SUMMARY AND CONCLUSION

Over the past three decades, dendrimers have emerged as a novel class of macromolecules with applications in a wide range of natural sciences. They are macromolecules possessing a highly regular molecular topology based on an iterative growth sequence of branching units. Starting from a small "core" molecule, this may lead to large globular structures that possess a high degree of molecular uniformity. The iterative branching not only leads to an efficient and symmetrical growth pattern but potentially to a rapid multiplication of functional groups, making these molecules attractive platforms for chemical functionality. Since the first application of dendrimers in catalysis in the mid 1990s this field has advanced rapidly. As a consequence, catalytically active dendrimers have emerged as a class of molecular catalysts, which have substantially enriched the field of homogeneous and to some extent heterogeneous catalysis.

The present thesis has described the development of some heterogeneous catalysts based on polymer supported dendrimers. Attachment of dendrimers to crosslinked polymer produced new catalysts with combined benefits of both dendrimers and heterogeneous catalysts. These were used as heterogeneous catalysts in selected reactions. All possible attempts were taken to avoid halogenated and aromatic solvents and toxic reagents. In short the present work has dealt with development of environmental friendly catalysts based on dendrimers.

The thesis is divided in to six chapters. An overview of solid phase organic synthesis, polymer supported catalysts and dendrimers was given in first chapter.

In chapter 2, the solid phase synthesis of poly(propylene imine) (PPI) and poly(amidoamine) (PAMAM) dendrimers was discussed. Solid phase synthesis
of the dendrimers were carried out on aminomethyl polystyrene, 3-nitro 4-aminomethyl polystyrene (DVB crosslinked) and aminated poly(methyl methacrylate) (DVB crosslinked) resins. The synthesis of dendrimers began from the primary amino pendant groups on the polymer supports. The primary amino group functioned both as the core of the dendrimer and the linker that connected the support and the dendrimer. The dendrimers were synthesized up to third generation by adopting the divergent approach used in their solution phase synthesis with suitable modification so that they could be successfully transformed to the solid phase. Poly(propylene imine) dendrimers were synthesized by an acetic acid catalyzed double Michael addition of acrylonitrile to the amino groups of the supports followed by reduction of the nitrile groups to amino groups using LiAlH₄ in THF. Poly(amidoamine) dendrimers were synthesized by double Michael addition of methyl acrylate to the amino groups of polymer supports in methanol followed by transamination using large excess of ethylene diamine. The progress of the solid phase synthesis was followed by FTIR spectroscopy, qualitative ninhydrin test, quantitative estimation of amino groups and solid state CP-MAS ¹³C NMR spectroscopy. After the synthesis, the dendrimers were detached from the polymer supports and analyzed using NMR spectroscopy and MALDI-TOF MS. The effect of degree of crosslinking of the supports on the synthesis was studied. A comparison between the two supports was also presented.

Chapter 3 has dealt with the application of polymer supported dendrimers as heterogeneous organocatalysts. Since the supported dendrimers described in this thesis are highly basic and the first, second and third generation dendrimers carry two, four and eight primary amino groups on the periphery respectively, the supported dendrimers performed well as efficient organocatalysts. After screening the catalytic activity these dendrimers in various reactions, Knoevenagel reaction and ring opening of epoxides, for which the catalysts showed better activity, were selected for further study.

Knoevenagel condensation between various carbonyl compounds and active methylene compounds were carried out in the presence of the supported
dendrimers. Various factors affecting the catalysis like amount of catalysts, solvent, temperature and electronic and steric nature of the substrates were studied in detail. The dendrimer catalysts showed excellent activity. Only 0.5 mole percent of catalyst was required to obtain excellent yield with in a short interval of time. About thirty styrene derivatives were prepared and all the reactions proceeded to completion with in a short period of time. The most important aspect of the catalysis by supported dendrimers was that high yields were obtained in polar protic solvents like ethanol and water. All the products were obtained in excellent yield, purity and 100% selectivity. Since no side reactions were observed and the reaction proceeded to complete conversion, no additional purification of the products was required. All products were characterized by ¹HMR and FTIR spectroscopic methods. The catalysts were recycled ten times with no loss of activity. The effect of generation of the dendrimer and the nature of the support on catalysis was also studied. It was found that, third generation dendrimers were better catalysts and better results were obtained when lightly crosslinked supports were used. Comparisons between the two dendrimers as well as the two supports were made.

