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The use of Cu and Zn salicylaldimine complexes as catalyst precursors in ring opening polymerization of lactides: ligand effects on polymer characteristics

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A range of monomeric tetra-coordinate copper (II) and zinc (II) complexes based on N,O-bidentate salicylaldimine Schiff base ligands has been synthesized and characterized using various spectroscopic techniques. These complexes were then evaluated as initiators in ring-opening polymerization of lactides at both 70 °C and 110 °C. The effect of structural changes in the complexes on the ability of these compounds to initiate lactide polymerization as well as the impact on the chemical and physical characteristics of the polymers obtained indicate that the coordination geometry of the metal complex, M–O bond length and substituents on the Schiff base ligand all play a role in the catalyst activity. Electronic factors were dominant in the case of the copper complexes while steric factors prevailed in the case of Zn initiators. Both the Zn and Cu complexes exhibit characteristics of living ring opening polymerization. Copyright © 2010 John Wiley & Sons, Ltd.

Supporting information may be found in the online version of this article.

Keywords: salicylaldimine complexes; copper Schiff base complexes; zinc Schiff base complexes; lactide polymerization; ring-opening polymerization

Introduction

Their biocompatibility and their degradation into nontoxic components (water and carbon dioxide via the Krebs cycle) make polylactides (PLAs) very useful for biomedical applications such as controlled drug delivery systems.^[1] Owing to their mechanical properties, PLAs are widely used in surgery as sutures, orthopedic applications, tissue engineering and biodegradable internal fixation devices for repair of fractures to small bones and joints.^[2]

The most important and general way to prepare high molecular weight PLAs is through ring opening polymerization (ROP). A number of different metal initiators and catalysts have been used in the ROP of lactides, including compounds of aluminum, lead, tin, zinc and bismuth. Currently almost all commercial PLAs are prepared using FDA-approved stannous octanoate as mediator.

Recently, catalysts based on Ca, Mg, Fe and Zn have received increased attention because these elements can be metabolized in the body.^[3] Zinc lactate which shows catalytic characteristics similar to stannous octanoate, has been proposed as a less toxic catalyst substitute for PLA production.^[4]

Our current interest is focused on zinc and copper metal complexes of salicylaldimine ligands which remain largely unexplored as catalysts for polylactides synthesis. Only a few reports concerning such complexes as lactide polymerization catalysts exist in the literature.^[5–8]

Chisholm *et al.*, for example, have briefly described the polymerization of DL-lactide with a three coordinate zinc phenoxy-imine complex containing bulky substituents on the phenoxy and imino rings (Fig. 1). $^{[5]}$

Zhang *et al.* investigated the polymerization of ε -caprolactone and DL-lactide using zinc and aluminum complexes containing pyrazole substituents.^[6] They reported that the zinc ethyl complexes (Fig. 2A) displayed relatively high catalytic activity in ε -caprolactone polymerization, giving high molecular weight polymers (number average molecular weight, $M_n = 58\,000, 100\%$, [monomer]:[initiator] = 200). It was, however, found that the process proceeds via a nonliving mechanism, thus leading to poor polydispersities. Only complex **2d** (Fig. 2A) was active for DL-lactide polymerization but unfortunately it yielded only atactic polymers.

Hung *et al.* reported L-lactide polymerization using dimeric zinc complexes with tridentate N,N,O Schiff base ligands (Fig. 3).^[7] These mediated controlled living polymerization.

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Figure 1. Three-coordinated zinc phenoxide complex used as lactide polymerization catalyst by Chisholm *et al.*^[5].



Figure 2. (A) Zinc ethyl; (B) zinc diphenolato complexes used for ROP of lactide by Zhang *et al.*^[6].

Copper complexes have been less frequently employed in ring opening polymerization of DL-lactide. A recent report by John *et al.* showed that phenoxy-ketimine copper complexes of the type shown in Fig. 4 efficiently catalyzed the ROP of

L-lactide under solvent-free conditions but only at fairly elevated temperatures (160–180 °C), producing poly-L-Lactides (PLLAs) of moderate molecular weights ($M_n = 8000-11\,000$, [M] : [I] = 50) and having narrow molecular weight distributions (polydispersity index, PDI = 1.3–1.4 at 70–80% conversion).^[8]

The relative success of phenoxy-imines in various polymerization reactions is presumably due to the scope for suitable tuning of the steric bulk and the electronics of the ancillary ligand and also due to their easy synthetic accessibility, as the phenoxy-imines are generally prepared via Schiff base condensation reactions. Despite extensive utility of phenoxy-imines in many important chemical transformations, their application in ROP of DL-lactide largely remains unexplored.

