SYNTHESIS, CHARACTERIZATION AND CATALYTIC PROPERTIES OF MACROPOROUS POLYMER METAL COMPLEXES

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CERTIFICATE

Certified that the work incorporated in the thesis "**Synthesis, Characterization and Catalytic Properties of Macroporous Polymer metal complexes**" submitted by Mr. Sunny Skaria, for the degree of Doctor of Philosophy, University of Pune was carried out by the candidate under my supervision in the Polymer Science and Engineering Unit, Chemical Engineering Division, National Chemical Laboratory, Pune, India. Materials obtained from other sources have been duly acknowledged in the thesis.

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[SUNNY SKARIA]

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CHAPTER I

INTRODUCTION

1. General Introduction

Merrifield's solid state peptide synthesis in 1963 opened up considerable research interest in reactive species anchored on insoluble supports suited to conducting organic, inorganic and biochemical transformations [1-3]. The study of these functional polymers has received considerable attention in organic syntheses and related research areas as/in: stoichiometric reagents, catalysts, protecting agents, analytical chemistry, hydrometallurgy/ chromatography, biologically and pharmacologically active systems, immobilisation of enzymes and agricultural chemicals [4-7]. The development of numerous new polymeric reagents, catalysts and supports has generated better awareness on the design of polymer synthesis, catalysis and separation science.

The polymer supported species used in chemical syntheses are polymeric reagents, polymeric protecting groups, polymer supported catalysts and polymeric mediators [8]. The initial investigations as chelating resins and chromatographic materials have resulted in hydrometallurgical and separation processes [9]. The high level of interest is reflected in the large number of publications that describe many new polymeric reactants applied to a rich variety of research fields.

This chapter deals with selective and brief coverage of the field of reactive polymers. The emphasis is on (i) preparation and structures of polymer matrices, especially polystyrenes and polyacrylates, (ii) their most synthetic and catalytic applications and (iii) the advantages and disadvantages of supported species.

1.1 Advantages and Disadvantages

The attachment of soluble homogeneous, reactive species onto insoluble polymer supports results in heterogeneous species with the retention of activity. The potential advantages offered by this immobilisation include ease of separation, isolation and purification of the particulate immobilised species from the reaction mixture. Thus, reagents could be used in excess circumventing downstream processing problems. This is a convenient methodology to drive equilibrium reactions closer to completion.

The loss of expensive and precious reactive species, such as optically active molecules or platinum group metal complexes, will be minimised due to efficient retention when supported on polymer matrix, thereby increasing recyclability and efficient use. Corrosive, noxious or toxic species are rendered safe on immobilisation. The vapour pressure of volatile hazardous species is depressed appreciably and the possibility of absorption of toxic low molecular mass compounds through skin, respiratory and digestive systems are drastically reduced. Thus supported systems are environmental friendly and offer cleaner chemistry.

In engineering terms, polymer supported systems can be used very flexibly in column and batch reactors and are suitable for gas and liquid phase reactions, due to the heterogeneity. Other advantages of polymer supported species are better rates and selectivity and depressed side reactions due to site isolation and 'infinite dilution'. In specific cases, the chemical and steric structure of the polymer backbone provides ideal microenvironment for reactions at the pendent reactive group. The nature of the backbone, the bulkiness of the substituents, polarity of the medium and porous nature impart some specificity to the transition state of the reaction leading to regiospecific or regeoselective reactions.

The disadvantages of the immobilised systems are the high initial cost of the supported species. Leaching out of the reactive species from the supported systems would annul all the advantages. The overall chemical and mechanical stability of the system can often be limiting. Diffusional limitations may be experienced, which would decrease the effective concentration of substrate in the vicinity of the reactive site and reduce the reaction rates, resulting in poor yields. The anticipated improvements in selectivity and depressed side reactions may not compensate for the higher costs.

1.2 Supports

The two types of polymeric matrices used are inorganic and organic supports. The inorganic supports tend to withstand high pressures, provide better thermal stability, have high mechanical strength, and are stable in organic solvents and mineral acids, but have limited flexibility of functionalisation [10]. A variety of reagents can be adsorbed on or intercalated in inorganic supports such as silica gel, carbon, graphite and zeolites. The organic supports employed may be either natural or synthetic. Polymeric reactants are generally based on synthetic polymers, while chelating resins are based on natural as well as synthetic polymers.

1.2.1 Natural supports

Among natural polymers, cellulose continues to be the material of choice. The chelating properties of cellulose based resins have been extensively investigated. These provide better exchange kinetics but have limited potential due to physical and chemical characteristics [11]. Other natural supports to have generated interests are chitin and chitosan [12,13].

1.2.2 Synthetic supports

1.2.2.1 Linear polymers

The linear polymers could be generated by either condensation [14] or addition polymerisation [15]. Polycondensation involves the reaction of bifunctional monomers. Vinyl polymers, widely used as supports, are synthesised by addition or more specifically free radical addition polymerisation using techniques like bulk, solution and suspension polymerisations.

1.2.2.2 Crosslinked polymers

Crosslinked polymers consist of insoluble infinite networks formed by inter-connection of linear chains and bridges. The crosslinking can be achieved either during polymerisation or as a separate reaction [16]. Crosslinked condensation polymers are formed from small difunctional reactants in presence of a tri or higher functional component.

Supports synthesised by addition polymerisation are preferred over condensation polymers, due to better chemical stability and mechanical strength. Crosslinked addition polymers are synthesised by the free radical polymerisation of a mixture of mono-vinyl and a multi-vinyl monomer. The polymer backbones consist of exclusively C-C bonds, which are hydrolytically stable over wide variations in pH. Acrylic and styrenic copolymers are the most extensively investigated supports.

1.3 Control of particle size

Crosslinked, beaded polymers have received greater interest inspite of some interesting results obtained with linear, soluble polymers. These are synthesised by suspension polymerisation [17].

Here, an organic layer consisting of vinyl monomer, crosslinking multi-vinyl monomer and polymerisation initiator is dispersed in an aqueous phase having water soluble polymers as droplet

stabiliser. As the suspension is agitated and heated, the initiator is cleaved generating radicals which initiate polymerisation in the droplets, slowly converting mobile liquid droplets into rigid solid particles or beads. The resultant copolymer beads are freed readily from residual monomers by solvent extraction. Each of the suspended monomer droplets undergoes individual bulk polymerisation and kinetically the system consists of large number of bulk polymerisation units.

Suspension polymerisation is by no means a simple process. A large number of synthesis parameters influence desired characteristics such as the particle size, internal and outer morphologies of polymer beads. The geometries of stirrer and reactor which govern shear distribution and system characteristics like viscosity and interfacial tensions between the monomer droplets and continuous phase all affect the particle morphology. Particle size is controlled by adjusting the interfacial tension between the aqueous and organic phases, their relative densities, viscosity of the continuous phase, volumes of dispersing and continuous phases and agitation rate. Lower monomer/water ratio and higher shear rates yield smaller particles.

The selection of the stabiliser, a water soluble synthetic or natural polymer, is critical in controlling bead size. The droplet stabilisers increase the viscosity of the continuous phase, reduce interfacial tension and prevent coalescence by forming a layer of adsorbed dispersant at the surface of the droplets [18].

1.3.1 Porosity : Control and Mechanism of formation

Crosslinked polymers are distinguished as gel type and macroporous resins on the basis of the crosslinking density. Gel type resins are formed by very low crosslinking density and do not possess a permanent porosity but swell in organic solvents. These have relatively small pore diameters and large effective surface area and give rise to high loading efficiency. Macroporous

resins are obtained at higher mole fraction (higher crosslinking densities) of multi-vinyl monomer (5-60%) and in presence of inert diluents (pore generating solvents). These have large pore diameter and relatively small surface area. Chemical modifications occur at the surface of the pores in the beads and hence highly crosslinked polymers are not easily functionalised. Phase separation occurs during polymerisation and permanent pores or holes of various sizes are created on extraction of the diluent and drying. The heterogeneity of macroporous network polymers are controlled by the type and amount of diluent as well as the crosslinking density. The macroporous morphology and pore formation has been extensively investigated for beaded, crosslinked styrene-divinyl benzene (S-DVB) copolymers [19].

The three main classes of porogens considered are: solvents for polymer structure (solvating), non-solvents for polymer, and finally polymeric porogens. Very large pores are generated by polymeric porogens and pore size is defined by the molecular mass [20]. Recently, polymeric porogens have received wider attention in the generation of monodisperse pores [21,22]. Solvating diluents generate small (micro) pores while nonsolvating ones produce large (macro) pores. As the solvating power of the diluent is lowered, the microspheres and micropores become bigger and microspheres become rigid and compact. Therefore, the polymer-solvent (diluent) interaction is the factor which primarily determines the pore size distribution [23]. The most complex but frequently explored are those systems formed with a nonsolvating diluent. As initially proposed by Kun and Kunin [24] and later experimentally observed by Jacobelli et al [25], the bead is a large agglomerate of microspheres (100-200 nm). Each microsphere results from the fusion of smaller nuclei (10-20 nm). High surface area arises from small pores (5-10 nm) present between the nuclei. The inter-microsphere results in mesopores (20-50 nm) with moderate surface

area, up to 100 m^2 /g. The larger pores, with pore volumes up to 3 cm^3/g, are located in between agglomerates and arise when a high volume of porogen is used.

Macroporous morphology in beaded polymers arises by a three stage process of production of gel microspheres, the agglomeration of these and the binding together of the agglomerates to form the beads [26]. A recent approach considers the occurrence of three critical events during polymerisation [27]. The first, the appearance of microgels, is dependent primarily on the mole fraction of crosslinking monomer and to a lesser extent on the porogen. Crosslinking density also influences the phase separation, which is responsible for the formation of microspheres.

The main differences observed in pore structure are attributable to differences in the critical concentration for polymer precipitation during the early stages of polymerisation, the tendency of precipitated polymer to agglomerate in microspheres and the entanglement degree of nuclear and inter-nuclear chains [28]. The solvating power changes with the diluent type. The precipitation is shifted to lower conversion with decreasing solvating power. In presence of precipitating (non-solvating) diluent, the precipitated polymer tends to agglomerate rapidly to form larger microspheres. Consequently, the diluent is distributed preferentially among microsphere agglomerates to form big pores. On the other hand the microspheres formed in the presence of a solvating diluent are rather small, and the diluent is distributed both within and outside the microspheres.

Recently, Coutinho et. al investigated the influence of the solvating power of pure diluents on the formation of porous structure and the swelling properties of S-DVB copolymers. A three dimensional parameter was arrived, which was found to be better than the Hildebrand solubility parameter at predicting the relationship between diluent type and pore structure formation. The

porous structure formation could be controlled by diluent mixtures composed of a good and a bad solvent [29].

Poly(alkyl acrylates/ methacrylates) are other supports to have generated interest in beaded forms, especially for the immobilisation of biocatalysts [30], as chromatographic supports, and as matrices for chelating resins and transition metal complexes [31]. Synthetic strategies to generate macroreticular glycidyl methacrylate-ethylene glycol dimethacrylate copolymers were extensively studied by Svec [32].

1.4 Syntheses of functional polymers

The synthetic routes to generate functional polymers are: (a) polymerisation of functional monomers, (b) polymerisation of non-functional monomer and its subsequent modification and (c) a combination of method (a) and (b).

1.4.1 Polymerisation of functional monomer

In this functional comonomer route the required functionality is incorporated covalently in the structure of a vinyl monomer used as a component in the polymerisation mixture to obtain the functional copolymer. The method avoids the problems of conducting reactions on polymer chains. Vinylic or acrylic derivatives are the typical functional monomers. The chemical structure of polymer can be varied over a wide range to obtain products with a particular combination of desirable properties. Copolymerisation allows a control of the properties through the relative mole fraction of functional monomer units. A prior knowledge of the reactivity ratios of the comonomers enhances the possibility of precise positioning of the functional group on a polymer chain. Functional polymers / crosslinked polymers can be prepared by ionic polymerisation or

preferably in good physical (bead) form by suspension polymerisation [33] *[section 1.3.1]*. Complex functional groups, especially chelating groups, can be readily coupled to polymerisable vinyl or acrylic functionalities [34]. Recent literature describe the syntheses and polymerisations of many unusual monomers, with intricate functional groups, especially pyridine derivatives [35].

The main shortcoming of the functional comonomer route is that a significantly high mole fraction of the functional group would be buried deep inside the inaccessible cores of highly crosslinked network. A partial solution to this problem is the delayed introduction of the functional monomer. Another draw back is that the polar functional groups tend to inhibit radical polymerisation resulting in enhanced chain termination and low molecular mass brittle polymers. Tougher high molecular mass copolymers can be synthesised only in large excess of nonpolar comonomers. This method has not been widely used due to limited stability of monomers, the difficulty in achieving broad spectrum of polymers with specific functional groups and generating polymers in bead form. The advantages outweigh the shortcomings in systems based on monomers with multi oxa (macrocyclic crown ethers), aza and thia ligands as well as macrocyclic crown ethers [36].

1.4.2 Chemical modification route

In this, the preferred route, functionality is introduced through the chemical modification of a performed linear or beaded crosslinked polymer. The interest in this route is due to the ease of derivatising commercial beaded polymer supports of known crosslinking density and porosity [37]. The reaction sequences used for the chemical modification of polymer supports should be as few as possible, since few reactions are free from side reactions [38]. The chemical modifications are usually in the more accessible sites in the polymer matrix and few, if any, are unavailable for later reaction. The functional group ought to be evenly spaced. Thus, the reaction conditions must

be carefully chosen to ensure that the reagents penetrate the crosslinked matrix throughout the reaction. This depends on factors such as the rate of modification reaction relative to the rate of diffusion of the reagent into the polymer matrix, and whether the group introduced facilitates or hinders the introduction of additional groups in the vicinity. A vast number of functional groups, especially chelating groups, have been incorporated into polymer networks [39].

The advantages and disadvantages of chemical modification route and functional comonomer route are presented in Table **1.1**.

Table 1.1

Derivatisation of copolymers by chemical modification and by comonomer route

Factor	**Chemical modification route**	**Functional comonomer route**
Availability	off the shelf product	Comonomer and polymer to be prepared
structure of groups	may be clear	well defined
number of groups	poor control	better control
distribution of groups	poor control and poorly defined	better control and better defined
overall chemistry	may be poorly defined	generally clear cut
access to groups	generally good	possibly limited
cost/convenience	low/high	higher /lower

1.4.3 Polystyrene support and its chemical modifications

A major segment of research in chemical modification of a preformed copolymer has focused on S-DVB copolymer [40]. Copolymers of varying physical characteristics like crosslinking density, surface area and porosity are available commercially. The options for initial chemical modification rely largely on the electron rich aromatic pendent group and its susceptibility to electrophilic substitution reactions. The different methods employed for the incorporation of required functional group to the copolymers are represented in Fig. **1.1**.

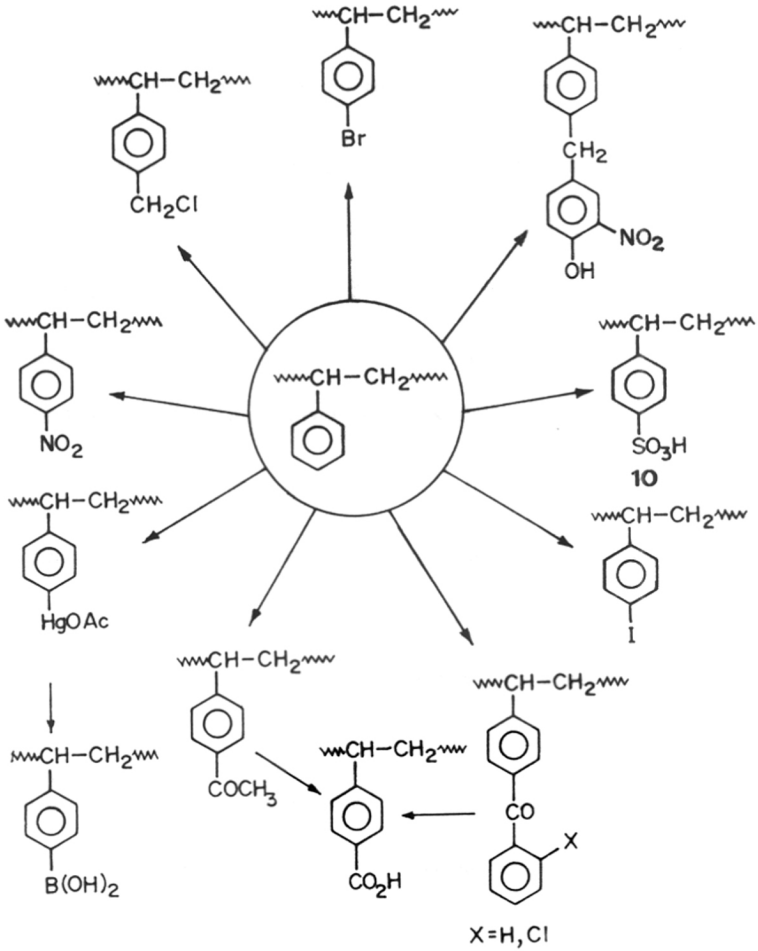
Halogenation and chloromethylation are convenient starting points for many other chemical transformations [41,42]. The chloromethyl derivative of S-DVB copolymers have been used to synthesise various polymer supported species such as polymeric reagents, catalysts and chelating copolymers. The chloromethylation procedure is hazardous and milder procedures have been developed recently [43].

Lithiated polystyrene is a suitable intermediate since this offers a facile attack on the aromatic ring by electrophilic species [44]. Another important and industrially accepted process is the sulphonation of polystyrenes [45]. Poly(vinyl pyridines) [46], poly methacrylates [47], poly (ace naphthylenes) [48] and polyacrylamide are other polymers found to be suitable for specific applications.

1.5 Features of polymer supported reactions

The attachment to a polymer chain changes the reactivity of functional groups from that supported on analogous groups on a small molecule. The conditions required for polymer supported species tend to be more drastic. The fundamental processes that dictate the overall reaction rates in heterogeneous reactions, especially in catalysis, are : (i) the rates of diffusion of

Fig. 1.1: Chemical reactions on styrene-divinyl benzene copolymer



substrates and products within the polymer matrix; (ii) the ratio of the molecular size of the reactant to pore size in the polymer; (iii) degree of swelling of the polymer and (iv) the intrinsic reaction rate at the active surface. With polymeric catalysts or reagents, the reactivities may be significantly influenced by the so called 'polymeric effects', the origin of which may be physical viz, the viscous diffusion effects, steric effects, site separation effects and local concentration effects, or chemical viz, microenvironmental and coordination.

The porosity and its distribution affect the performance of functionalised porous polymers. The kinetics of chemical reactions are controlled by the diffusion into the microparticles and this diffusional limitation is related to the crosslinking density and size of the penetrant molecules. In gel type crosslinked structures, which tend to swell in solvent, the extent of swelling is inversely proportional to crosslinking density. Thus, lower crosslinking density is desired for large sized penetrants [49].

The design of a new reactive polymer must consider factors which affect the activity. It should be stable to the reagents and solvents used for the functionalisation and subsequent reactions. It should also consider chemical behaviour of the support which depends on physical form, crosslinking density, the flexibility of chain segments and the degree of functionalisation. Polymer bound catalysts, reagents and substrates are prepared primarily from porous crosslinked polymer beads. These polymers will only swell but never dissolve in any solvent. Solvents affect the reactivity of polymer supported species. The primary function of a solvent is to increase the size of the pore by swelling the polymer lattice. Most catalytic sites would be at the surface of the pores, deep inside the beads and for reactions to take place the low molecular mass reactants must diffuse into the pores in the polymer beads. The reaction will be very slow in microporous

polymers unless solvent is used to swell the beads to increase the porosity. Macroporous polymer supports, with accessible functional groups, will not generally present any problems. However, when the functional groups are buried deep within the densely crosslinked regions, the choice of the reaction medium will gain importance. Poorly swollen resin retards the rotation of unattached molecules imbibed in the matrix while swollen polymer exhibits a high internal viscosity and the crosslinks restrict the long range mobility of chain segments. Thus, the collision frequency of substituents attached to different chain segments is reduced substantially.

The role of a solvent in the reaction of functionalised copolymer is rather complex. An ideal solvent should meet the following requirements: (1) it should have the correct solvating characteristics to aid any chemical transformation being carried out. (2) it should interact with the polymer matrix to optimise the mobility of reagent molecules.

At high loading of functional groups the swelling characteristics of polymer supported reagents or substrates would be altered [50]. Quaternisation of tertiary amino groups linked to chloromethylated S-DVB copolymers is known to dramatically change the copolymer characteristics. Similar observations have been made in Wittig reactions conducted using polymer supported phosphonium salts, where the functional group changes from ionic to ylide and finally, to phosphine oxide groups [51]. An equilibrium comes into play when the diffusion of low molecular mass reactants in and out of the polymer beads is rapid relative to its intrinsic reactivity. Depending on the equilibrium, when the diffusion is faster, the low molecular mass reactant is concentrated within the beads and will result in faster rate of reaction. When intrinsic reactivity is higher, diffusional limitations would lead to a lower reaction rate as compared to low molecular mass analogues. The position of equilibrium depends on many factors such as the polarity of the

medium and polymer as well as polarity of the solvent relative to the substrate. Hence, the choice of the solvent is crucial. The reaction will occur uniformly throughout the beads if low molecular mass reactant can diffuse into and product can diffuse out of the pores freely throughout the reaction.

The reaction will be diffusion controlled when diffusion of low molecular mass reactant into and product out of the polymer beads is slower than the intrinsic reactivity observed in low molecular mass analogues. The rate of diffusion obviously depends on many factors such as extent of swelling and interactions between the polymer and reactant. Factors which affect the rates of reaction in crosslinked polymers are rather complex, for even relatively simple reactions. Changes may constantly be occurring as the reaction proceeds. The polymer supported reactions display size and porosity based substrate selectivity over and above that shown by their homogeneous counter parts [52].

1.5.1 Site isolation

The reactivity of functionalised polymer is altered by site isolation. The interactions between two functional groups are statistically limiting on attachment to a polymer. There has been considerable experimentation and debate concerning the possibility of achieving site isolation of functional group bound to crosslinked polymers [53].

In principle, it is possible to introduce functional groups onto permanent three dimensional polymer networks in such a manner that each group experiences a state analogous to infinite dilution in homogeneous solution. Such a situation could be important for producing species such as coordinatively unsaturated metal complexes that would be destroyed by rapid self condensation under homogeneous conditions [54].

There is also considerable potential for the attachment of symmetrical polyfunctional compounds at one end leaving the other end free to be chemically transformed [55] to inhibit undesired bimolecular reactions and to induce unimolecular reactions not normally observed in homogeneous systems [56].

Site isolation is generally favoured in lightly crosslinked systems [57] at low loading (<5%) of pendent functional groups. However this does not always lead to site isolation, especially when the distribution of bound groups is nonuniform and results in high local concentrations. The site-site interactions and long range flexibility will be less favoured at higher crosslinking densities [58].

1.5.2 Microenvironmental effects

The discussions presented above indicate that reactivity of functional group inside a polymer medium is governed by its microenvironment. Polar groups produce significant field effect at neighbouring sites. The microenvironment is altered when the tendency of polymer to absorb low molecular mass compounds is strong. A classical example of reaction where in the reactivity is altered by neighbouring ionic groups is the alkali induced ionisations of poly(acrylic acid) and poly(methacrylic acid) [59].

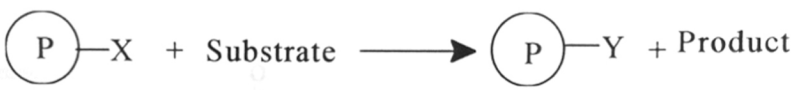
1.5.3 Steric effects

The reactivity of functional group is depressed on direct attachment to the polymer backbone due to steric crowding. This depressive effect is diminished with increase in the distance between the functional group and the polymer backbone. Steric effects also come into play when the solvent does not interact favourably with either the polymer or bound species. The intrinsic reactivity of a species is not altered by attachment to a macromolecule but it is confined to a smaller volume

compared to the low molecular mass analogue. Therefore, the interactions between the groups are potentially greater. Solvent swells crosslinked polymer and surrounds the functional group to generate situation similar to that experienced by low molecular mass analogues.

1.6 Polymer supported reagents

Polymer supported reagents carry a chemically reactive functional group which needs to be used in stoichiometric amounts in a one step process to convert low molecular mass substrates into products. The active functional group of the support is consumed during the reaction and the spent reagent/ by-product remains attached to the polymer structure. The reaction can be represented as :



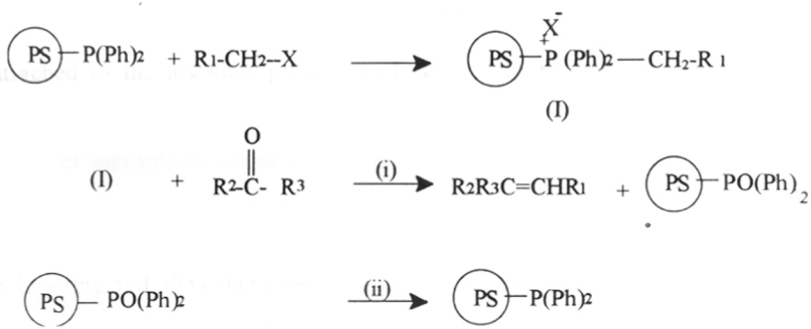
Polymer supported reagents can be prepared either by the physical adsorption (ionic binding) or by the covalent binding of a reagent to polymeric matrix. The former is generally not preferred since they may decompose/ desorb during the reaction and cannot be recycled. The covalently bound reagents are stable and can be regenerated and recycled.

Many hygroscopic, pyrophoric and explosive reagents have been immobilised on polystyrene supports for organic reactions as substrates and/ or catalysts. These include aluminium chloride [60], p-toluene sulphonic acid, perfluoroalkane sulphonic acid [61]. Reagents like chromium (VI) species are highly toxic. The quaternary trifluoro acetochromate (VI) polymer prepared from Amberlyst A-26 with chromium trioxide and trifluoro acetic acid showed greater activity for oxidation of secondary alcohols without the toxic effects [62]. Polymeric percarboxylic acids have

been prepared from polystyrene analogues of benzoic acid and benzoyl chlorides [63]. The supported peracids are relatively stable and selective and can be recycled.

1.6.1 Recyclable polymer supported reagents

Polymer supported reagents offer better selectivity and are recyclable [64]. The Wittig reaction is widely used for the regiospecific introduction of carbon double bonds. The expensive reagent and the problems associated with product separation are the major draw back of the reaction. Polymer supported Wittig reaction eases the product isolation. A generally useful Wittig reaction sequence is:



(i) $NaCH_2S(O)Me$, Me_2SO;

(ii) $HSiCl_3$, Benzene

1.6.2 Polymeric halogenating agents

These have generated considerable interest in the halogenation of olefins since these provide better selectivity and are relatively free from undesirable side reactions. Crosslinked styrene/polyvinyl pyridine-bromide complexes brominate alkenes highly stereoselectively [65].

Recently, bromine complexes of polymers bearing basic units like pyridines have been tested for the role of polymer matrices on reactivity [66].

1.6.3 Polymeric condensing agents

Dicyclohexyl carbodiimide (DCC) and similar condensing agents are used extensively for amide bond formation in peptide synthesis. A major difficulty with DCC is that the byproduct of the reaction (N,N-dicyclohexyl urea) tends to crystallise which complicates the purification procedure. Polymer bound insoluble carbodiimide derivatives overcome this recovery problem [67] and have generated interest in oxidation of highly sensitive alcohols (Motaff's reaction) and many other reactions related to the conversions of carboxylic acids [68]. The by-product (urea) remains attached to the insoluble polymer and can be readily recovered and reconverted into carbodiimides.