Ring opening of epoxides with anilines was efficiently catalyzed by supported-dendrimers. Various 2-amino alcohols were synthesized from different epoxides and anilines in the presence of catalytic amounts of the supported-dendrimers. The influence of reaction conditions and nature of substrates were studied in detail. The reaction proceeded effectively in polar solvents at 50 °C. Only 2 mol% of the third generation dendrimer was required for completion of the reaction. Sixteen 2-amino alcohols were synthesized, isolated and characterized. Dendrimers of different generations were studied and found that the catalytic activity increases with increase in generation. Comparison between the two dendrimers showed that the PAMAM dendrimers were more efficient catalysts. The influence of the support on the catalytic activity was studied and found that the polystyrene supported catalysts were more active.
Chapter 4 has described the synthesis of polymer supported dendrimer metal complexes. The polymer supported dendrimers were used as ligands for the preparation of polymer-supported dendrimer-metal complexes by ligand exchange method in aqueous medium. The metal complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Pd(II), Ag(I) and Zr(IV) were prepared. The influence of various factors like reaction time, temperature and pH of the reaction medium, presence of a co-solvent and the degree of crosslinking of the polymer support were studied. The role of the support’s properties and generation of dendrimer in complex formation were studied. From these experiments, suitable reaction conditions were optimized. Generally, complex formation was effective at room temperature, at natural pH of the reaction mixture in the presence of acetone as co-solvent with in a period of 12 h. It was observed that, PAMAM dendrimers were more efficient in complex formation compared to the PPI dendrimer of the same generation. The complexes prepared in this manner were characterized by various analytical techniques like FTIR, UV-Vis, TG-DTA, EPR and Solid state NMR. From these analytical data structures of the complexes were predicted.

In chapter 5 applications of polymer supported dendrimer metal complexes as heterogeneous catalysts was described. After screening the polymer supported dendrimer metal complexes as heterogeneous catalysts against a number of reactions two reactions were identified for detailed study.

Polymer-supported dendrimer-Mn(II) complexes were found to be highly efficient catalysts in the oxidation of secondary alcohols to ketones under mild conditions. Compared to many previously reported polymer supported catalysts, the present complex showed high activity. The influence of the catalyst concentration, solvent and temperature on the catalytic activity was studied. Only 5 mol % of the catalyst was required to drive the reaction to completion. As described in the case of earlier catalysts, the catalytic activity was maximum in polar solvents. Oxidation of various alcohols was carried out in the presence of different oxidants like K2Cr2O7, KMnO4 and urea-hydrogen peroxide adduct (UHP). The problems observed during the application of strong oxidizing agents could be effectively overcome when the mild oxidizing agent UHP was used. In
many cases, the ketones were isolated in excellent yields. It was observed that PAMAM-Mn(II) complex showed better activity and stability compared to PPI-Mn(II) complexes. Comparable activity was shown by both polystyrene and poly(methyl methacrylate) supported catalysts. The catalyst was recycled up to four times without considerable loss of activity. The ketones formed were isolated and characterized by various spectral methods.

Polymer-supported dendrimer-Pd(II) complexes were used as heterogeneous catalysts in the three component Mannich reaction between aldehydes, ketones and anilines to give β-amino ketones. Various factors influencing the reaction were studied and the condition for the maximum yield was optimized. The reaction proceeded well in ethanol in the presence of 2 mol% of the catalyst. A number of β-amino ketones were synthesized and isolated with excellent yields. The products were characterized using FTIR and 1HNMR spectroscopies. The catalyst after washing with ethyl acetate was recycled six times without considerable loss of activity. In the case of Pd(II) complex also, better activity was shown by the PAMAM complex. Comparison of the catalyst supported on the two supports showed that the poly(methyl methacrylate) supported catalysts were more active.

The sixth chapter of this thesis has dealt with synthesis and characterization of polymer supported dendrimer encapsulated metal nanoparticles and their use in heterogeneous catalysis. Polymer supported PAMAM dendrimer nanoparticle conjugates of Pd, Cu, Ag, Ni and Co were prepared by chemical reduction of the corresponding supported dendrimer-metal complexes using hydrazine-hydrate in methanol.

The supported dendrimer-metal nanoparticle conjugates were characterized by UV-Vis spectroscopy, TG/DTA, SEM, AFM and TEM. The Pd, Cu, Ag and Ni nanoparticles were stable and showed long shelf life. It was observed that the nanoparticles prepared using first and second generation dendrimers were agglomerated while the nanoparticles prepared using the third generation dendrimers were well separated and of uniform size.
The Pd-nanoparticle conjugate prepared was used as catalyst in Suzuki coupling between aryl boronic acid and aryl halides. By varying the reaction conditions, the most suitable condition required to get better yield was arrived at. The efficiency of the catalyst was proved by preparing various biphenyls. Better results were given by the third generation dendrimer-nanoparticle conjugates as the nanoparticles were of smaller size and well-separated; they offered more surface area for heterogeneous catalysis. The catalyst was recycled four times without loss of activity. On further recycling a gradual loss of metal ions was observed and this may be due to the decomposition of the dendrimer backbone during the course of the reaction.

In general, the thesis has described the synthesis, characterization and environmental friendly catalysis by different polymer-supported dendrimers, their metal complexes and nanoparticle conjugates. The possibilities of recycling of the catalysts were explored along with chances to avoid the use of aromatic and halogenated solvents. The thesis opens new possibilities of development of environmental friendly and efficient catalysts based on supported dendrimers. In short the thesis has contributed to organic synthesis, heterogeneous catalysis and green chemistry.