Because of the relative paucity of reports on the use of zinc and especially copper complexes as ring-opening polymerization initiators, we embarked on a study of these complexes in such processes. Here we report the synthesis and use of several Cu and Zn phenoxy-imine complexes in DL-lactide polymerization. These complexes offer the advantage of being stable in air, unlike aluminum complexes, and are also easier to prepare. In addition, the steric and electronic effects of substituents on the phenoxy and imino rings on polymerization activity were also investigated. A kinetic study of the ROP of DL-lactide was carried out and correlated with the nature of the ligands complexed to the metal atom, metal-oxygen bond length and geometry of the complexes. In addition, an attempt was made to understand the effect of the salicylaldimine ligands on stereoselectivity of the DL-lactide polymerization and its influence on T_q of the resulting polymers. The characteristics and morphology of the resulting PLAs are also discussed.

Experimental

General Procedures

Ligands and metal complexes were synthesized using standard Schlenk techniques under nitrogen using a dual vacuum/nitrogen Schlenk line. The NMR spectra were recorded on a Varian Gemini 2000 spectrometer (¹H at 200 MHz, ¹³C at 50.3 MHz) at room temperature using tetramethylsilane as an internal standard. The chemical shifts are reported in δ (ppm) and referenced relative to residual proton signals for the NMR solvent. Infrared spectra were recorded on a Perkin Elmer Paragon 1000 PC FT-IR spectrophotometer as KBr pellets for solids or between NaCl plates for oils. ESI-MS spectra were obtained on a Waters API Q-TOF Ultima spectrometer calibrated with NaF. UV-Vis spectra were recorded on a GBC UV-Vis S920 spectrophotometer as dichloromethane solutions. Microanalyses were performed at the University of Cape Town's micro analytical laboratory. Size exclusion chromatography was performed at the University of Mauritius using a Polymer Standards Service (PSS) apparatus with



Figure 3. NNO-tridentate Schiff's base Zn complex used by Hung et al.^[7].



Figure 4. Copper complexes used for ROP of L-lactide by John et al.^[8].



Figure 5. Chemical structure of Cu and Zn complexes synthesized.

a refractive index detector. Calibration was done using polystyrene standards. THF was used as eluent at a flow rate of 1.0 ml min⁻¹. Scanning electron microscopy (SEM) samples were prepared for analysis according to the following protocol. A thin layer of polymer was spread on a metal mount. The samples were then coated with gold for 90 s in a 20 mV argon atmosphere on S150A sputter coater. Analysis was done on a Leo 1430VP scanning electron microscope. Differential scanning calorimetry was performed on TA Instrument Q100 Differential Scanning Calorimeter. For DSC analysis, each sample was weighed (7–8 mg). T_g and enthalpies of fusion (ΔH_m) were measured. The DSC cell was purged with nitrogen gas flow of 50 ml min⁻¹. Experiments were performed in aluminum hermetic pans using a heating and cooling rate of 5 °C min⁻¹. T_m was determined by the first scan while T_g was determined by the second scan.

X-ray Crystallography

X-ray crystallography of some of the metal complexes were performed on a Rigaku R-AXIS IIc diffractometer. Diffracted intensities were measured at ambient temperature, using graphite-monochromated Mo-K_{α} radiation ($\lambda = 0.71073$ Å) from a RU-H3R rotating anode operated at 50 kV and 90 mA. Ninety oscillation

photographs with a rotation angle of 2° were collected and processed using the CrystalClear software package. Empirical corrections were applied for the effects of absorption using the REQAB program under CrystalClear. The structures were solved by direct methods^[14] and refined using full-matrix least-squares calculations on F_2 (SHELXL-97)^[15] on all reflections, both programs operating under the WinGX program package.^[16]

Anisotropic thermal displacement parameters were refined for all nonhydrogen atoms; the hydrogen atoms were included as a riding contribution except for those of the amine groups, which were located from difference maps and refined with fixed isotropic thermal parameters. Structural illustrations have been drawn with ORTEP-3 for Windows under WinGX.^[17]

Synthesis of Ligands

The salicylaldimine ligands were prepared via Schiff base condensation of the appropriate 2-hydroxybenzaldehyde and aromatic amine using a published procedure (Scheme 1).^[9] The synthetic procedure is described using the synthesis of **HL**¹ as an example.

To a Schlenk tube containing salicylaldehyde (12 mmol) and formic acid (0.5 ml) in methanol (15 ml) was added aniline (16 mmol). The resulting orange-brown reaction mixture was



$$\begin{split} \textbf{HL}^1 &: \ R = \textbf{i} - \textbf{Pr}, \ R_1 = R_2 = \textbf{H}, \\ \textbf{HL}^2 &: \ R = R_1 = R_2 = \textbf{H}; \\ \textbf{HL}^3 &: \ R = \textbf{H}; \ R_1 = \textbf{t} - \textbf{Bu}; \ R_2 = \textbf{t} - \textbf{Bu}; \\ \textbf{HL}^4 &: \ R = \textbf{i} - \textbf{Pr}; \ R_1 = \textbf{t} - \textbf{Bu}; \ R_2 = \textbf{H}; \\ \textbf{HL}^5 &: \ R = R_1 = \textbf{H}; \ R_2 = \textbf{Cl}; \\ \textbf{HL}^6 &: \ R = \textbf{i} - \textbf{Pr}; \ R_1 = \textbf{H}; \ R_2 = \textbf{Cl}; \\ \textbf{HL}^7 &: \ R = \textbf{i} - \textbf{Pr}; \ R_1 = \textbf{t} - \textbf{Bu}; \ R_2 = \textbf{t} - \textbf{Bu}; \end{split}$$

