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### **Summary of Achievements :**

Our study on catalysis of ethylene polymerization has led to two interesting observations:

1. Simple half sandwich titanium (IV) and zirconium (IV) complexes of fluorenyl amido ligands bearing aromatic substituent's on the amido nitrogen which lead to very high molecular weight linear poly (ethylene) s. It is expected that such catalyst could be very useful for the synthesis of rheologically interesting polyethylenes without entanglements.
2. An *ansa*- $\eta$ -5-monofluorenyl cyclohexanolato zirconium complex was prepared and shown to be active for the polymerization of ethylene, leading to poly(ethylene)s with long chain branches (> 6 carbons) at 60 and 80C, whereas, at 100C, methyl branches were observed in addition to the long chain branches. Long chain branches are formed as a result of  $\beta$ -H transfer reaction followed by reincorporation of the resulting macromonomers of ethylene into the growing polymer chains. The methyl branches result from  $\beta$ -H elimination followed by 2, 1-insertion of the  $\alpha$ -olefin into the [Zr]-H species. To the best of our knowledge this is the first example of a zirconium complex that exhibits such diverse polymerization behaviour. Long chain branched linear polyethylenes are interesting materials, having the properties of linear polyethylenes and the processability of branched polyethylene.

We have recently concluded a study on molecular approaches to tailor the interfaces towards the objective of preparing polymer - layered clay nanocomposites. Several unique organic modifiers for clay have been synthesized and used for preparing exfoliated nanocomposite of clay with poly (aryl carbonate) using a technique of intercalative melt polycondensation.

We have recently initiated research in the area of copolymers of L(+) Lactic Acid, an area where very little prior work exists.

My group in NCL, Pune is one of the few groups engaged in basic research towards polymer synthesis using a diversity of techniques, all of which are not practiced in any other research group in India.

### **Major Contributions :**

Our research has been recognized by an ability to use sound principles of chemistry to create new properties in polymers. In diverse areas of polymers, namely, polyolefins , biodegradable polymers or nanocomposites, our approach has led novel methods to create new structures in polymers leading to useful properties. Thus, our work enables rational understanding between synthesis, structure and properties of polymeric materials

### **Publications during the period in peer reviewed journals:**

1. U. Subramanyam and S. Sivaram, Synthesis and Characterization of Poly(higher--olefin)s using Nickel (-diamine) / Methylaluminumoxane Catalyst System : Effect of Chain Running on Polymer Properties, J. Polym. Sci. Polym. Chem., 45, 191 (2007). {IF 3.971}

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2. S. Radhakrishnan, B.T.S. Ramanujam, A. Adhikary and S. Sivaram, High Temperature Polymer-Graphite Hybrid Composites for Bipolar Plates: Effect of Processing Conditions on Electrical Properties, *J. Power Sources*, 163, 702 (2007). {IF 3.792}
  3. U. Subramanyam and S. Sivaram, Kinetics of Hexene-1 Polymerization using [N,N'-diisopropyl benzene)-2,3-(1,8-naphthyl)-1,4-diazabutadiene] Dibromo nickel / Methylaluminoxane (MAO) Catalyst System, *J. Polym. Sci., Polym. Chem.* 45, 1093 (2007). {IF 3.971}
  4. R. Gnaneshwar and S. Sivaram, End-Functional Poly(methyl methacrylate)s via Group Transfer Polymerization, *J. Polym. Sci., Polym. Chem.* 45, 2514 (2007). {IF 3.971}
  5. T.E. Sandhya, C. Ramesh and S. Sivaram, Copolyesters Based on Poly(butylenes terephthalate)s Containing Cyclohexyl and Cyclopentyl Ring: Effect of Molecular Structure on the Thermal and Crystallization Behavior, *Macromolecules*, 40, 6906 (2007). {IF 4.539}
  6. M.G. Dhara, D. Baskaran and S. Sivaram, Synthesis of Amphiphilic Poly(methacrylate-b-ethylene oxide) Copolymers from Monohydroxy Telechelic Poly(methyl methacrylate) as Macroinitiator, *J. Polym. Sci., Polym. Chem.*, 46, 2132 (2008). {IF 3.971}
  7. S.R. Mallikarjuna and S. Sivaram, Polycarbonate - Clay Nanocomposites via in situ Melt Polymerization *Ind.Eng.Chem.Res.*, 49, 2217 (2010) {IF 1.758}
  8. R. Gnaneshwar and S. Sivaram, Addition of a Silyl Ketene Acetal to  $\alpha$ ,  $\beta$ -Unsaturated Cyclic Anhydrides, *Synthetic Communication*, 40, (16) 2353 (2010) {IF 0.961}
  9. S.R. Mallikarjuna and S. Sivaram, Influence of Structure of Organic Modifiers and Polyurethane on the Clay Dispersion in Nanocomposites via in-situ Polymerization, *J. App.Polym.Sci.*, 118, 1774 (2010) {IF 1.203}