems can be overcome by copolymerizing the monomer with nonpolar inactive comonomers
An important type of chelating polymers obtained by
using this technique is the series of polymers made from vinyl crown compounds (36,37).

1.3.1.3 Polymerization of Condensation Monomers Containing Chelating Groups .

The earliest method of forming chelating polymer resins was condensation polymerization of monomers containing the chelating ligand (18). Prime examples have included polymers formed by condensation of formaldeyhyde with reactive phenols and/ or amines such as 8-hydroxyquinoline, pyrogallolcarboxylic acid, an$\overset{r}{\text{th}}$anilic acid and o-aminophenol. Resins formed in this way have generally been found to be unsatisfactory (18), both for the lack of chemical stability owing to the polar bridges in the main chain and poor structural integrity. In the past, polymerization and crosslinking reactions employed in the preparation of resins were often poorly defined and destroyed, or at least altered, the functional groups present in the monomer. However, this synthetic route has the advantage in that a great variety of highly functional monomers can be easily obtained and polymerized(38). Unless the reactions are optimized by using model compounds, the true structure of the polymer is difficult to establish.

Other types of common condensation reactions such as polyester and polyamide formation have been used to obtain chelating polymers; for example, a series of polyamides formed by condensation of EDTA anhydride with various diamines(18). In most cases, the presence of hydrolytically unstable groups in the polymer chain has limited commercial applications.

1.3.2 Theory

The reactivity and selectivity of complexation of polymer supported chelating ligands may be seriously changed owing to the altered physical environment. The origin of such changes may be physical effects such as diffusion, steric factors, site-separation, local concentration effects, etc. or it may be chemical effects such as microenvironmental interactions, cooperative etc. In order to study the complexation of chelating polymers the thermodynamic and kinetic effects of each step in the multistep chelate formation process must be considered. The complexes may be cationic, neutral, or anionic with different types of calculations for each. The theory involved in monomeric complex formation has been related to polymeric analogues(39).

The interactions of all ion exchange resins involve multiphase heterogeneous systems. When an exchanging ion in solution approaches an ion exchange resin particle, it encounters a more or less stagnant thin film or solution layer at the interface, commonly called the Nernst film, before moving into and diffusing through the particle itself. Diffusion cannot occur unless electroneutrality is maintained; thus, the diffusion process in ion-exchange resin requires one ion to move out as the others move in (18).

1.3.3 Kinetics

It has been long recognised that the rate of ion exchange reactions is controlled by the diffusion in the case of simple synthetic ion exchange resins. For chelate formation, the rate of chemical reaction varies over a considerable range so that the chemical reactions may determine the over all rate of chelate formation rather than the diffusion process. If the rate of chelate formation is too low, then the resin may not be commercially viable. A commercial resin Dowex A-1 has been used to study the kinetics of interactions with a series of metal ions. It has been found that where chelates were not formed the rate determining step was the particle diffusion. On the other hand where chelate formation was involved, the slowest step was a second order chemical reaction (18). It has been suggested that the kinetics can be controlled by particle diffusion, film diffusion, or chelate forming reactions depending upon the particular ion and its ionic strength (18,40).

1.3.4 Stability Constants

The most important character of polymer ligands is reflected on the stability constant of their metal complexes. The characteristics of the stability of polymer-metal complexes are summarized (18,41).

(i) The stability is usually much higher than the complex of the corresponding monomeric analogues.

(ii) The stepwise formation of a multidentate complex is often not observed, i.e, fully coordinated metal complex is formed alredy at the first stage of the complexation reaction.

(iii) When a stepwise formation of a multidentate complex is observed the stepwise stability constants usually increase with the degree of coordination, which is contrary to the behaviour of the monomeric ligand.

(iv) A distortion of polymer chain in some cases reduces the stability of its metal complex owing to the polymer backbone configuration.