Scheme 1. Synthesis of ligands (HL¹-HL⁷).

stirred at room temperature for approximately 15 h. During this time a yellow solid precipitated from the solution and was isolated by vacuum filtration, washed with cold methanol and dried under vacuum. The salicylaldimine ligands were obtained as light yellow to orange-yellow solids in yields of 65–93%. Full characterization data for the ligands are given in Tables S1 and S2 in the Supporting Information.

Synthesis of Copper Complexes Cu(1-6)

The general procedure for the preparation of the copper complexes is given here. Copper acetate monohydrate (0.5 mmol) and the appropriate Schiff base ligand (1 mmol) were placed in a round-bottom flask, followed by methanol (20 ml). The resulting reaction mixture was stirred under reflux for 4 h under a nitrogen atmosphere. During this time a solid precipitated from solution. The reaction mixture was cooled to 0 °C for approximately 15 min and the solid isolated by vacuum filtration. Complexes were recrystallized by slow diffusion of ethanol into a concentrated dichloromethane solution of the complexes at -4 °C. All complexes were obtained as dark green crystals.

bis[N-(2,6-diisopropylphenyl)-salicylaldiminato]copper(II), Cu(1)

Yield, 62%; m.p. > 300 $^{\circ}C$ (dec); UV–vis. λ_{max} (nm) CH_2Cl_2 soln: 286, 328, 386, 630, 660.

bis[N-(phenyl)-salicylaldiminato] copper(II), Cu(2)

Yield, 57%; m.p. $>\!280\,^{\circ}C$ (dec); UV–vis. λ_{max} (nm) CH_2Cl_2 soln: 277, 336, 376, 631, 661.

bis[N-(phenyl)-3,5-di-tert-butyl salicylaldiminato] copper(II), Cu(3)

Yield, 73%; m.p. >290 (dec); UV-vis. λ_{max} (nm) CH_2Cl_2 soln: 280, 320, 386, 632, 653.

bis[N-(2,6-diisopropylphenyl)-3-tert-butyl-salicylaldiminato] copper(II), **Cu(4)**

Yield, 62%; m.p. >270 (dec); UV-vis. λ_{max} (nm) CH_2Cl_2 soln: 284, 328, 384, 633, 657.

bis[N-(phenyl)-5-chloro-salicylaldiminato] copper(II), Cu(5)

Yield, 58%; m.p. > 295 $^\circ C$ (dec); UV–vis. λ_{max} (nm) CH_2Cl_2 soln: 274, 333, 372, 628, 657.

bis[N-(2,6-diisopropylphenyl)-5-chloro-salicylaldiminato] copper(II), **Cu(6)**

Yield, 73%; m.p. > 280 $^{\circ}C$ (dec); UV–vis. λ_{max} (nm) CH_2Cl_2 soln: 276, 335, 375, 629, 662.

bis[N-(2,6-diisopropylphenyl)-3,5-di-tert-butyl salicylaldiminato] copper(II), **Cu(7)**

Yield, 51%; m.p. >260 $^{\circ}$ C (dec); UV–vis. λ_{max} (nm) CH₂Cl₂ soln: 278, 326, 368, 620, 656.

Synthesis of bis[N-(2,6-diisopropylphenyl)-salicylaldiminato] zinc(II), Zn(1)

To a clear yellow solution of **HL**¹ (1.0 g, 3.6 mmol) in ethanol (20 ml) was added zinc acetate (0.39 g, 1.8 mmol) and the mixture refluxed for 2 h. During the reaction time, a yellow solid precipitated from the solution. The solid was isolated by vacuum filtration. The product was recrystallized using a mixture of CH₂Cl₂/EtOH (1:2) at -4 °C, giving a cream-colored solid. Yield 0.55 g, 48%. FT-IR (cm⁻¹, ATR): $\nu_{C=N} = 1614 \nu_{C-O} = 1277$, ESI-MS [M + H]^+ = 626 m/z calculated for $C_{38}H_{44}N_2O_2Zn.\ ^1H\text{-}NMR$ (CDCl_3 298 K) δ (in ppm) 1.19 [d, 12H, CH(CH₃)₂], 3.01 [m, 2H, CH(CH₃)₂], 6.98 (t, 2H, Ar); 7.09 (d, 2H,Ar); and 7.20 (m, 4H, Ar), 7.36 (m, 2H, Ar) 7.43 (m, 4H, Ar), 8.30 (s, 2H, CH=N). ¹³C-NMR (CDCl₃) δ (in ppm), 177.01 (N=CH), 173.39 (aromatic C-OH), 145.88 (aromatic <u>C</u>-N=C), 137.01 (aromatic C2/6-ⁱPr), 135.31 (C4/6 on OH-containing aromatic ring), 126.31, (C3/5 on ⁱPr containing aromatic ring), 123.24, (C4- on ⁱPr containing aromatic ring), 118.12 (C5 OH-containing aromatic ring), 113.82 (aromatic C-C=N), 27.44 [CH-(CH₃)₂], 22.21 [CH-(CH₃)₂]. Anal. calcd for C₃₈H₄₄N₂O₂Zn C, 72.91; H, 7.64; N, 4.47. Found: C, 72.47; H, 7.89; N, 4.45

