

7.1 Summary of the Work

Most of the works discussed in the field of dendritic catalysis were using dendrimers or hyperbranched polymers. Focus of present thesis was on the new trend in dendritic architecture, *i.e.*, dendronized or dendrigraft polymer. During the last few years, dendronized as well as dendrigraft polymers were well documented for their application in the field of material science due to their structural perfection. Nobody, within our knowledge, have tried these systems for catalytic applications, particularly, the synthesis of these systems on a polymer support. The present thesis has attempted to undertake the challenge to synthesize the dendrigraft architecture on polystyrene support. The intention was to create the dendrigraft architecture having large amount of peripheral functionality even at the low generation level. The present approach was centred on the synthesis of dendrigraft systems on the polystyrene support and functionalization of the periphery of the low generation polymer.

In the present thesis, we have developed a novel family of dendrigraft amidoamine polymers having pentaerythritol, glycerol and ethylene glycol initiated polyepichlorohydrin as core. The graft from or divergent method along with solid phase strategy was adopted for the synthesis. The different generations G0, G1 and G2 were synthesized and characterized. Characterization of dendrigraft amidoamine polymer

having pentaerythritol initiated polyepichlorohydrin as core has been done after photolytic cleavage of the same from the support. Amount of amino group in the G0, G1 and G2 series was found to be comparable for dendrigraft polymer having ethylene glycol and pentaerythritol initiated polyepichlorohydrin as core while the same was found to be higher for dendrigraft polymer having glycerol initiated polyepichlorohydrin as core. This may be due to the monodispersity and high molecular weight of glycerol initiated polyepichlorohydrin compared to other polycore polyepichlorohydrin.

In chapter 3 of thesis, an attempt was made to develop a highly efficient dendritic copper catalyzed method for the conjugation of aromatic 1, 2-diamine with aldehydes and ketones. The copper complexes of G0, G1 and G2 dendrigraft polymer having glycerol initiated polyepichlorohydrin as core were synthesized and characterized, were found to be excellent catalysts for the synthesis of benzimidazole derivatives *via* the reaction between 1, 2-phenylenediamine with carbonyl compounds. The reaction occurred even with low generation *ie.*, GLR-G0-Cu polymer. After optimizing the reaction conditions, a detailed study of the synthesis of benzimidazole derivatives was done with GLR-G2 copper catalyst. Comparison of GLR-G2-Cu catalyst with nondendritic copper acetate was also done. The main features of the synthesis include: air was used as the terminal oxidant, ethanol was used as the solvent, only small amount of catalyst was needed to drive the reaction and water was the only by-product in this reaction. All the reactions were performed at room temperature and it showed outstanding tolerance of both aldehydes and ketones. The synthetic protocols are

straightforward, safe, environmentally clean, and free from halogenated solvents or any other additives such as a co-catalyst or acid. Procedural simplicity, simple recovery and reusability of catalysts meet the requirements of benign chemistry.

The chapter 4 of thesis has discussed the development of a highly efficient dendritic copper catalyzed procedure for the synthesis of 1,2,4,5 tetra-substituted imidazoles based on one pot four component condensation of 1,2 diketone, aldehyde, amine and ammonium acetate under benign conditions. The copper complexes of G0, G1 and G2 dendrigraft polymer having ethylene glycol initiated polyepichlorohydrin as core were synthesized and characterized and they were found to be excellent catalysts for the 4CR reaction between 1,2 diketone, aldehyde, amine and ammonium acetate. The reaction occurred well even with low generation ie. EG-G0-Cu catalyst. After optimizing the reaction conditions, a detailed study of synthesis of tetra-substituted imidazole derivatives was done with EG-G2 copper catalyst. A brief investigation on the synthesis of tri-substituted imidazole derivative was also done. EG-G2-Cu catalyst was compared with EG-G2-Pd catalyst and found that EG-G2-Cu catalyst was superior to EG-G2-Pd with respect to the reaction time. The main features of the synthesis are: ethanol or water was used as the solvent, even small amount of catalyst was found to drive the reaction and the reaction was found to be feasible under solvent free condition also. All the reactions were performed at room temperature and outstanding tolerance of functional groups was noticed. The synthetic protocols are straightforward, safe, environmentally clean, and free from halogenated solvents or any other additives such as a co-catalyst or acid.