The stability constants or equilibrium constants are determined by pH titrations using the modified Bjerrum (18,42) method. When a metal ion (M) forms a complex with N ligands(L), the successive stability constant K_i and the overall stability constant K_j can be given as:

$$ML_{i-1} + L \rightleftharpoons ML_i , \qquad i = 1 \sim N$$

$$K_i = [ML_i] / [M_{i-1}] [L]$$

$$j$$

The formation function $\bar{n}$, which represents the average number of ligands bound to the metal ion is given by

$$\bar{n} = \sum_{j=1}^{N} j K_j [L]^j \Big/ \left(1 + \sum_{j=1}^{N} K_j [L]^j \right)$$

The plots of $\bar{n}$ vs p[L], i.e., -log [L], are called formation curves. When [L] is determined experimentally and when the dissociation constant of LH is known ,$\bar{n}$ can be calculated:

$$\bar{n} = ([L]_t-[L]-[LH])/[M]_t$$

where $[M]_t$ and $[L]_t$ are total concentrations. The assumptions that the main complex species at $\bar{n} = n-1/2$ are ML_{n-1} and ML_n and their concentrations are almost the same leads to

$$K_n = 1 / [L]_{\bar{n}=n-1/2}$$

The K_n value is obtained as the p[L] value at $\bar{n} = n-1/2$ on the formation curve. By modification of the equations to suit particular types of polymer ligands and using the experimental results obtained from the pH titrations of these ligands with and without metal atoms present, overall stability constants for each metal-polymer complex can be obtained and compared.

1.3.5 Ion Selectivity

From the practical standpoint, the selectivity i.e., preference for one ion over another of chelate forming fibres is more important than their metal-complex stability constants. It is comparatively easier to determine the selectivity. Even for monofunctional ion exchange resins, there is considerable ion selectivity. The factors that enhance ion selectivity are electroselectivity, the general preference for counterions of higher valence, which increases at low concentrations and with resins of high internal molality. Ionic-solvation variations and swellingpressure changes also encourage ion selectivity of crosslinked resins. The most important factor is comparative stability constants.A small difference in the stability constants of the complex between a polymeric ligand and the different metal ions can enable the selective adsorption of a particular ion by the polymer under specific conditions. Experimental conditions such as total concentration of solution, temperature, pH, etc affect the ion selectivity.

1.3.6 Adsorption of Metal Ions and Organic Molecules

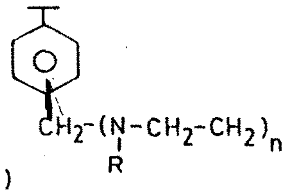
The polymer ligands can bind various metal ions. Therefore, insoluble resins or films of these polymers have been used for adsorption of metal ions(41). Removal of toxic metal ions from water or collection of trace precious metals from sea water is strongly desired from the social standpoint of cleanup of the environment and of energy saving. Selective adsorption of metal ions is especially important, which is realized only by using polymer ligands and by making use of the dependencies of the stability of the metal complex upon the structure of the ligands as well as upon the kind of metal ions. A small difference of the stability constant of the complex between polymer ligand and metal ion enables the selective adsorption of metal ion by the polymer. Although it is possible to adsorb some definite metal ion from a mixture of metal ions in special cases,it is not yet possible to adsorb any desired metal ion selectively from a mixture. The adsorption of metal ions has been reviewed(41,43-46).

Polystyrene, crosslinked with DVB, containing pendant iminodiacetic acid type groups has been especially used as a metal-binding resin showing excellent ability to adsorb metal ions selectively and its behaviour was studied in detail (41). Iminodiacetic acid group was also incorporated into polyacrylamide gel by aminomethylation of the N-methylolpolyacrylamide with iminodiacetic acid disodium salt. The polymer showed high stability constants with Ca(II), Mn(II), Hg(II), Zn(II), and Cu(II) ions (47)

Polyamine ligands such as ethylenediamine, diethylenetriamine, or triethtlenetetramine are excellent chelating agents. They were bound to chloromethylated PS resins,and the resulting polyamine resins adsorbed Cu^{2+} ions effectively(48). Similar polymers containing ethylenediamine groups bound to copolymers of glycidylacrylate-ethylenedimethacrylate and of glycidilacrylate-methylenebisacrylamide were prepared and their complex with cu^{2+} was studied(49). In the same polymer having monoamine ligands instead of diamine, -OH groups also coordinate to metal ions resulting in chelated structures (33). High selectivity to Cu,Zn,Fe,Ni and Co was observed.

Crosslinked PS with pendant polyamine (I) adsorbed metal ions selectively in the following order at pH 6:

$Hg^{2+} > Cu^{2+} > Cd^{2+} > Ca^{2+}$ (50)



(I)

R = H, CH_2CH_2COONa, CH_2COONa, CH_2CH_2SH, CS_2Na

Polymers with pendant bipyridine groups were obtained by homopolymerization of 6-vinylbipyridine and 4-vinyl-4-methylbipyridine(51). Bipyridine was also bound to crosslinked PS beads, and complexation of the polymers with Cu(II), Co(II), Ni(II), Fe(II), and Fe(III) in tetrahydrofuran was described and comparison was made with that of vinylbipyridine homopolymers (52).