1.6.4 Polymeric acylating and alkylating agents

Polymeric acylating and alkylating agents are used in organic syntheses. Poly(vinyl pyridine) and polymer bound 4-dimethyl amino pyridine have been used effectively in esterification and acylation reactions [69]. 4-(Dimethyl amino) pyridine and its analogues have gained importance as super nucleophilic acyl transfer catalysts in nonaqueous media [70]. Polymeric 4-(dialkyl amino)pyridines (PDAAP) have been evaluated as enzyme mimics in the hydrolysis of 4-nitrophenyl alkanoates. The catalytic activity of some PDAAP in aqueous media has been documented [71]. Polymer bound reagent provide good selectivity and selectively generate mono substituted products.

1.6.5 Reagents and catalysts for regioselective reaction

Polymer bound chiral reagents have succeeded in generating high enantiomeric excess (*ee*) in asymmetric syntheses. Chiral aminoalcohol prepared from (*S*)tyrosine and borane in tetrahydrofuran reduced alkyl phenyl ketones quantitatively to secondary alcohols in 76-97 % *ee* [72].

1.6.6 Miscellaneous reagents

Polymer bound photosensitiser, Rose Bengals, has been used to probe certain structural parameters in the polymer itself. Peroxides covalently anchored on polymers have been used to initiate free radical vinyl polymerisations [73,74].

1.6.7 Reactions with polymer bound substrates

Polymer supported substrates have been reviewed recently [75]. Organic substrates could be bound to polymer supports to conduct reactions as a heterogeneous species and then detached from the polymer. A general problem associated with this strategy is that the desired polymer products cannot be completely separated from the contaminating polymer byproducts after each reaction. Consequently, the reaction sequences need to be very short unless each polymer supported reaction leads specifically to a single product at high yields. However this field of research has generated considerable interest due to advantages arising from site isolations.

1.6.7.1 Polymer supported protecting groups

Protecting groups are used in organic syntheses to prevent a potentially reactive group from reacting with a reagent used for the conversion of other groups in the substrate [76]. In a homogeneous medium it is difficult to selectively transform one functionality of a symmetrical difunctional group. Functionalised insoluble polymers have been marginally successful in these synthetic strategies. 1-Polystyryl-2,2-dimethyl-1,3-propane diol was used to protect one aldehydic group of terephthaladehyde through acetal linkages, while the other aldehydic group underwent a variety of organic transformations like Wittig, Grignard etc. Subsequently the aldehyde group was deprotected with formic acid in chloroform [77].

1.7 Polymer bound catalysts

Catalysts can be classified as either heterogeneous or homogeneous. Heterogeneous catalysts are finely divided functional catalytic groups (metal or metal oxides in case of transition metal catalysts) supported on carbon, silica, alumina, zeolite and some other inorganic supports. These catalysts are very durable (reusable), can be readily separated from reactants and products but are frequently less selective and active. Heterogenising of homogeneous catalyst, which combines the advantages of the two, can be achieved by attaching the homogeneous catalyst to an organic polymer in a manner that the ligand sphere of the metal is essentially unchanged and the attached complex is bathed (wetted) by solvent and reactants.

Thus, a polymeric catalyst is a conventional catalytic species supported on a macromolecular backbone which is used in catalytic quantities relative to reaction substrates. Performance of a polymeric catalyst is influenced by physical and chemical properties of the support. In addition, the efficiency is related to other factors such as: (a) properties of both catalyst and reactants, since

these determine the activation energy of the reaction; (b) distribution coefficient of the reactant between the solution and catalyst and (c) the nature of the solvent.

1.7.1 Industrial applications

Only few commercial applications involving polymer supported catalysts are reported notwithstanding the great burst in research activity. This includes ion exchange resins, primarily sulphonated S-DVB copolymers, widely used for acid catalysed reactions in industrial chemistry and in waste water treatment.

1.7.2. Comparison with inorganic catalyst supports

The polymeric supports offer several unique advantages compared to inorganic supports. These supports have virtually inert backbones and are therefore excellent for preventing unwanted side reactions in catalyst cycles or in the synthesis strategies. Simple chemistry is employed in the synthesis of polymeric catalyst. The polymers offer high degree of functionalisation resulting in a large number of active sites (high loading). The number of active sites available on surface of metal oxides is relatively low and molecular diffusion of the substrate on to the bulk of catalyst is very limited. In some cases the polymer also stabilises the coordinative unsaturated metal sites. Polymer support also offers unique opportunity for the design of multifunctional catalysts.

Despite several potential advantages, polymeric catalysts have limitations. The most pertinent one is the deactivation when used for long term in flow reactors due to leaching of metal from polymer support. Many polymers are physically robust which results in attrition during catalytic process in stirred reactors. In contrast to metal oxides, polymer supports can not be regenerated by burning off carbonaceous deposits due to instability at higher temperatures. In addition, metal oxides are inexpensive, readily available in wide ranges of purity and physical properties such as

surface area, pore size distribution, particle size and shape and are resistant to crushing and attrition.

1.7.3 Polymer supported base and acid catalysts

The synthetic parameters of various catalysts and their industrial applications have been reviewed [78]. Poly(vinyl pyridine) and its derivatives are widely used as acid scavengers and in the esterification reactions of acid chloride and carboxylic acids [79]. Polymer supported disubstituted aminopyridines are promising super bases [80]. Polymer substituted alkoxides have been used for the elimination of hydrogen bromide from 2-bromooctane and p-toluene sulphonic acid in dimethyl sulphoxide [81]. The hydroxide forms of commercial anion exchange resins are the simplest and readily available polymer supported bases. They are used in reactions like base hydrolysis of esters, aldol condensations, Michael additions of stabilised carbanions, etc. The catalytic potentials of various polymer supported chiral amines have been studied; a case in point is polyethyleneimine catalysed hydrolysis of aspirin [82].

Acid catalysis, the most frequently applied process in organic chemistry, has always been of critical importance in chemical technology. Sulphonated polystyrenes, the most successful catalyst, is used in the hydration of propene and its esterification with acetic acid [83].

1.7.4 Catalysis by transition metal complexes

The activity of transition metal complex catalysts originates from the binding of reactants to the open coordination site of the metal complex and their subsequent transfer to the product, thereby generating a free catalyst. Hence, the prime requirement for catalytic activity is that the species present in solution should be coordinatively unsaturated, permitting the reactants to form bonds to the metal ion. A loss in activity is noted when the complex dimerises during the opening of the

active site. Hence, the basic requirement for metal complex to function as catalyst is the availability of open coordination sites and isolation of reactive binding sites. An important property of transition metal complexes is their ability to coordinate groups in a specific manner leading to high regio- and stereo-specificity in the ensuing catalytic reaction. Coordinative unsaturation, the template effect and substrate activation are basic to all reactions homogeneously catalysed by transition metal complexes.

1.7.5 General features of polymer bound transition metal complexes

The optimum polymeric catalyst for a particular reaction can be determined by variation of number of parameters. These are: (a) nature of support, (b) nature of metal complex, (c) degree of crosslinking and (d) nature of solvent.

The properties of catalyst formed by the chemical binding of soluble transition metal complexes to a polymer lies in between those of homogeneous and heterogeneous catalysts. The advantage of anchoring catalytically active transition metal complexes on to polymer matrix has been discussed in *Section 1.1*. Considerable research efforts have gone into the immobilisation of these complexes. The polymer transition metal complexes are markedly useful as immobilised catalysts in a variety of reactions such as hydroformylations, carbonylations, oxidations, polymerisation and in asymmetric synthesis.

The syntheses and catalytic properties of polymer supported hydrogenation catalysts have been reviewed [84]. Polymer bound transition metal complexes such as palladium, ruthenium, and rhodium complexes have generated interest as hydrogenation catalysts [85]. The immobilisation of Wilkinson catalyst, rhodium phosphine complex, has generated much interest [86]. The synthesis and catalytic properties of poly(vinyl pyridine)-rhodium complexes as carbonylation

catalyst of methanol has been reported [87]. The successful immobilisation of Wacker catalyst, palladium complex, has been recently reported by Sherrington [88]. The high thermal stability of the new polybenzimidazole matrix allows the use of catalyst at higher temperature. The catalytic activity and selectivity of the polybenzimidazole-palladium complexes are comparable with the conventional cyano functionalised S-DVB copolymer-palladium complexes.

1.7.6 Metal complexes in Oxidations

Transition metal peroxides, particularly peroxo, alkyl peroxo and hydroperoxo complexes, are extremely important reactive intermediates in catalytic oxidations involving molecular oxygen, hydrogen peroxide and alkyl hydroperoxides as oxygen sources. Peroxide complexes are potential oxygen donors to organic substrates but only a few of them are reactive. The reactivity depends on physical criteria such as solubility in organic substrates and chemical criteria, such as the nature of metal, geometry of complex and availability of vacant and releasable coordination sites for complexation of substrate as well as the overall charge on the reagent.

As rationalised by Sheldon and Kochi, metal catalysed oxidations can be conveniently divided in two types designated as homolytic and heterolytic [89]. Homolytic oxidations involve free radical intermediates and are catalysed by first row transition metals, characterised by electron oxidation-reduction steps. The hydrocarbon substrates are not coordinated to the metal, and are oxidised outside the coordination sphere. Consequently the coordination is not selective and does not preserve stereochemical configuration of the substrate. Heterolytic oxidations generally require activation of the substrate by coordination to the metal and are generally highly selective and stereospecific. These do not involve free radical intermediates and use second and third transition metals, which either conserve their oxidation states or change it by a two electron reduction step.

In several situations the metal can act both as homolytic and heterolytic catalyst. For example, vanadium complexes catalyse the epoxidation of allylic alcohols by alkyl hydroperoxides stereoselectively [90] and involve vanadium (V) alkyl peroxides as intermediates. Vanadium (V) alkyl peroxide complexes such as (dipic) VO(OOR)L, which do not have any coordination site for the complexation with alkenes to occur, react homolytically [91].

In summary, the homolytic or heterolytic nature of oxidation is principally governed by the nature of the metal, ligands and substrate, the availability of coordination sites.

1.7.7 Polymer supported phase transfer catalysts

The reaction mechanisms and kinetics of S-DVB copolymer supported phase transfer catalysis has been reviewed [92]. A variety of synthetic applications of supported phase transfer catalysts such as quaternary ammonium ions were reported by Regen [93]. Liquid-liquid or solid-liquid phase separated reactions are accelerated by the addition of phase transfer catalysts such as organophilic onium salts or crown ethers or cryptands. The catalysts aid the transfer of anions across the phase boundary either by complexing with attendant metal cation or replacing it in an ion pair equilibrium. Polymeric phase transfer catalysts are insoluble polymers which have covalently bound catalytically active functional groups for reactions between anions and neutral organic substrates. The active functional group may be quaternary ammonium or phosphonium ions, crown ethers, cryptands, grafted poly(ethylene glycols) [94-96]. The reactions can be conducted in triphase mixtures of organic liquid, solid or aqueous inorganic salt and solid catalyst. The chemical reactions take place within the polymer support or at the polymer surface. The toxicological problems of crown ethers can be avoided by immobilising on to a polymeric

support. Recently, Shuji et. al have investigated the phase transfer reactions of octyl bromide with potassium thiocyanide, catalysed by polymer supported imidazoles [97].

1.8 Polymer bound chelating agents

The history of the early development of chelating resins was reviewed in 1957 by Miller [98]. The first chelating resins, found suitable for selective adsorption, were based on the imino diacetic acid functional groups. The range of stability constants for the resin-metal complexes were three orders of magnitude greater than that of an ordinary sulphonic acid resin.

Chelating groups such as amine, heterocyclic nitrogen, carboxylic acid, phosphonic acid, thiol and Schiff base can be bound covalently to polymers to generate chelating copolymers suited to selective removal and recovery of metal ions from aqueous solutions. Since toxic and valuable metal ions are generated extensively in machinery, catalysts, electronic industry and other applications, the removal and separations of metal ions from complex sources, industrial effluents and waste water are of great public concern. This has generated a rapid growth in the study and synthesis of ion exchange resins and chelating copolymers for the selective separation of metal ions. The selectivity of chelating copolymers far exceed that noted with conventional ion-exchange resins.

The mechanisms of metal adsorption from an aqueous solution by chelating and cation resins are similar. However, the exchange of metal cations in solution with the protons on the resin does not involve dehydration of the metal ion for cation exchange resins, but for chelating resins it does; and the metal ion is bound by a combination of outer sphere ionic and inner sphere covalent forces [99].

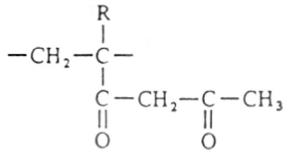
The coordination of all vacant valencies in the metal ion results in a very strong bond, and this in turn, ensures greater selectivity than that can be achieved with cation exchange resins.

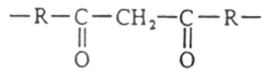
All transition metals are known for their ability to form strong coordination compounds and thus a very good selectivity for transition metals (over non transition metals) can be achieved with all chelating resins. Reasonable selectivity for one or more metals can also be achieved, since theoretical considerations derived from valence bond theory and experimental analytical techniques predict that the stability constants of metal complexes will depend primarily on the electronic configuration of the metal and only to a minor extent on the ligand. A linear relationship has been established between metal stability constants and the sum of the first and second ionisation potentials of the metal; being the ionisation potential as a measure of the tendency of the metal to accept electrons from the ligand. The size and charge of metal ion have only a marginal effect in determining the selectivity of the chelating resin. In the first transition series, the strength of the coordination compound almost invariably increases according to the well known Irwing -Williams series $Mn^{+2} < Fe^{+2} < Co^{+2} < Ni^{+2} < Cu^{+2} > Zn^{+2}$ [100]. Therefore, copper can be extracted selectively from a solution containing manganese, iron, nickel, cobalt and zinc. To find a ligand that reverses this general trend at any stage and to incorporate that specific ligand into a polymeric matrix is far more difficult. This has been a challenge for chemists for some time now. For example, a number of research workers have attempted to incorporate the well known nickel specific ligand dimethyl glyoxime into a polymeric matrix. Although nickel selective resins based on this ligand have been made, they have suffered from other problems, such as hydrolytic stability of ligand functional group or lower selectivity. The various chelating groups employed in the syntheses of chelating copolymers are shown in Table **1.2**.

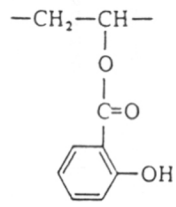
Coordinating groups	Repeating units of polymer ligands
Amines $-NH_2$, $>NH$, $\geqslant N$	$-CH_2-CH(NH_2)-$ $-NHCH_2CH_2-$ $-CH_2-CH-$ (with $CH_2NHCH_2CH_2NR_2$) $-CH_2CH(CH_2NR_2)-$ $-NH-CH(CH_2)_4NH_2-CO-$
Nitrogen of heterocyclic compounds	$-CH_2-CH-$ (pyridyl) $-CH_2-CH-$ ($N=N-$ quinolyl-OH) $-NH-CH(CH_2)-CO-$ (imidazolyl) $-CH_2-CH-$ (imidazolyl) $-CH_2-CH-$ (CH_2-O pyridyl) $-CH_2-NH$ biphenyl $NH-CH_2-$ (pyridyl)
Schiff base $>C=N-$	$-OH$ $CH=N$ $N=CH$ $HO-$ $-CH_2-CH(N=CH-C_6H_4-OH)-$ $-CH_2-CH(C(=N-OH)-C(=N-OH)-CH_3)-$
Alcohols $-OH$ carboxylic acids $-COOH$	$-CH_2-CH(OH)-$ $-CH_2-C(R)(COOH)-$ $-CH(COOH)-CH(COOH)-$

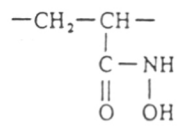
Table 1.2 . : Various polymeric ligands employed for metal complexation

Ketones $>C=O$
esters, amides

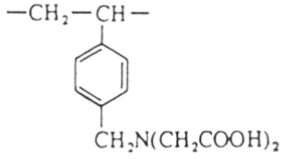


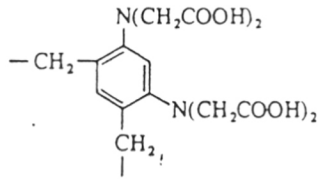


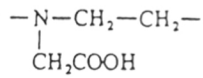




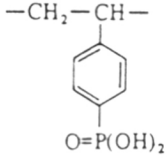
Aminopoly-
carboxylic acids

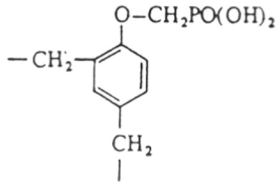




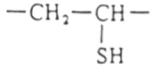


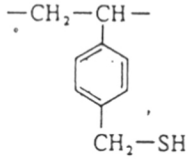
Phosphonic acids
$-PO(OH)_2$

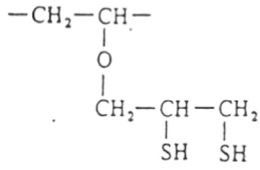


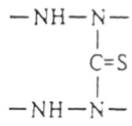


Thiols
$-SH$









1.9 Polymer metal complexes

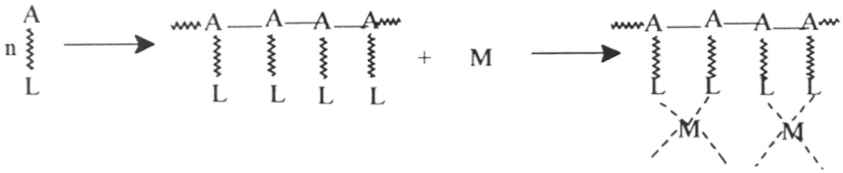
This metal complex consists of a polymer ligand, which is surrounded by polymer chains or is located in a polymer network. The simplest method to generate a polymer-metal complex is to treat a polymeric ligand L' with a solution of complex possessing ligand L [101]. The metal complexation is achieved by mixing the polymer chelant with metal ion solution. The structure and characteristics of the polymer metal complexes depend on the number of coordinating groups present in the polymer ligand. With a polydentate polymer-pendant coordinating group, the coordination structure would be precise and stable. The best polymeric polydentate ligand is S-DVB with iminoacid type group.

The other type of polymer metal complexes formed by the chain linking of bifunctional ligand through the complexation with metal ions, are known since 1950 as semiconducting organic molecules. The third type of polymer metal complex is formed by the polymerisation of monomeric ligand-metal complexes. An example is the radical polymerisation of methacrylate monomer co-ordinated to Co(III). Homo/ copolymerisation would generate polymer metal complexes of defined structure but this strategy is of limited scope since polymerisation is difficult to control because of strong interactions between the polymerisation initiator and the metal [102]. Pictorial presentation on the syntheses of different types of polymer-metal complexes is given in Fig. **1.2**.

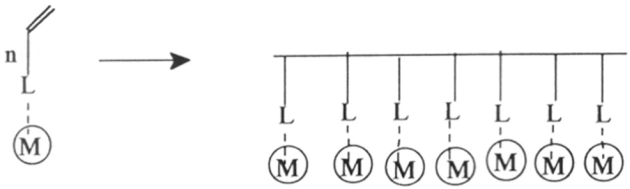
The most important applications of polymer metal complexes would be their use as immobilised reagents. Ruthenium complexes of poly(vinyl pyridines) are known to convert solar energy into chemical energy. Polymers with bipyridyl ruthenium complexes have been synthesised and used for the conversion of solar energy. The redox properties of polymer containing redox reagent,

Fig.1.2. **Different methodologies of polymer-metal complex syntheses**

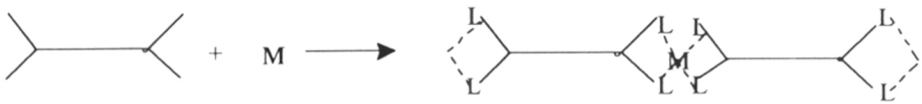
1. Polymerisation of functional monomer followed by metal coordination



2. Polymerisation of metal containing monomers



3. Polymer formation through metal coordination



ferrocene has been synthesised and the redox potential has been evaluated [103]. A recent review describes the synthesis and evaluation of metal containing polymers [104].

1.10 Characterisation of polymer-metal complexes

The modification of polymer supports, polymer-transition metal complexes and the reactions using these reagents can be studied by a number of techniques. While each technique has limitations, a combination of techniques needs to be used to provide better and accurate results.

Elemental analysis is a simple and essential test for carbon and hydrogen. The technique has some validity for element gained or lost in the reaction such as nitrogen, halogen, sulphur and phosphorous. Gravimetric analysis is useful for reactions of crosslinked polymers since this leads to significant changes in mass at higher temperature. However, interpretation would be difficult if side reactions occur, which lead to volatilisation of metal ions. Chemical titration method is widely used for the characterisation of various chelating copolymers and polymers containing groups such as phenols, acids and bases.

1.10.1 Physico-chemical methods

The detailed account of various techniques useful for the characterisation of polymer metal complexes has been reviewed [101]. Instrumental techniques are suited to the characterisation of polymer supported species, especially polymer supported transition metal complexes. The coordination of a polymer ligand to metal ions or to metal complexes and the structure of the resulting polymer metal complexes can be investigated by Infra-red (IR) spectroscopy, nuclear magnetic resonance (NMR), electron spin resonance (ESR) and X-ray analysis. Other techniques

like optical rotatory dispersion or circular dichroism are suited to the study of microenvironment around metal ions.

IR is most frequently used to determine the chemical structure of the crosslinked polymer matrix and its functional groups. The adsorption of ligand is usually shifted on complexation with metal ions. Thus, the adsorption of pyridine assigned at 1580 cm^{-1} is shifted up by about 30 cm^{-1} on complexation in cis-[$Co(en)_2Py.Cl$] [105]. Spectrochemical characterisations are widely used for the determination of the structure of organometallic species and to locate the binding of the species in polymer supported catalysts. The polymer bound species can be well characterised by comparing the spectra with that of molecular analogues. It is possible to make differential observations with Fourier transform infra-red spectroscopy. This is suited to the characterisation of metal complexes, especially supported metal carbonyls. High quality spectras are obtained with thin polymer membranes. A number of methods have been developed to study catalyst beads in presence of liquid reactant [106] and gaseous reactants.

The coordination structure of polymer metal complexes can be investigated by electron spin resonance spectroscopy. The interaction between the spin of the central metal ion and the co-ordinated ligand influences the absorption pattern and its g (gyration constant) value, which in turn is used to study the metal-ligand bond.

The extended X-ray adsorption fine structure [EXAFS] appears to offer the greatest potential for characterising polymer-metal complexes since this gives a detailed information regarding the microenvironment of the metal as it is surrounded by ligands since this defines the catalytic activity. Reed et. al characterised analogues of Wilkinson alkene hydroformylation catalyst

bonded to phosphine functionalised S-DVB copolymer [107]. The EXAFS technique has become widely accessible with easy availability of synchrotron radiation.

Nuclear magnetic resonance spectroscopy is an efficient tool for the characterisation of soluble functional polymers. ^{1}H and ^{13}C NMR are widely used to determine tacticity and compositions of copolymers. ^{31}P NMR has been used for the characterisation of polymer supported phosphine-rhodium complexes. The highly functionalised copolymer gave high signal strength and showed a nearly uniform environment for phosphorous through out the polymer. The structures of the polymer-metal complex and the molecular analogues were assigned from NMR spectra. Proton magnetic spectra has not been used for structural analysis of polymer-metal complex because of poor solubility of polymer. and broadening of the spectrum on complexation.

X-ray photoelectron spectroscopy [XPS] has been an useful technique to characterise metals in polymers as it provides the binding energies of the core electrons. The method is a means to compare different forms of a given sample and provides precise evidence of changes in metal oxidation state due to catalysis. The data can occasionally be used to determine absolute oxidation states. Srinivas et. al investigated the catalytic activity of polymer supported-palladium complexes on the hydrogenation of alkenes activated by different methods and discussed the binding energy of synthesised palladium atoms [108].

Polymer supported catalysts have also been characterised by quantitative electron microprobe analysis to determine the distribution of reactive groups, profiles of metals and other elements

within individual beads of polymer. Particle is sectioned, mounted and traversed with an electronbeam in vacuum system and the emitted X-ray signals provide quantitative elemental analysis of roughly 1 μm^3 volume of the sample.

1.10.2 Stability Constant

The most important character of polymer ligand is the stability constant of the respective metal complex. The stability constant of polymer-metal complexes are most frequently higher than their monomeric analogues. It is determined by modified Bjerrum method [1955] and is mostly applicable to the soluble polymer metal complexes [109]. Recently, methods have been developed to determine stability constant of heterogeneous polymer bound dispheroxime iron complexes by ligand competitive method [110].

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Chapter II

Experimental

EXPERIMENTAL

2.1 GMA-EGDM Copolymer beads

2.1.1 Materials

Glycidyl methacrylate (GMA), also known as 2,3-epoxypropyl methacrylate, obtained from Fluka A/G, Switzerland was used as received in the preparation of macroporous reactive GMA-EGDM copolymers. Ethylene glycol dimethacrylate (EGDM), also known as 1,2-ethane diol dimethacrylate, obtained from Fluka A/G, Switzerland was also used as received. Cyclohexanol and lauryl alcohol, used as pore generating solvents were obtained from M/S Aldrich Chemical Co. (USA). Poly(vinyl pyrrolidone) obtained from M/S. Polysciences, USA was used as protective colloid. Azobis(isobutyronitrile) [AIBN], obtained from M/S SISCO, India was used as the initiator after reprecipitation in ethanol.

2.1.2 Polymerisation of glycidyl methacrylate-ethylene glycol dimethacrylate

The synthesis was conducted in 1 litre double walled cylindrical reactor of 11 cm diameter and 15 cm height (Fig. **2.1**). The continuous phase comprised of one weight percent aqueous solution of poly(vinyl pyrrolidone) (PVP). The discontinuous organic phase consisted of glycidyl methacrylate, crosslinking divinyl monomer, ethylene glycol dimethacrylate, polymerisation initiator AIBN and a mixture of cyclohexanol and lauryl alcohol used as pore generating solvent. The ratio of aqueous phase to organic phase was 2.8:1.0. The discontinuous organic phase was introduced into the aqueous phase, stirring was set at 300 rpm and the temperature was maintained at 70°C by circulating hot water. The polymerisation was continued for normally 3 hours. The copolymer obtained in beaded form was separated by decantation, washed with

methanol, water and dried at room temperature under reduced pressure. The compositions of synthesised GMA-EGDM copolymers are presented in Table **2.1**.

TABLE 2.1

Composition of glycidyl methacrylate (GMA)-ethylene glycol dimethacrylate (EGDM) copolymers synthesised. Polymerisation temperature = 70°C; Time = 3 hours; Water = 250 cm^3 ; Poly(vinyl pyrrolidone) = 2.5 g and AIBN = 0.6 g.

