Chapter 1
Introduction and Objectives

The developments in chemical science and technology have been crowned by the introduction of polymer supported organic synthesis by Letsinger and Merrifield. Even though a lengthening list of experimental difficulties has been charted by the solid-phase experimentalists, the method was widely adopted by chemists and technologists. Merrifield’s findings were heavily quoted by organic chemists and the replica of the solid-phase method was reported by many of these practitioners. Thus a detailed catalog of experimental ensemble covering both peptide and nonpeptide methodology is available now.

Several active fields of research have emerged after Merrifield’s announcement of the revolutionary idea of solid phase peptide synthesis as an alternative to the conventional synthesis of peptide fragments in homogeneous systems. In some of these areas, the polymers are used as supports for grafting catalysts, reagents, enzymes and biomolecules. Also solid phase polymers find wide application in synthesising proteins, oligosaccharides, and oligonucleotides. One of the oldest and very popularly known applications of polymeric systems is as ion exchange resins in effecting separation of mixtures of ionic species. In such a context a more useful and modified form of ion exchange resins in the selective separation of metal ions appears to be polymer supports bearing ligand functions. The donor groups on the solid polymer supported ligand systems capable of
complexing with metal ions would exhibit selective affinity for the metal ions present in the mixture and hence can be expected to bring about better separation of the components.

In the general enthusiasm for using polymer supported ligand systems as metal ion separators, attempts to study the structural aspects of the polymer metal complexes formed on the system seem to be given scant attention, not to mention about the variety of structurally novel species that could be generated on them. Polymer metal complex can be considered as a metal complex containing a polymer ligand presenting a remarkably specific structure in which central metal ions are surrounded by polymer chain. These types of polymer metal complex show interesting and important characteristics, especially catalytic activities different from the low molecular weight counterparts. Metalloenzyme is a kind of polymer metal complex present in nature, where metal ions are surrounded by a giant protein molecule. Such a protein molecule which has a definite three dimensional structure often gives the central metal ion subnormal co-ordination structure and oxidation state by arranging the co-ordination sites stereospecifically or by distorting the co-ordination directions. In order to throw light upon the effect of the giant biomolecules surrounding the metal ion, extensive studies of the structure of synthetic polymer metal complexes are highly helpful.

Polymer metal complexes are markedly useful as immobilised catalyst for practical use and sometimes much more active than the corresponding monomer analogs due to the specificities of this large ligand molecules. In order to elucidate the effects of polymer ligand on the catalysis by polymer metal complex, the structure of the complex must be unambiguous. Considering the above facts, the first part of the present thesis is mainly aimed at developing some of the polymeric ligand systems with various donor sites and characterise their metal complexes.

The generation and characterisation of mixed ligand complexes assumes great significance in the light of innumerable catalytic reactions where such species are implicated as transition states and in bioinorganic chemistry which simulate
several important biological functions with cleverly designed model cofactors that are essentially special mixed ligand complexes. Various works were reported on the preparation of mixed ligand complexes in solution phase and their characterisation. But in homogeneous conditions the formation of these mixed complexes depends on their formation constants and also on the geometry and for complexes with comparatively smaller formation constants values the formation is incomplete and the characterisation is difficult due to the absence of a structurally singular species. To overcome these difficulties, a polymer supported strategy was developed for the synthesis of mixed ligand complexes. These studies are the main theme of the second part of this thesis.

1.1 Objectives of the work

The present work involves the following aspects.

1) Selection and synthesis of suitable polymer supports, in solid form with appropriate crosslinking, in size and shape convenient for working with metal ions in solution in laboratory scale.

2) Functionalisation of the granular polymer support by appropriate chemical methods so that variety of ligand functions could be generated on the support appreciably separated and capable of interacting efficiently with metal ions in solution. The surface functionalisation could thus graft N, NN, OO, NO and SS donor ligand functions on the polymer support. The identity and the extent of ligand function on the support could be estimated by suitable techniques.

3) An attempt was made to study the affinity of various polymer supported ligand systems (P*L) developed towards a variety of transition metal ions and correlate the metal ion uptake with the available ligand functions on the polymer support.
4) The metal ion uptake by P*L systems was essentially by complexation. This comparatively unattended fact has been explored in detail for metal complexes generated by chemical and spectral studies.

5) Depending the nature of P*L system employed, the metal ion complexes to the polymer support are expected to carry with them a definite amount of anions for charge compensation so that the complex could be of the form P*L (MX) B These are verified.

6) The anions incorporated along with metal ions on the P*L systems could be such that they could be co-ordinated or existing in the ionic form. Spectral studies are made to characterise the species.

7) Attempts are also made to induce the associated anions, which generally tend to remain ionic to co-ordinate on to the metal ions in the P*L (MX) B species by controlling the reaction conditions like the selection of solvents, temperature, etc.

8) An interesting aspect of P*L (MX) B systems (named as the first series of complexes) is that they could be used as ‘precursor complexes’ to generate a variety of novel tailor made mixed ligand complexes by making them react with any desired ligands taken in solution. The strategy could be tried, in principle, to obtain any type of metal-ligand chromophores P*L ML’, where ‘L’ is any desired ligand and M denotes metal fragment with or without the anion originally present.

9) Though a very much workable strategy, the results of a number of trials as above to develop series of P*LML’ species, however, met with some difficulties. There seems to be a strong dependence on the formation constants of ML2 and ML’2 in generating P*LML’. Based on this, attempts have been made to generate mixed ligand complexes of several selected ligands.
10) Attempts are also made by alternate strategy to develop several second series of mixed complexes denoted above.

Section 2.1 gives a brief overview of the synthesis, characterisation and application of polymer supported ligands and polymer metal complexes and Section 2.2 gives a brief review about the synthesis and structural aspects of mixed ligand complexes. Chapter 3 describes the materials employed, methods of preparation and analytical details. Chapter 4 gives a detailed account of the synthesis, analysis, and metal uptake studies of a series of polymer supported ligand systems. The preparation and characterisation of the metal complexes of these polymeric ligands are described in Chapter 5. Chapter 6 gives a detailed account of the preparation and characterisation of mixed ligand complexes on polymer supports and in Chapter 7 the important results are summarised.

1.2 References