CHAPTER 1

INTRODUCTION AND OBJECTIVES
The chemistry of functionalised polymers, their synthesis, structural modification and application in chemistry and chemical technology have continued to receive immense attention during the last few decades. The chemistry and applications of these functional polymers depend largely on the characteristics of the specific active functional groups. The architectural characteristics of the macromolecule influence the behaviour of these functional groups. The interdependence of the polymer microstructure and reactivity of functional groups in functionalised polymers dictates the applications of such systems in a number of areas of functional and technological interest. A polymer-metal complex is composed of a synthetic polymer and metal ions. Its synthesis represents an attempt to give an organic polymer with inorganic functions. Catalytically active polymers can be obtained by introducing a metal complex to a polymer backbone, and it is reasonable to assume that the metal complex bound to the polymer would show a specific type of catalytic behaviour, reflecting the properties of the polymer chain. Synthetic polymer-metal complexes exhibit high catalytic efficiency. In the case of metalloenzymes such as oxidase and haemoglobin, where a metal complex is the active site, the macromolecular protein part plays a significant role and controls the reactivity of the metal complex. Thus, research on the catalytic activity of polymer-metal complexes has attracted considerable interest in recent years.

In the macromolecular metal complexes, physicochemical properties and chemical reactivities of the complex moieties are often strongly affected by interaction with the surrounding three dimensional polymer matrix. The nature of the polymer backbone, the conformation of the macromolecular chain, the microenvironment of the reactive functional groups, the relative occurrence of functional groups in the
Investigations of the effect of the variables of macromolecular structure on complexation would contribute to the study of polymeric complexing agents which find varied applications in metal ion separation, preconcentration and recovery of trace metal ions, catalysis, organic synthesis, waste water treatment, nuclear chemistry, pollution control, hydrometallurgy and in the modelling of mechanochemical and bioinorganic systems.

Polymer metal complexes are markedly useful as immobilised catalysts for practical use because it is more reactive than the corresponding monomer analogs due to the specificity induced by the macromolecular matrix. The chemical reactivity of the functional groups in the polymer is dependent on the nature of the polymer backbone, molecular nature of the crosslinking agent, relative amount of the crosslinking agent in the copolymer, pore-size and pore-volume of the polymer particles, separation of the functional groups from the backbone of the polymer support and on the solvation characteristics of the polymer matrix. The development of a catalyst formulation should therefore take into account not only by the chemical nature and distribution of the active species but also the design of the catalyst. This involved factors such as the average pore-size, the variation in pore-size and adequate mechanical strength. Catalysis may be defined as the art of manipulating chemical molecules in order to facilitate their transformation along the desired reaction pathway.
The content of this Thesis is a correlation between the variables of macromolecular structure, complexing ability of ligand and catalase-like activity of polymer-metal complexes. For these investigations crosslinked polystyrene-supported Schiff base- and polyacrylamide-supported glycine-metal complexes were used. The preparation of these crosslinked polymer, functionalisation to incorporate various ligand functions by polymer-analogous reactions, physicochemical investigations of the polymeric ligands and their complexes, study of the interdependence of the macromolecular parameters and trends of complexation and the catalytic activity of specific systems were carried out here.

Chapter 2 describes the background of the present work, a brief analysis of existing literature on synthetic, analytical and catalytic activities of polymer-metal complexes. Here emphasis is given to typical illustrative examples of the formation of important types of polymer-metal complexes, illustration of catalytic and important applications of polymer-metal complexes.

The synthesis, characterisation and catalytic activity of the various polymer-metal complexes are picturised in Chapters 3, 4, 5 and 6 respectively. The purpose of undertaking the work is to synthesise a more efficient polymer-supported catalyst to portrait the enzyme-like activity and also trace out the diverse aspects of complexation of insoluble crosslinked polymer ligand in an aqueous heterogeneous environment.

Chapter 3 illustrates the complexation behaviour of Schiff bases supported on polystyrene supports. The preparation of ethyleneglycol dimethacrylate (EGDMA)-, butanediol dimethacrylate (BDDMA)-, hexanediol diacrylate (HDODA)-, tetraethyleneglycol diacrylate (TTEGDA)-, and divinyl benzene (DVB) (microporous and macroporous)-crosslinked polystyrenes are described here. By varying the amount of crosslinking agent and monomer, polymers with varying degree of crosslinking were prepared. On varying the nature and extent of the crosslinking agent and reactivity of macromolecule system, the metal ion uptake exhibits diversity. Complexing ability of the ligand function in
differently crosslinked polymers were investigated towards Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) ions. The different polymeric ligands and their metal complexes were characterised by infrared, ultraviolet-visible and electron paramagnetic resonance spectroscopy and also by scanning electron microscopy analysis.

Chapter 4 describes the investigation of the complexation characteristics of glycine functions supported on N,N'-methylene-bis-acrylamide (NNMBA)-crosslinked polyacrylamide supports. The complexation studies of glycine functions supported on NNMBA-crosslinked polyacrylamide in different structural environments are also discussed here.

Chapter 5 describes the thermogravimetric studies of complexes of various polymeric metal complexes. In this section, attempts have been made to analyse the phenomenological and kinetic aspects revealed by the nonisothermal thermogravimetric curves. The purpose is to investigate whether there is a correlation between the decomposition kinetics of metal complexes with the nature and extent of crosslinking and how thermal stability varies with various metal complexes.

Chapter 6 describes the catalase-like activity of various crosslinked polystyrene-supported Schiff base-metal complexes. The catalase-like activities of polyacrylamide-supported glycine-metal complexes are also discussed in this chapter. This makes a comparative study of the catalytic behaviour of hydrophobic polystyrene and hydrophilic polyacrylamide systems. These investigations are conducted with Fe(II), Fe(III), Co(II), Ni(II) and Cu(II) metal complexes by altering various conditions of catalysis. On changing the nature of support and crosslinking agent, catalysts exhibit considerable difference in reactivity. The catalytic activity of the metal complexes of the polystyrene-supported Schiff base and polyacrylamide-supported glycine were followed. In the two systems catalytic activity of the polymer metal complexes decreased in the order: Co(II) > Cu(II) > Ni(II) > Fe(II) > Fe(III). The variation in reactivity with metal ions can be explained in terms of coordination geometry and nature of crosslinking agent. The high catalytic activities of Co(II) and Cu(II) complexes are due to the
unsaturation of its coordination geometry. But Fe(II) and Fe(III) complexes have no considerable reactivity. The degree of crosslinking has significant importance in the decomposition reaction of hydrogen peroxide. Various crosslinks of 2-20 mol% were studied for these investigations. In polystyrene system, in all crosslinking agents the catalytic activity decreased in the order: 20 > 12 > 8 > 4 > 2. But in NN MBA-crosslinked polyacrylamide system it decreased in the order: linear > 12 > 8 > 4 > 20 > 2.

Chapter 7 is the experimental part of the thesis. The final section gives a summary of the results of these investigations covering the macromolecular characteristics and nature of the support in polymeric systems.