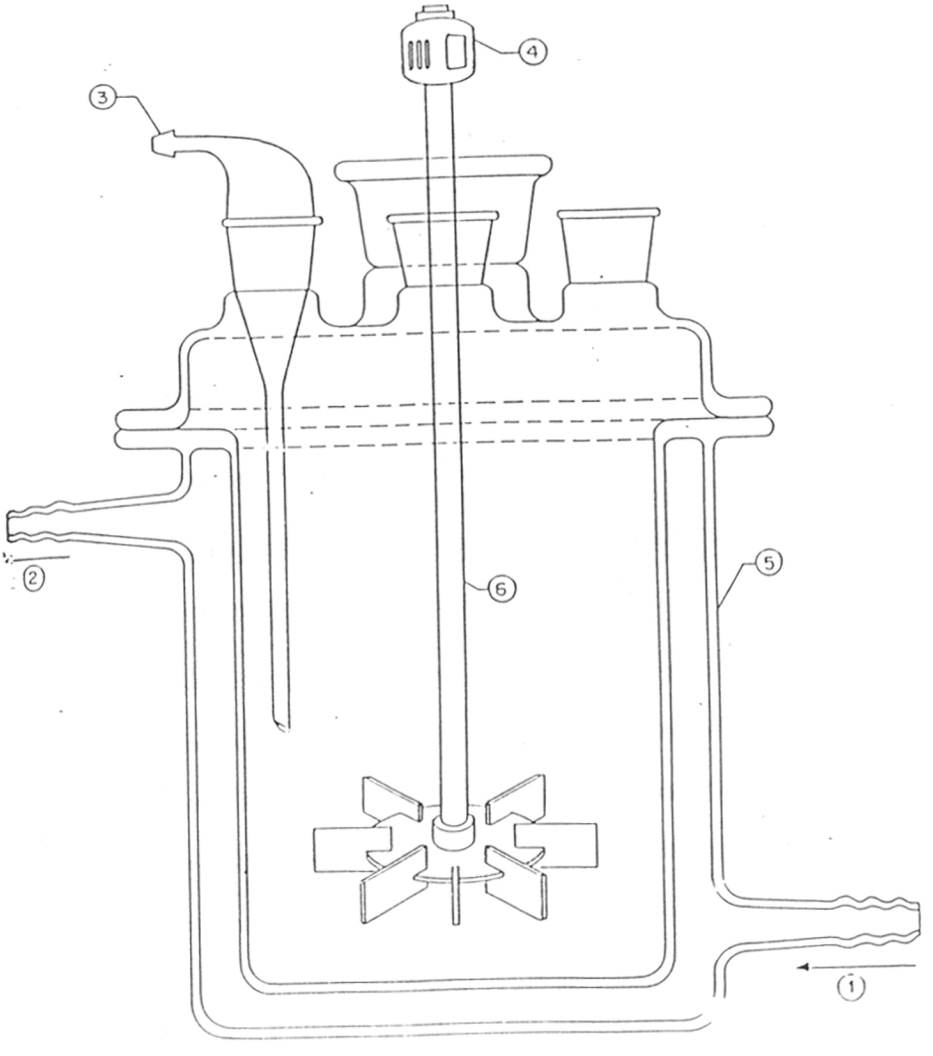
GMA cm^3	EGDM cm^3	CL	mmole of epoxy/ g polymer	copolymer yield %
28.7	4	10	6.1677	95
24.3	8.4	25	5.2161	98
19.3	13.4	50	4.1374	96
13.7	19.0	100	2.9325	95
7.4	22.1	125	1.717	100

CL = crosslinking density

2.2 Characterisation of copolymer beads

The specific surface area measurements, based on single point nitrogen adsorption method, more popularly known as BET method, were conducted using Quantachrome (USA) Quantasorb. The pore size distribution and pore volume were determined by mercury intrusion porosimetry in the

Fig. 2.1. Laboratory scale assembly for suspension polymerisation reactor



(1) HOT WATER INLET (2) HOT WATER OUTLET (3) NITROGEN BUBBLER
(4) STIRRER MOTOR (5) REACTOR FLASK (6) STIRRER

pressure range of 0-4000 Kg/cm with an Autoscan 60 mercury porosimeter from Quantachrome, USA. The copolymer beads were dried at 150°C under vacuum prior to analysis.

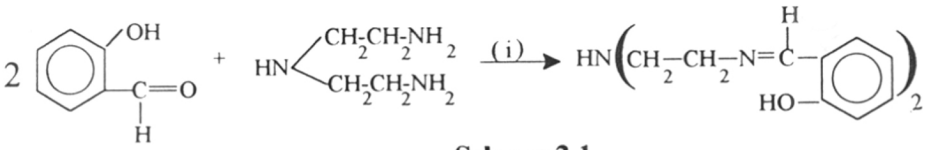
The epoxy content of copolymers were determined by a modified hydrochloric acid-dioxane method [1]. The polymers were first swelled in 5 cm^3 of pure 1,4-dioxane by stirring at room temperature for three hours. To this a known excess of hydrochloric acid (0.2N in dioxane) was added and stirring was continued for 8 hours. The excess hydrochloric acid was estimated by pH titration with standard methanolic sodium hydroxide solution. The neutralisation point was taken as the midpoint of the break in the curve.

2.3 Synthesis of Ligands

2.3.1 Bis(2-hydroxy benzylidene amino ethylene) amine

Diethylene triamine was obtained from Loba Chemie., India. Salicylaldehyde was obtained from SRL (India) limited. The chemicals were vacuum distillated prior to use.

The bis(2-hydroxy benzylidene amino ethylene) amine was synthesised by reported procedure [2]. 0.1 mole [10.317 g] of diethylene triamine in 75 cm^3 dry ethanol was stirred with 0.2 mole [24.43 g] salicylaldehyde in presence of 4.0 g 4 A molecular sieve for 30 minutes each at 10°C and 30°C. The molecular sieves were filtered out and the product concentrated and analysed by infra-red spectroscopy and elemental analysis. The reaction is presented in **Scheme 2.1**.



Scheme 2.1

(i) Ethanol,

IR: 3440 cm^{-1} (O-H); 2960 cm^{-1} (C-H); 1628 cm^{-1} (C=N).

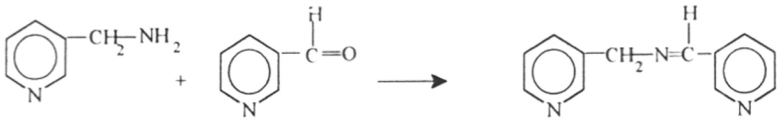
2.3.2 Bis(picolyl) amines

3-Amino methyl pyridine (pyridine-3-methanamine), 2-amino methyl pyridine (pyridine-2-methanamine), 2-pyridine carboxaldehyde and 3-pyridine carboxaldehyde were from Aldrich Chemical Co. USA., and were used as received. Sodium borohydride was from Loba Chemicals, Mumbai, India. Ethanol obtained from Loba Chemicals was used after distillation.

2.3.2.1 Bis(3-picolyl) amine

2.3.2.1.1 N-3-Pyridylidene-3- pyridine methanamine

Schiff base, N-3-pyridylidene-3-pyridine methanamine was prepared by treating 0.1 mole (10.80 g) 3-aminomethyl pyridine (3-pyridine methanamine) in 50 cm^3 absolute ethanol with 0.1 mole (10.71 g) 3-pyridine carboxaldehyde in 50 cm^3 ethanol under stirring. The whole mixture was stirred at room temperature for 3 hours in presence of 5.0 g of 4 A molecular sieves. The product was filtered and was concentrated by evaporating the ethanol from the product using a rotavap. The product Schiff base was analysed by infra-red spectrophotometry. The yield was quantitative. The reaction is presented in **Scheme 2.2**.



Scheme 2.2

2.3.2.1.2 Reduction of N-3-pyridylidene 3-pyridine methanamine

2.3.2.1.2.1 High pressure hydrogenation with Raney nickel catalyst

Raney nickel catalyst was prepared from nickel aluminium alloy according to reported procedure [3]. The hydrogenation of N-3-pyridylidene-3-pyridine methanamine was carried out using Raney nickel catalyst at 8 atmosphere pressure at 100°C. 0.1 mole [19.70 g] of N-3-pyridylidene-3-pyridine methanamine was dissolved in 100 cm^3 absolute ethanol and was taken in 250 cm^3 Parr reactor. 2.0 g Raney nickel catalyst was added and the reactor was closed. Hydrogen was passed into the reactor, the pressure of the system was maintained at 10 atmosphere and the reaction was continued for three hours. The product was separated by filtration and was concentrated by evaporation on a rotavap. The bis(3-picolyl) amine trihydrate formed was precipitated by adjusting the pH of the ethanolic solution to 4 with dilute hydrochloric acid. The yield was 45%. The bis(3-picolyl)amine and its trihydrate were analysed by elemental analysis, proton nuclear magnetic spectroscopy and by infra-red spectroscopy.

2.3.2.1.2.2 Reduction with sodium borohydride

0.05 mole [9.985 g] N-3-pyridylidene pyridine-3-methanamine was dissolved in 75 cm^3 ethanol and to this stirred solution 0.075 mole (2.35 g) sodium borohydride in 50 cm^3 aqueous ethanol was added and the mixture was stirred for 12 hours. Then 0.025 mole (0.9 g) sodium borohydride was added and the stirring was continued further for 12 hours at room temperature. The reaction

was monitored by thin layer chromatography (TLC). The product was filtered out and the filtrate was repeatedly extracted with dichloromethane. The dichloromethane was evaporated on a rotavap. The trihydrate of bis(3-picolyl)amine was precipitated by acidification with dilute hydrochloric acid. The yield was 65%. The reaction is presented in **Scheme 2.3a**

Scheme 2.3a

2.3.2.2 Bis(2-picolyl) amine

N-2-pyridylidene-2-pyridine methanamine was synthesised from 2-pyridine carboxaldehyde and 2-pyridyl methanamine as the procedure presented in Section **2.3.2.1.1**. The Schiff base, N-2-pyridylidene-2-pyridine methanamine was reduced by the procedure presented in Section **2.3.2.1.2.2**. The yield was 60%. The reaction is presented in **Scheme 2.3b**

Scheme 2.3b

^{1}H NMR is presented in Fig. **2.2.** The values are 6.7-8.4 (aromatic protons correspond to 8H), singlet at 3.8 corresponds to 4 methylene protons and a broad peak at 2.6, for secondary amino group, corresponds to ^{1}H.

IR: 3340 cm^{-1} (pyridine); 3000 cm^{-1} (C-H); 1578 cm^{-1} (C=N of Pyridine).

Elemental Analysis : C : 72.4 %; H : 6.68 %; N : 20.6 %.

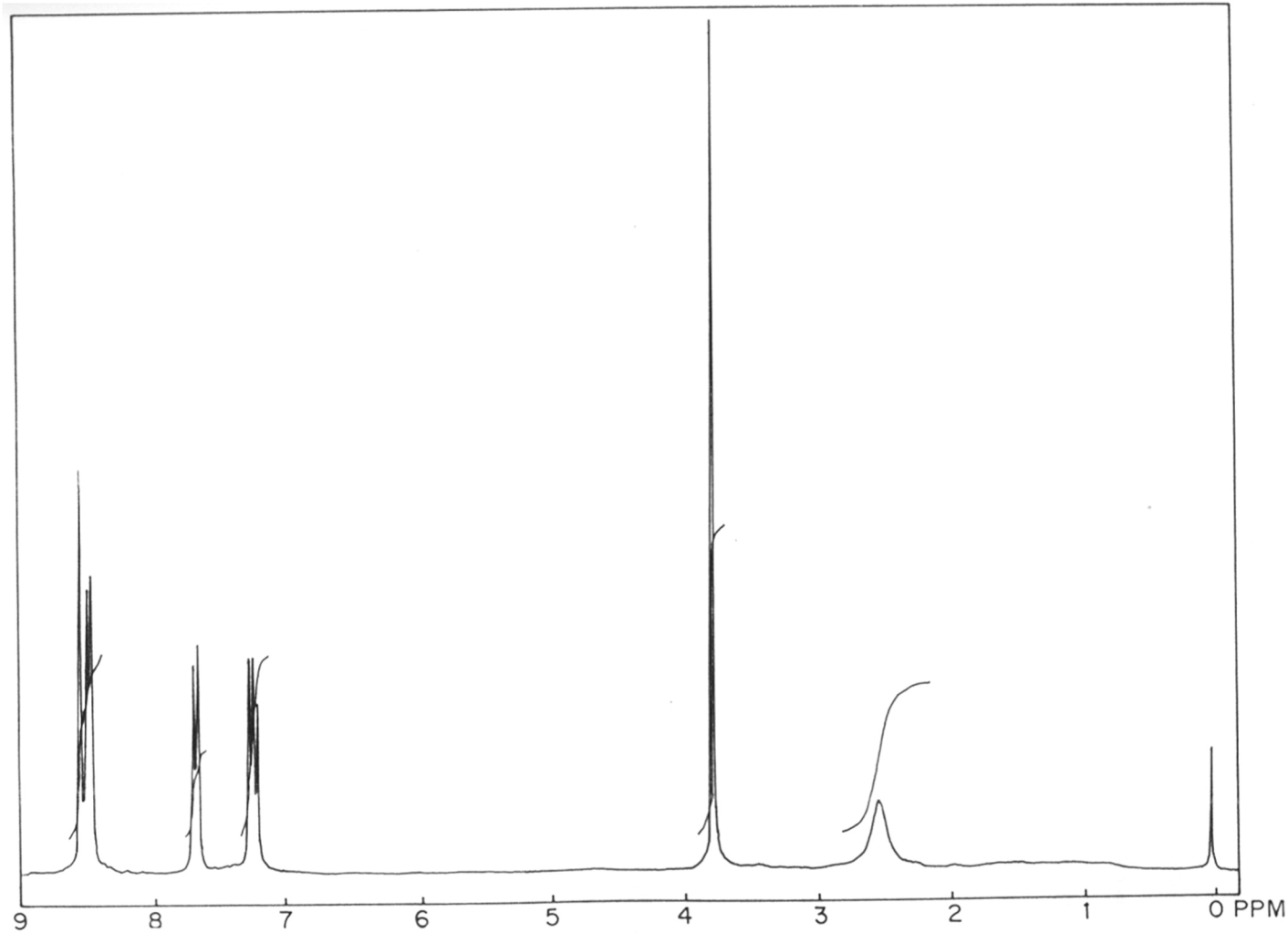


Fig. 2.2. 1HNMR spectra of bis(2-picolyl) amine.

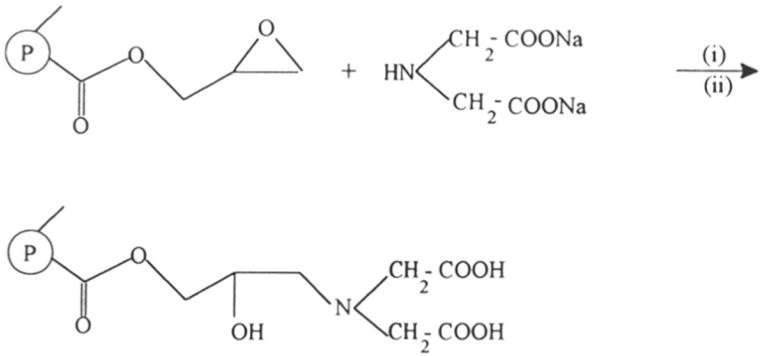
2.4 Chelating Copolymers

The following chelating copolymers were synthesised by the modification of macroporous GMA-EGDM copolymers: (i) Imino diacetic acid (IDA) copolymer; (ii) Schiff Base copolymer; (iii) Diethylene triamine (DETA) copolymer; (iv) Diethylene triamine tetraacetic acid (DTA) copolymer; (v) Bis(2-picolyl) amine copolymer; (vi) Bis(3-picolyl) amine copolymer and (vii) Dithiocarbamate copolymer.

2.4.1 Imino diacetic acid (IDA) copolymer

Imino diacetic acid was obtained from Aldrich Chemical Co., USA. Disodium salt was prepared by dissolving imino diacetic acid in 1.0N sodium hydroxide solution. The GMA-EGDM copolymer was modified by refluxing 5.0 g of copolymer beads (having 8.60 mmole epoxy group) with 100 cm^3 aqueous solution containing 5.71 g (43 mmole) disodium imino diacetate at pH 11.5 for 24 hours. The concentration of imino diacetic acid : epoxy group in polymer was 5.0: 1.0. The resultant imino diacetic acid incorporated beads were washed with distilled water and thrice with 0.2N hydrochloric acid and 0.2N sodium hydroxide. After a final washing with 0.2N hydrochloric acid, the beads were dried under vacuum at 30°C. The reaction is represented in Scheme **2.4.** The spectrum of copolymer is presented in Fig. **2.3b.**

Scheme 2.4



Imino diacetic copolymer

Scheme 2.4

(i) water, reflux; (ii) dilute hydrochloric acid

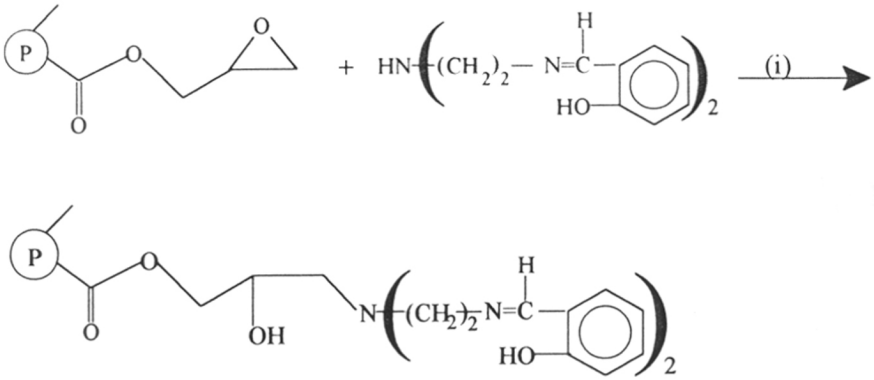
Elemental Analysis: Nitrogen content of IDA chelating copolymer was 1.61 Wt.%.

IR: 3400 cm^{-1} (O-H); 2920 cm^{-1} (C-H); 1726 cm^{-1} (C=O).

Capacity of copolymer (Chemical titration) 1.12 mmole of univalent Na^+ ions/g.

2.4.2 Pentadentate bis(2-hydroxy benzylidene amino ethylene) amine copolymer

10.0 g (29.36 mmole) of GMA-EGDM copolymer beads were refluxed with 18.25 g (58.70 mmole) of pentadentate bis(2-hydroxy benzylidene amino ethylene) amine in 100 cm^3 1,4-dioxane for 24 hour under stirring. The modified copolymer beads were filtered, washed with 1,4-dioxane, ethanol and water. Finally, the derivatised beads were soxhlet extracted with 1,4-dioxane and dried under vacuum at 50°C. The yield of derivatised polymer beads was 11.25 g. The reaction is represented in Scheme **2.5**.



Schiff Base Copolymer

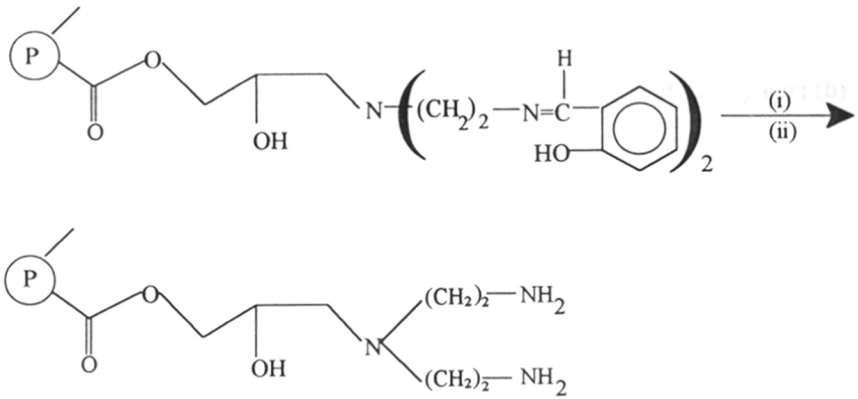
Scheme 2.5

Elemental Analysis: C : 53.85%; H : 5.69% ; N : 2.84%.

IR: 3420 cm^{-1} (OH), 2980 cm^{-1}(C-H); 1728 cm^{-1} (C=O); 1628 cm^{-1} (C=N).

2.4.3 Diethylene triamine copolymer

5.0 g of polymeric bis(2-hydroxy benzylidene amino ethylene) amine copolymer was heated with 75 cm^3 of 6N hydrochloric acid for 12 hours at 60°C. The yellow beads turned red due to cleavage of imine bond and generated free aldehyde in solution. The copolymer beads were washed free from salicylaldehyde with ethanol. Neutralisation with 0.2N sodium hydroxide solution yielded the diethylene triamine chelating copolymer. Yield was 4.9 g. The synthesis is presented in Scheme **2.6**. The Infra-red spectrum of the copolymer is presented in Fig. **2.4**.



Diethylene triamine Copolymer

Scheme 2.6

(i) 6N Hydrochloric acid; (ii) 0.2N sodium hydroxide

Elemental analysis : N : 2.62%.

IR : 3430 cm^{-1}(O-H); 3350 cm^{-1}(N-H); 2960 cm^{-1}(C-H); 1728 cm^{-1}(C=O).

2.4.4 Diamino tetraacetic acid copolymer

The tetraacetic acid copolymer was synthesised by the N-acetylation of the diethylene triamine chelating copolymer. Sodium monochloroacetate was prepared by neutralising 11.90 g chloroacetic acid solution in 40 cm^3 distilled water with sodium bicarbonate at 5°C. 4.0 g of copolymer was stirred at pH 10 with sodium chloroacetate solution at 70 °C for 16 hours. The tetraacetic acid copolymer formed was washed repeatedly with 0.1N hydrochloric acid, 0.1N sodium hydroxide and distilled water. The reaction is presented in Scheme **2.7**. The IR spectra of the copolymer is presented in Fig. **2.3a**.

Fig. 2.3. Infra-red spectra of (a) diethylene triamine tetraacetic acid copolymer; (b) Imino diacetic acid copolymer.

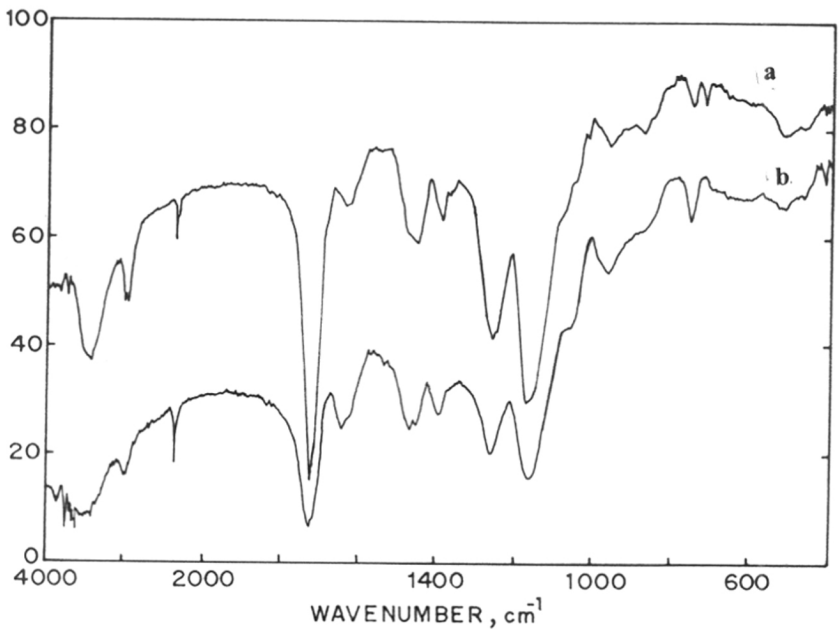
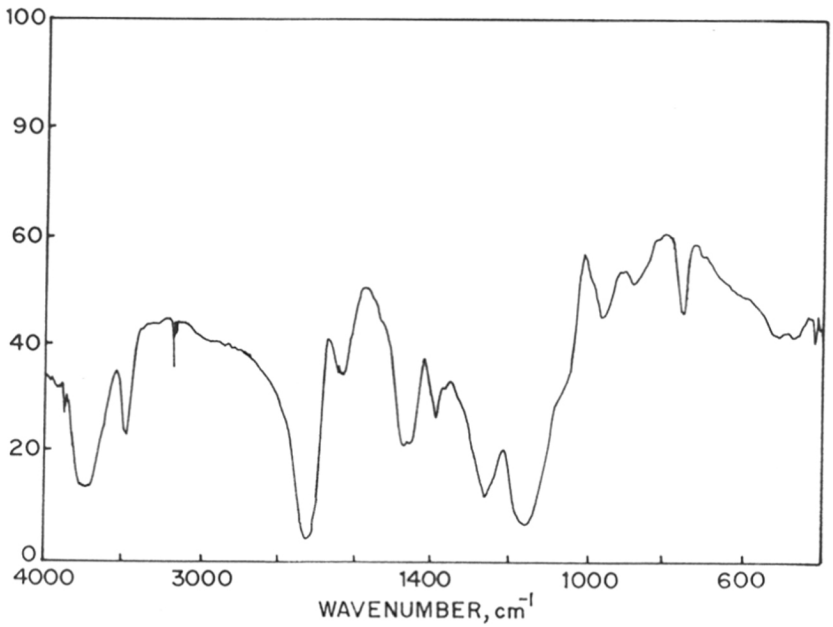
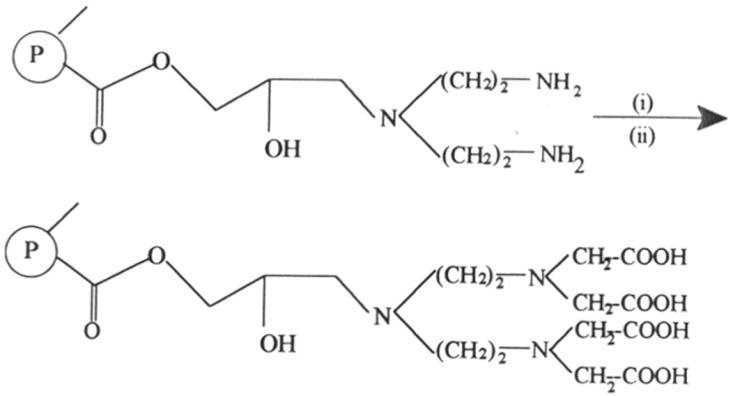


Fig. 2.4 Infra-red spectrum of diethylene triamine copolymer





Diamine tetraacetic acid Copolymer

Scheme 2.7

(i) Cl-CH_2-COONa, 70°C; (ii) dilute hydrochloric acid

Elemental analysis: N : 2.46%.

2.4.5 Bis(2-picolyl) amine copolymer

An ethanolic solution containing 6.8 g (34.4 mmole) bis(2-picolyl) amine was stirred at 70°C with 5.0 g GMA-EGDM copolymer beads (equivalent to 8.6 mmole epoxy units) for 24 hours. The modified yellow coloured polymer beads were filtered out, washed with ethanol, 1N sulphuric acid, 0.2N sodium hydroxide, water and finally with ethanol. The structure of copolymer are presented in Fig. **2.5a**.

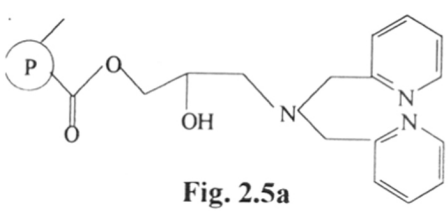


Fig. 2.5a

Elemental analysis: C : 51.96%; H : 6.62% and N : 2.29%.

IR : 3400 cm^{-1}(O-H); 3300 cm^{-1} (pyridine); 2960 cm^{-1}(C-H); 1728 cm^{-1} (C=O); 1580 cm^{-1} (Pyridine, C-N).

Chemical Titration = 0.21mmole/copolymer.

2.4.6 Bis (3-picolyl) amine copolymer

The bis(3-picolyl) amine copolymer was synthesised and purified by reacting GMA-EGDM copolymer with bis(3-picolyl) amine by procedure presented in Section **2.4.5.** The structure of the copolymer is presented in **Fig. 2.5b.**

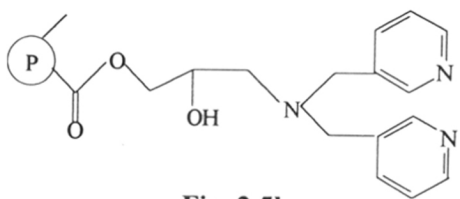


Fig. 2.5b

Elemental Analysis: C: 51.84 %; H: 6.48 %; and N; 2.29 %.

Titration value: 0.43 mmole /copolymer.

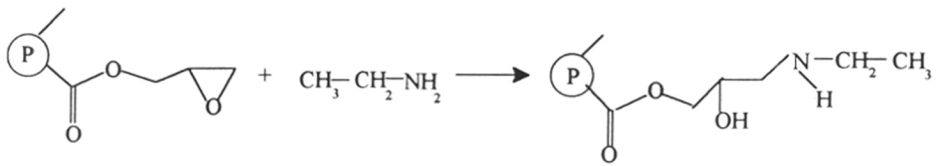
2.4.7 Dithiocarbamate copolymer

This was prepared in two steps. The ethyl amine copolymer was prepared in the first step. This was reacted with carbon disulphide to form the dithiocarbamate copolymer.

