Chapter 7

Conclusion and Outlook

The chemistry and technology of polymer supports and polymer supported reactions has been a subject of intense research during the last three decades. This was emerged as a new area of research in chemical sciences after the historical announcement of solid phase peptide synthesis in 1963 by R. B. Merrifield. The polymer supported strategy is widely used in synthetic organic chemistry and inorganic chemistry to overcome some of the serious limitations of the reactions in homogeneous phase. The concept of the use of insoluble crosslinked polymers as supports for reactive functional species has reduced the efforts of the usual reaction work-up considerably. The problem of contamination can be avoided by this novel method. For this and many other reasons, the polymer supported strategy has been extended to innumerable multistep synthesis in the field of chemistry and other related areas. The method has been successfully extended to the area of transition metal complexes also.

Polymer supported analogues of transition metal catalysts are currently being vigorously investigated. It is believed that resin binding will provide typical homogeneous catalytic chemistry and the convenience and economy of heterogeneous catalysts. Resin binding can change the steric environment and consequently the substrate specificity found in homogeneous systems. It should
provide catalytic sites containing a single metal atom, avoiding the formation of ligand-bridged species which are inactive in solution phases.

Chelate forming polymers are resin supports that incorporate chelating ligands by covalent bonding. Ion exchange resins represent the most prominent class of chelating polymer and generally contain the multifunctional ligands attached at one point. In the past, the principal commercial interest in chelating polymers has been in the selective removal and recovery of multivalent metal ions from solutions. Much higher ion selectivities have been obtained than with conventional ion-exchange resins and the metal ions are generally much more strongly retained. More recently polymer chelating of monovalent metal ions (using crown complexes) and multivalent anions has been accomplished. Some of these polymer based second shell complexes are finding application in ion selective electrodes and ion exchange membranes.

In the general strategy of using polymer supported ligands for metal ion separation the structure of the metal complex formed on polymer support is of prime importance.

In recent years polymer - metal complexes has been of great interest to chemists, biologist and industrialists because they came to understand that it is not only an excellent model for metalloenzymes, but also leads to developments of highly efficient catalysts. The microenvironment around the metal ion on polymer support is of great importance regarding its use in various fields of chemistry and biology.

Recently, there has been a wide interest in the study of mixed ligand complexes due to its theoretical importance and practical usefulness. The transition states of catalysis and different enzymatic processes are structurally analogous to mixed ligand complexes. To understand the mechanism of the above processes the structural study of mixed ligand complexes is important. The preparation and characterisation of mixed ligand complexes in homogeneous conditions meet with
some problems regarding the completion of reaction and separation of complex. In this context it is useful to prepare mixed ligand complexes on polymer supports whereby the problem in solution phase can be avoided.

The thesis primarily deals with the preparation of various polymer supported ligand systems, the metal uptake studies of these ligands, the preparation and characterisation of metal complexes of polymer ligands, and the preparation and characterisation of some mixed ligand complexes on polymer supports. Styrene-divinyl benzene copolymer forms excellent support for the designing of polymer supported metal complexes. Ligating systems were introduced into these well-defined, swellable and mechanically stable polymer networks through a series of polymer analogous functional transformation reactions.

Several factors are important in selecting the type of polymer to be used to support a given reactive group. These include the ease of preparation of potentially useful polymers and the ease with which these polymers can be obtained in a good physical form. Also the polymer should be chemically inert to unwanted substrates under the conditions of functional transformation and complexation reactions. Polystyrene crosslinked with different extents of DVB were prepared for the present work and it was found that 2% DVB-crosslinked polystyrene is most suitable because it can be obtained in granular form and also the maximum amount of ligand functions can be introduced on to this polymer.

The polymeric ligands developed are polystyrene supported dithiocarbamate (P*SS), polymer supported ethylene diamine (P*NN), polymer supported Schiff base (P*NO), polymer supported acid (P*OO), polymer supported azodye (P1*NO) and polymer supported acetyl acetone (P1*OO). These ligand systems were prepared following simple organic reactions and the functionalisation was confirmed by suitable chemical methods and also by IR spectroscopy. The extent of functionalisation was determined by directly estimating the functional group or by determining the residual chlorofunctionality remaining after respective functionalisation.
The affinity of various polymer supported ligand systems developed towards a variety of transition metal ions was tried by solid-solution phase reactions. The metal ions investigated are Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$, VO$^{2+}$, Zn$^{2+}$, Cd$^{2+}$ and Hg$^{2+}$. Studies were generally restricted to neutral pH but in a few cases a pH dependant uptake capacity was also monitored. The uptake capacity was found to be varying with the ligand system employing and the trend emerged for various metal ions is related to the stability constants of complexes on the support. Anion dependant study showed that there is a significant influence of the type of anion of the metal salt employed on the metal uptake capacity and the difference is attributed to the difference in formation constants of different metal salts.