Synthesis of bis[N-(2,6-diisopropylphenyl)-3-tert-butyl-salicylaldiminato] zinc (II), Zn(4)

To a clear yellow solution of **HL**⁴ (0.60 g, 1.78 mmol) in THF (10 ml) was added NaH (0.045 g, 1.88 mmol). Immediately effervescence

was observed. The yellow mixture was stirred at room temperature under nitrogen for 1 h. The reaction mixture was filtered under nitrogen into another Schlenk tube and the solvent was removed under vacuum. The residue (Na salt of ligand) was washed with pentane (2 × 5 ml) and used without further purification in the subsequent step. The sodium salt of the ligand and zinc acetate (0.172 g, 0.78 mmol) were placed in a two-necked round-bottom flask followed by ethanol (20 ml). The resulting yellow mixture was stirred under nitrogen at room temperature for 4 h. During this time, a yellow solid precipitated. The solid was filtered and washed with cold methanol. Recrystallization was performed using a mixture of CH₂Cl₂/EtOH (1:2) at -4° C. Yield 0.52 g, 89%. FT-IR (cm⁻¹, KBr pellet): $\nu_{(C=N)} = 1598$, $\nu_{(C-O)} = 1272$. ESI-MS [M + H]⁺ = 739 m/z calculated for C4₆H₆₀N₂O₂Zn.

¹H-NMR (CDCl₃ 298 K) δ (in ppm) 1.19 [d, 12H, CH(C<u>H</u>₃)₂], 1.39 [s 18H, C(C<u>H</u>₃)₃], 3.03 [m, 2H, C<u>H</u>(CH₃)₂], 6.53 (2H, Ar), 6.94 (t, 6H, Ar) 7.41 (m, 2H, Ar), 8.31 (s, 2H, C<u>H</u>=N). ¹³C-NMR (CDCl₃) δ (in ppm), 175.92 (N=CH), 172.65 (*aromatic* C_-OH), 146.94, (*aromatic* C_-N=C), 142.82, 141.90 (*aromatic* C2/6⁻ⁱPr), 139.13, (*aromatic* C3^{-t}Bu), 135.26, 132.78, (C4/6 on ^tBu containing aromatic ring), 127.12, (C3/5 on ⁱPr containing aromatic ring), 124.69 (C4- on ⁱPr containing aromatic ring), 117.96 (C5 on ^tBu containing aromatic ring), 114.85 (*aromatic* C_-C=N), 35.28 [C-(CH₃)₃], 28.46 [C-(CH₃)₃], 25.31 [CH-(CH₃)₂], 22.65 [CH-(CH₃)₂]. Anal. calcd for C₄₆H₆₀N₂O₂Zn C, 74.8; H, 8.20; N, 3.80. Found: C, 75.27; H, 7.89; N, 3.45.

Polymerization

DL-Lactide (0.72 g, 0.005 mol) was dissolved in dioxane or toluene (5 ml) in a Schlenk tube and the required amount of catalyst/initiator was added. The reaction mixture was refluxed at 70 or 110 °C (depending on the solvent used) under vacuum. After the required reaction time, the solvent was removed and the crude material was analyzed by ¹H-NMR in CDCl₃. The integration values of the methine proton of the monomer ($I_{CH_{monomer}}$) and that of polymer ($I_{CH_{polymer}}$) were used to calculate the percentage conversion as shown in eqn (1).

$$\% \text{ Conversion} = \frac{I_{\text{CH}_{\text{polymer}}}}{I_{\text{CH}_{\text{monomer}}} + I_{\text{CH}_{\text{polymer}}}} \times 100$$
(1)

Polymer Characterization

Polymers were characterized using NMR spectroscopy, DSC analysis, scanning electron microscopy and size exclusion chromatography.

Results and Discussion

Synthesis of Schiff-base Complexes

The Schiff-base complexes were prepared by the reaction of the appropriate phenoxy-imine ligand with copper or zinc acetate in a 2:1 mole ratio of ligand to metal precursors (Fig. 5). The mononuclear complexes **Cu(1)** and **Cu(5)** have previously been reported by us when used as a catalyst in the oxidation of phenol.^[9] The other complexes are new and were obtained as green complexes for Cu and pale yellow solids for the Zn complexes. All complexes were found to be stable but some decomposition is observed over time when the complexes are dissolved in various organic solvents. This is especially true of the zinc complexes.