2.4.7.1 Ethyl amine copolymer

5.0 g of GMA-EGDM polymer beads were stirred with 1.36 g of ethyl amine in 75 cm^3 1,4-dioxane : water mixture (50 : 50 V : V) for 12 hours at 60°C. The modified copolymer beads were filtered and washed with distilled water, 0.2N hydrochloric acid, 0.5N sodium hydroxide,

distilled water, ethanol and dried under vacuum at 40°C. The yield of the modified ethyl amine copolymer was 5.23 g. The reaction between ethyl amine and GMA-EGDM copolymer is presented in **Scheme 2.8**.



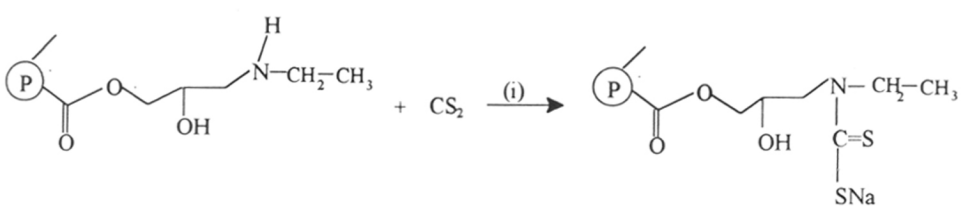
Ethyl Amine modified copolymer

Scheme 2.8

IR: 3440 cm^{-1} (O-H); 3330 cm^{-1} (N-H); 2900 cm^{-1} (C-H); 1536 cm^{-1} (N-H, bending).
Elemental Analysis: N: 1.76%.

2.4.7.2 Dithiocarbamate copolymer

The ethylamine derivatised copolymer was reacted with carbon disulfide in distilled water in presence of alkali. 5.0 g of the ethyl amine copolymer was treated with 4.0 g (50 mmole) carbon disulfide in presence of excess sodium hydroxide (3.0 g). The whole mixture was stirred at 65°C for 10 hours. The reaction is presented in Scheme **2.9**.



Dithiocarbamate copolymer

Scheme 2.9

Elemental Analysis : C : 54.8%; H : 5.86 %; N : 1.59%; S : 3.4 %.

2.5 Characterisation of Chelating copolymers

2.5.1 Capacity of chelating copolymers

The acid capacity of aminoacetic and amine copolymers were determined by chemical titration methods [4]. 0.5 g of the derivatised copolymer were converted into the protonated (acid) form by equilibrating with 50 cm^3 1N hydrochloric acid. The protonated beads were filtered and thoroughly washed with distilled water to remove adhering acid. Then the beads were shaken with 20 cm^3 of 0.1N sodium hydroxide solution for 24 hours at room temperature. The beads were filtered out and the resultant sodium hydroxide solution was titrated with 0.1N hydrochloric acid. The mmoles of sodium hydroxide consumed by the protonated chelating copolymers were determined by back titration with hydrochloric acid.

2.5.2 Degree of functionalisation

The amount of ligand loaded relative to epoxy group was calculated from the nitrogen content of the chelating copolymer.

The mmole of ligand / gram of copolymer 'L' was calculated as

$$\frac{(N \times 10)}{n \times 14}$$

where 'n' is the number of nitrogen atoms in the chelating ligand and 'N' is the Wt.% of nitrogen in the copolymer obtained from elemental analysis.

2.6 Complexation of Metals

The metal complexation experiments were conducted to investigate the affinity of the polymeric ligands towards metal ions and to find out the optimum condition for the adsorption of metal ions and thus to remove selectively the specific metal ion from a mixture of metal ions.

Potassium hydrogen phthalate, potassium chloride, hydrochloric acid and sodium hydroxide of analytical grade were used to prepare buffer solutions of varying pH ranging from 1-7. The metal salts, copper sulphate pentahydrate ($CuSO_4.5H_2O$), cupric chloride hexahydrate ($CuCl_2.6H_2O$) nickel chloride hexahydrate ($NiCl_2.6H_2O$) and cobalt chloride hexahydrate ($CoCl_2.6H_2O$) used were of analytical reagent grade. These salts were used to prepare the stock solutions in distilled water. Buffers were prepared by standard procedure [5]. The pH meter was standardised prior to use. All pH measurements were conducted at 25°C.

The metal stock solutions were prepared by dissolving 0.1 g of respective metal salts in the buffer and making up to 100 cm^3 in standard volumetric flasks with the buffer. This was diluted 10 fold to prepare 0.01 Wt.% metal salt solution. This buffered metal ion solution was used for chelation experiments.

2.6.1 Chelation Experiments

The metal complexation experiments were conducted in batch process. 0.1 g of chelating copolymer was shaken with 100 cm^3 0.01 Wt.% buffered metal salt solution for 24 hours at 25°C. The metal ion concentration present in the solution was determined prior to and after the equilibration. The metal ion adsorbed by the copolymer was calculated from this difference

between the initial and equilibrated metal ion concentration. The standard solutions for atomic absorption spectroscopy were prepared from analytical grade metal ion salts in respective buffers.

2.6.2 Adsorption kinetics

0.1 g copper sulphate pentahydrate ($CuSO_4.5H_2O$) was dissolved in potassium hydrogen phthalate-sodium hydroxide buffer of pH 6 and was made up to 1 litre in standard volumetric flask. 1.0 g of chelating copolymer was stirred in this solution at room temperature. 2 cm^3 of solution was withdrawn at regular intervals and the metal concentrations in the solutions were estimated by atomic absorption spectroscopy.

2.6.3 Desorption kinetics

The desorption of chelated metal were conducted at pH 1 and with stronger acids. The desorption kinetics were studied with solutions under conditions over which desorption was substantially high. The time profile for desorption was studied by withdrawing samples at regular intervals.

2.6.4 Distribution coefficient

The distribution coefficient was evaluated by determining the metal ion concentration in an equilibrated solution by atomic absorption spectroscopy (AAS). The distribution coefficients of metal ions are characteristic for each specific chelating copolymer. These were determined for metal ions as a function of pH according to Roozemond's method [6]. Thus the distribution coefficient for each chelating copolymer was estimated using the expression:

$$\text{Distribution coefficient} = \frac{[\text{metal ion}] \text{ in the polymer phase}}{[\text{metal ion}] \text{ in the aqueous phase}}$$

2.6.5 Selectivity of the copolymer

solution containing known amounts of differing metal ions was equilibrated with 0.1 g of chelating copolymer for 24 hours at room temperature. The equilibrated concentrations of all metal The selectivity of copolymers were estimated by competitive chelation method. A buffered ions was determined by AAS. The difference between the initial and equilibrated concentration was the capacity of the copolymer for the specific metal at that pH. The selectivity coefficient of the chelating copolymer for the metal ion A over metal ion B was calculated as

$$K a/b = \frac{[A]^b}{[\bar{A}]^b} \frac{[B]^a}{[\bar{B}]^a}$$

where the bars indicate the copolymer phase.

2.6.6 Hydrolytic stability of Schiff base copolymer

The hydrolytic stability of a chelating copolymer was estimated by shaking the copolymer with varying solutions. The hydrolytic stability of the polymeric Schiff base was determined at varying conditions such as in neutral, acidic and in basic media. The hydrolysis of the polymeric pentadentate Schiff base was studied by determining the amount of salicylaldehyde liberated from the copolymer by ultra-violet spectroscopy.

2.6.7 XPS study of Polymeric catalyst

XPS [ESCA-3MK, VG Scientific, UK] of the vanadium chelated copolymers were taken using Mg Kα after the evacuation of the sample at 10^{-8} Torr.

2.7 Catalyst preparation

The polymer bound catalysts were prepared by equilibrating the metal ion solutions with the polymeric chelating agents. The polymer bound metal complexes in various atmospheres were synthesised and employed for a variety of catalytic conversions. The polymeric catalysts synthesised were: (i) Dithiocarbamate-vanadium complex catalyst; (ii) Imino diacetate and diamino tetraacetate-vanadium (V) complex catalyst and (iii) Schiff base / Bis(picolyl) amine-copper chloride complex catalyst.

2.7.1 Polymeric dithiocarbamate-vanadium salt catalyst

The catalyst was prepared by complexing the dithiocarbamate copolymer with 0.01 Wt.% solution of vanadyl sulphate in distilled water for 24 hours at room temperature. The blue coloured vanadium chelated copolymer was washed with water, ethanol and dried. The amount of vanadium incorporated in the copolymer was estimated by measuring the difference in the vanadium ion concentration before and after the complexation.

2.7.2 Imino diacetate and diamino tetraacetate-vanadium (V) complex catalyst

The sodium metavanadate solution was prepared from ammonium metavanadate [7]. Ammonium metavanadate was dissolved in 0.1N sodium hydroxide solution and nitrogen gas was bubbled into it for five minutes to flush out ammonia. The pH of the resultant solution was adjusted to 4 by addition of dilute hydrochloric acid and the concentration was adjusted to 0.1 Wt.%. 1.0 g of diamino tetraacetic acid copolymer and imino diacetic acid copolymer were added and shaken for 24 hours at room temperature. The polymer beads were filtered off, washed with water, ether and dried under vacuum at 40°C. The vanadium ion present in the copolymer was determined, after

the elution of the vanadium ions with sodium hydroxide solution, by atomic absorption spectroscopy (AAS).

2.7.3 Polymeric Schiff base-copper chloride catalyst

The polymer bound Schiff base-copper chloride catalyst was prepared in dry N,N-dimethyl formamide (DMF). 0.01 mole (1.71 g) copper (II) chloride was dissolved in 50 cm^3 DMF in 250 cm^3 stoppered Erlenmeyer flask, 0.5 g Schiff base copolymer was added and shaken for 24 hours at 30°C. The resultant beads were filtered, washed with DMF and finally with dry ethanol. The metal ion present in the copolymer was estimated by eluting the metal ions with 0.1 hydrochloric acid and then analysing by AAS. The pyridine adduct of the bound metal complex was prepared by treating the copper complex with 25 molar excess pyridine in 50 cm^3 dry ethanol for 24 hours. The resultant beads were filtered and then washed thoroughly with ethanol and dried under vacuum. The amount of copper leached out from the polymeric Schiff base-metal complex was determined from the amount of copper ions in ethanol.

2.8 Oxidation of phenols

The general procedure used for the preparation of quinones is as follows: The catalyst was taken (10% by weight of substrate) in methanol and a slight molar excess of tertiary butyl hydroperoxide (tBHP) (10-15 mmole) was added and stirred for few minutes to activate the catalyst. 10 mmole of corresponding phenol dissolved in 25 cm^3 was added to this and stirred at room temperature. The reaction was monitored by thin layer chromatography. After the reaction, methanol and catalyst were removed, ice cold water was added and extracted with

dichloromethane. The dichloromethane layer was washed with sodium thiosulphate, water, brine, concentrated and the crude was purified by column chromatography to yield the product.

The melting points are uncorrected. ^{1}H NMR spectra were recorded in 80 and 90 MHz. Infra-red spectroscopy were taken on Shimadzu IR-470 spectrophotometer.

2.9 Epoxycyclisation of hydroxy methyl furans

To a stirred mixture of the diamino tetraacetic acid-vanadium complex catalyst (0.20 g) in 25 cm^3 dry dichloromethane (DCM), 70% tertiary-butyl hydroperoxide (tBHP) (1 cm^3; 0.0075 mol) was added. The mixture was stirred for 5 minutes. to activate the catalyst, as shown by the appearance of red colour. A solution of hydroxy methyl furan (0.005 mol) in 2 cm^3 DCM was added and the mixture was then stirred at room temperature for 6 hours. The copolymer beads were filtered off and the products were purified by column chromatography on silica gel column using 6% acetone in petroleum ether 60/80. The products were analysed by infra-red spectroscopy and ^{1}H NMR.

2.10 Polymerisation of acrylamide

The polymerisations were conducted in 50 cm^3 stoppered flasks. 20 cm^3 sulphuric acid of pH 2 was taken in the flask and cyclohexanone and acrylamide were added. The contents were purged with oxygen free nitrogen for three minutes. The polymeric initiator, 5 Wt.% with respect to monomer was added. The flasks were stoppered, thermostated at 30°C and shaken for 12 hours. The polymeric initiator was separated by filtration and polyacrylamide formed was precipitated by addition to an excess of methanol. The precipitated polyacrylamide was dissolved in distilled water, reprecipitated in methanol and dried under vacuum at 40°C. The intrinsic viscosity of

polyacrylamide samples were estimated in 1M sodium nitrate solution at 30°C with an Ubbelohde viscometer. The constants 'K' and 'a' were taken as 3.73×10^{-4} dL/g and 0.66 [8].

2.11 Electrocatalytic reduction of Dioxygen

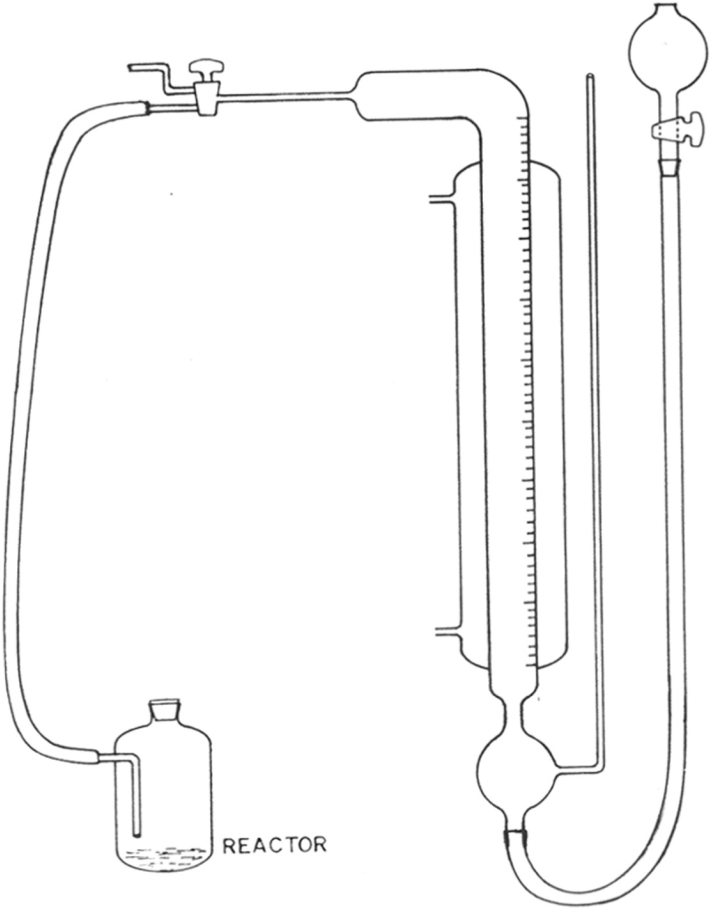
Cyclic voltammetric experiments were conducted in 0.1M tetrabutyl ammonium tetra fluoroborate in N,N-dimethyl formamide (DMF). The solutions in the cell were purged with argon for 30 minutes prior to the analysis. The voltammogram of oxygen reduction in a suspension of powdered Schiff base copolymer-copper (II) complex (catalyst) (0.1 g) in DMF was taken after continuous bubbling of oxygen into the cell. The effect of pyridine on the electrocatalytic properties of the polymeric complexes was investigated by repeating the scan in presence of 3 mmole (0.24 g) of pyridine without altering the conditions. The results were compared to standard emf of oxygen reduction conducted without catalyst under identical conditions. All potential values reported were against a standard calomel electrode (SCE). The experiments were performed on a PAR 173 function generator and the data was recorded on a model RE0091 X-Y recorder.

2.12 Oxidative coupling polymerisation of 2,6-dimethyl phenol

The oxidative coupling polymerisation of 2,6-dimethyl phenol (DMP) was investigated in 1,2-dichlorobenzene at atmospheric pressure in pure oxygen at 25°C under differing concentrations of catalyst and the external coordinating ligand. The reaction was monitored by the oxygen uptake using a gas burette filled with paraffin oil. A constant oxygen pressure was maintained during the reaction by adjusting the height of the oil leveling bulb of the manometer. The Schematic diagram of the assembly is presented in Fig. **2.6**.

In a typical experiment, The polymeric catalyst, polymeric Schiff base-copper complex or the polymeric bis(picolyl) amine-copper complex, containing about 1.2×10^{-5} mole of copper and 5×10^{-4} mole of pyridine were taken in 15 cm^3 1,2-dichlorobenzene. Oxygen was flushed for 30 minutes. 2×10^{-3} mole (0.245 g) DMP in 5 cm^3 of 1,2-dichlorobenzene was added. The system was closed and was stirred vigorously under oxygen atmosphere. The oxygen consumption was monitored and reaction was allowed to proceed until the oxygen uptake was complete. The catalyst and precipitated reddish tetramethyl diphenoquinone were filtered out and poly(phenylene oxide) [PPO] formed was precipitated by pouring the filtrate mixture into acidic methanol. The PPO obtained was dissolved in chloroform, reprecipitated in methanol and purified further by washing with excess methanol. The molecular mass of the PPO was determined from the intrinsic viscosity obtained from dilute solution viscometry in toluene at 25°C. The constants 'K' and 'a' were taken as 28.5×10^{-3} dL/ g and 0.68 respectively. The glass transition temperature, Tg, of the poly(phenylene oxide) was determined on Mettler DSC 30.

Fig. 2.6. Laboratory scale assembly for oxidative coupling polymerisation of 2,6-dimethyl phenol.



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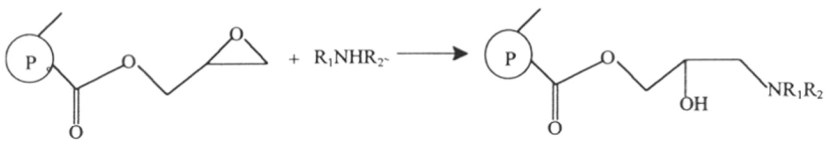
Chapter III

Syntheses And Metal Complexation Studies of Chelating Copolymers

3. Results and Discussion

3.1 Support Synthesis and Characterisation

Glycidyl methacrylate (GMA) copolymers have been evaluated as supports for chromatography, enzyme immobilisation and for selective chelation [1-3]. GMA copolymers are hydrophilic relative to the extensively used S-DVB copolymers and possess more reactive epoxy (oxiranyl) group amenable to modification with reagents having nucleophilic amine, thiol, hydroxy functionalities. The reaction of epoxy group with amines is a nucleophilic addition in which the nitrogen atom attacks the least protected carbon atom of epoxide ring, particularly in neutral and basic media. Reactions of amines with glycidyl acrylate/ methacrylate copolymers have been investigated for the kinetics and mechanism [4-5]. This is represented in Scheme **3.1**.



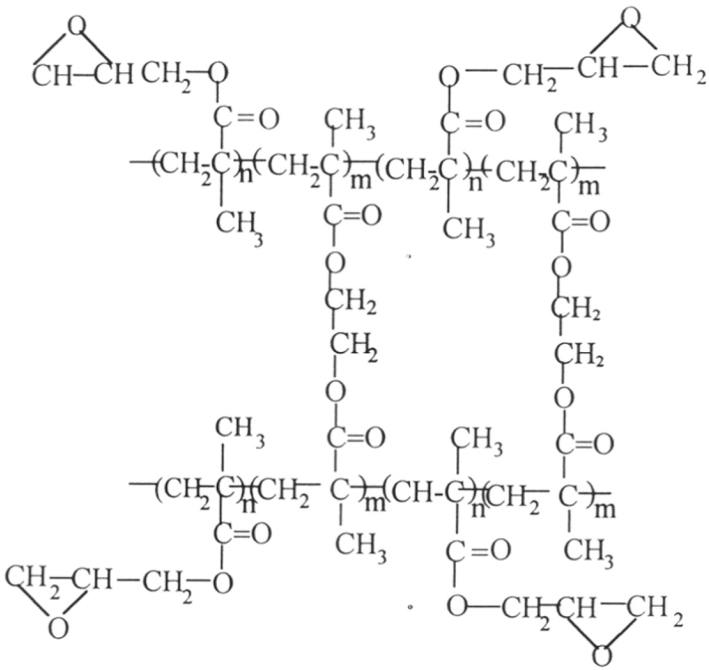
Ethylene glycol dimethacrylate [EGDM] is the preferred crosslinking comonomer. Other crosslinking divinyl monomers such as divinyl benzene and tetramethylene glycol dimethacrylate have generated limited interest [6]. Recently, chelating polymers based on glycidyl methacrylate and more hydrophilic crosslinking divinyl monomers were shown to possess better adsorption/desorption rates [7]. Glycidyl methacrylate copolymers of widely varying physical characteristics such as crosslinking density, hydrophilicity/ hydrophobicity have been synthesised.

The distribution of GMA and EGDM sequences along the chain is random and thus the copolymer formed is a network. A schematic of glycidyl methacrylate-ethylene glycol dimethacrylate copolymers is presented in Fig. **3.1**.

The existence of a shell was observed in GMA-EGDM copolymer beads synthesised by suspension polymerisation and this was attributed to the interfacial tension. The inner and outer morphologies of the formed copolymer beads could be related to the composition of the polymerisation mixture, while the inner porosity was found to be dependent on the composition of the diluent mixture. The relative volumes of the components determine the surface area, morphology and physical properties of macroporous GMA-EGDM copolymers [8,9].

In the present work, GMA-EGDM copolymers were synthesised by suspension polymerisation in a three necked jacketed cylindrical polymerisation reactor. The oil phase containing the functional monomer GMA, crosslinker divinyl monomer EGDM, pore generating inert diluent (a mixture of cyclohexanol and lauryl alcohol) and polymerisation catalyst (azobisisobutyronitrile) was dispersed in 250 cm^3 of one weight percent aqueous solution of poly(vinyl pyrrolidone). The combined volume of GMA and EGDM was maintained constant. The total volume of both phases was so adjusted that the height of the liquid phase was equal to the inner diameter of the reactor. The polymerisation was conducted in nitrogen atmosphere at 70°C for three hours. Copolymers of varying compositions were synthesised by varying the amounts of comonomers so as to generate copolymers of specific crosslinking density. Crosslinking density of copolymers was taken as the mole percent of the crosslinking monomer relative to mole of functional monomer GMA, since polymerisations were taken to completion. Permanent pore structure was generated by the inclusion of nonsolvating porogen such as cyclohexanol and lauryl alcohol in the monomer

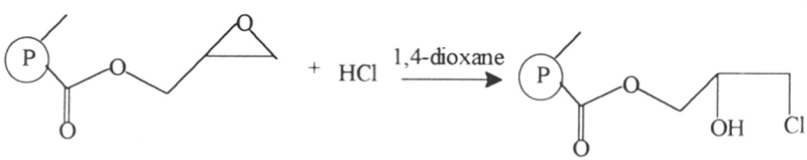
Fig. 3.1 : Schematic network of GMA-EGDM copolymer



feed. The copolymer bead particles obtained were in the range 250-400 μm. The scanning electron micrograph of the porous beads are presented in Fig. **3.2**.

The pore size and its distributions in the copolymers were determined by mercury intrusion method. Mercury porosimetry provides good estimates of pore size (radii) and pore size distribution above 20A°. However, pores of smaller radii (< 20A°) are determined by nitrogen adsorption isotherm method, more popularly known as BET method. The results indicate a bimodal distribution of pore in the copolymers. A graph of pore volume against normalised differential volume (dv/r) of the copolymers are presented in Fig. **3.3a**. and Fig. **3.3b**. The surface area of the copolymers were determined by a single point BET adsorption method.

The epoxy content of the copolymer was determined by a simplified hydrochloric acid-dioxane method [10]. Hydrochloric acid adds to epoxy groups in a wide variety of organic solvents producing chlorohydrin. The basic reaction of hydrochloric acid with epoxy polymer is :



The experimentally determinable epoxy content data works out to be between 75-80% of the theoretical epoxy content for easily accessible small ligands such as hydrochloric acid.

3.2 Imino diacetic acid copolymer

Imino diacetic acid (IDA) based resins, known since 1950, are well investigated [11] and commercial production started in 1960. The initial work involved the use of condensation polymers as the matrices and was used in the chromatographic separation of cobalt (II) and nickel

Fig. 3.2a : Scanning Electron Micrograph of GMA-EGDM (100% CL)copolymer beads, before seiving (286 times magnification).

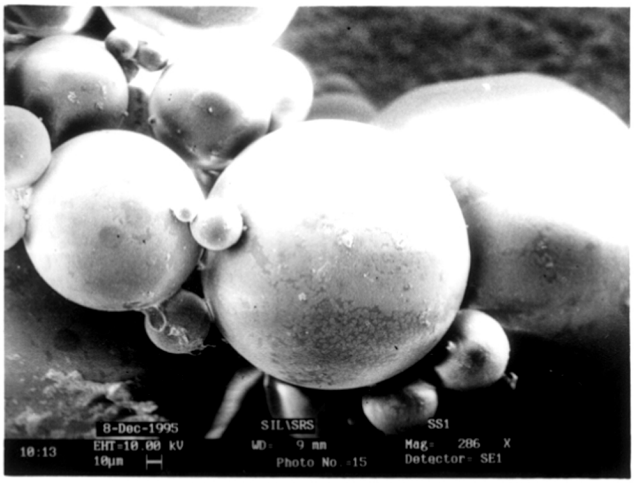


Fig. 3.2b : Scanning Electron Micrograph of GMA-EGDM (100% CL) copolymer beads, after seiving (50 times magnification).

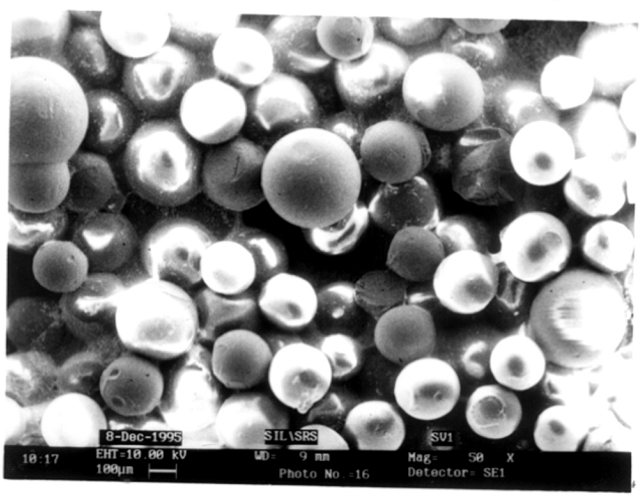


Fig. 3.3a : Mercury porosimetry graph of GMA-EGDM (100% CL); as (dv/dr) verses log pore volume in A°.

