# PREFACE

## Introduction

Dendrigraft polymers or Dendronized polymers are currently under intense investigation with respect to various applications, including the synthesis of hierarchically structured materials, catalysis, applications in biosciences, as well as optoelectronic applications. In Dendronized polymers, the focal points of the dendrons are attached to the pendant functional groups at the repeat units along the polymer backbone. Multiple branching levels characterize the architecture of these molecules, in analogy to dendrimers and hyperbranched polymers. Their core is not a single unit, but a polymeric chain. Main distinguishing feature of these polymers is their synthesis, based on grafting reactions with polymeric side chains serving as backbone. In the case of branched polymeric core, the term Dendrigraft polymer was more appropriate than Dendronized polymer, because, dendritic units are grafted on the polymeric chain. In the synthesis of dendritic molecules, multistep solution chemistry presents a synthetic challenge, because of the need to purify products at every stage. In solid phase synthesis, no purification is required during intermediate stages. Reactions are driven to completion by the addition of excess reagents. In this technique, the product is anchored onto the support and after the reaction, the excess reagents are removed by filtration. Also, one can study the solution chemistry of the product by cleaving the same from the resin loaded polymer. The concept of dendritic polymer together with solid phase strategy has been applied. We have tried to establish Merrifield resin supported dendrigraft polymer as heterogeneous catalyst for organic transformations. The present thesis envisages the synthesis and characterization of dendrigraft polymers on Merrifield resin and the application of metal complexed dendrigraft polymers in the field of heterogeneous catalysis.

**The motivation behind the work**

- Peripheral functionality of PAMAM and PPI dendrimers developed previously from this laboratory were in the order of 1 to 2 mmols/g for G0 to G2 generations. So the present focus was to increase the amount of functionality at the low generation level itself.
- Dendronized polymers reported so far were based on linear polymeric core, the same synthesized from branched polymeric core are only few. So the present focus was to develop dendrigraft polymers having branched polymeric core.
- Reported dendronized polymers having linear polymeric core were synthesized using solution phase strategy, the same synthesized using solid phase strategy was not reported yet. So the present focus was to develop dendronized or dendrigraft polymers using solid phase strategy.

**Objectives of the Work**

- To design and develop Dendrigraft polymers having linear ethylene glycol initiated polyepichlorohydrin as core on a resin support.
- To design and develop Dendrigraft polymers having branched glycerol and pentaerythritol initiated polyepichlorohydrin as core on a resin support.
- To study the nature of Dendrigraft polymers after cleaving from the support.
- To synthesize and characterize Copper and Palladium Complexes of Dendrigraft polymers having Ethylene Glycol, Glycerol and Pentaerythritol initiated Polyepichlorohydrin as core.

- To evaluate the catalytic properties of polymer supported copper and palladium complexes of dendrigraft polymers in organic chemical transformations.

**The thesis is presented in seven chapters, a brief summary of which is given here.**

**Chapter 1** is a general introduction to Dendritic Polymers, especially Dendrimers, Dendrigraft polymers and Dendronized polymers; the concept of solid phase organic synthesis and polymer based catalysis. A detailed review of the scientific literature relevant to the development of dendrigraft polymers, solid phase organic synthesis and dendritic polymer based catalysis are also included.

**Chapter 2** describes the synthesis and characterization of dendrigraft polymers having ethylene glycol, glycerol and pentaerythritol initiated polyepichlorohydrin as core, anchored on Merrifield resin. Methods like IR and solid state $^{13}C$ NMR spectroscopy and TG-DTG are used to characterize the products of the reaction. Photolytic cleavage of dendrigraft polymer from the resin was achieved and solution chemistry of the dendritic polymer was studied.

**Chapter 3** demonstrates the synthesis and characterization of copper complex of dendrigraft polymer having glycerol initiated polyepichlorohydrin as core. The catalyst was employed for the study of synthesis of Benzimidazole derivatives via the reaction between o-phenylenediamine and aldehydes or ketones. The experimental parameters were optimized, scope of substrates and reusability of the catalyst were studied. The mechanism of the reaction was also proposed. The use of the catalyst resulted in good yield of the products.

**Chapter 4** demonstrates the synthesis and characterization of copper complex of dendrigraft polymer having ethylene glycol initiated

polyepichlorohydrin as core. The catalyst was employed for the synthesis of tetra-substituted imidazoles by a reaction between 1,2 diketone, aldehyde, amine and ammonium acetate. The experimental parameters were optimized, scope of substrates and reusability of the catalyst were studied. The mechanism of the reaction was also proposed. The catalyst was found to be an excellent one for the synthesis of tetra-substituted imidazoles.

**Chapter 5** demonstrates the synthesis and characterization of palladium complex of dendrigraft polymer having ethylene glycol initiated polyepichlorohydrin as core. The catalyst was employed for the synthesis of Benzoxazole derivatives by a reaction between o-aminophenol and aldehyde. The experimental parameters were optimized, scope of substrates and reusability of the catalyst were studied and the mechanism of the reaction was proposed. The Pd complex of dendrigraft EG-G2 polymer was found to be a good catalyst for the synthesis of benzoxazole derivatives.

**Chapter 6** demonstrates the synthesis and characterization of chiral dendrigraft polymer having pentaerythritol initiated polyepichlorohydrin as core and its copper complex. The synthesized catalyst was employed for the study of Aza Diels Alder reaction between aldimines and cyclohexenone. The experimental parameters were optimized, scope of substrates and reusability of the catalyst were studied and the mechanism of the reaction was proposed. The chiral catalyst derived from dendrigraft PEN-G2 was found to be an excellent catalyst for the synthesis of isoquinuclidines with high enantiomeric excess.

**Chapter 7** presents the summary, major achievements and future outlook of the present study.