Spectral Characterization of Complexes

The copper complexes were characterized by IR and UV spectroscopy, elemental analysis and mass spectrometry (ESI). The zinc complexes were characterized using similar techniques together with ¹H NMR spectroscopy. The main features of the IR spectra of the copper complexes is the shift of the v(C=N) band from around 1615 cm⁻¹ in the ligand to around 1602 cm⁻¹ in the complexes. Similar shifts are observed for the zinc complexes. In this case the shift is from ~1615 to ~1598 cm⁻¹. In all cases the complexation is further confirmed by the disappearance of the v(O-H) band which normally occurs in the region of 2800–3000 cm⁻¹. The original v(C-O) band of the phenoxy group in the free ligand (1269–1279 cm⁻¹) also shifts to higher frequencies on coordination to the metal.

Owing to the paramagnetic nature of Cu⁺² complexes, we were unable to study these complexes via NMR spectroscopy. The d¹⁰, Zn⁺² complexes were, however, amenable to NMR studies, giving clear ¹H NMR spectra in CDCl₃. The main features in the NMR spectra of these complexes are the shift in the signal of the imine proton to δ 8.30 ppm in **Zn(1)** and δ 8.31 ppm in **Zn(4)**.

Complexes were also characterized using ESI mass spectrometry. In all cases parent ions for the different complexes were observed. The series of copper complexes showed similar fragmentation patterns. In the case of the copper complexes a typical fragmentation pattern consisted of initial demetallation of the complex producing the free ligand. The remaining fragmentation pattern resembles that of the free ligand. The Zn complex **Zn(1)** shows only a weak parent ion, with the remaining fragmentation pattern being very similar to that of the free ligand. The ESI mass spectrum of **Zn(4)** shows a fairly intense molecular ion at *m/z* 737. There is very little fragmentation of the parent ion observed, which seems to point to the relative stability of the complex under the condition employed to carry out the mass spectral analysis.

The UV-vis spectra of the copper complexes show four bands in the region 220–400 nm. The first two bands around 235 and 275 nm can be assigned to $\pi - \pi^*$ transitions while the third band around 305 nm is due to a $n-\pi^*$ transition. A fourth band not present in the ligand spectra can be assigned to a metal to ligand charge (MLCT) transfer band which involves electrons in the n orbital of the C=N functionality. These spectra are similar to those reported for analogous Cu⁺² complexes. This seems to indicate that we are dealing with distorted square planar geometries. Full characterization data for the copper complexes are given in Table 1.

X-Ray Structure of Complexes

Cu(4) and **Zn(4)** were further characterized by single crystal X-ray diffraction. The crystallographic parameters for these two complexes are given in Table 2 and the structures shown in Fig. 7. It should be noted that the crystal structures for the complexes **Cu(1)** and **Cu(5)** have previously been reported by our group (Fig. 8).^[9] X-ray crystallography of **Cu(4)** and **Zn(4)** revealed that the Schiff base ligands bind to the metal in a bidentate fashion with two ligand moieties interacting with the metal center.

The copper complex **Cu(4)** has a distorted square planar geometry around the metal center. The structure for **Cu(4)** resembles that of **Cu(1)** and **Cu(5)** reported recently.^[9] As was the case for **Cu(1)**, complex **Cu(4)** also adopts a *trans* arrangement. This is most likely due to the presence of the bulky iso-propyl groups on the aromatic ring which is bonded to the imino nitrogen. This is unlike the structure for an anlogous compound in which the N-aryl

Table 1. Characterization data for copper(II) salicylaldiminato complexes Cu(1) – Cu(7)								
			Anal. found (calcd)			IR spectra (cm ⁻¹) ^b		
Complex	Formula	M^+ (calcd) ^a m/z	С	Н	Ν	ν(C=N)	ν(C-O)	
Cu(1)	$C_{38}H_{44}CuN_2O_2$	624 (624.31)	72.90(73.11)	7.11(7.10)	4.45(4.49)	1602	1323	
Cu(2)	$C_{26}H_{20}CuN_2O_2 \cdot 1/2H_2O$	455 (455.99)	67.85(67.17)	4.17(4.42)	6.01(6.14)	1606	1327	
Cu(3)	$C_{42}H_{52}CuN_2O_2$	680 (680.42)	74.57(74.14)	7.73(7.70)	4.13(4.12)	1609	1317	
Cu(4)	C ₄₆ H ₆₀ CuN ₂ O ₂	736 (736.53)	74.81(75.01)	8.17(8.21)	3.78(3.80)	1602	1318	
Cu(5)	$C_{26}H_{18}Cl_2CuN_2O_2 \cdot 1/2H_2O_2$	^c 525 (525.89)	58.41(58.49)	3.23(3.46)	5.54(5.34)	1606	1322	
Cu(6)	$C_{38}H_{42}Cl_2CuN_2O_2$	^c 694 (694.20)	65.46(65.84)	6.12(6.11)	3.77(4.04)	1610	1322	
Cu(7)	$C_{54}H_{76}CuN_2O_2{\cdot}2H_2O$	848 (848.74)	73.62(73.32)	8.73(9.06)	2.53(2.97)	1610	1324	
a Deserved as ESI sparstra unless otherwise stated								

^a Recorded as ESI spectra unless otherwise stated.