It is expected that a crosslinked polymer ligand might form a more stable complex with metal ions than a noncrosslinked polymer,and that it might show some selectivities for metal ions due to its rigid network structure.Thus polyvinylpyridine (PVP) partially crosslinked with α w dibromobutane revealed the stability of metal complex more than one order higher than that of noncrosslinked polyvinylpyridine(53). The ratio of metal ions adsorbed and its dependencies on the extent of crosslinking varies with each metal ion.A higher degree of crosslinking results in a lower degree of metal ions adsorption and in a lower stabiity of the resulting metal complex, because of the structural strain caused by high degree of crosslinking. Adsorption of Cu ions is dependent on the degree of crosslinking while that of Hg ions is not much affected. It is therefore possible to prepare resins which adsorb only Hg ions selectively by controlling the degree of crosslinking. The PVP resins with 31% crosslinking adsorb only Hg ions from the mixture of Hg and Cu ions at a pH below 2 (53).

Polymers containing dithiocarbamate or thiocarbonyl groups have been used as metal chelating agents(54).

1-Vinyl-4,5-dicarboxyimidazole and 2-styryl-4,5-dicarboxylic acid imidazole were polymerized in the presence of 5% DVB. The resulting polymers were studied for swelling behavior and pH dependent complexation of Cu(II), Ni(II), Cd(II), Zn(II) and Hg(II) in aqueous solutions (55). 3-Vinylpyrazoles (isomeric to vinylimidazoles), substituted in position 4 and 5 with auxillary chelating groups (aldehyde, oxime, ester), were copolymerised in the presence of the diallylic species bis (3-vinyl -5- pyrazolyl) ketone to yield, after saponifiation, poly(vinylpyrazolecarboxylic acid) chelating resins with very high binding capacity (up to 8 meq/g) for Cu (II), Ni(II), Zn(II) and Mn(II) (56).

p-Vinylbenzoylacetone was prepared from vinylbenzaldehyde and polymerised which readily forms complexes

comlepxes with Ni(II),Cu(II),Co(II)and Au(II)(57).A diketone resin was also obtained by alkylation of chloromethylated PS (crosslinked with 8% DVB) with pentane -2,4-dione sodium salt. Square planar complexes of the polymer with Cu (II)and (II) Ni(ii) and octahedral complexes with Fe (III)and Cr (III) were observed (58).

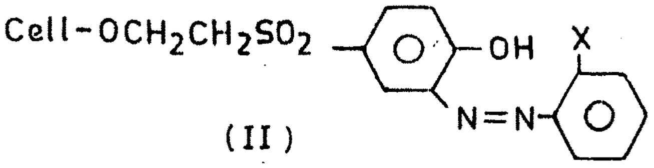
Catechol resins for adsorption of heavy metal ions Cd(II),Pb(II),Hg(II),and Cr(VI) from waste water were prepared from chloromethylated polystyrene(19).

Delepine reaction of chloromethylated PS with hexamethylenetetramine yielded aminomethyl PS, which upon alkylation with ligands carrying the chloromethylaryl group leads ,in one step to chelating polymers of the pyridylimine, hydroxyquinoline or hydroxyoxime type (19).

Crown ethers have attracted attention in recent years, because they bind metal ions remarkably, selectively, especially alkaline and alkaline earth metal ions. The selectivity is dependant on the number and chemical structure of the ring member as well as on the steric factors of the ring . 4-Vinylbenzo-15-crown-5 and-4-Vinylbenzo-18-crown-6 were prepared by various methods and their homopolymers studied extensively (37,59). Polymeric crown ethers with a spacer between the backbone polymer and crown group have been reported (60,61). Cyclic polyamines(Cyclam) bound to PS showed high selectivity for

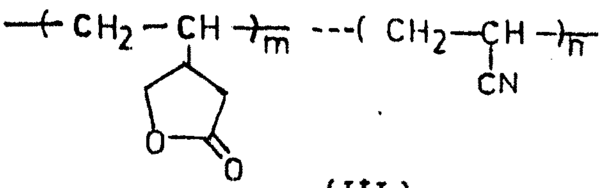
Cu(II) adsorption(62).

