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Well-Defined Aminophenolate Zinc and Magnesium Complexes as Excellent Inhitiators for the ROP of Lactides

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Summary: A series of molecular homo and heteroleptic zinc and magnesium compounds with aminophenolate ligands $[(\mu,\eta^2\text{-}L^2)ZnEt]_2$ (**1**), $[(\eta^2\text{-}L^2)Zn(\mu\text{-}BnO)]_2$ (**2**), $[Zn(\eta^2\text{-}L^2)_2]$ (**3**), $[Zn(\eta^2\text{-}L^3)_2]$ (**4**), $[Mg(\eta^2\text{-}L^3)_2]$ (**5**) (L^2-H = *N*-[methylene(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-cyclohexylamine, L^3-H = *N*-[methylene(2-hydroxy-3,5-di-*tert*-butylphenyl)]-*N*-methyl-*N*-methyl-1,3-dioxolaneamine) have been prepared and characterized. The homoleptic complexes **3–5** are most probably a mixture of diastereoisomers that in solution show an interesting dynamics which plays an important role in their catalytic behavior. The complexes **2–5** are efficient initiators in ring-opening polymerization (ROP) of lactides to produce polymers with desired molecular weight and narrow polydispersity.

Keywords: aminophenolates; lactides; magnesium; polymerization; zinc

Introduction

Ring opening polymerization (ROP) of cyclic esters derived from renewable resources is an attractive route to polyesters that find application in many areas ranging from bulk packing materials to medicine.[1] Polylactides (PLAs) production can be brought by enzymatic, organic or metal coordinate catalysis and the latter has attracted a great deal of attention because it offers high stereoselectivity and yields polyesters with exceptional weight control and narrow polydispersity (PDI).[2] Particularly suitable for this purpose are zinc and magnesium compounds with N,O-donor functionalized ligands because they are colorless, often inexpensive and biologically benign.[3] Our research has focused on the design and development of aminophenolate based initiators for controlled synthesis of PLAs. Detailed studies in solid state and in solution provided insight into the effect of catalyst architecture on lactide polymerization behavior.

Discussion

The aminophenolate ligands L^2-H and L^3-H are well suited for the synthesis of monomeric magnesium and zinc complexes. As shown in Scheme 1 two equivalents of bi/tridendate (L^2-H/L^3-H) ligand react with $ZnEt_2$ or $MgBu_2$ to form tetrahedral $[Zn(\eta^2\text{-}L^2)_2]$ (**3**) or octahedral $[M(\eta^2\text{-}L^3)_2]$ (**4**, M = Zn; **5**, M = Mg) compounds.[4,5] Instead, treatment of L^2-H with $ZnEt_2$ in 1:1 molar ratio gave heteroleptic complex $[(\mu,\eta^2\text{-}L^2)ZnEt]_2$ (**1**) which could be converted to dimeric complex $[(\eta^2\text{-}L^2)\text{-}Zn(\mu\text{-}BnO)]_2$ (**2**) after addition of benzyl alcohol.[5] All compounds are colorless, soluble in polar organic solvents and in toluene. Most of them are moisture sensitive. Interestingly, $[Zn(\eta^2\text{-}L^2)_2]$ is stable in air for several hours what is an important feature for commercial application. The complexes **1**–**5** were formulated on the basis of elemental analysis, NMR spectroscopy and in case of **3**–**5**, an X-ray analysis.

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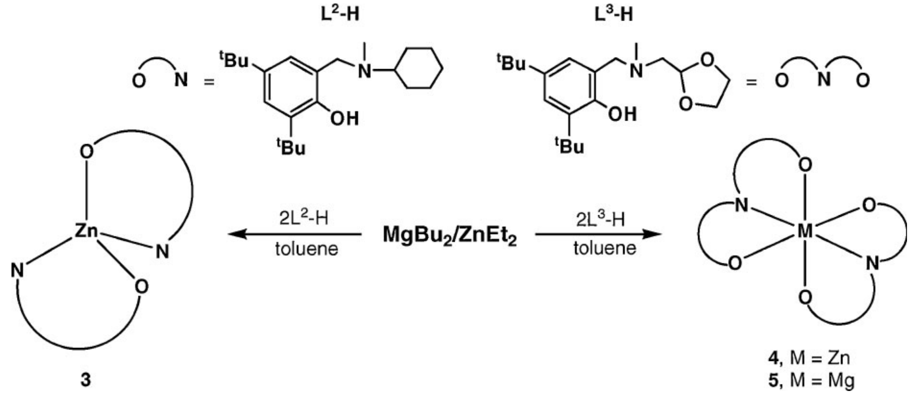

Scheme 1.
Synthesis of homoleptic magnesium and zinc compounds.