In chapter 5 of the thesis, the development of a dendritic palladium catalyst for the conjugation of o-aminophenol with aldehydes was discussed. The developed palladium complexes of G0, G1 and G2 dendrigraft polymer having ethylene glycol initiated polyepichlorohydrin as core were characterized and were found to be good catalysts for the synthesis of benzoxazole derivatives *via* the reaction between o-aminophenol with aldehydes. The reaction occurred even with low generation *ie.*, EG-G0-Pd catalyst. After optimizing the reaction conditions, a detailed study of the synthesis of benzoxazole derivatives was done with EG-G2 palladium catalyst. The palladium catalyst of different series such as EG-G2-Pd, GLR-G2-Pd and PEN-G2-Pd were found as active catalysts for the synthesis of benzoxazole. The main features of the synthesis were; air was used as the terminal oxidant, ethanol was used as the solvent, only small amount of catalyst was needed to drive the reaction and water was the only by-product in this reaction. Even though the reactions are feasible at room temperature, reactions were carried out at moderate temperature, 50⁰C. The catalyst showed outstanding tolerance of functional groups on aldehyde. The synthetic protocols are straight forward, safe, environmentally clean, and free from halogenated solvents.

Chapter 6 of the thesis has elaborated on the development of a highly efficient chiral dendritic copper catalyzed method for the cycloaddition of cyclohexenone with aldimines. The copper complexes of chiral G1 and G2 dendrigraft polymer having pentaerythritol initiated polyepichlorohydrin as core were characterized. Aza Diels-Alder reaction between systems like imines and cyclohexenone are rare and reported

works are base catalyzed or catalyzed by other metals under homogeneous conditions. It was found that copper complexes could catalyze aza Diels-Alder reaction like Diels-Alder reaction. The reaction occurred more efficiently with high generation dendrigraft polymer in comparison with low generation G1 dendrigraft polymer. After optimizing the reaction conditions, a detailed study of aza Diels-Alder reaction was done with chiral PEN-G2 copper catalyst. The main features of the synthesis are: only small amount of catalyst was needed to drive the reaction and all the reactions were performed at room temperature. The catalyst performed well with good diastereoselectivity and good enantiomeric excess. All the catalysts reported in this thesis could be recycled.

Procedural simplicity, simple recovery and reusability of catalysts meet the requirements of benign chemistry. So the synthesized catalysts will be of wide practical application in similar reactions. Further investigation on the application of these catalysts for other organic reactions is in progress.

7.2 Major Achievements

- Even though there are large number of reports on dendronized polymer having linear polymeric core, amidoamine dendrigraft polymer having polyepichlorohydrin as core is a new one.
- Within our knowledge, there are only two reports on dendrigraft polymers having branched polymeric core. We have developed dendrigraft polymers having branched polymeric core like glycerol and pentaerythritol initiated polyepichlorohydrin as core.

- So far, no reports have appeared on the synthesis of dendrigraft polymers on a solid resin support. The present thesis has demonstrated the success of the approach to certain extent in developing the dendrigraft polymer on a resin support.
- As expected, the amount of amine functionality increased from G0 to G2 dendrigraft polymer.
- The present attempt to cleave the dendrigraft polymer from the support was successful. Molecular mass obtained in the case of G0 dendrigraft polymer was agreeable with the theoretical value. But G1 and G2 dendrigraft polymers showed defective structure.
- Metal complexes of dendrigraft polymers for catalytic applications were not yet reported. We have succeeded in developing metal complexes of dendrigraft polymers and used them as catalysts.
- Even though benign catalysts were reported for the synthesis of benzimidazole and tetra-substituted imidazole derivatives, the catalysts discussed in the thesis are more beneficial in terms of their heterogeneous nature.
- Generally, palladium catalysts are reported for C-C coupling reactions; the developed palladium catalyst was successfully used for synthesis of benzoxazole and tetra-substituted imidazole derivatives.
- We have succeeded in carrying out the aza Diels Alder reaction with excellent enantiomeric excess using chiral modified dendrigraft polymer catalyst.

7.3 Future Outlook

Catalysis reactions of metal complexes of dendrigraft polymers were studied in the thesis. No attempt was made to study the catalytic efficiency of the metal free polyamines. Hence it could be desirable to study the performance of dendrigraft polyamine as a base catalyst. Periphery modification can be done with more acidic functionality like p-toluene sulphonyl fluoride in order to further increase catalyst efficiency. Comparison of solid phase strategy for the synthesis of dendrigraft polymers can be compared with solution phase strategy. Other easy cleavage strategies have to be developed to cleave the dendrigraft polymer from the support. The nature of the dendrigraft polymers having glycerol and ethylene glycol initiated polyepichlorohydrin as core could be studied in detail after photolytic cleavage from the resin. We have to develop methods to synthesize dendronized polymers with perfect structures on a solid support. Palladium nano particles embedded in dendrigraft polyamine could be used as catalysts for several organic reactions. Application of present catalysts could be explored for the synthesis of various heterocyclic compounds using MCR strategy.