A major thrust made in the present study is on the generation and characterisation of metal complexes of the various polymer supported ligand systems mentioned. The metal complexes were prepared by the general procedure and characterised by spectroscopic methods. IR spectra showed that the anions are present in the non-coordinated form in the complexes. Attempt was made to force the anion to co-ordination by changing the solvent and also by using anions with higher formation constants for their metal salt and it was seen that when acetate was used as the anion it remain co-ordinated to the metal.

Electronic spectral studies suggest square planar structure for the complexes. Since the functional groups available on the solid polymer surface are widely separated each metal ion would be able to link with only one ligand function on the polymer surface and the vacant co-ordination sites are satisfied by water molecules since the reactions were carried out in aqueous conditions.

The cases of Cu$^{2+}$ and VO$^{2+}$ systems were studied in detail by ESR measurements. Spectral measurements indicate nearly square planar structure to Cu$^{2+}$ complexes. The $A_{11}$ and $g_{11}$ values fitted well with the reported correlation plots and $a^2$ values indicate the strength of the inplane sigma bonding.
The spectral data of various vanadyl complexes generated on various polymeric ligand systems were also studied which indicate 5-co-ordinate character for all complexes. The nature of charge compensating anions were studied by IR methods while the electronic spectra gave the indication of their geometry. ESR spectra were also analysed in detail.

Knowing the structure of these polymer metal complexes P*SL(MX) simple strategy was tried to use them as precursor complexes to generate various mixed ligand complexes. In P*SL(MX) the metal centre is hooked on to the polymer support essentially by chelation with the exposed portion of the metal bearing weakly co-ordinated solvent molecule. The parent complex P*SL(MX) thus on treating with a solution of any selected ligand (say A) could be expected to generate new mixed ligand complexes with A replacing the water molecule from the co-ordination sphere. The preparative method involved is extremely simple but some difficulty was associated with the method with regard to the formation and stability aspects of the expected complexes. In many cases it was found that the polymer bound metal ions in P*SL(MX) get cleaved and come out in solution. Trials with several series of ligand systems indicate that there is dependency of formation constants of individual complexes on the extent of stabilisation of mixed ligand complexes on the polymer support. After considering the formation constants of various metal complexes, a few typical ligands were selected to generate the 'second series' of complexes. These include species like acetate, phthalate, oxalate, etc. Using these ligands several novel mixed ligands complexes were generated from the precursor P*SL(MX) species by simple work-up. Their characterisation was done by appropriate spectral methods. IR spectra give indication about the formation of the mixed complexes. Electronic spectra suggest square planar structure for these complexes. The case of Cu\(^{2+}\) and VO\(^{2+}\) were studied in detail by EPR.

Attempts were also made to prepare novel mixed ligand complexes by reacting known bis chelate complexes of some bivalent metal ions with some of the
P*SL system developed. The nature of the resulting complexes were probed by different spectral techniques.

The synthetic strategy based on polymers as support materials receives much attention during the last few decades. The advantages of the Merrifield's method have been thoroughly investigated by various groups of workers and the usefulness of this method was widely extended to other areas of chemistry and other interdisciplinary fields. The present thesis is an attempt to throw a glimpse primarily into the area of polymer supported metal complexes and particularly into polymeric mixed ligand complexes. A series of metal complexes were prepared in styrene based copolymer systems and the microenvironmental participation of the polymers was investigated. Spectral results from UV-VIS, IR and EPR methods were useful in establishing the structure of the metal complex analogues. The metal complexes gave well-defined EPR spectra at room temperature. The mixed ligand complexes were found to be stable under normal conditions of temperature and pressure. The extra stability showed by these mixed ligand complexes, in contrast to their low molecular weight counterparts, is attributed to the 'polymer effect'.

The foregoing studies give only a glimpse to the immense possibilities of the chemistry of polymer supported metal complexes with special reference to mixed ligand complexes. An extension of these studies could provide much information about the synthetic strategy, structural aesthetics, thermodynamic stability, kinetic response and spectral behaviour of these classes of compounds.