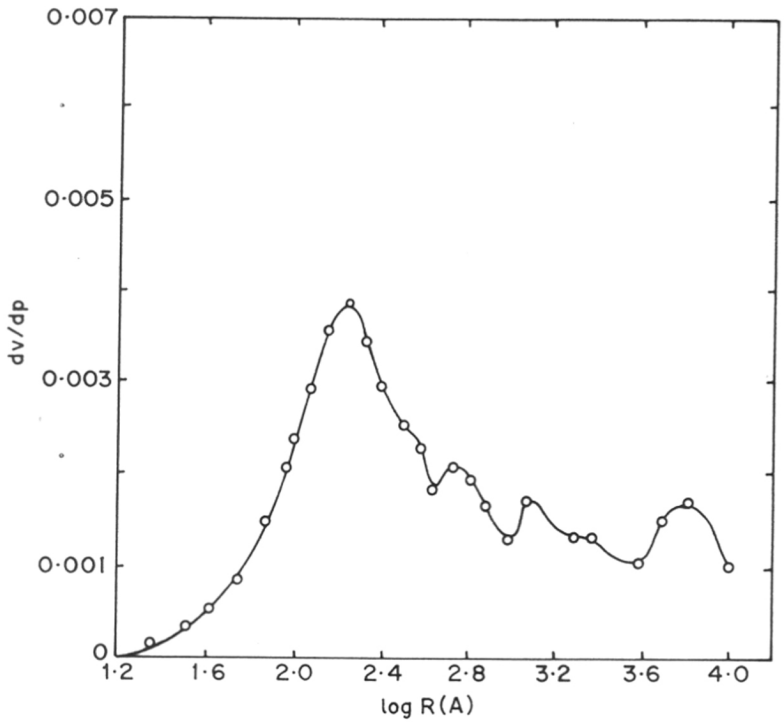
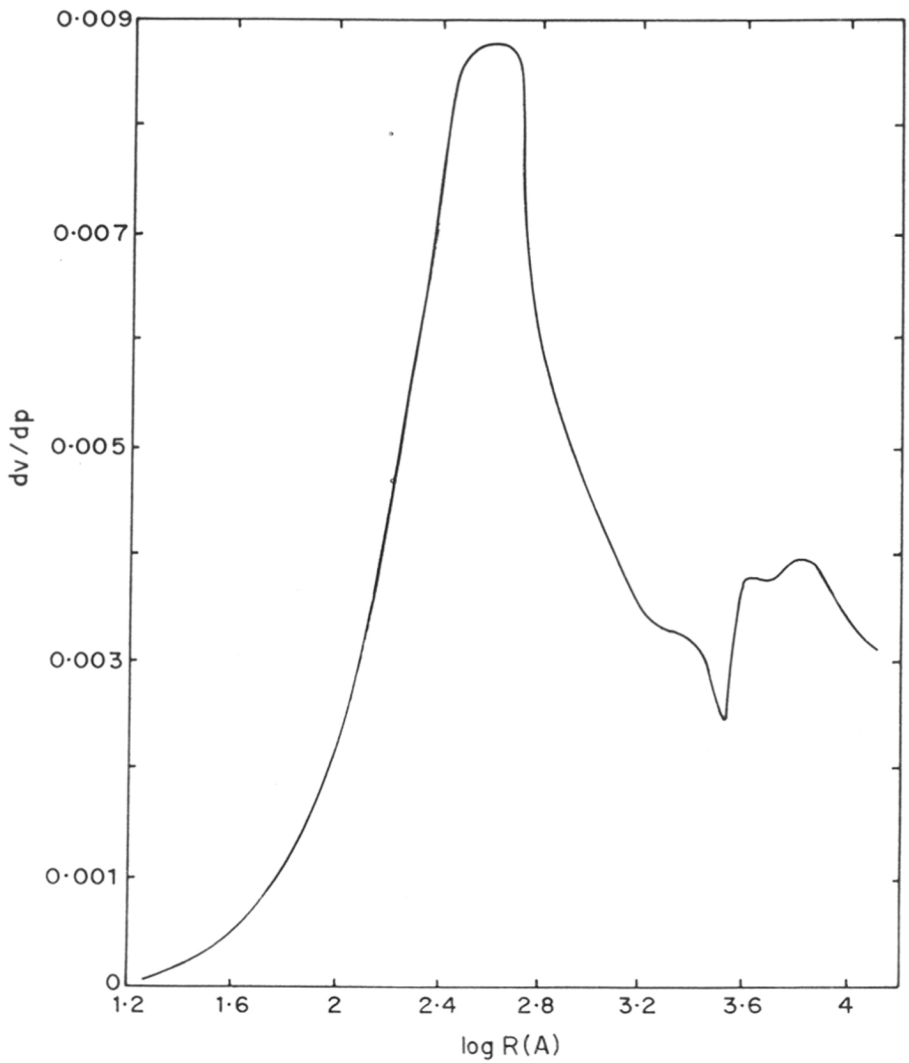


Fig. 3.3b : Mercury porosimetry graph of GMA-EGDM (125% CL); as (dv/dr) verses log pore volume in A°.



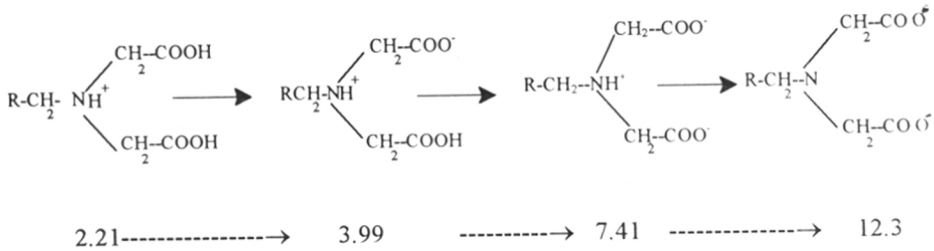
(II) [12]. Methods soon emerged to attach this ligand to crosslinked polystyrenes [13]. Commercially available imino diacetic acid resins are listed in Table **3.1**.

Table 3.1 : Commercially available imino diacetic acid chelating copolymers [14].

Trade Names	Manufacturer
Duolite ES466	Duolite International
Dowex A-1	Dow Chemical
Amberlite IRC-718	Rohm & Haas
Diaion CR-50	Mitsubishi
Unicellex	Unitica
Chelex -100.	Bio-Rad
Wofatit - CM-50.	Veb. Chemie. Kembrait, Bitterfield, GDR.
Lewatit TP-207	Bayer

The first patent literature describes the preparation of IDA resin with basic back-bone containing epoxy group by heating poly(epoxy butadiene) with diethyl ester of imino diacetic acid followed by hydrolysis with sodium hydroxide [15]. D'Alelio patented chelating polymers based on copolymers of glycidyl acrylate/ methacrylate with amino acids. The synthesis and properties of macroporous GMA-EGDM copolymer with IDA chelating group was first reported by Kalal [16]. The synthetic route involved reaction of GMA-EGDM copolymer with diethyl ester of imino diacetate and subsequent alkaline hydrolysis to generate the free imino diacetic acid group.

Imino diacetic acid forms 1:1 complex with different metal ions, though 1:2 metal : ligand complex may also occur [17]. The copolymer acts as a tridentate ligand by coordinating through the imino nitrogen atom while binding through two carboxylic oxygen atoms. The pka values of the imino diacetic acid is represented as:



Here, imino diacetic acid is attached to macroporous GMA-EGDM copolymer beads by a one pot synthetic procedure. GMA-EGDM copolymer of 125% crosslinking density was used in this reaction. The surface area of the copolymer beads was 152 m^2/g. The pore volume was 0.74 cm^3/g. The theoretical epoxy content of the copolymer was 1.717 mmole/g. Various methodologies were investigated to generate chelating copolymers such as conducting the reaction in either organic or aqueous environment. Organic solvents of varying polarities were used and in aqueous environment the pH was also altered to have a high loading of imino diacetic acid. An aqueous environment and a pH of 11.5 was found most suited for the reaction. Imino diacetic acid was converted into disodium imino diacetate by dissolving in 1N sodium hydroxide solution. GMA-EGDM copolymer beads were refluxed for 36 hours in this solution while the pH was maintained at 11.5. The molar ratio of epoxy group : imino diacetic acid was 1.0 : 5.0. The imino diacetic acid concentration and solvent type are known to affect the extent of modification by altering the local concentration of the reagent around the polymeric epoxy group [18]. The derivatised beads were filtered and the acid form was generated by washing the copolymer with 0.5N hydrochloric acid.

The degree of modification was estimated by chemical titration method [19] as well as from elemental analysis for nitrogen. Nitrogen content was estimated as 1.61 Wt.%, which corresponds to a ligand content of 1.12 mmole/g of copolymer. Thus, 60% of epoxy groups in the copolymer

were converted into imino diacetate groups. The copolymer was transformed into the acid form by treating with 0.2N hydrochloric acid and then titrating with standard 0.1N sodium hydroxide solution. The low value for ligand modification noted by the titration method arises from the diffusional constraints since the chemical titration method generally describes the accessible ligand sites while elemental analysis locates all derivatisation sites.

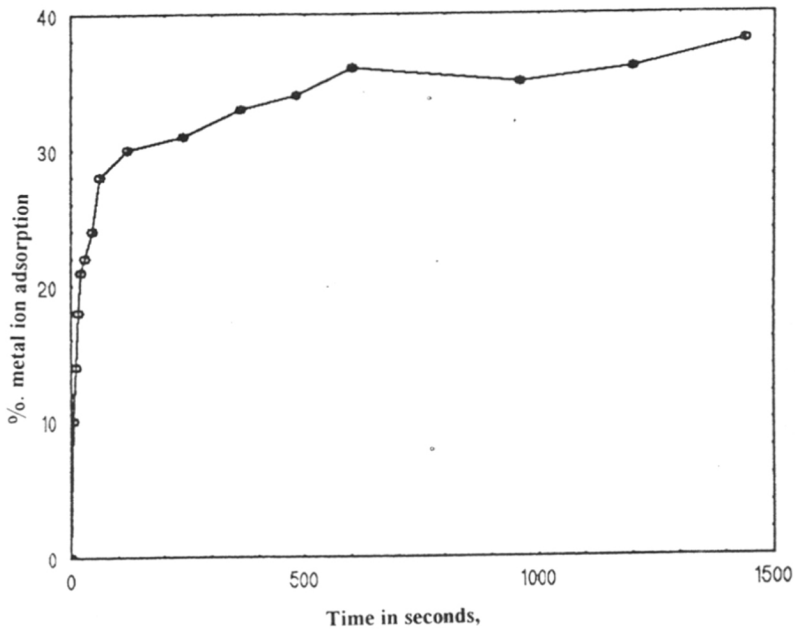
The metal complexation experiments were conducted in noncompetitive batch process in the pH range 1-6 with sulphates of copper, nickel and cobalt and metal ion capacities of copolymer was determined. The metal ion concentrations in the solutions were determined by atomic absorption spectroscopy which was calibrated in a quadratic method. The adsorption capacity of the copolymer was found to increase with pH, due to greater stability of the metal complexes at higher pH. The chelating copolymer showed maximum adsorption for copper ions at all pH. The adsorption capacity of the copolymer towards different metal ions, presented in Table **3.2**, does not agree with the Irwing-Williams series, since affinity for cobalt exceeds that for nickel ions [20]. This deviation from normal behaviour originates from a change in the chelating ligand at higher pH due to the involvement of hydroxyl group in the coordination and thus the ligand in the chelating copolymer acts as a tridentate, which is known to favour the adsorption of cobalt. The metal ions could be quantitatively desorbed from the copolymer at pH 1. The copolymer readsorbed metal ions without any loss in capacity.

The kinetics of copper ion adsorption by the copolymer was studied at pH 6 corresponding to the maximum adsorption. The data is presented in Fig. **3.4**. The $t_{1/2}$ of the copolymer was 20 minutes which is lower than that estimated for the commercial Dowex -1 resins. This could be due to the greater porosity and hydrophilic character of GMA-EGDM relative to S-DVB copolymer and its homogeniety[21].

Table 3.2 : Metal ion capacity of IDA copolymer as a function of pH

pH	Cu^{2+} mmole/ g	Ni^{2+} mmole/ g	Co^{2+} mmole/ g
1	0.0	0.0	0.0
2	0.04	0.0	0.0
3	0.13	0.0	0.02
4	0.15	0.01	0.04
5	0.16	0.05	0.09
6	0.17	0.1	0.08

Fig. 3.4. Adsorption kinetics of Iminodiacetic acid copolymer

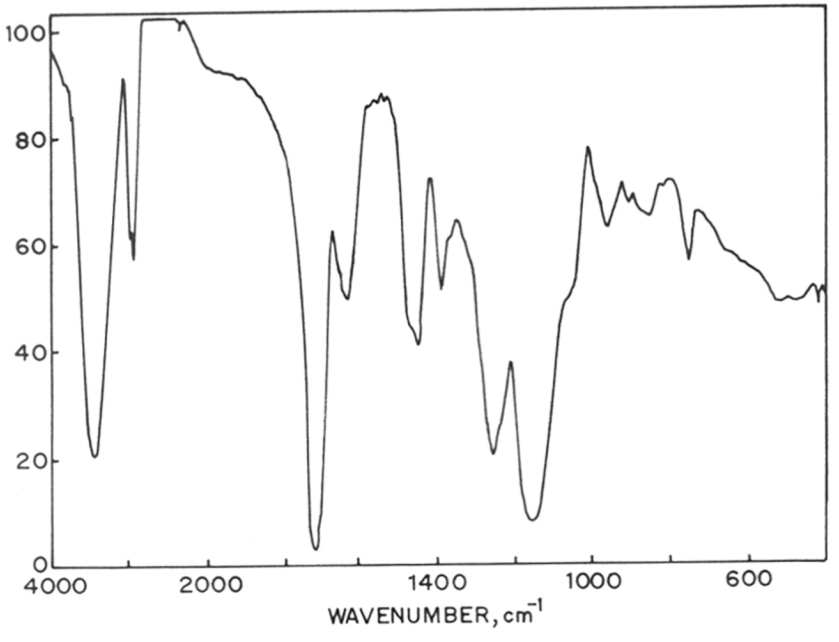


3.3 Schiff base and other multidentate ligand polymers

Multidentate chelating agents form more stable complexes compared to monodentate or bidentate analogues [22]. Thus, the immobilisation of multidentate ligands onto polymeric supports is a better approach to synthesise polymer bound transition metal complexes.

The synthesis of GMA-EGDM copolymer from a molar feed ratio of 50 : 50 is presented in Section **2.1.1**. The pore volume was 0.50 cm^3/g and the surface area was 108 m^2/g. Pentadentate Schiff base was synthesised [Section **2.3.1**] [23] and reacted with hydrophilic GMA-EGDM copolymer to generate polymeric Schiff base [Section **2.4.2**]. The polymeric Schiff base was hydrolysed to generate diethylene triamine [Section **2.4.3**] copolymer and acetylated to synthesise the diamino tetraacetic acid copolymer [Section **2.4.4**]. The chelating properties of these copolymers towards divalent metal ions were investigated. The two primary amino groups of the diethylene triamine react with two molecules of salicylaldehyde resulting in the Schiff base while the secondary amino group of the diethylene triamine remains intact. The IR spectrum (neat) of Schiff base in Fig. **3.5** shows characteristic peak at 1628 cm^{-1} for the imino group. The copolymer beads were refluxed with Schiff base in 1,4-dioxane for 24 hours. The molar ratio of ligand : epoxy group was 2.5 : 1.0. The covalent bond formation by reaction between the polymer and the Schiff base proceeds via the epoxy and the secondary amino group. The elemental microanalysis showed the nitrogen content of the copolymer to be 2.84 percent. This corresponds to 0.67 mmole of Schiff base per gram of copolymer. The value implies 28% ligand loading with respect to experimental and 23% relative to theoretical epoxy content respectively. Infra-red spectroscopy of the modified copolymer shows characteristic peak of Schiff base at 1628 cm^{-1}. It was also clear from the spectra that some of the epoxy group had remained intact and that the

Fig.3.5. Infra-red spectra of polymeric Schiff base.



imino group frequency merges with the residual double bond frequency of the copolymer matrix. The restriction posed by the stiff pores present in the nonswelling copolymer for the diffusion of the bulky pentadentate Schiff base towards the epoxy group and the steric difficulty of the secondary amino group in reacting with the epoxy group lead to a low binding of the bulky pentadentate ligand.

The diethylene triamine copolymer was generated by acid hydrolysis of the polymeric Schiff base with 6N hydrochloric acid at 60°C for 12 hours. The Schiff base of salicylaldehyde and diethylene triamine readily undergoes hydrolysis in acidic as well as basic media generating salicylaldehyde and amine. The amino group generation was qualitatively estimated by ninhydrin test [24]. This indirect derivatisation was evolved to avoid crosslinking reaction between primary amino group and epoxy groups which would complicate the ligand structure. The acid capacity of the copolymer was estimated as 0.43 mmole per gram of copolymer, calculated by chemical titration of the protonated form of diethylene triamine with 0.1N sodium hydroxide. The IR spectroscopy of the DETA copolymer does not show any additional characteristic peak over and above that noted for the polymeric Schiff base. Epoxy group frequency was absent in spectra, indicating that the residual epoxy groups underwent ring opening reaction in presence of acid. The microanalysis shows that the copolymer contains 2.62 Wt.% of nitrogen.

The acetylation or carboxymethylation is a known process to generate imino diacetic or amino acid chelating copolymers. The poly(aminoacetic acid) can be synthesised from polyamines [25]. In the present work, the diamino tetraacetic acid copolymer was generated by the reaction of diethylene triamine copolymer with sodium chloroacetate at 70°C for 16 hours. The pH was maintained at 10 during the reaction. The acid capacity of the derivatised copolymer was

determined by chemical titration with standard 0.1N sodium hydroxide solution as 1.82 mmole of univalent sodium ions/g copolymer.

The hydrolytic cleavage of the polymeric Schiff base was studied by estimating the amount of salicylaldehyde liberated from the copolymer in 0.1N sodium hydroxide and 0.1N hydrochloric acid solutions. The salicylaldehyde liberated from the copolymer was estimated at 257 nm. The capacity of Schiff base copolymers to bind copper, nickel and cobalt metal ions were investigated under static, noncompetitive batch process in the pH range 3-6. The copolymer was hydrolytically unstable at lower pH. The Schiff base copolymer shows maximum adsorption capacity for copper ions at all pH. The uptake of copper ions by Schiff base copolymer from 100 cm^3 0.01 Wt.% copper sulphate solution was 48% which corresponds to 0.19 mmole/g copolymer. The adsorption capacity of Schiff base copolymer is presented in Table **3.3**. The adsorption capacity of the copolymer towards different metal ions is in accordance with Irwing-Williams series [19]. Diethylene triamine (DTA) copolymer shows a similar but diminished trend in the activity. The adsorption capacity of the DTA copolymer is presented in **Fig. 3.6**. The adsorption data indicates that 29% of ligands take part in coordination with metal ions. Schiff base coordinates to the metal ions through imine bond. The IR spectrum of the Schiff base copolymer is presented in Fig. **3.7**. The adsorption frequency of imine in the Schiff base copolymer changes on co-ordination to the metal ion from 1630 to 1645 cm^{-1}.

The copolymer with diamino tetraacetic acid (DETA) showed higher metal ion adsorption capacity relative to the other two multidentate chelating copolymers. The adsorption capacity of DETA copolymer at different pH is presented in Fig. **3.7**. DETA forms 1 : 2 as well as 1 : 1 metal : ligand complexes. Unlike the imino diacetic acid ligand, DETA shows normal adsorption behaviour for metal ions, absorbing 64% metal ions from 0.01 Wt.% copper sulphate solution.

Table 3.3 : Metal ion capacity of Schiff base copolymer as a function of pH

pH	Cu^{2+} mmole/ g	Ni^{2+} mmole/ g	Co^{2+} mmole/ g
1	ND	ND	ND
2	ND	ND	ND
3	0.04	0.01	0.02
4	0.10	0.03	0.05
5	0.16	0.05	0.09
6	0.19	0.11	0.11

Fig. 3.6. Metal ion adsorption capacity of Diethylene triamine copolymer.

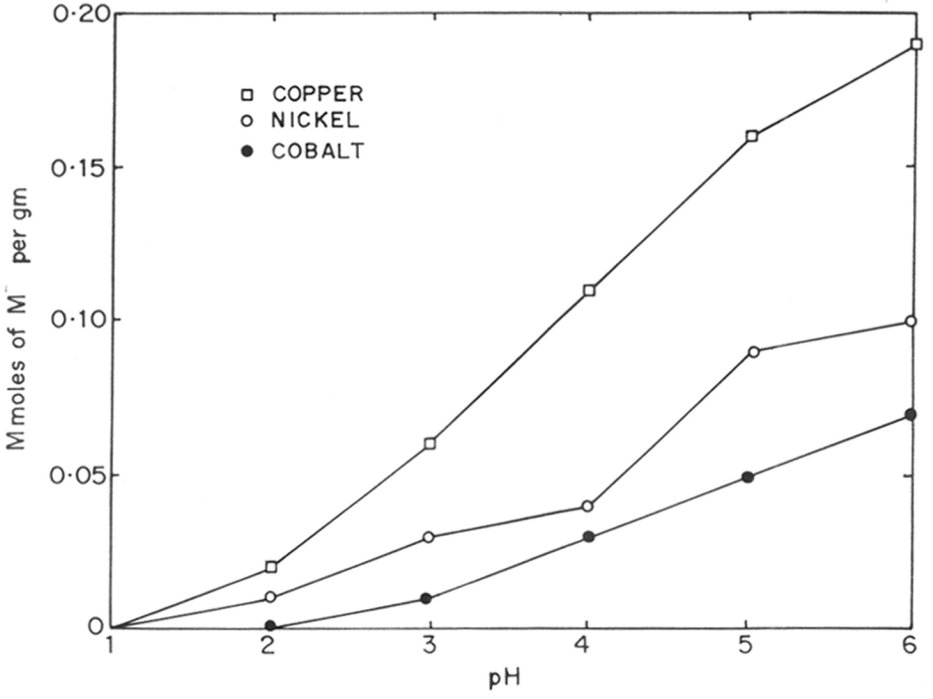
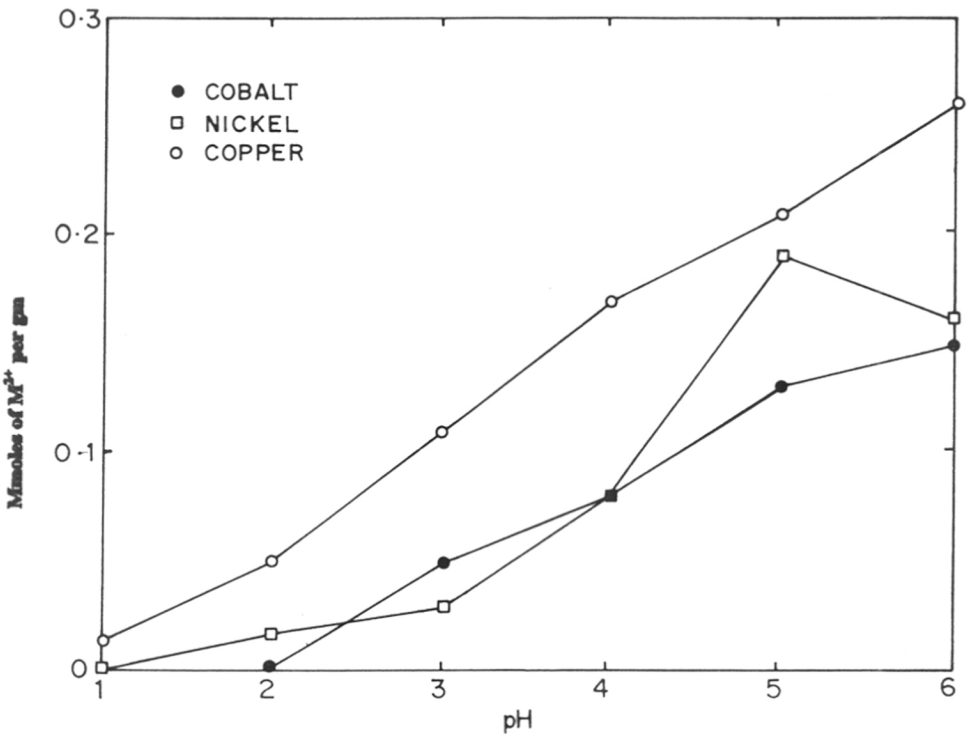


Fig.3.7. Metal ion adsorption capacity of Diethylene triamine tetraacetic acid copolymer



The adsorbed metal ions was eluted by 0.1N hydrochloric acid. The chelating copolymer readsorbed metal ions without any loss in the capacity.

3.4 Bis (picolyl)amine Chelating Copolymer

The tridentate nitrogen ligands based on different bis(picolyl) amines form stable complexes with copper ion in acidic media. The high selectivity resulted in the use of bis(picolyl) amine attached to polystyrene matrices in hydrometallurgical processes and many are available commercially as Dowex XFS 4196, Dowex XFS 4195 [26,27]. Recently, picolylamine anchored on hydrophilic copolymers have received much interest as these offer better rates of adsorption. The nature of complexation of tridentate bis(picolyl) amines have been investigated. The coordination is significant with Cu (II) ions even at a low pH such as 2.

The present study pretains to the synthesis of tridentate bis(picolyl) amines bound covalently to beaded macroporous reactive glycidyl methacrylate copolymers. The metal ion adsorption capacity and distribution coefficients of the chelating copolymers were investigated. The selective separation of copper ions in the presence of other divalent metal ions were studied.

The GMA-EGDM copolymers were synthesised from a GMA : EGDM molar feed ratio of 31.5 : 68.5 as reported in Section **2.2**. The crosslinking density of the copolymer was estimated from the feed molar ratio of divinyl monomer, ethylene glycol dimethacrylate, to the functional monomer, glycidyl methacrylate. The pore volume of the bead was 0.74 cm^3/g and the surface area was 152 m^2/g. The synthesis of bis(picolyl) amine is reported in Section **2.3.3**. The amino group reacts with the epoxy group of the copolymer. The nitrogen estimation indicated that bis(2-picolyl) amine copolymer [copolymer (I)] contains 0.29 mmole of bis(2-picolyl) amine while bis(3-picolyl) amine copolymer [copolymer (II)] has 0.48 mmole of bis(3-picolyl)amine per gram. This

corresponds to approximate 17% and 29% ligand loading with respect to the epoxy content in copolymer. The chemical titration of the protonated form of the chelating copolymer (I) with 0.1N sodium hydroxide showed 0.21 mmole of ligand per gram of copolymer. The chemical titration value ascertains the amount of accessible ligands. IR spectra of chelating copolymers in potassium bromide pellets having absorption peaks at 3460 cm^{-1} (OH), 3300 cm^{-1} (pyridine), 1728 cm^{-1} (C=O) and 1575 cm^{-1} (C-N bond of pyridine) is presented in Fig. **3.8**.

The metal ion capacities of chelating copolymers were determined as a function of pH by an equilibrium batch process. The data shows that the chelating copolymers have adsorption capacity towards bivalent metal ions. The uptake of copper ions is highest over a wide range of pH, from 1-7. The copolymer (I) showed a better adsorption capacity for cobalt ions relative to nickel ions. This does not agree with the well known Irwing-Williams series [20]. The maximum uptake of copper ions is 0.19 mmole/g for chelating copolymer (I). This implies that 61% ligands are involved in the coordination of metal ions. The adsorption capacities of the chelating copolymer (I), based on bis(2-picolyl) amine, for Cu(II), Co(II) and Ni(II) are presented in Fig. **3.9**.

The chelating copolymer (II), based on bis(3-picolyl) amine, also showed a preferential adsorption of copper ions over other metal ions. Despite a higher ligand density, the metal ion adsorption capacity of copolymer (II) was very low. The maximum adsorption capacity of the copolymer was 0.09 mmole/g for copper at pH 7. The uptake of cobalt and nickel ions were relatively very low. The extremely low uptake capacity of the chelating copolymer (II) is due to the formation of a less preferred 6 membered chelate ring with metals. The adsorption data agrees with stability and ionisation constants noted for the monomeric analogue [28]. The pk_1 and pk_2 are significantly larger for bis(3-picolyl) amine as compared to bis(2-picolyl) amine as a

Fig. 3.8. : Infra-red spectrum of bis(3-picolyl) amine copolymer.

