Introduction and Objectives
"I am inclined to think that the development of polymerization is, perhaps, the biggest thing that chemistry has done, where it has had the biggest effect on everyday life. The world would be a totally different place without artificial fibres, plastics, elastomers etc. Even in the field of electronics what would you do without insulation? And there you come back to polymers again.

Lord Todd

The chemistry of functional polymers, their synthesis, structural modifications and applications in chemistry and chemical technology have continued to receive immense attention during the last few decades. From the lowly throwaway candy wrapper to the artificial heart, polymers touch our lives as does no other class of materials, with no end to new uses and improved products in sight. Polymer supports are widely used in synthetic organic chemistry to overcome many of the operational limitations of the conventional solution phase reactions. Polymer-supported strategy was employed for mechanistic investigations of organic reactions. Such experiments have the historical charm of establishing the kinetic effects in multi polymer systems, migratory aptitudes or rearrangeable groups embedded in crosslinked macromolecular matrices and in trapping of short-lived intermediates. The chemistry and applications of these functional polymers depend largely on the characteristics of the specific active functional groups. The macromolecular
structural features of the polymer support have been proved to contribute significantly to the reactivity of the functional groups.

The important advantages of polymer-supported strategy are the simplification of product work up, easy separation and isolation. The attachment of functional groups to insoluble crosslinked polymers can bring about significant reactivity changes by possible restricted interaction of functional groups. The insolubility makes the functional groups mutually inaccessible. The polymer acts as an insolubilizing medium for the attached species. A high degree of crosslinking, a low level of functionalisation, low reaction temperature and the development of electronic charges near the polymer backbone tend to encourage this situation which may be similar to mimic the solution conditions of infinite dilution. The attachment of macromolecular matrix can also solve the problems of lability, toxicity or odour, often experienced with low molecular weight reagents.

Polymers find use in organic synthesis either as passive supports or as active supports. In passive supports, the polymer functions as a heterogeneous matrix to which a low molecular substrate is covalently bound, allowed to react with various reagents and finally cleaved from the polymeric support in a modified form. In active supports the substrate attached to the insoluble polymer effects a synthetic or catalytic transformation on a soluble substrate. This group includes polymer-bound reagents in which the active site is consumed during the course of the reaction and polymer bound catalysts where the active site catalyses numerous chemical transformations. Here comes the importance of polymer-metal complexes which act as polymer bound catalysts.
A polymeric catalyst is a conventional catalytic species supported on a macromolecular backbone, which is used in catalytic quantities and can be reused many times without loss of activity. The performance of a catalyst is influenced by the physical and chemical properties of the support. Heterogenation of homogeneous catalysts by attaching them to polymers leads to improved stability and selectivity since the catalysts produced combine the advantages of the heterogeneous and homogenous catalysts. The distribution and accessibility of the active sites control the activity of the catalysts. When the catalyst species is supported on a polymer its catalytic action is essentially maintained while problems associated with the use of conventional soluble catalysts such as emulsification are eliminated. The costly catalyst can be effectively retained in this method and can be readily reused.

In polymer-supported transition metal catalysts, the desired metal complex is generally attached to the functionalised polymer by equilibration of the polymer with a metal complex having similar or weak ligands. The mode of attachment depends on the nature of the transition metal complex and the amount of the crosslinking in the polymer. The nature of the support, nature of the metal complex, degree of crosslinking and the nature of the solvent optimize the polymeric catalyst for a particular reaction. Thus catalysis may be defined as the art of manipulating chemical molecules in order to facilitate their transformation along the desired reaction pathway.

The purpose of the present work is to synthesise some efficient polymer-supported metal complexes and to portrait the catalytic activity in ester
hydrolysis and also to trace out the diverse aspects of complexation of insoluble crosslinked polymeric ligands in an aqueous heterogeneous environment. For this purpose, metal complexes of 4-20 mol% NN MBA-crosslinked polyacrylic acids and copolymers of acrylic acid and N-vinyl-2-pyrrolidone were prepared and characterised.

1.1 Organisation of the Thesis

For convenience this thesis has been arranged in seven chapters as outlined below.

**Chapter 1** is a brief introduction to the history and importance of functional polymers including a brief perspective to polymer bound metal complexes and the objectives of the present work.

**Chapter 2** is a retrospective survey of polymer-metal complexes with special emphasis on their synthesis, classification and catalytic activity.

**Chapter 3 & 4** present the details of results and discussion. It includes the synthesis and characterisation of solid supports, metal ion complexation of polymeric ligands and optimization of conditions of complexation. Complexing ability of the ligand function in different linear and crosslinked systems was investigated. Swelling studies of polymeric ligands and metal complexes were also carried out.

**Chapter 5** describes the catalytic activity of metal complexes of 4 to 20 mol% NN MBA-crosslinked polyacrylic acid and acrylic acid–N-vinyl-2-pyrrolidone.
copolymers. This makes a comparative study of the catalytic behavior of (a) crosslinked homo polymer system and crosslinked copolymer system and, (b) linear copolymer system and crosslinked copolymer system. These investigations were conducted with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) metal complexes by altering various conditions of catalysis. On changing the nature of the support and crosslinking agent, considerable difference in catalytic activity was observed.

Chapter 6 describes the reagents used, methods of preparation of the polymer-supported ligands and metal complexes, analytical and physicochemical methods and other experimental procedures employed in the present study.

Chapter 7 gives a summary of the results of these investigations covering the macromolecular characteristics and catalytic activity of polymer-supported metal complexes and the future scope of the present work.