CATALYTIC ACTIVITY OF N-DONOR STABILIZED TIN(II) CATIONS IN ROP OF L-LACTIDE

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Aliphatic polyesters, such as polylactide (PLA), are recently of great interest due to their biodegradable and biocompatible properties. One of the synthetic approach for producing these polymers is based on the ROP of cyclic esters initiated by metal complexes.[1] In industry, most linear aliphatic polyesters are produced by ROP in the presence of $Sn(Oct)_2$.[2] $Sn(Oct)_2$ enjoys its popularity due to its low cost, robustness and versatility. On the other hand, it exhibits a relatively low catalytic activity. This disadvantage can be overcome by using discrete tin(II) cations as highly catalytically active alternatives. Recently, the ROP of L-lactide (L-LA) catalyzed by aminoether−phenolate based tin(II) cation was reported.[3] Macromolecular parameters of the isolated PLA exhibited a good control over the polymerization. Following the stabilization of the tin(II) cation [{2-((CH$_3$)C=N(C$_6$H$_3$-2,6-iPr$_2$))-6-CH$_3$O-C$_5$H$_3$N}SnCl][SnCl$_3$][4], we report here the synthesis of a series of tin(II) ionic compounds containing α-iminopyridine ligands L^{1-3} (L^1 = 2-(CH=N(C$_6$H$_2$-2,4,6-Ph$_3$))C$_5$H$_4$N, L^2 = 2-(CH=N(C$_6$H$_2$-2,4,6-tBu$_3$))C$_5$H$_4$N and L^3 = 1,2-(C$_5$H$_4$N-2-CH=N)$_2$CH$_2$CH$_2$). The reaction of L^1 and L^2 with $SnCl_2$ led to the formation of neutral adducts [L^1→$SnCl_2$] and [L^2→$SnCl_2$]. The preparation of the desired ionic compounds was achieved by subsequent reactions with an equivalent of $SnCl_2$ or $GaCl_3$. In contrast, ligand L^3 containing four donor nitrogen atoms showed the ability to ionize $SnCl_2$ and also $Sn(OTf)_2$ yielding [L^3→SnCl][SnCl$_3$] and [L^3→Sn(H$_2$O)][OTf]$_2$. Selected catalysts were further tested in the ROP of L-lactide with the aim to synthesize linear PLA, as well as star-shaped PLAs with various polyalcohol-based cores. Finally, a DFT computational study was performed to evaluate the steric and electronic properties of the ionic tin(II) species together with their ability to interact with the L-lactide monomer.

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