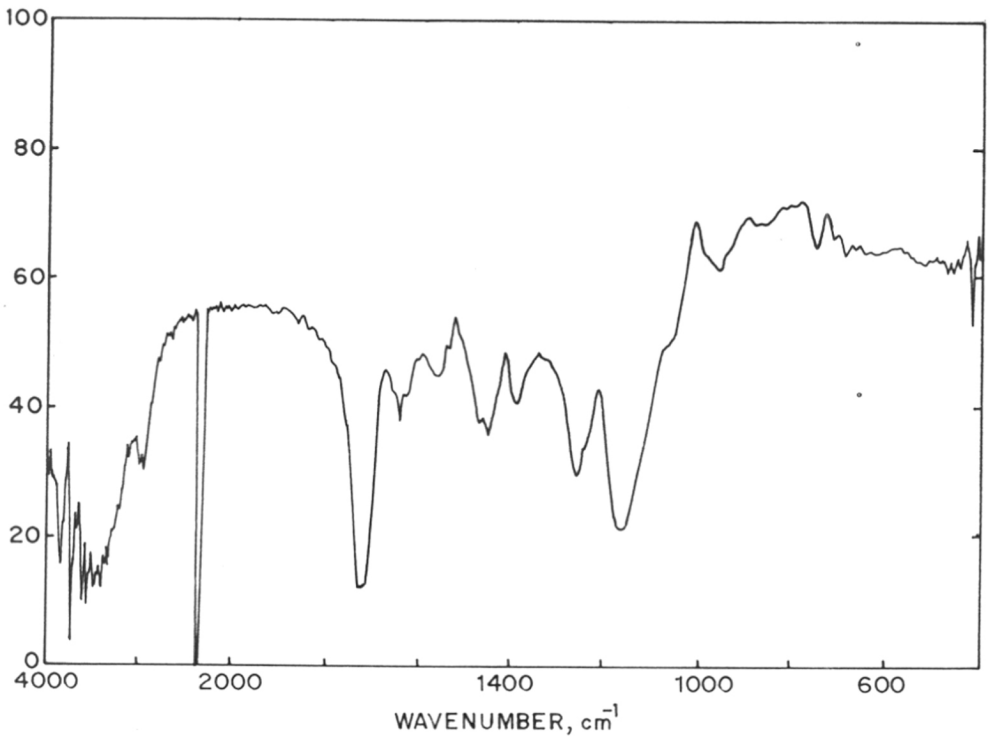
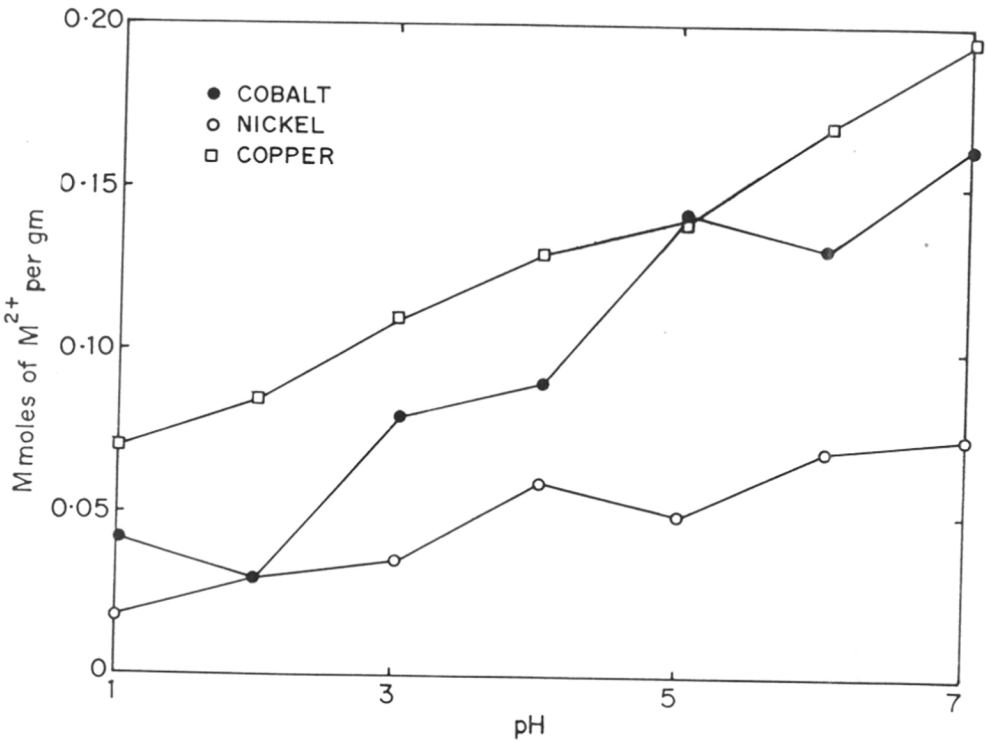


Fig. 3.9. Metal ion adsorption capacity of bis(2-picolyl) amine copolymer.



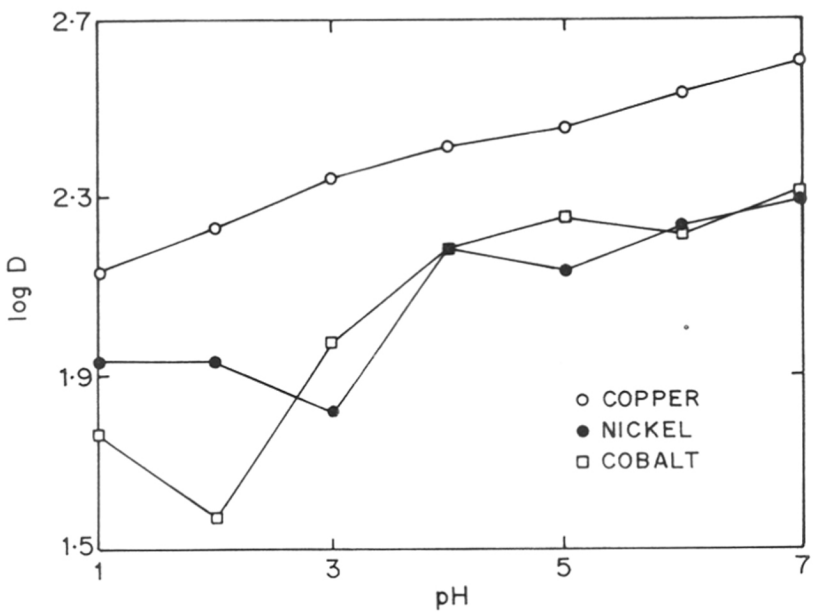
result of the greater distance between the pyridine and side chain nitrogens, while pk_3 differs only slightly. The values are presented as:

Ligand	pk_1	pk_2	pk_3
2-BPA	1.12	2.60	7.30
3-BPA	2.95	3.90	7.15

The distribution coefficient values are characteristic of a chelating copolymer and is calculated according to Roozemond's method [29] for 0.01 Wt.% metal ion solution. The distribution coefficients (D) of chelating copolymer (I) is presented as pH verses log of D in Fig. **3.10**. Copper ions showed higher distribution coefficient values which implies the selectivity of this ion over the other metal ions. It is noted that copper ions show highest distribution coefficient at all pH. This indicated to a higher affinity of bis(2-picolyl) amine chelating copolymer towards copper ions.

The selectivity of metal ions were determined under competitive metal ion adsorption conditions. The data shows that chelating copolymer (I) selectively adsorbs copper ions from the aqueous solutions containing cobalt and nickel ions. The selectivity of copper ions over cobalt ions at pH 2 is 39:1 and at pH 5 it is 27:1. The chelating copolymer also has remarkable selectivity for copper ions over nickel. From an aqueous solution containing equimolar amounts of copper, nickel and cobalt ions at pH 2, the respective metal uptakes were 6 mg, 0.015 mg and 0.008 mg per gram of copolymer. The data implies that the ligand has higher affinities for copper and nickel, inspite of higher uptake of cobalt ions at higher pH.

Fig. 3.10 Metal ion distribution coefficient of bis(2-picolyl) amine copolymer verses pH



The kinetics of adsorption was studied for copper ions at pH 6. The $t_{1/2}$ of the chelating copolymer (I) is 15 minutes. This corresponds to the time at which the chelating copolymer adsorbs 50 percent of the equilibrated metal ions. The desorption of the adsorbed metal ions were conducted with 4M sulphuric acid as well as with the complexion EDTA at pH 10. The metal desorption in sulphuric acid was found to be 85% while that with EDTA was 80%. The chelating copolymer readsorbed metal ions without any loss in activity.

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Chapter IV

Catalysis with Polymer Bound Vanadium Catalyst

4. Catalysis with Polymer Bound Vanadium Catalyst

4.1 Introduction

Catalytic quantities of metals such as molybdenum or titanium dramatically increase decomposition rates of hydrogen peroxide and alkyl hydrogen peroxides [1]. The epoxidation of propylene by these metals in the presence of alkyl hydroperoxides is strategically important. The Halcon process uses a soluble molybdenum complex with tertiary butyl hydroperoxide (tBHP) while Shell has patented a heterogeneous catalyst involving titanium on silica [2,3].

The cheap availability of alkyl hydroperoxides offers a number of advantages. These have been regarded as highly reactive reagents and the oxidation behaviour is extremely attractive because of the inertness to most organic molecules in the absence of a catalyst. This tremendous potential to develop a particular catalyst to selectively move the oxidation in the predetermined direction has generated considerable research activity [4]. These combination catalysts are less corrosive than peroxy acids and hydrogen peroxide. The coproduct, alcohol, can be dehydrated, reduced and recycled.

Transition metals, which are capable of achieving and sustaining formally high oxidation states and d° electronic configuration, seem to be best suited as catalysts for epoxidation of alkenes by alkyl hydroperoxides. The highest oxidation state attained *in situ* is the one always found to catalyse the reaction. The preferred catalytic order of transition metals is Mo(VI) > W(VI) > V(V) > Ti(IV). The metal must be capable of forming an oxo-metal (M=O) bond and possess Lewis acid character to withdraw electrons from the peroxidic oxygen of alkyl hydroperoxide. It is clear that cleavage of the peroxo species is heterolytic. Iron and cobalt, with two comparable and accessible oxidation states differing by a single unit, tend to promote homolytic peroxy

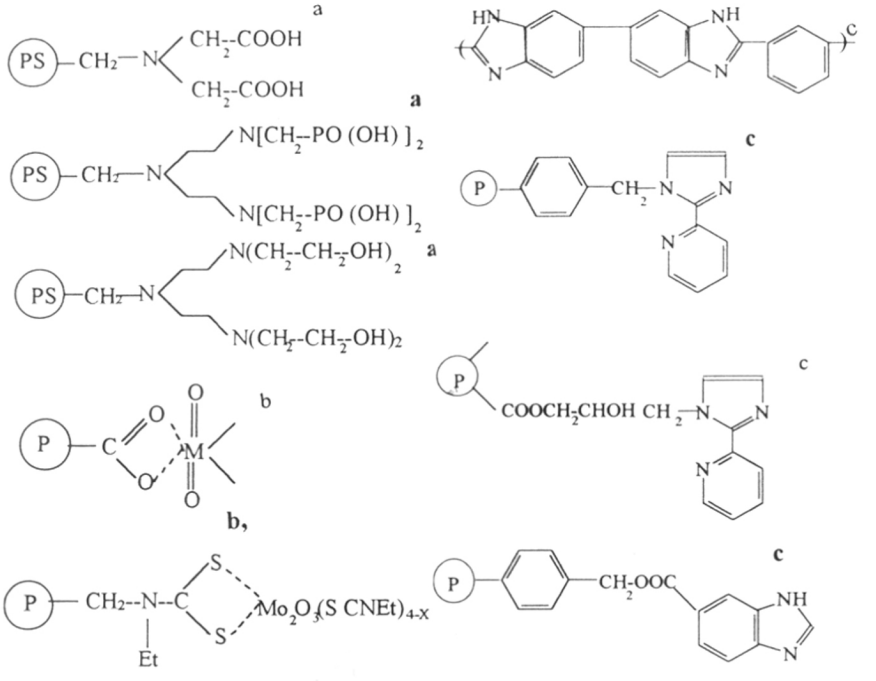
linkage and a free radical chain transfer is observed in oxidation of olefins [5,6]. Detailed mechanisms on the catalytic properties of transition metal peroxo complexes were postulated [7,8]. A schematic presentation of the catalytic epoxidation of alkenes by transition metal peroxo complexes is presented in Scheme **4.1**.

The discovery of vanadium bromoperoxidase, an enzyme carrying vanadium (V) in marine algae that catalyses oxidation of halides by hydrogen peroxide, has renewed attention towards the reactivity of vanadium peroxide. Vanadium (V) ion coordinates the peroxides and the reactivity of vanadium peroxy complex is rich and varied. These complexes undergo a variety of net two electron oxidation reactions like epoxidation, hydroxylation and oxidation of primary and secondary alcohols to aldehydes and ketone [9]. Vanadium compounds are less efficient and selective relative to molybdenum for epoxidation of unactivated olefins, but are highly active for allylic alcohols [10].

4.2 Supported transition metal peroxo complexes

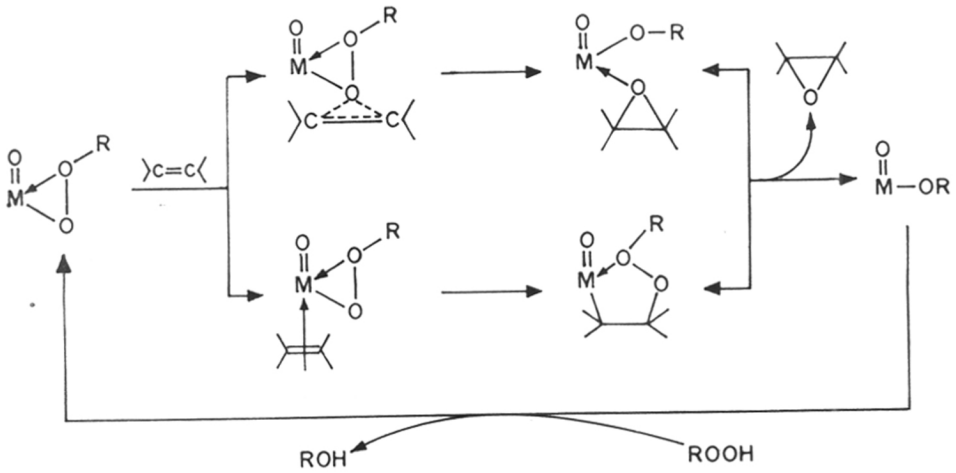
The first polymer transition metal peroxo complex is the HWO_4^{--} supported on Amberlite IRA 400, reported by Allen and Nigie [11]. Recently, Sherrington reviewed the role of polymer bound transition metal oxidation catalysts in the field of organic synthesis [12]. The tremendous growth of research activity in the polymer supported transition metal-peroxo complexes noted in the past few years are summarised in Table **4.1**.

Table 4.1. : Structures of polymer ligands



a---ref. 13, b---ref 14. C----ref.15.

Scheme 4.1: Mechanism of epoxidation of alkenes by transition metal peroxocomplex



4.3 The present study

The objective of the present study is to immobilise vanadium on macroporous GMA-EGDM copolymer supports in different environments generated through dithiocarbamate, diacetic acid and tetraacetic acid ligands. Vanadyl sulphate and sodium metavanadate were immobilised and evaluated for the catalytic conversion of substituted phenols to quinones, oxidative cyclisation of furan carbinols and polymerisation of acrylamide.

4.4 Oxidation of substituted phenols to quinones

4.4.1 Introduction

The highly functionalised character of quinones offers considerable potential in the syntheses of organic molecules and has been successfully used to generate natural products, vitamins and their intermediates [17,18]. Biogenetic pathways involve oxidative utilisation of phenols. The effective catalysts for the oxidation of phenols to the corresponding quinones are chromic oxide [19], ferric chloride [20], silver oxide [21], manganese dioxide [22], ceric ammonium nitrate [23] and Fermi's salt. Heterogeneous catalysts are of current interest in organic transformations such as oxidation of phenols due to mildness, ease of separation and enhanced reactivity and selectivity [24].

Dithiocarbamates form stable complexes with metal ions. Polymeric dithiocarbamates have practical importance in complexation of heavy metal ions, the separation of metal ions and in catalysis [25]. A shortcoming is the instability in strong acids and the inability to regenerate. Epoxidation of cyclohexene by molybdenum complexes of dithiocarbamate resin has been reported [26]. Polymer bound dithiocarbamate-iron (II) complex has been used to initiate the

redox polymerisation of acrylamide at room temperature in conjunction with hydrogen peroxide [27].

In the present study, glycidyl methacrylate-ethylene glycol dimethacrylate (GMA-EGDM) copolymer was modified with ethyl amine and xanthated to obtain dithiocarbamate copolymer. The dithiocarbamate copolymer was chelated with vanadyl sulphate in aqueous solution. The catalytic potential of vanadium chelated copolymer for the oxidation of substituted phenol was determined.

4.4.2 Experimental

Ethyl amine and carbon disulfide were from Loba Chem., Mumbai, India. The glycidyl methacrylate-ethylene glycol dimethacrylate copolymer was synthesised as discussed in Section **2.1** The synthesis of dithiocarbamate copolymer and its vanadyl sulphate complex are reported in Sections **2.4.7** and **2.6.1**.

4.4.3 Results and Discussion

The copolymer was synthesised from a GMA : EGDM mole ratio of 50 : 50 and the crosslinking density was 100. The epoxy content of the copolymer was 2.936 mmole /g. The copolymer beads were in the range 250-400 μm.

The complexation of vanadyl ion was conducted by equilibrating 1.0 g dithiocarbamate copolymer beads with 0.01 Wt.% aqueous solution of vanadyl sulphate for 24 hours. The vanadium ion coordinated in the copolymer beads was calculated from the difference between the initial and final concentrations of vanadium ions in the solution. The vanadium ion coordinates to the metal

ion through the sulphur atom of the dithiocarbamate group [28]. The AAS indicated that 0.01 g vanadium ion was incorporated per gram of dithiocarbamate copolymer.

Vanadium coordinates and forms a peroxo complex in presence of hydroperoxides. This peroxo vanadium complex can undergo both heterolytic as well as homolytic cleavage and the intermediate peroxo complex catalyses the oxidation of phenols to the corresponding quinones. The polymer supported vanadium peroxo complex is active even in protic solvents such as methanol, where as the corresponding homogeneous system fails. Though hydrogen peroxide also forms stable complexes with vanadium ions, tertiary butyl hydroperoxide is preferred, as hydrogen peroxide forms strong coordination with vanadium ion and results in harsher reactions such as coupling / polymerisations. The polymeric dithiocarbamate-vanadyl sulphate catalyst was recyclable with only a marginal loss in catalytic activity. A general reaction scheme is presented in Scheme **4.4.1**.

Scheme 4.4.1 : General reaction Scheme of Phenol oxidation

(i) Dithiocarbamate copolymer-vanadium salt complex and tBHP in methanol at room temperature.

Substrates done:

1. **Hydroquinol** --------→ ***P*-Benzoquinone**.

   Yield: 95%; MP: 111 °C; IR (neat) : 2800 cm^{-1} (C-H); 1685 cm^{-1} (C=O); 1605 cm^{-1} (C=C); ^{1}H NMR : 6.9 δ (s, 4H).

2. **2,6-Dimethyl phenol** --------→ **2,6-dimethyl benzoquinone**.

   Yield : 70%; MP : 68° C; IR (neat) : 2850 cm^{-1} (C-H); 1680 cm^{-1} (C=O); 1645 cm^{-1} (C=C); 1600 cm^{-1} (C=C); ^{1}H NMR : 1.8 δ (bs, 6H); 6.9 δ (d, 2H).

3. **3,5-Dimethyl phenol** ------→ **3,5-dimethyl benzoquinone**.

   Yield : 68%; MP : 68 °C; IR : 2850 cm^{-1} (C-H); 1680 cm^{-1} (C=O); 1645 cm^{-1} (C=C); 1600 cm^{-1} (C=C); ^{1}H NMR : 1.8 δ (bs, 6H); 6.9 δ (d, 2H).

4. **Glycol** ------→ **2-methoxy 1,4-benzoquinone**.

   Yield : 72%. MP : 134 °C; IR : 2900 cm^{-1}(C-H); 1640 cm^{-1}(C=O); 745 cm^{-1}(C-O);. ^{1}H NMR : 3.8 δ (s, 3H); 6.9 δ (d, 2H); 8.2 δ (s, 1H).

5. **4-tertiary butyl Catechol**------→ **4-tertiary 1,2-benzoquinone**.

   Yield : 80%. MP : 64 °C; IR (neat) : 2950 cm^{-1}(C-H); 1680 cm^{-1}(C=O); 1600 cm^{-1}(C=C); ^{1}H NMR : 1.2δ (s, 3H); 6.9 δ (d, 2H); 7.6 δ (s, 1H).

6. **2-Methyl phenol** ------→ **2-Methyl benzoquinone.**

Yield 75% MP : 67 °C; IR : 2860 cm^{-1}(C-H); 1672 cm^{-1}(C=O); 1590 cm^{-1}(C=C); ^1H NMR : 1.9 δ (s, 3H); 6.9 δ (d, 2H); 6.6 δ (s, 1H).

7. **2-Naphthol** ----------→ **1,2-Naphthoquinone;**

Yield 65%; 3000 cm^{-1}(C-H); 1712 cm^{-1}(C=O); 1685 cm^{-1} (C=O); 1605 cm^{-1}(C=C); ^1H NMR : 7.5 δ (m, 4H); 8 δ (d, 1H); 8.2 δ (d, 1H).

The polymeric dithiocarbamate-vanadium peroxo complex system was failed to catalyse oxidation of salicylaldehyde and 2-nitro phenol. This may be attributed to the electron withdrawing property of the substituents in the substrates.

4.5 Catalysis with polymer supported aminoacid-vanadium complex

4.5.1 Oxidative cyclisation of furan carbinol

Crosslinked S-DVB resins with bis(phosphonomethyl)amino and bis(2-hydroxyethylamino) functional groups readily form metal complexes with oxo vanadium and oxy molybdenum ions. These polymer complexes selectively catalyse the epoxidation of (*E*)-geraniol with tBHP [29]. Sherrington observed faster rates of reactions with metal peroxo complexes of molybdenum supported on GMA-EGDM copolymer as compared to the rate with peroxo complex supported on S-DVB polymer [30]. Spiroketals and hydropyranones are important subunits of a variety of naturally occurring compounds. These hold considerable interest currently and a great deal of synthetic work is directed towards their facile synthesis. Also, the epoxy cyclisation of hydroxy methyl furans has emerged as one of the most useful methods to obtain hydropyranones. 2-Furyl

carbinols undergo an oxidation sequence producing a pyrenone derivative when treated with any of several oxidising agents including peracids, meta chloroperbenzoic acid (MCPBA), pyridinium chlorochromate (PCC) and bromine [31-34].

Here, we report the synthesis of a new oxo vanadium (V) complex anchored onto a GMA-EGDM copolymer with diamino tetraacetic acid ligand and its remarkable catalytic activity and selectivity towards the epoxycyclisation of hydroxymethyl furans with 70% tBHP.

The synthesis of macroreticular GMA-EGDM copolymer (feed molar ratio 50:50) is presented in Section **2.1**. The synthesis of polymer supported diamino tetraacetic acid is reported in Section **2.4.4**. The hydroxymethyl furans were synthesised according to a reported procedure [35]. The synthesis of polymer bound diamino tetraacetic acid-vanadium complex is reported in Section **2.6.2**.

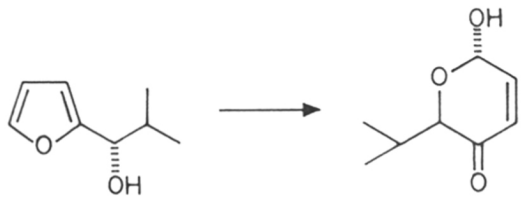
The surface area and pore volume of the GMA-EGDM copolymer beads were 108 m^2g^{-1} and 0.50 cm^3 g^{-1} respectively [Section **2.2**]. The modification of copolymer to diamino tetraacetic acid copolymer is reported in Section **2.4.4**. The acid capacity was 1.82 mmole/ g of the copolymer, as determined by chemical titration [36]. Vanadium incorporated in the copolymer was 11.6 mg/g. The polymeric vanadium formed red peroxo complex on reaction with tertiary butyl hydroperoxide.

Hydroxy methyl undergoes epoxycyclisations in presence of several catalyst systems like peracids such as MCPBA, PCC and vanadium acetyl acetonate ($VO(acac)_2$)-tertiary butyl hydroperoxide system [37]. The disadvantages of these systems are that the catalyst cannot be recycled and the

reaction does not proceed in a diastereoselective manner. The reaction is presented in Scheme 4.5.1..

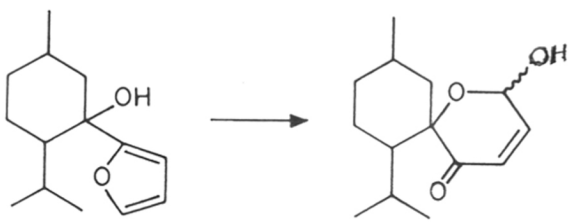
In the present case, when hydroxy methyl furans ***4.5.1a*** and ***4.5.1b*** were subjected separately to epoxidation with 70% tBHP in presence of catalytic amounts of diamino tetraacetic acid-V-incorporated copolymer at room temperature, the corresponding hydropyranones were obtained in 45 and 52% yields respectively. It may be noted that the epoxy cyclisation of hydroxymethyl furan took place in the presence of diamino tetraacetic acid-V-polymer catalyst in diastereoselective (3:1) manner. No such stereoselectivity was observed for both MCPBA and $VO(acac)_2$. The V-peroxo species, formed by addition of tBHP to vanadyl group, initially epoxidises one of the furan double bonds. Ring opening and cyclisation then proceed leading to the desired hydropyranones. It was expected that the double bond linked directly to the hydroxy the alkyl chain would undergo the reaction regioselectively, and the resultant dioxabicyclo hexene derivatives could rearrange to furanones. On the other hand, the rearrangement may proceed with the cleavage of C_2-O bond to give the hydroxy-2-one carbonyl products, the tautomers of hydroxy pyranones. The epoxide formation and ring cleavage of the epoxide is in the direction governed by the relative stability of the cyclic vanadate intermediates. However, the peracid oxidation may also involve epoxidation at a remote double bond of the furan nucleus, rearrangement of the primary products to the hydroxyone dicarbonyl compounds, and cyclisation. The polymer-vanadyl coordination may be a sterically better complexation and hence displays better stereoselectivity. The catalyst was recovered and reused at least three times with a marginal loss in activity and with retention of selectivity. The advantages of the present catalyst system include higher catalytic activity and the reaction, remarkably, proceeds in a diastereoselective fashion.

Scheme 4.5.1: Epoxycyclisation of Furan Carbinols



4.5.1a

Yield : 45%; IR (neat) $\nu max/cm^{-1}$: 3615-3335; 1717; 1683; 1610; 1453; 1386; 1307; 1250; 1115; 1045; 961; 859; 756. δ_H ^{1}HNMR; (200 MHz, $CDCl_3$) : 0.85 (3H, d, *J* 6Hz); 1.05 (3H, d, *J* 6Hz); 2.4 (1H, m); 3.9 (1H, *J* 2Hz); 4.4 (1H, d, *J* 2Hz); 5.65 (1H, d, *J* 2Hz); 6.1 (1H, d, *J* 8Hz); 6.9 (1H, dd, *J* 8 and 2 Hz).



4.5.1b

Yield : 52%; IR (neat) $\nu max/cm^{-1}$: 3820-3390; 1717; 1683; 1618; 1453; 1369; 1306; 1250; 1132; 1115, 1045; 961; 859; 755. δ_H ^{1}HNMR; (200 MHz, $CDCl_3$) : 0.8-1.0 (9H, m); 1-4-1.9 (7H, m); 2.3 (1H, m); 3.9 (1H, br.s); 5.25 (1H, d, *J* 2Hz); 6.2 (1H, d, *J* 2Hz); 6.9 (1H, dd, *J* 8 and 2 Hz). M/z (relative intensity): 238 (M^+, 6); 155 (10); 137 (10); 95 (35); 84 (100); 81 (35); 69 (14).

