Summary of the Work

The thesis entitled Studies on Geometrically and Electronically Altered Metal Complexes Supported on Polymer Matrix enlists a wide array of structurally modified copper(II), oxovanadyl(IV), cobalt(II) and cobalt(III) complexes. The main objective of the work was to point out the possibility of obtaining well defined and structurally homogeneous macromolecular metal complexes fixed on a solid organic support. The fulfilment of this objective also pave path for the modification of usual structures of monomeric complexes. The generation of these new forms would allow to achieve an important development of chemical processes involving heterogeneous catalysts, giving the opportunity of tailoring the structure active sites and then of controlling products type and distribution.

The organic matrix, mainly crosslinked polystyrene, appears more suitable to be functionalised with chemical species which can act as ligands for fixation of transition metal ions/metal complexes to give structurally uniform macromolecular metal complexes. 2% DVB-crosslinked poly-4-vinyl pyridine also provides good binding sites for metal ions/complexes. By varying the amount of σ donor and π donor and acceptor characteristics of the ligands at the active site the extend of charge transfer from central metal to the ligand site and the overall activation of the complex moiety will vary in a corresponding fashion.

This redistribution of electron density is accomplished not only by changing ligands but more subtly by changing their orientation with respect to the central metal.

In the series of systems studied all polymer supported metal complexes gives anisotropic EPR spectra and made this spectral analysis easier. IR and UV spectra of the solid polymer samples were taken for assigning their structures.

The first chapter gives a general introduction about polymer supported metal complexes and polymer supported ligands, chelating resins, etc. Main achievements of the work is enlisted in chapter 2. Materials and reagents used for this work and the important instruments employed are mentioned in chapter 3. This chapter also contains the way by which various metal complexes, polymer supports, polymer supported ligands and polymer supported complexes are represented in this thesis. Chapters 4, 5 and 6 entirely contains complexes of copper(II) with coordination number four, five and six, respectively. In copper(II) with coordination number 4 mixed ligand complexes of copper with or without anion in the polymer support is described. The usual structure of four coordinated species could modify so as to generate asymmetric complexes on polymer support is also dealt with in chapter 4. Five coordinated species discussed in chapter 5 is synthesised by reacting together usual four coordinated complexes with polymer supported monodentate ligands. Four-coordinated species are modified to five coordinated species with the use of polymer supported ligands. Polymer support **C, D** and **E** are used there. Four-coordinated copper(II) complexes with pyridine and DVB-crosslinked 4-vinyl pyridine gives six-coordinated copper(II) species which were considered in chapter 6.

Geometrically modified five-coordinated oxovanadyl complexes on polymer supports comprising mixed ligands and six coordinated oxovanadyl

complexes obtained by modifying usually occurring five-coordinated species with polymer supports like **C** or **D**, were described in chapter 7.

Mixed ligand complexes of cobalt(II) and cobalt(III) on polymer support is described in chapter 8. Usual structures of cobalt(II) complexes were modified with the use of polymeric monodentate ligands. Also rate of anchoring of some similar complexes on polymer supports **C** and **D**, dioxygen intake occurs while the modification of usual structures of cobalt(II) complexes takes place with the help of polymer support were followed and studied in chapter 8.

The work presented in this thesis in section 7.2 has been published in the proceedings of POLYMER '94 held at Research Centre, IPCL Vadodara as details given below.

Title of the work:

1. Polymer support based route to generate mono-Schiff-base and asymmetric bis-Schiff-base complexes (Polymer Science Recent advances, Vol. 1, 214-221, 1994, Edited by I. S. Bharadwaj).
2. Investigation on the possible role of ligand framework on reversible dioxygen binding in cobalt(II) complexes (Paper sent in 30th Annual Convention of Chemists conducted at Udaipur).
3. Use of polymer-support for generation of novel electronically and geometrically modified metal complexes (Paper presented in recent advances in polymers held at Moti, Tabela, Indore, 1995).