^b Recorded as nujol mulls between NaCl plates.

^c Recorded as electron impact spectra.

Table 2. Crystallographic parameters				
	Cu(1) ^a	Cu(4)	Cu(5) ^a	Zn(4)
Empirical formula	$C_{38}H_{44}CuN_2O_2$	C ₄₆ H ₆₀ N ₂ O ₂ Cu	$C_{26}H_{18}CI_2N_2O_2Cu$	$C_{46}H_{60}N_2 O_2Zn$
Mr	624.3	736.5	524.9	738.3
Crystal system	Triclinic	Tetragonal	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -4	C2/c	<i>P</i> -1
a (Å)	8.0725(16)	14.3631(10)	23.634(7)	10.9182(2)
b (Å)	10.2332(9)	14.3631(10)	9.337(2)	12.2249(2)
<i>c</i> (Å)	11.7022(3)	9.8445(7)	15.087(5)	16.0998(3)
α (deg)	60.62(2)	90	90	90.0420(10)
β (deg)	76.39(3)	90	137.343(7)	103.0180(10)
γ (deg)	81.64(4)	90	90	97.9420(10)
V (Å ³)	818.2(1)	2030.9(2)	2256(1)	2072.46(6)
Ζ	1	2	4	2
D_{calc} (g cm ⁻³)	1.27	1.204	1.54	1.183
μ (MoK _{$lpha$}) (cm ⁻¹)	7.0	5.8	12.32	6.3
Temperature (K)	293(2)	100(2)	293(2)	100(2)
2θ range (deg)	$4.0 < 2\theta < 54.0$	$7.6 < 2\theta < 56.4$	$7.6 < 2\theta < 54.0$	$3.4 < 2\theta < 50.6$
Absorption correction	Empirical	psi-scan	Empirical	psi-scan
Data/restraints/par.	3230/0/206	4914/0/238	2235/0/151	7491/1/485
$R_1 \left[l > 2\sigma(l) \right]$	0.055	0.0326	0.032	0.063
wR ₂ (all reflections)	0.119	0.0695	0.0909	0.0726
Max/min residual electron density (e Å $^{-3})$	0.45; -0.86	0.336; -0.190	0.27; -0.35	0.386; -0.341
^a Data from reference [9]				

group is an unsubstituted phenyl group. The structure of the latter compound reported by Repo *et al.* shows a *cis* arrangement of N₂O₂ donor atoms.^[10] These authors claim that in this case the driving force for this arrangement is the ease of $\pi - \pi$ stacking of the N-phenyl rings. No such $\pi - \pi$ stacking is observed in our copper complexes, presumably due to the presence of the isopropyl substituents. The selected bond angles and bond lengths for **Cu(4)** and **Zn(4)** together with those of the previously reported structures, **Cu(1)** and **Cu(5)**, are given in Table 3. Full crystallograhic data for the two new complexes are given in the Supporting Information.

Comparison of **Cu(1)** and **Cu(4)** with each other show that the latter exhibits greater degree of distortion. This is clearly seen when comparing the O–M–O bond angles. For **Cu(4)** this is 151.32° while for **Cu(1)** it is the expected bond angle of 180° .

The zinc complex **Zn(4)** exhibits a distorted tetrahedral geometry. The N-Zn–N angle in **Zn(4)** is 124.77° and is similar to values obtained for analogous salicylaldimine complexes.^[11] The O–Zn–O angle in **Zn(4)** is 107.13° and is once again within the same range of similar complexes. The two Zn–O bond lengths are very similar, being around 1.93 Å, which corresponds well with other Zn salicylaldimine complexes.

Preliminary Polymerization using DL-Lactide

The solubility of the complexes prepared was determined in various solvents at different temperatures in order to determine the initial polymerization conditions. Preliminary polymerization reactions were thus carried out and the results are shown in Table 4. As previously found for a range of other metal-alkoxide and aryl-oxide complexes, the polymerization is assumed to most probably occur via a coordination–insertion mechanism into an



Figure 6. Plot of ln[M]₀/[M]_t vs time for DL-lactide polymerization initiated using (A) Cu(4), (B) Cu(7), (C) Zn(1) at 70 °C in toluene.