4.6 Redox Polymerisation of Acrylamide

The polymerisation of acrylic monomers can be initiated by redox pairs consisting of low molar mass transition metal complexes and a suitable reagent [38]. The susceptibility of organic compounds to oxidation by quinquivalent sulphuric acid solutions has been quantitatively surveyed by J.S. Littler and W.A. Waters [39]. Thus, ammonium metavanadate-cyclohexanone pair in dilute sulphuric acid media has been evaluated for the polymerisation of acrylates [40]. Polymeric heterogeneous initiators are advantageous over the corresponding homogeneous pair in the recyclability of the catalyst and leads to polymers relatively free from ionic impurities or reactive end groups [40,41]. Commercially pertinent polyacrylamide of very high molecular weights are prepared either by reverse emulsion or reverse microemulsion polymerisations. These methodologies have been extensively investigated by Candau et.al [42].

The primary objective of this study is to use a macroporous polymeric ligand-vanadium complex in combination with cyclohexanone to induce redox reaction, particularly polymerisation of water soluble monomer such as acrylamide. The molecular weight of the polyacrylamide obtained was compared with that synthesised by the corresponding homogeneous pair under identical conditions.

The macroreticular GMA-EGDM beads was prepared from a GMA : EGDM feed mole ratio of 50 : 50. The concentration of oxiranyl group present was 2.94 mmole/g of polymer. Surface area of the copolymer beads were estimated to be 108 m^2/ g. The pore volume was determined to be 0.50 cm^3/ g.

The imino diacetic acid copolymer [copolymer (I)] was synthesised by a one step process as presented earlier in Section **2.4.1.** The acid capacity of the copolymer was to be 1.19 mmoles of univalent sodium ions / g of copolymer (I). The nitrogen content of copolymer (I) was 1.81 Wt.%, which indicates 45% modification of oxiranyl group in the copolymer.

The copolymer carrying a diamino tetraacetic acid [DTA] ligand [copolymer (II)] was synthesised by a multistep process presented in Section **2.4. 4.** Diethylene triamine was incorporated in the base copolymer in this manner to generate a diamine moiety. A homogeneous substitution was obtained by this process. This indirect mode of derivatisation was worked out to avoid additional crosslinking of copolymer by the reaction of primary amino groups with the oxiranyl in the copolymer which would result in a decreased capacity [43]. The capacity of the copolymer (II) was evaluated as 1.92 mmole/g of univalent sodium ions.

Vanadium ions exist as VO_2^+ in acidic solutions. The coordination of VO_2^+ to amino acids is through the oxygen atom of the carboxylate ion and nitrogen atom of the amino group [44,45]. The complexation of vanadium ion were effected by contacting an acidic solution of metavanadate ion of pH 2 and 3 with acetic acid copolymers. There was only a marginal difference in the absorption of vanadium ions at the two pH. The coordination of vanadium ions on the copolymeric ligands was estimated by atomic adsorption spectroscopy as 0.120 and 0.176 mmoles Vanadium ions / g of copolymers I and II respectively at pH 2.

The polymerisation of acrylamide is through a free radical mechanism, which is shown to occur in all vanadium oxidations. The coordinated vanadium ion hydrates in acidic aqueous medium and complexes with cyclohexanone. Propagation is followed by termination either by combination of two growing radicals or through chain transfer to metal ions. This complex reacts with the

monomer yielding the primary radical, which initiates the polymerisation. The mechanism of polymerisation is presented in Scheme **4.6.1**.

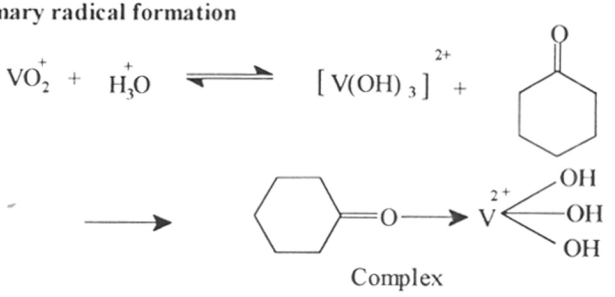
The relative efficiencies of the homogeneous metavanadate ion-cyclohexanone and the heterogeneous copolymer-vanadium ion-cyclohexanone as initiator systems for the polymerisation of acrylamide were examined under identical conditions. The molecular masses of polyacrylamide obtained are presented in Table **4.2**. The molecular mass of the polyacrylamide obtained under heterogeneous conditions is four fold higher than that obtained with homogeneous catalyst system. The yield of polyacrylamide formed by homogeneous catalyst system was low, probably due to the disappearance of quinquivalent vanadium ions in the solution as the reaction proceeds. The polymerisation of vinyl monomers are influenced by the cyclohexanone concentration and the acidic strength of the reaction medium [47]. Polymerisations does not proceed when pH exceeds 2.25 and / or cyclohexanone concentration recedes below 5 Wt.%. In the heterogeneous system at higher volumes of cyclohexanone, the polyacrylamide yield was quantitative. However, the molecular mass was low. This points to an increase in the concentration of initiator species with the volume of cyclohexanone. The recyclability of the catalyst, DTA were checked for three cycles and there was no change either in the molecular mass or yield of polyacrylamide formed.

4.6 X-Ray Photoelectron Spectroscopy (XPS) of Polymeric Vanadium catalysts

In the past two decades electron spectroscopy has been applied to several interesting applications in chemistry. The pioneering work of Seighban and his coworkers in high resolution electron spectroscopy resulted in a technique named by them as electron spectroscopy for chemical analysis (ESCA). In ESCA, a specimen is irradiated by soft X-rays and the resulting photoelectrons are dispersed through either a magnetic field or a electrostatic field. ESCA or XPS

Scheme 4.6.1. : Mechanism of redox polymerisation of vinyl monomer by vanadium (V) Cyclohexanone system

1, Primary radical formation



$$\text{Complex} \longrightarrow R\cdot + V^{4+}$$

2, Initiation by primary radical

$$R\cdot + M \xrightarrow{K_i} RM\cdot$$

3, Propagation

$$RM\cdot + M \xrightarrow{K_p} RM_2\cdot$$

$$RM_{n-1}\cdot + M \xrightarrow{K_p} RM_n\cdot$$

4, Linear termination by V^{5+}

$$R\text{-}M_n\cdot + V(OH)_3^{2+} \xrightarrow{K_{t1}} \text{Polymer} + V^{4+}$$

$$R\text{-}M_n\cdot + VO_2^+ \xrightarrow{K_{t2}} \text{Polymer} + V^{4+}$$

$$R\text{-}M_n\cdot + VO.OH^{2+} \xrightarrow{K_{t3}} \text{Polymer} + V^{4+}$$

Table 4.2: **Polymerisation of Acrylamide**

Catalyst	[M] mole/dm^{-3}	[CH] mole/dm^{-3}	[V]×10^{4} mole/dm^{-3}	yield %	[-η] dL/g	-$\bar{M}v$×10^{-4}
IDA	0.7	0.025	4.5	95	4.1	13.3
DTA	0.7	0.025	4.5	95	3.7	11.4
DTA	0.7	0.050	4.5	100	2.5	6.3
AMV	0.7	0.025	4.5	45	1.7	3.5

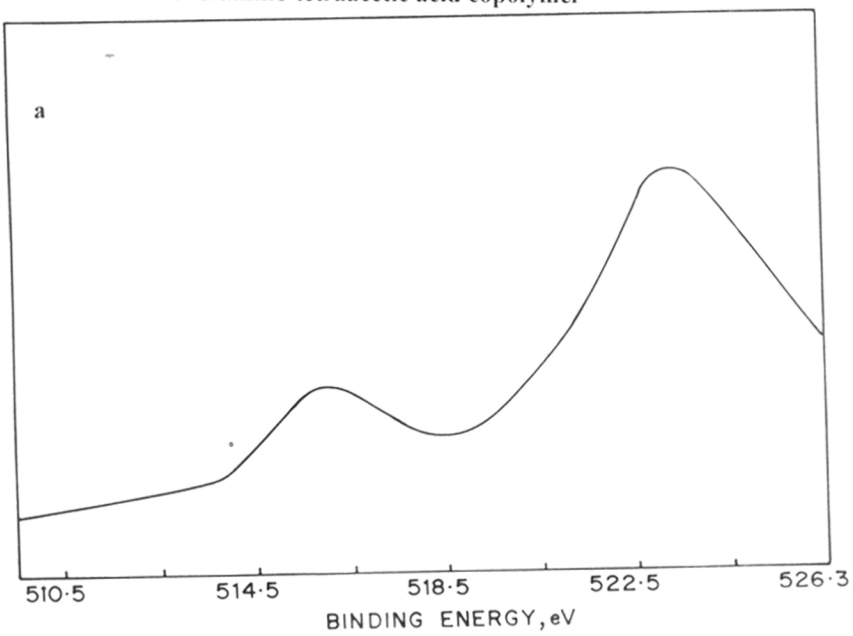
All the reactions were carried out at pH 2 and at 30°C for 24 hours.

IDA = Imino diacetic acid-vanadium (V) complex; **DTA** = Diamino tetraacetic acid -vanadium (V) complex; **AMV** = Ammonium metavanadate in homogeneous conditions; **[M]** = Concentration of monomer, acrylamide in water; **[CH]** = Concentration of cyclohexanol; **[V]** = Concentration of vanadium ions.

is concerned with the kinetic analysis of electrons yielded out of a specimen when it's subjected to photons or electrons. ESCA has been widely used to characterise supported metal catalysts.

The present study deals with the XPS characterisation of three vanadium chelated copolymers in different ligand environments. XPS analysis of diamino tetraacetic acid copolymer-vanadium complex (DTA catalyst) shows that oxidation state of the coordinated vanadium ion was +5. The measured binding energies were 515.5 eV and 523.5 eV which corresponds to 2p electron of vanadium atom [48]. Two different microenvironments were noted for the nitrogen atoms in the modified copolymer with binding energy values of 398/399 eV, 401 and 402.5 eV which corresponds to N_{1s} electrons of nitrogen atom. The former correlates well with non-coordinated nitrogen. Metal coordination shifts the binding energy to 402.5 eV. A similar trend was noted for imino diacetate copolymer-vanadium complex as well. The XPS of vanadium atom and nitrogen atoms are presented in Fig. **4.1.** The binding energy for all other elements are presented in Table **4.3**. Thus, all nitrogen atoms of the ligand are not coordinated to metal ions. The dithiocarbamate copolymer-vanadium complex shows characteristic binding energy for sulphur atoms at 162 and 164 eV and for vanadium ion at 523 eV. The XPS of sulphur atom is presented in Fig.**4.2.** Nitrogen atom present in the copolymer shows a binding energy of 398 eV, which indicates that nitrogen atom in the copolymer is not involved in the coordination.

Fig. 4.1 X-ray photoelectron spectroscopy of (a) vanadium ion and (b) nitrogen atom of diamino tetraacetic acid copolymer



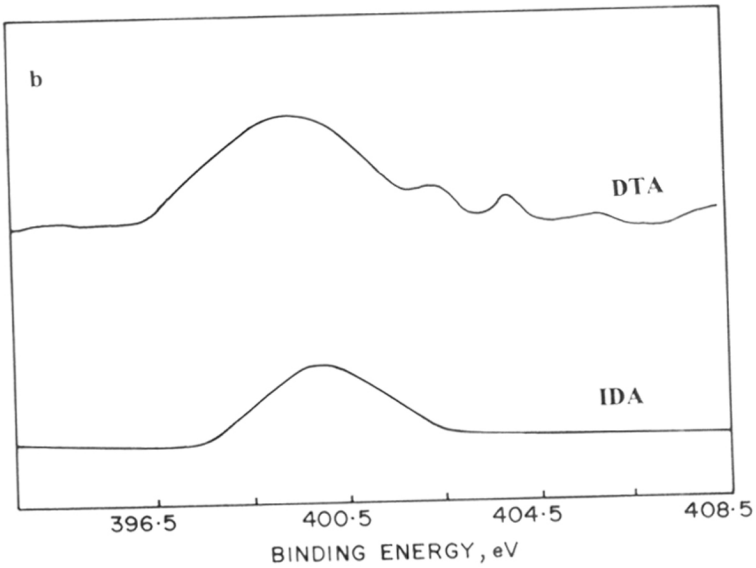
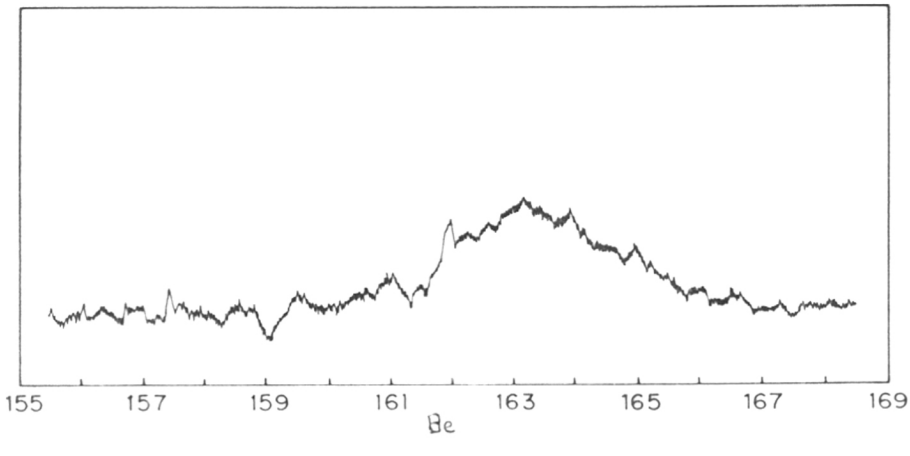


Table 4.3 : XPS studies on complexes

	Binding Energy (eV)			
	C_{1S}	N_{1S}	O_{1S}	V_{2P}
IDA	285	398, 401.1	532	517
DTA	285	398, 399, 402.5	532.2	515.5,523.5
DVC	285	398	532	522.6

IDA: Imino diacetic-vanadium complex; **DTA** : Diamino tetraacetic acid-vanadium complex and **DVC** : Dithiocarbamate -vanadium complex.

Fig. 4.2. XPS Peak of Sulphur atom in Dithiocarbamate copolymer-vanadium complex



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Chapter V

Redox Reactions with Polymer-Metal Complexes

5. Redox reactions with Polymer-metal complexes

Metal catalysed reactions of dioxygen are very important processes and there is sustained interest in their mechanisms [1-4]. Natural oxidation systems have evolved from the biosynthesis of oxidatively stable polydentate ligands for metals that can confer specificity as subtle as the difference between dioxygen transport and oxygenase or deoxygenase activity. This specificity is partially due to dioxygen reduction. Active site models based on carefully chosen polydentate ligands have been especially helpful in clarifying between cobalt, iron and copper dioxygen systems. Novel approaches have emerged with attachment of these multidentate ligands onto polymer supports [5-6]. Heterogeneous chelating polymer-metal complexes suited to catalysis are synthesised by the covalent binding of chelating agent to reactive polymer followed by coordinate complexation of metal ion [7].

Poly(phenylene oxide) [PPO] is a high volume engineering thermoplastic and much research has gone into the development of new catalyst systems [8-10]. The catalyst used for the oxidative coupling polymerisation is copper chloride-pyridine system in presence of molecular oxygen. The reaction proceeds through electron transfer which are mediated by the complex in presence of molecular oxygen. Heterogeneous polymer bound copper chloride catalysts have generated interest as this process yields poly(phenylene oxide) with fewer impurities [11-14].

The objective of the present study is to investigate the catalytic potentials of heterogeneous polymer supported copper chloride catalyst for the oxidative coupling polymerisation of 2,6-dimethyl phenol in presence of molecular oxygen and to correlate the electrocatalytic reduction of dioxygen with the catalytic property of the complex.

5.1 Oxidative coupling polymerisation

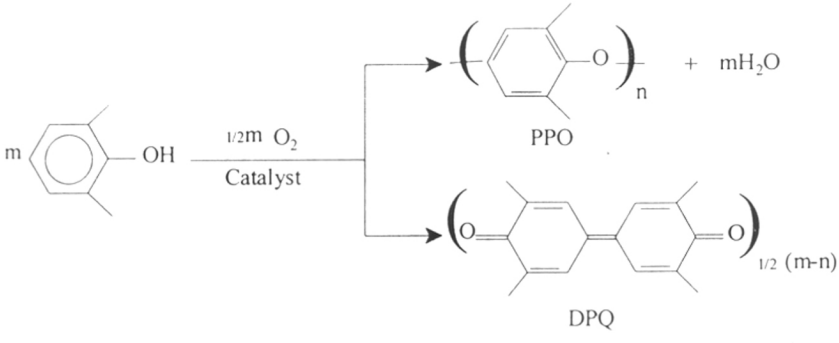
The Schiff base-metal complexes catalyse a variety of reactions like oxidations, hydroxylations and epoxidations [15]. The catalytic potentials of cobalt complex of such multidentate Schiff bases attached to polystyrene matrices have been investigated for the oxidation of substituted phenols [16].

The synthesis of the polymeric Schiff base-copper chloride catalyst is presented in Section **2.7.1.** The amount of copper coordinated was determined by AAS, after desorption with 0.1N hydrochloric acid, as 0.24 mmole/ g. The copper ions are coordinated through the C=N bond of the chelating copolymer, as seen by the shift in the IR frequency from 1630 to 1641 cm^{-1}. The IR spectrum of polymeric Schiff base copper complex is presented in Fig. **5.2b**. The pyridine adduct of the polymeric Schiff base complex was prepared by treating the complex with 25 molar excess of pyridine in 50 cm^3 dry ethanol for 24 hours.

In presence of pyridine, a competition would exist between the two coordinating ligands, polymeric Schiff base and pyridine for the copper ions. The relative affinity of the two ligands towards copper ions would depend on the stability of the resultant complex. In case, if affinity of pyridine exceeds that of the Schiff base, especially in large excess of pyridine, there would be considerable leaching out of copper. Thus, as an initial study the amount of copper ions leached out from the polymeric complex in presence of a known large excess of pyridine was estimated. The amount of copper ion leached out/ desorbed by pyridine when present in 25 molar excess of polymeric ligand, in 50 cm^3 ethanol was only 0.6%, even after equilibration for 48 hours. This indicates the high stability of polymeric Schiff base-copper complex compared to homogeneous

Fig. 5.1. Mechanism of oxidative coupling polymerisation of 2,6-Dimethyl phenol

1, Oxidative polymerisation of 2,6-dimethyl phenol



2, Elementry mechanism of copper complex catalysed phenol oxidation

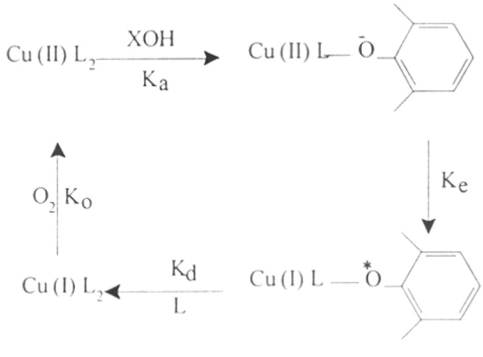
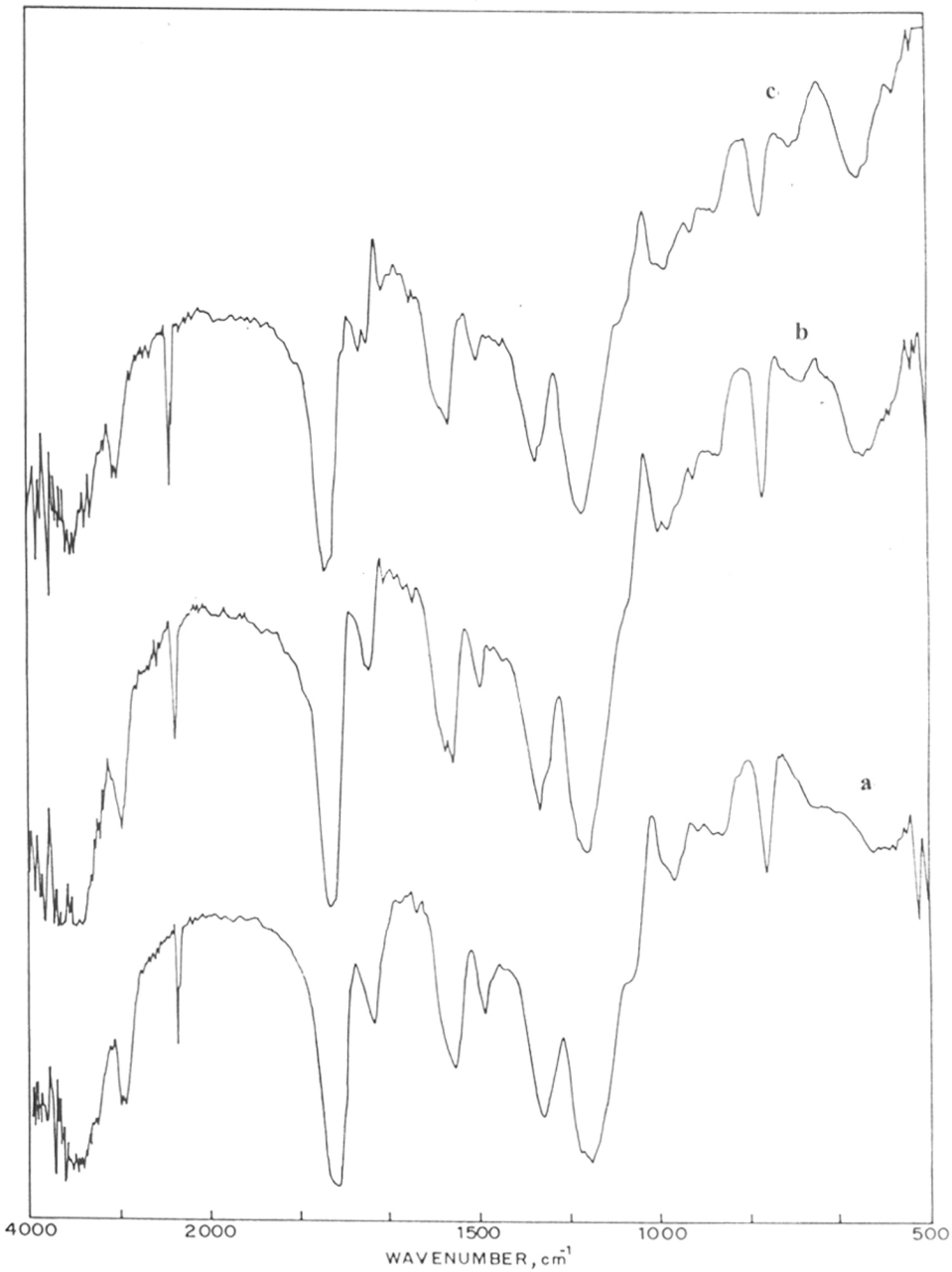


Fig. 5.2. : Infra-red Spectra of polymeric Schiff base (a); Polymeric Schiff base-copper chloride complex (b); and its pyridine adduct (c).



soluble pyridine-copper complex and that the heterogeneous catalyst could be evaluated for the oxidative coupling.

Substituted phenols are oxidatively coupled by number of homogeneous and heterogeneous catalysts like copper-pyridine complex and other metal salts in presence of molecular oxygen [17-19]. The underlying fundamental mechanisms related to phenols have been extensively investigated [20-21]. The reaction involves electron transfer. The polymer copper complex coordinates with the phenoxy ion and electron is transferred from the substrate to cupric ion. Molecular oxygen brings Cu(I) back to Cu(II) and thus completes the catalytic cycle. A schematic of the mechanism is presented in Fig. **5.1**. Oxidative coupling of phenols either forms poly(phenylene oxide) by C-O coupling or quinones upon C-C coupling. The selectivity of the catalyst depends on the structure of the complex. The electron transfer is an intra-complex process, and the electronic as well as the steric factors of the ligand in copper complex dictates the rate and selectivity of the reaction. Tsuchida et.al reported an increase in the oxygen binding property of cobalt-salen complex in the presence of an external coordinating ligand [22]. The vinyl pyridine copolymers have enhanced reversible binding of oxygen relative to pyridine [23].

The reaction was carried out under varied conditions such as changing the concentration of catalyst, substrate 2,6-dimethyl phenol (2,6-DMP) and solvent. The various conditions employed in the polymerisation is presented in Table **5.1**. The polymer yield was 60% in chloroform and 80% in orthodichlorobenzene. The polymeric Schiff base-copper chloride catalyst was inactive without the external pyridine ligand. The polymeric Schiff base copper complex, complexes with pyridine. This was confirmed by infra-red spectroscopy by the absorbence corresponding to

Table 5.1: Oxidative coupling polymerisation of 2,6-dimethyl phenol

Batch. No:	Catalyst	$[Cu]\times10^5$	$[Pyridine]\times 10^4$	Yield, %
1	**S-Cu**	1.2	0.0	0.0
2	**S-Cu**	1.2	5.0	70
3	**S-Cu**	1.2	2.5	75
4	**3-BPA-Cu**	0.6	2.5	80
5	**2-BPA-Cu**	1.2	0.0	0.0
6	**2-BPA-Cu**	1.2	2.5	85
7	**2-BPA-Cu**	1.2	5.0	90

Solvent = 1,2 dichlorobenzene; temperature = 30°C; under oxygen atmosphere of pressure 1 bar.

S-CU = Polymeric Schiff base-copper chloride complex; **3-BPA-Cu** = Polymeric bis(3-picolyl) amine-copper chloride complex, **2-BPA-Cu** = Polymeric bis(2-picolyl) amine-copper chloride complex.

coordinated pyridine at 1615 cm^{-1} in Fig. **5.2c**. The solid state ultra-violet spectroscopy (diffused reflectance spectroscopy) of the polymeric complex is presented in Fig. **5.3** and **5.4**. The spectrum of green coloured polymeric Schiff base-copper chloride exhibits charge transfer bands at 382 nm, 280 nm and broad band in the d-d transition range at 642 nm. The pyridine adduct of the complex shows a bathochromic shift with values at 384 nm, 289 nm and 652 nm. The electron spin resonance spectroscopy (ESR) X-band of the copolymeric Schiff base-copper chloride catalyst and its pyridine adduct at room temperature is shown in Fig. **5.5** and **5.6**. The values are comparable to the reported values of S-DVB Schiff base-copper complex [24]. The polymeric Schiff base-copper (II) complex shows values at g_1 = 2.057, g_2, g_3= 2.27 and A_1 = 127 as compared to 2.04, 2.07, 2.23 and 130 for reported values. The pyridine adduct of the complex also showed similar values as g_1, g_2 = 2.05, g_3 = 2.257 and 135 [24]. The data indicates that the geometry of the copper complex does not change from the destorted tetrahedral in presence of the external ligand. Presence of pyridine catalyses the oxygen transfer reactions. At a catalyst mass equivalent to 0.024 mmole of copper and 0.5 mmole of pyridine, poly(phenylene oxide) formed was a maximum of 80%. The molecular mass of polymer formed based on intrinsic viscosity from dilute solution viscosity, was low. The value, 0.114 dL/g corresponds to a viscosity average molecular mass (M_v) of 7000. The low molecular mass is due to the diffusional constraints posed by the rigid polymer support to the growing polymer chain of oxy phenylenes. Despite the higher rate of electron transfer generally observed in polymeric ligands, the slow reaction rate may be attributed to slow rate in the first step, the coordination of phenoxy ion onto the copper ion present deep within the rigid polymeric network. As the reaction proceeds, the colour of the solution turns deep red and diphenoquinone precipitates out. The glass transition

Fig. 5.3 : Diffused reflectance spectroscopy of Polymeric Schiff base-copper chloride complex.

