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Group IV complexes as initiators for the ring opening polymerization studies: Ligand and metal screening

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The complexation of salicylbenzoxazole ligand 2-(5-X-benzoxazol-2-yl)-6-R¹-4-R²-phenol, L with titanium, zirconium and hafnium alkoxides selectively formed either mononuclear L₂M(OR)₂, 1-9 or oxo-bridging dinuclear complexes [(μ-O)L₂M(OR)]₂, 10-12 depending on the substituents on salicylbenzoxazole ligands. The ligands which have R¹=R²=H or Br on the phenol moiety afforded mononuclear complexes 1-9. Notably the ligand which has R¹=R²=Cl substituent on the phenol ring afforded oxo bridged dinuclear complexes 10-12. The substituents on benzoxazole ring (X=H or Cl) does not influence the nuclearity of complexes. All these complexes were fully characterized by various spectroscopic techniques including elemental analysis and X-ray crystallography. In ring-opening polymerization (ROP) of rac-Lactide (rac-LA), all these complexes produced isotactic rich (P_m upto 0.78) and alkoxide terminated polymers with narrow molecular weight distributions (MWDs) with predictable molecular weights (M_n). Ring-opening copolymerization (ROC) of L-lactide (L-LA) and ε-caprolactone(ε-CL) to yield block copolymers was also studied. In particular, dinuclearZr complex (11) was found to exhibit extremely high activity in homo polymerisation of rac-LA and ROC of L-LA and ε-CL which is comparable with the previously reported active group IV complexes. Additionally, homo polymerisation of epoxides [rac-cyclohexene oxide (CHO), rac-propylene oxide (PO) and rac-styrene oxide (SO)] were also investigated. The reactivity of these monomers in homopolymerization promoted by these complexes varied in the order of CHO>PO>SO. The yield and molecular weight of the polymers increase with the prolonged reaction time. The complexes which have electronegative substituents on the phenol ring and oxazoline ring (5, 6, 8, 9, 11 and 12) improved the catalytic ability sharply. DFT studies have been carried out on ROP of LAs initiated by both the Ti and Zr complexes. The results indicate that the activation barrier height for the ring opening transition state of lactide monomer for Zr(IV) complex is low and hence facile compared to Ti(IV) complex. From density functional theory (DFT) calculations we explained the mechanistic pathways for ROP of lactide promoted by Ti and Zr complexes in detail.

Biography

Sreenath Pappuru is a highly motivated and enthusiastic Organometallic and Polymer Chemist with a Masters degree in Organic Chemistry (2008-2010) from Sri Venkateswara University, Tirupathi, Andhra Pradesh and currently pursuing PhD in IIT Madras (from 2010) in Sustainable Polymer Chemistry/Organometallic Chemistry. He has achieved best poster award during PhD in International Symposium on "Nature Inspired initiatives in Chemical Trends" (NIICT-2014), March 2-5, 2014.

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