M-O bond.^[12a-d] Polymer end-group analysis via ¹H NMR was used to gain some insight into the polymerization mechanism.^[12b] An ¹H NMR (CDCl₃) spectrum of a sample of an oligolactide exhibits two main signals at δ 1.6 ppm (d, CH₃) and δ 5.2 ppm (q, CH). A weak singlet located at δ 8.26 ppm corresponding to the Schiff base's imino group (HC=N) was also observed in the spectrum. This indicated that initiation of polymerization of DLlactide by the complexes occurred via insertion of one molecule of lactide into the M-O bond of the catalyst, via acyl-oxygen bond cleavage (Scheme 2). The result of this is the presence of an imino end group in the growing oligomer. This process was further confirmed by carrying out a reaction of DL-lactide with **Zn(1)** in a 1:1 mole ratio and following the reaction via ¹H NMR spectroscopy. Over time signals are observed at 1.62, 5.2 and 8.26 ppm similar to those observed in the oligolactide's spectrum discussed above.

End-group analysis was also used to determine the molar mass of polymers using eqn (2). A good relationship between this value and the theoretical value further confirms living polymerization via the coordination–insertion mechanism. For instance, **Cu(4)** resulted in M_n (H NMR) compared with 4500 for M_n (theoretical) of 5000 using [M]:[I] = 50 at 44% conversion. Similarly good relationships were also obtained for other calculated values.

$$M_{\rm n}(^{1}{\rm H}{\rm NMR}) = \frac{I_{\rm CH_{polymer}}/4}{I_{\rm HC} = N/2} \times 144$$
 (2)

where $I_{CH_{polymer}}$ is the peak height of methine proton in the polymer spectrum and I_{HC}_{N} is the peak height of the HC=N proton in the polymer spectrum.

The initial polymerization results showed that only two copper complexes, **Cu(4)** and **Cu(7)**, and one zinc complex, **Zn(1)**, gave reasonable conversion of the monomer. These complexes were thus used for further studies to establish the optimum polymerization conditions. Reactions were performed at both 70 and 110 $^{\circ}$ C. In addition, kinetic studies using the more active metal complexes were also conducted. This is discussed in more detail in the next section.

Kinetic Studies

The kinetics of the ring opening polymerization at 70 °C, using the two copper complexes **Cu(4)** and **Cu(7)** and as well as the zinc complex **Zn(1)** as catalyst precursors, were investigated in more detail. Linear plots were obtained for graphs of $\ln[M]_0/[M]_t$ against time, where $[M]_0$ is the initial monomer concentration, while $[M]_t$ is the monomer concentration at time *t*, indicating that the polymerization exhibited living characteristics (Fig. 6). Linearity is observed for all [M]: [I] ratios, where [I] is the initiator concentration. It can also be observed that the fastest reaction rates are obtained at lower [M]: [I] ratios. An increase in [M]: [I] ratios lead to a significant decrease in reaction rate. This is quite marked for the copper complex, **Cu(7)**.

The k_p values for the copper and zinc complexes were determined from the gradients of the plots of $1/t(\ln[M]_0/[M]_t)$ vs [I], where [I] is the initiator concentration (Table 5). **Cu(4)** showed the lowest rate constant of polymerization while **Zn(1)** showed the highest rate. This might be related to M–O bond strength. The M–O bond length for **Cu(4)** is shorter than that of **Zn(1)** (Table 3). The latter therefore has a weaker bond which should facilitate monomer insertion into the M–O bond.



Figure 7. X-ray structure of (A) Cu(4) and (B) Zn(4).



Figure 8. X-ray structures of Cu(1) and Cu(5).^[9].

Structure – Polymerization Relationship using X-ray Crystallography

With a view to assessing whether the geometry imposed by the four-coordinate ligand might account for polymerization activities and selectivities, the crystal structures of some of the active and inactive complexes were determined using single crystal X-ray diffraction. Complexes Cu(1), Cu(2) and Cu(6) did not initiate polymerization even when the reactions were carried out for extended periods at 100 °C. These complexes have no substituents on the phenoxy moieties. X-ray studies showed that Cu(1) adopts a square planar geometry (Fig. 7). Cu(5), with a Cl substituent in the para position but without any ortho substituent on the phenoxy

	Chemistry				
Table 4. 1 mol l ⁻¹	Preliminary po	lymerization resul	lts using [M] :	[I] = 50, [M] =	
Complex	Solvent ^a	Temperature (°C)	Time (h)	Conversion (%) ^b	
Zn(1)			48	55	
Zn(4)			48	26	
Cu(1)			48	с	
Cu(2)			48	с	
Cu(3)	Toluene	70	48	с	
Cu(4)			35	55	

Cu(5)			24	18		
Cu(6)			48	с		
Cu(7)			35	80		
Cu(3)	Dioxane	100	68	10		
Cu(6)	THF		65	с		
Cu(7)	Dioxane		48	89		
^a Solvent used depended upon solubility of complex.						

^b Determined from ¹H NMR.