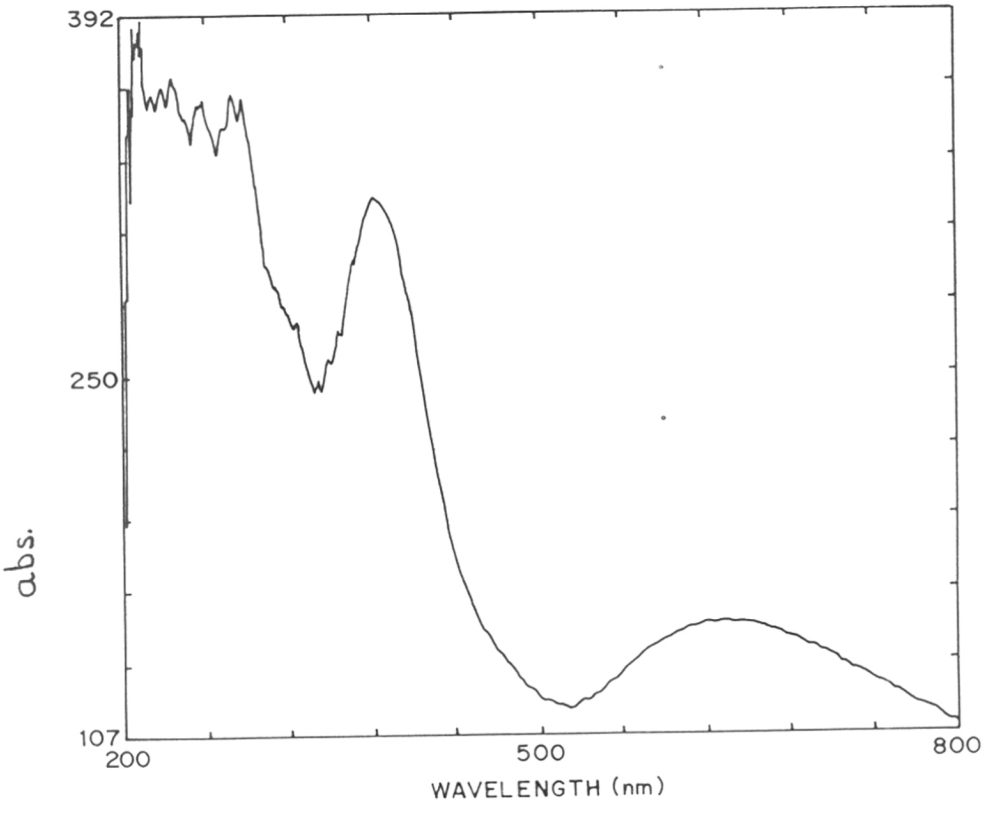


Fig. 5.4. : Diffused reflectance spectroscopy of polymeric Schiff base-copper chloride-pyridine adduct.

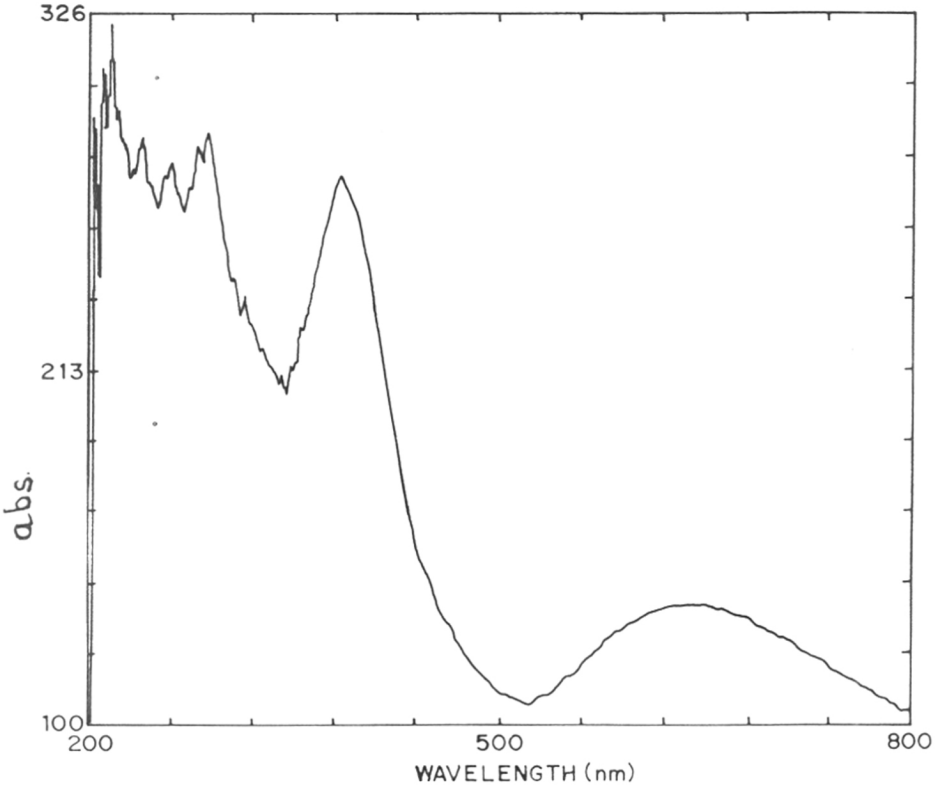


Fig. 5.5. : Electron spin resonance spectroscopy of polymeric Schiff base-copper chloride complex

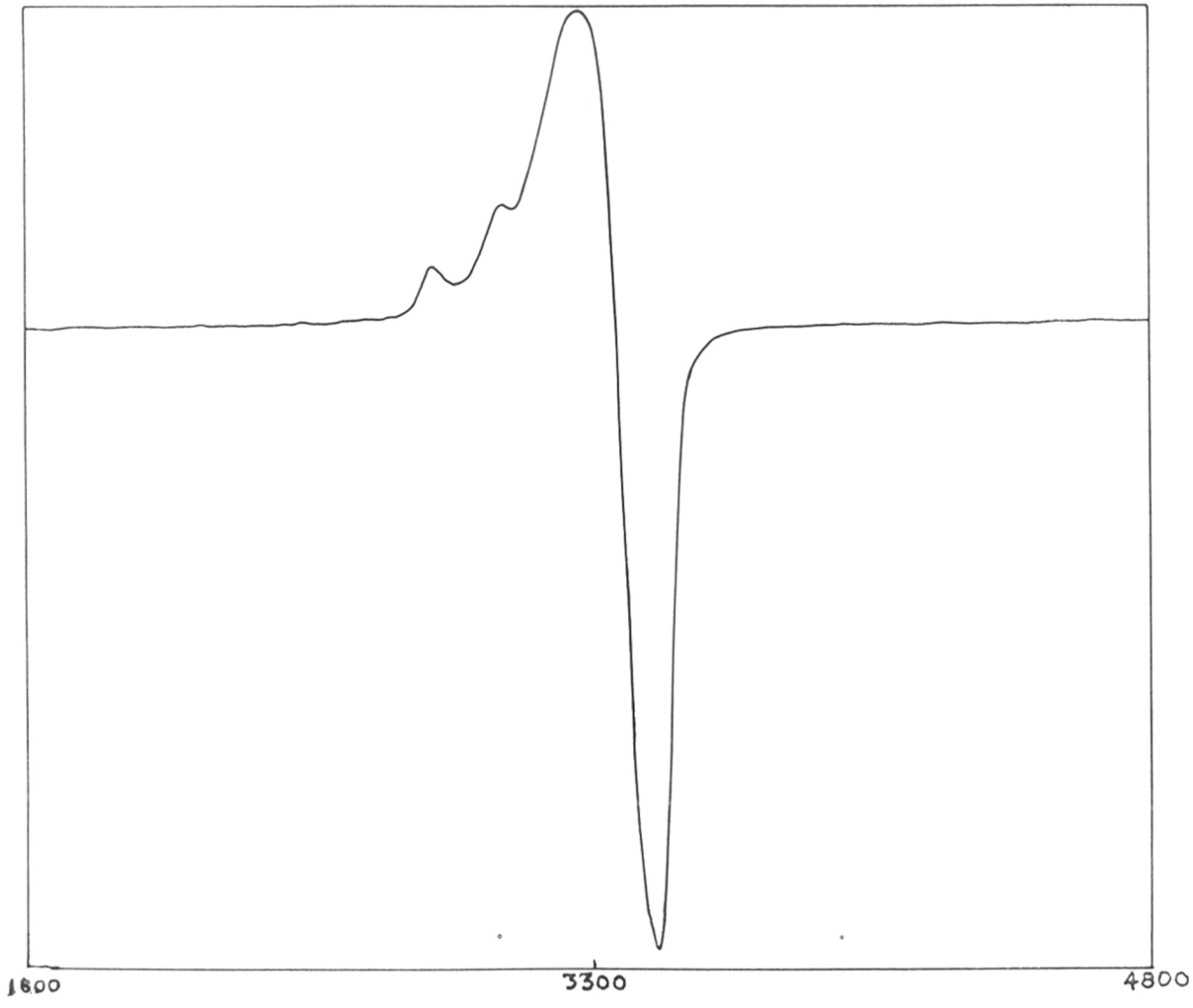
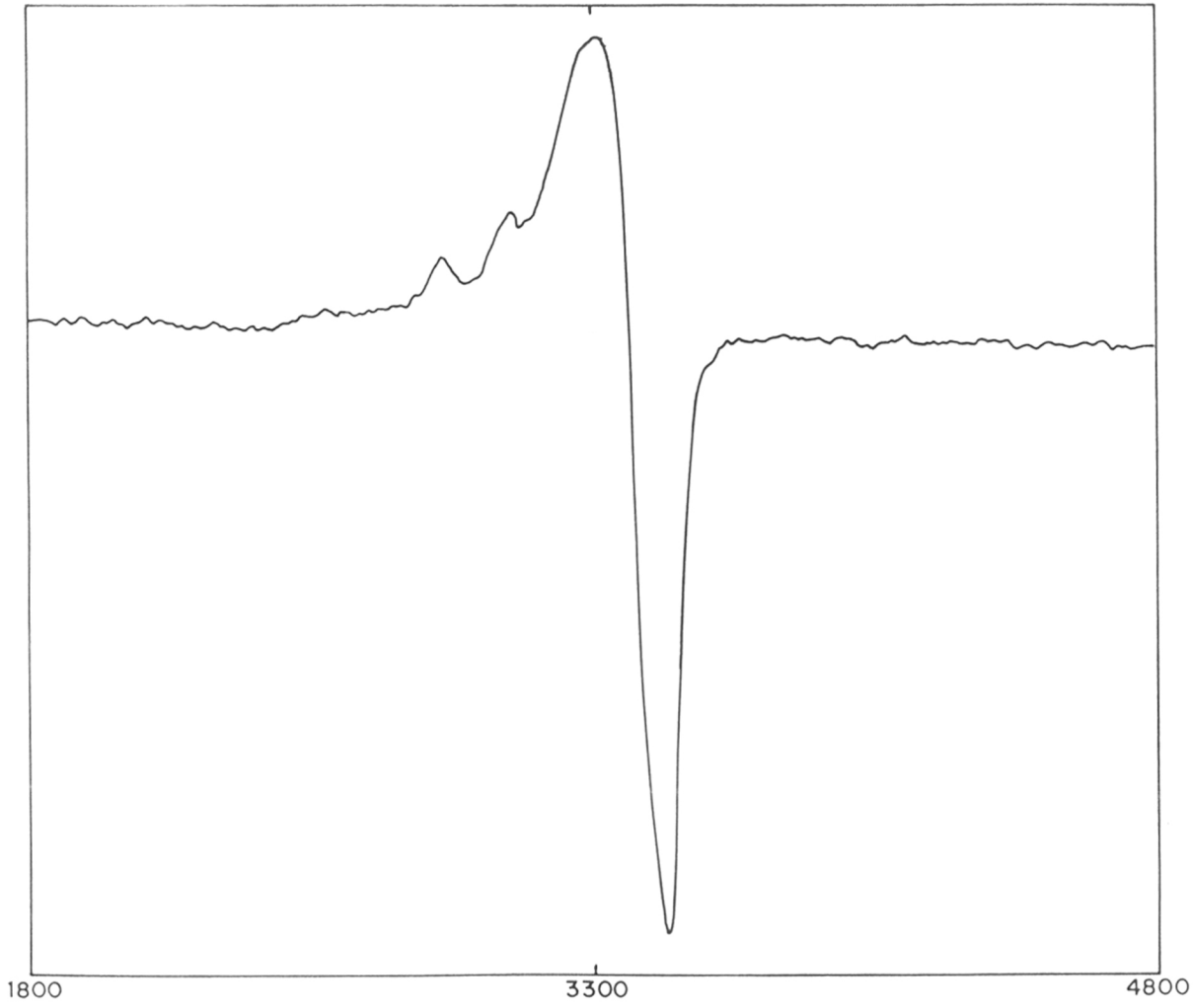


Fig. 5.6. : Electron spin resonance spectroscopy of polymeric Schiff base-copper chloride complex-pyridine adduct.



of the low molecular mass oligomeric PPO obtained was 185°C.

The bis(picolyl) amine copolymer catalyses oxidative coupling polymerisation of 2,6-dimethyl phenol. The copolymer yields only diphenoquinone without any external coordinating ligand. Presence of pyridine in the reaction medium enhances the catalytic activity of the complex and yielded poly(phenylene oxide) in 80% yield. The conditions at which polymerisations have been carried out are presented in Table **5.1.** Bases known to catalyse the polymerisation, as it facilitate the formation of phenoxy ion. In the present study we have not observed any change in the yield or reaction time in presence of sodium hydroxide. The molecular mass of poly(phenylene oxide) formed was calculated by viscometery. The intrinsic viscosity value was obtained as 0.104 and the Tg was 170°C.

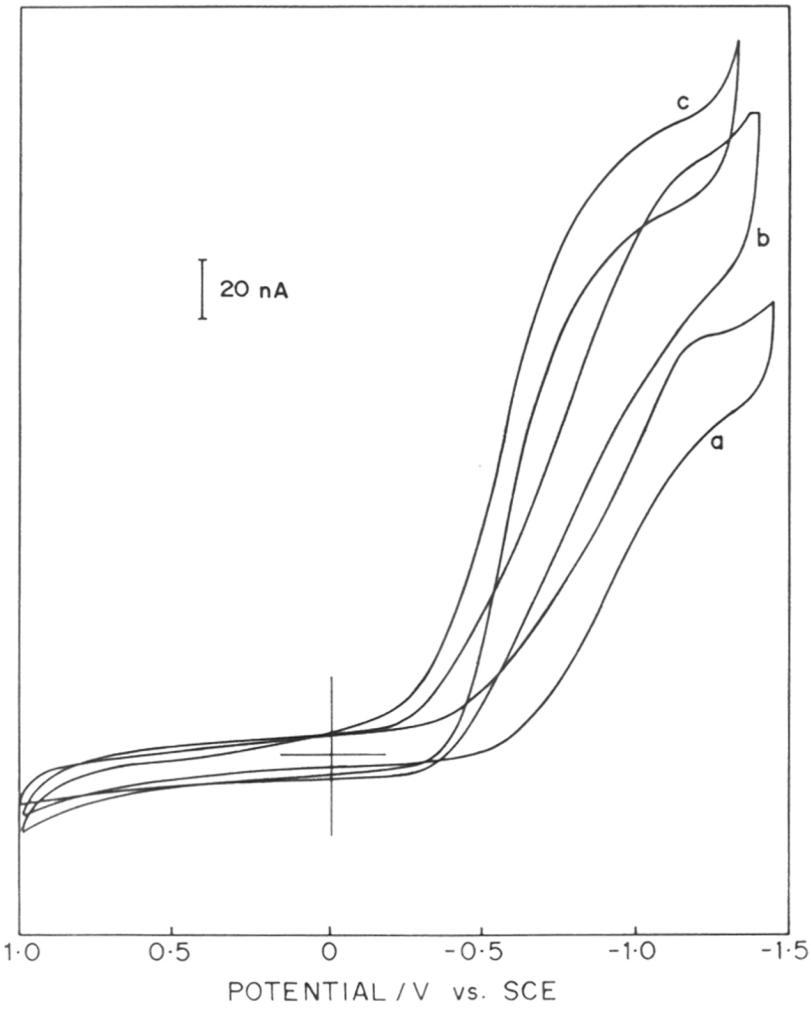
5.2 Electrocatalytic reduction of Dioxygen

Electrocatalytic reduction of oxygen with transition metal complexes is of considerable research interest [25]. Recently, the electrocatalytic reduction of oxygen with copper (II) hexaazamacrocyclic complex has been reported [26]. There have been no report on the electrocatalytic reduction of dioxygen in presence of polymer supported species. Cyclic voltammetry is a widely used technique to investigate redox potential of the system.

The present investigation deals with the dioxygen reduction capability of the polymeric Schiff base-copper chloride catalyst, which is a requisite property of a catalyst. The cyclic voltammetric experiment is presented in Section **2.9**. The electrocatalytic reduction of molecular oxygen was studied by cyclic voltammetry in N,N-dimethyl formamide (DMF). The reduction potential of

oxygen in DMF was obtained as -1.2 V. The cyclic voltammetry data showed that polymeric complex catalyst does not shift over potential of dioxygen reduction. The coordination of pyridine to this polymeric complex catalyst reduced the over potential of dioxygen reduction by more than 300 mV. The cyclic voltammograms are presented in Fig. **5.7**. Redox properties are related to structural and /or electronic parameters. These are typical of a specific complex and can be modified by subtle changes in the reaction medium [27]. The copper complexed on the copolymer coordinates with the pyridine in the solution which stabilises the reduced Cu(I) state of the complex and activates the redox process. The reduced Cu(I) catalyses the reduction of oxygen and brings down the over potential of dioxygen by 300 mV.

Fig. 5.7. : Cyclic Voltammogram of dioxygen reduction; (a) : without catalyst; (b) : with polymeric Schiff-copper complex and (c) : in presence of polymeric Schiff base-copper chloride catalyst and pyridine.



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Chapter VI

Conclusions and Recommendations

6. Conclusion and Recommendations

6.1 Conclusions

Macroporous glycidyl methacrylate-ethylene glycol dimethacrylate copolymer beads of varying crosslinking density and porosity were synthesised. The optimum synthetic parameters of polymerisations were investigated. The porous copolymer beads were characterised for the epoxy content and for pore size and its distributions. These reactive copolymers were then reacted with various reagents to generate chelating copolymers such as (i) imino diacetic acid (IDA); (ii) Schiff base copolymer; (iii) diethylene triamine copolymer; (iv) diamine tetraacetic acid copolymer (v) bis(2/3-picolyl) amine copolymers and (vi) dithiocarbamate copolymer. Imino diacetate group was introduced in the copolymer by a one pot synthesis. Other above mentioned multidentate ligands were also introduced onto the copolymer by the reactions with suitable reagents. The chelating properties of these copolymers were investigated under static condition as a function of pH. All the chelating copolymers showed good adsorption capacity towards bivalent metal ions such as Cu(II), Co(II) and Ni(II). These hydrophilic copolymers show better adsorption as well as desorption rates. The pentadentate Schiff base copolymer forms stable complexes with metal ions in organic conditions, but is not applicable as chelating copolymer for the preconcentration of metal ions, since the copolymer is hydrolytically unstable and undergoes cleavage in acidic as well as basic conditions. The bis(2-picolyl) amine copolymer was found to adsorb copper ions even at acidic conditions and has very good selectivity for copper ions at low pH. These copolymers can be effectively used to remove copper ions from electroplating bath, where high acidic solutions are normally employed. The distribution coefficient of the copolymer towards various metal ions was investigated. The selectivity of the bis(2-picolyl) amine

copolymer was investigated under competitive conditions. The diamino tetraacetic acid copolymer generated by a three step process has comparably good capacity for metal ions but lacks selectivity. The desorption of metal ions was carried out with acidic solutions of pH 1 or below.

The dithiocarbamate copolymer was generated by a two step process. The copolymer was first derivatised with ethyl amine and subsequently xanthated to generate the dithiocarbamate copolymer. Vanadyl sulphate was introduced into the copolymer by equilibrating the dithiocarbamate copolymer with the metal ion solution. The formation of peroxo complex was attained *in situ* by treating the vanadium chelated copolymer with tertiary butyl hydroperoxide (tBHP). These peroxo complexes catalyse the oxidation of substituted phenols at room temperature. The polymeric dithiocarbamate-vanadium complex catalyst is recyclable. The condition most suited for the oxidations were investigated.

Diamino tetraacetate copolymer was complexed with sodium metavanadate solution to generate the polymer-metal complex. The polymeric vanadium peroxo complex was generated *in situ* on reaction with tBHP. This vanadium peroxo complex catalyses the epoxycyclisation of furan carbinols (hydroxy methyl furans) under ambient condition. Epoxycyclisation of hydroxy methyl furans is a convenient method to synthesis phermones. The polymeric catalyst provides better selectivity.

Ammonium metavanadate, in presence of cyclohexanone, initiates the redox polymerisation of vinyl monomers such as acrylamide. The polymeric metavanadate of imino diacetate and diamino tetraacetate were prepared by equilibrating the metavanadate solution of pH 2 with the respective copolymer. Acrylamide polymerisations were conducted at differing concentrations of

cyclohexanone and polymeric catalysts. The polyacrylamide obtained at low concentrations of cyclohexanone have higher molecular mass than that obtained at high concentration of cyclohexanone. It was observed that the molecular mass decreases with increase in cyclohexanone concentration. The molecular mass of polyacrylamide obtained under heterogeneous condition is four times higher than that obtained with homogeneous ammonium metavanadate under same condition.

The vanadium chelated copolymers were characterised by X-ray photoelectron spectroscopy (XPS). The presence of vanadium in the copolymers was noted from the corresponding binding energy of the copolymers.

Polymeric Schiff base-copper chloride was prepared by equilibrating copper chloride solution in N,N-dimethyl formamide (DMF). The catalytic potentials of the polymeric Schiff base-copper chloride complex and its pyridine adduct were investigated for the oxidative coupling polymerisation of 2,6-dimethyl phenol in presence of molecular oxygen. The oxidative coupling polymerisations were carried out in varying conditions such as varying concentrations of catalyst, substrate and the external ligand, pyridine.

The polymeric Schiff base-copper chloride catalyst and its pyridine adducts were characterised by infra-red spectroscopy, electron resonance spectroscopy and also by diffused reflectance spectroscopy. The data indicates that pyridine complexes with polymeric Schiff base-copper chloride, but does not change the geometry of the complexes. The catalytic potentials of polymeric bis(picolyl) amines were also investigated for the polymerisation of 2,6-dimethyl phenol. The bis(picolyl) amine copolymer catalyses the oxidation of phenols, yielding 20% quinones in presence of molecular oxygen. The addition of external ligand into the catalyst

system changes the catalytic activity and yields poly(phenylene oxide) in 80%. The dioxygen reduction property of the polymeric Schiff base-copper chloride catalyst was evaluated using cyclic voltammetry. The polymeric Schiff base-copper chloride was found to be inactive without the external ligand, but its pyridine adduct changes the reduction over potential of dioxygen by 300 mV.

6.2 Recommendations

Glycidyl methacrylate copolymers are known as supports for chromatography, enzyme immobilisation etc. The copolymers synthesised with more hydrophilic comonomers could provide faster rates of adsorption for metal ions in aqueous environment. Copolymers of good metal capacities could be synthesised by derivatisation of functional monomers with metal specific ligands and its subsequent polymerisation with suitable comonomers.

Though styrene-DVB copolymers are extensively investigated as supports for immobilisation of transition metal complexes, GMA copolymers hitherto have not received much attention as catalyst supports. Catalytically important transition metal complexes can be immobilised on these macroporous copolymers and could be investigated as prospective organic polymer supported metal complex catalysts. Polymeric vanadium peroxo complexes could be used to selectively catalyse a variety of reactions such as epoxidations and hydroxylations etc. The polymeric vanadium complex could be used as recyclable, selective and environmental friendly catalyst systems.

Polymeric imino diacetate and polymeric diamino tetraacetate vanadium complexes could be used to synthesise high molecular mass vinyl polymers such as polyacrylamide and polyacrylonitrile

with fewer metal ion impurities. An investigation on the rates of polymerisation of acrylamide would give better understanding of the polymerisation recipe and one could apply the polymeric catalyst to tailor the molecular mass of polymer formed.

Polymeric Schiff base-copper chloride catalyst shows reversible dioxygen binding properties. The complex in presence of pyridine could reduce the over potential of oxygen by 300 mV in N,N-dimethyl formamide. The dioxygen reduction property of the complex could be tailored to a higher extent by evaluating the system under differing conditions such as varying the nature of solvents and the external coordinating ligand. The cyclic voltammetry investigations could be used to correlate the dioxygen reduction over potential with the catalytic activity and selectivity of the polymeric complex towards oxidative coupling polymerisation of 2,6-dimethyl phenol. A better catalyst system for oxidative coupling polymerisation of 2,6-dimethyl phenol could be chosen by carefully adjusting the ligand concentration, ligand : metal ratio and the type of external ligand. The stability of polymeric metal complexes would provide a better understanding regarding the optimum condition at which the catalyst could be employed circumventing any loss in activity (metal leaching). Electron spin resonance spectroscopy of polymer-metal complex at low temperatures could be carried out to understand the ligand environments and geometry of the complex.

List of Publications

1. Redox polymerisation of acrylamide by polymer supported vanadium (V) ion.

   Sunny Skaria, C. R. Rajan and S. Ponrathnam; *Polymer* (in press).

2. Porous thiiranyl polymers : Newer supports for immobilisation of penicillin G-acylase;

   Sunny Skaria, E. Sreenivasarao, S. Ponrathnam, K.K. Kumar and J. G. Shewale, *Eur. Polym. J.* (in press)

3. Polymer anchored vanadium salt for epoxy cyclisation of hydroxy furan carbinols.

   N.S.V. Raju, **Sunny Skaria**, S. Ponrathnam and A. Sudalai; *J. Chem. Res.* (S), 203 (1996).

4. Polymer supported vanadium salt as a catalyst for phenol oxidations,

   S. Suresh, **Sunny Skaria** and S. Ponrathnam, *Synth. Commn.*, **26**, (11) 2113 (1996).

5. Novel polyelectrolytes based on poly ethylene glycol methacrylate copolymer,

   J.S. Gnanaraj, R.N. Karekar, **Sunny Skaria** and S. Ponrathnam,

   Bull. Electrochem. Soc. India; (in press).

6. Immobilisation of Penicillin g-acylase on polymer supports,

   E.Sreenivasarao, **S. Sunny**, C.R. Rajan, S. Ponrathnam, K.K. Kumar, J.G. Shewale and P. Ellaiah, Paper presented in 47th National IPA conference, Chandighar, 1994.

7. Highly copper selective bis(picolyl) amine chelating copolymer based on Poly(glycidyl methacrylate).

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam, *Polym. Bulletin* (Communicated).

8. Redox catalytic property of polymeric Schiff base-copper chloride catalyst,

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam,

   J. Appl. Polym. Sci., (communicated).

9. Studies on comb like polymer blend with poly(ethylene oxide)-lithium perchlorate salt complex electrolyte.

   J.S. Gnanaraj, R.N. Karekar, **Sunny Skaria**, C.R. Rajan and S. Ponrathnam

Polym. Commn (communicated).

PATENTS FILED

1. A process for the preparation of hydrolytically stable macroporous beads

   E.Sreenivasarao, **S. Sunny**, A. Kotha, C.R. Rajan and S. Ponrathnam

   Indian Patent (1085/DEL/93).

2. A process for the preparation of immobilised penicillin g acylase using macroporious glycidyl methacrylate beads.

   E.Sreenivasarao, **S. Sunny**, A. Kotha, C.R. Rajan and S. Ponrathnam

   Indian Patent (316/DEL/94).

3. A process for the preparation of bis (picolyl) amines

   Sunny Skaria, Varsha Gadage, R. Ravishankar, C.R. Rajan and S. Ponrathnam

   (Indian Patent filed)

4. An improved process for the preparation of bis (picolyl) amines

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam

   Indian Patent filed)

5. A process for the preparation of macrporous bis(picolyl) amine polymers

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam

   (Indian Patent filed)

6. A process for the selective separation of copper ions using macroporous bis(picolyl) amine polymers.

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam

   (Indian Patent filed)

7. A process for the preparation of poly(phenylene oxide) using copper bound to macroporous bis(picolyl) amine copolymers.

   Sunny Skaria, Varsha Gadage, C.R. Rajan and S. Ponrathnam

   (Indian Patent filed)