

1. Abstract

A series of bis(pyrrolidene) Schiff-base aluminum complexes have been synthesized and fully characterized. ^1H NMR studies and X-ray diffraction analysis confirmed that these complexes adopt monomeric structure with a five-coordinated aluminum center. The complexes have all been investigated as initiators for the ring-opening polymerization of *rac*-lactide in the presence of 1 equivalent of benzyl alcohol. All polymerizations show living characteristic as evidenced by the linear correlation between molecular weight and percentage conversion, in conjunction with the narrow PDIs. In addition, the observation of relatively narrow PDI values (*ca.* 1.1) throughout the course of polymerization suggests no significant degree of transesterifications operates in this system. The kinetic studies revealed that the rate of polymerization was controlled by the diamine backbone substituent with the rate depending on the backbone flexibility. The rates of polymerization decrease in the order 1,3-propylene > 2,2-dimethyl-1,3-propylene > 1,4-butylene > *rac*-1,2-cyclohexylene > 1,2-ethylene >> 1,2-phenylene. Microstructure analyses of the resultant polylactides by Homonuclear decoupled ^1H NMR technique disclosed the isotactic-biased stereocontrol of the entire series of complexes. Polylactide with highly isotacticity ($P_m = 0.80$) was produced by the aluminum complex with 2,2-dimethyl-1,3-propylene backbone. DFT calculations on the *rac*-lactide ring-opening mechanism revealed a strong complex bite angle dependence of the polymerization rate. The extent of the stereoselectivity was found to be governed by the steric congestion of the complex propagating site and the steric interactions of an inserting lactide monomer with the last enchainment unit.

Keywords: Polylactide, aluminum, ring-opening polymerization, *rac*-lactide, DFT calculation