Cellulose bound to β-hydroxyazo compound (II) was reported to adsorb uranyl ions selectively(63).



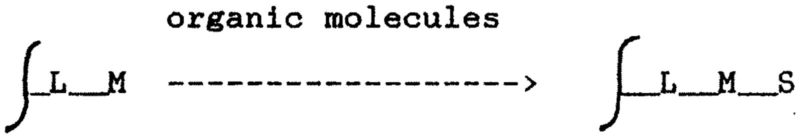
(II)

Utilization of these chelating polymers in the form of a film would develop new indusrial applications(41). The film from the copolymer of 3-Vinyl-1, 4 - butyrolactone and acrylonitrile(III) trasported alkaline metals actively(64).



(III)

The coordination reaction of resin-bound metal ions can be used for adsorption of coordinating organic molecules, which can be isolated from each other when they are in a mixture (41).



The complex of Zn^{2+} and Cu^{2+} with carboxymethyl-aminated agarose was packed in separate coloumns. Human blood serum was passed through the col~~o~~umns and its components were clearly separated(65).

1.3.7 Application of Chelating Polymers

The main applications for chelating polymers are based on the high selectivity of the materials for particular ions. Specific removal of a precious or toxic metal ions, in mining or pollution situation, where it is present in very low concentrations and in a mixture of ions, can drastically reduce the energy and material requirements. However, they have not been used yet in large scale commercial operation, except in some water- softening areas where undesirable multivalent ions such as Ca^{2+} and Mg^{2+} replace monovalent ions(18). One potentially useful example of this technology is in the use of the new membrane cells for the electrolysis of brine. Iminodiacetic acid chelate resins are often used to purify brine before electrolysis. A series of new copper-selective amino-pyridine Dowex resins were designed for large scale hydrometallurgical separation of copper from its ores. Chelating polymers in hydrometallurgical separation have been reviewed(19). Chelating resins such as amidoximes, poly(hydroxamic acids), etc have potential use in selective removal of precious metal from sea water. Commercial chelating resins have mainly been used in analytical applications, especially in the preconcentration step. They also have many potential applications for the selective removal and recovery of metal ions from industrial waste.

Another promising new application for chelating resins is in nuclear- medicine applications where very short lived isotopes must be removed quickly and selectively from mother and daughter ions. A recent example is the use of a pyrogallol- formaldehyde polymer made for the separation of ^{68}Ga and ^{68}Ge ions(18).

Ion exchange have been widely used as polymeric catalysts and reagents in many commercial aplications(18). A thorough review(66) details the use of chelating polymers as redox catalysts and reagents in many applications.

1.4 Scope of the Present Investigation.

The driving force for the continued interest in the field of chelating polymers is because of their potential applications in environmental and analytical chemistry and mining industries. Both ion selectivity and the stability of metal ligand complex for these polymer are much improved compare to the conventional ion exchange resins.

The main objective of the present work was to check the feasibility of preparing a natural polymer based sorbents for transition metal ions. We opted for cellulose derivatives as polymer supports because cellulose is a versatile, omnipresent natural polymer with excellent mechanical properties. By controlling the degree of substitution of cellulose derivatives, the number of available reaction sites (hydroxyl groups) as well as the hydrophobic/hydrophilic balance of polymer can be varied.

Transition metal complexes with Schiff bases as ligands have been the most widely studied coordination compounds. Increased interest in the coordination complexs of Schiff bases is due to their novel structural features, unusual magnetic properties and usefulness in biological processes. However, relatively little work has been done on the polymer supported Schiff bases. Recently,Sanyal and Singh (67) and sreekumar,et al,(68-70) have reported on the chelating polymers containing pendant Schiff bases. In all these cases chloromethylated polystyrene was used as polymer support.

In the present work, cellulose derivatives such as ethyl cellulose and cellulose acetate, both with degree of substitution ranging from 2.25-2.5, were reacted with excess of diisocynates followed by isolation and converting the free isocyanate groups into amino groups. The modified cellulose derivatives with pendant amino groups were then treated with salicyldehyde, 2-hydroxy-1-naphthaldehyde, or diacetyl monoxime to yield cellulosics anchored Schiff bases. These polymers were then char~~e~~acterised mainly by IR spectroscopy, and by elemental analysis and chemical methods. Adsoption of transition metal ions eg. Mn^{++},Co^{++},Ni^{++}, Cu^{++} and Zn^{++}, by the polymers was determined using complexometric titrations.