Table 1.
Polymerization of *L*-lactide with initiators [I] **2–5**.

Intiator [I]	[I]/*L*-LA/BnOH	t(min)	conv(%)^a	$10^{-3}M_n{}^b$	$10^{-3}M_n^c$	PDI^b
$[Zn(\eta^2\text{-}L^2)_2]$	1/100/1	60	99	16.73	14.38	1.16
$[(\eta^2\text{-}L^2)Zn(\mu\text{-}BnO)]_2$	1/100/0	120	98	15.38	14.23	1.09
$[Zn(\eta^2\text{-}L^3)_2]$	1/100/1	70	90	15.98	13.08	1.20
$[Mg(\eta^2\text{-}L^3)_2]$	1/100/0	30	95	16.82	14.03	1.31
$[Mg(\eta^2\text{-}L^3)_2]$	1/100/1	15	96	16.51	13.83	1.14

Genaral polymerization conditions: toluene (10 mL), T = 25°C, [I] = 0.025, ^{a}conversion determined by ^{1}H NMR, ^{b}determined by GPC, PDI calibrated with polystyrene standards

The NMR analysis for tetrahedral complex **3** indicated the presence of three isomers in its solution. The octahedral complexes **4–5** in solution exist in equilibrium with five-coordinate species having one oxolane fragment dangling.

The complexes **1–5** were tested for the ROP of lactide and the results are collected in Table 1.[6] Active initiators gave polymers with molecular weights in close agreement with calculated values and narrow PDI characteristic for well controlled living propagation. The monomeric tetrahedral **1** and **3** were inactive, but **3** in the presence of benzyl alcohol formed a very efficient initiator and polymerized 100 equiv. of L-lactide with high conversion within 1 h. An end group inspection showed that polymer chains were terminated with one benzyl ester and a hydroxy group. The heteroleptic complex **2**, which possesses the structure of a ‘‘single-site’’ initiator, was - to our surprise - less active than homoleptic zinc compound. Polymerization of *L*-LA initiated with **2** ([I]/*L*-LA of 1/100) achieved high conversion within 2 hours. The study of PLLA showed the benzyloxy ester and the hydroxy end groups, suggesting that the initiation occurred through the insertion of the benzyloxy group into *L*-lactide. The octahedral magnesium complex **5** in the absence of benzyl alcohol initiated polymerization of *L*-LA in high conversion within 0.5 h and study of isolated polylactides indicated the hydroxy and an aminophenolate ester chain end. Similar zinc complex **4** was also an efficient initiator after addition of benzyl alcohol and polymerized *L*-LA in molar ratio [I]/*L*-LA/BnOH = 1/100/1 within 70 min.

Conclusion

In conclusion, five zinc and magnesium complexes with aminophenolate ligands have been prepared and characterized. The most effective for controlled catalytic polymerization of *L*-lactide were homoleptic **3**–**5** in the presence of BnOH. The key role in high activity of homoleptic complexes play dangling of aminophenolate ligand triggered by monomer activated mechanism.

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[6] Representative procedure for lactide polymerization. The monomer L-LA was placed in a Schlenk flask and an initiator dissolved in dry CH2Cl2 was added. The reaction was stirred at the desired temperature for a prescribed time. Next, at certain time intervals about 1mL aliquots were removed for determination of the conversion using 1H NMR. After reaction was completed it was quenched with methanol, the solution was concentrated in vacuum and the polymer was precipitated with an excess of cold methanol. Filtration and drying in vacuum yielded a white polymer.