^c No polymerization observed.

ring, also showed low monomer conversion. The X-ray structure of Cu(5) also showed a square planar geometry with a regular arrangement of the phenyl groups and the molecule adopting a cis configuration (Fig. 8). It is thought that the absence of bulky substituents on the ligands makes the catalyst more susceptible to deactivation via the dimerization of the metal centers. Such dimerization often involves μ -oxo or μ -hydroxy bridges. On the other hand sterically bulky groups around the metal prevent such dimerization and thus prolong the catalyst life-time.^[13] In addition other sterically bulky groups in the vicinity of the metal center retard any unwanted side reactions such as transesterification reactions, thus increasing polymer yield.^[18] They also prevent catalyst deactivation via the formation of μ -oxo dimers.

Cu(3) has di-substituted phenoxy rings with bulky t-butyl groups at the ortho and para positions to the phenoxy moiety but surprisingly no ROP of DL-lactide took place at 70 °C while only 10% monomer conversion was observed when the reaction is performed at 100 °C. Cu(3) also lacked substituents on the imino bound aromatic ring. Van Wyk et al. have shown that salicylaldimine ligands which do not contain substituents on the imino bound aromatic rings tend to coordinate in a cis arrangement.^[9] This arrangement leads to increased steric crowding around the metal center, unlike the trans arrangement,

Table 3. Sele	Table 3. Selected bond lengths and bond angles obtained from X-ray data							
Complex	∠N–M–O (deg)	∠O−M−O (deg)	M–O (Å)	M–N (Å)	Geometry			
Cu(1)	91.39(9)	180	1.999(2)	1.869(2)	Distorted square planar			
	88.61(9)							
Cu(4)	93.13(5)	151.42(7)	1.8959(11)	1.9769(13)	Distorted square planar			
	95.76(5)	143.41(8)						
Cu(5)	93.56(6)	88.07(8)	1.901(1)	1.985(1)	Distorted square planar			
	151.86(6)							
	119.99(5)							
Zn(4)	116.05(5)	107.15(5)	1.9280(12)	1.9837(13)	Distorted tetrahedral			
	93.76(5)		1.9294(11)	2.0088(13)				
	95.42(5)							

Applied



Scheme 2. Coordination-insertion mechanism for ring-opening polymerization of DL-lactide.

Table 5. The $k_{\rm p}$ values of DL-lactide polymerization using copper and zinc complexes in toluene at 70 $^\circ \rm C$					
Complex	$k_{\rm p} ({ m mol}^{-1}{ m dm}^3{ m h}^{-1})$				
Cu(4) Cu(7) Zn(1)	0.869 2.777 2.839				

which forces the phenyl rings away from the metal center, reducing steric interaction and thus leading to higher polymerization activities.^[14]

The most active copper complexes have *ortho* t-butyl substituents on the phenoxy ring and *ortho* isopropyl substituent on the imino-bound ring. The enhanced activity of**Cu(4)** and **Cu(7)** are most likely due to electronic factors rather than steric factors. If the latter were dominant then one would have expected a decrease in activity as the bulky ^tBu group in the 3 position would have blocked access of the monomer to the catalyst active site, thus retarding the polymerization process. The phenoxy oxygen is most likely to act as a π -donor ligand. In this case an electron rich substituent in the *ortho* position such as the ^tBu in the 3-position of the phenoxy group will increase electron density on the phenoxy oxygen and enhance its π -donor ability, leading to a weaker M–O bond. A comparison of the Cu–O bond in **Cu(1)** (no ^tBu substituent) and **Cu(4)** (with ^tBu substituent) shows that the latter has a longer and thus a weaker Cu–O bond (Table 3).

The ability of **Cu(7)** to mediate ROP of DL lactide at such high conversions can be explained by the fact that it has ^tBu substituents at positions *ortho* and *para* to the hydroxyl group. This would lead to a further increase in the π -donor ability of the phenoxy group, thus further weakening the M–O bond and therefore leading to a higher rate of monomer insertion into the M–O bond. In addition the high degree of substitution on the aromatic rings helps protect the metal site against undesired side reactions as previously shown by Kerton *et al.*^[19] That electronic effects are more significant than

steric effects can be deduced from the fact that the k_p value of **Cu(7)** is three times faster than that of **Cu(4)**.

The situation is reversed in the case of the zinc complexes. Here a t-butyl substituent in the 3-position of the salicylaldimine ligand retards the polymerization process. Steric effects are now dominant. This is largely due to differences in the electronic configuration of zinc (d10) as opposed to copper (d9). In the zinc complexes the ability of the phenoxy O to act as a π -donor is prevented by the fact that the metal has no empty d orbitals to accept electrons from the phenoxy group. We thus postulate that, in the case of the zinc complexes, steric factors now outweigh electronic factors.

As expected, X-ray crystallography data show that the copper complexes have a distorted square planar geometry around the metal center, while the zinc complexes showed a distorted tetrahedral geometry [Fig. 8(b), Table 3]. DL-lactide can approach the Cu metal center unhindered from either the bottom or top of the coordination plane while the tetrahedral zinc complexes provide a more hindered access. Structural data showed that the inactive complex, **Cu(1)**, has the shortest Cu–O bond length and thus the strongest Cu–O bond. This would render the insertion of the monomer into the Cu–O bond more difficult. X-ray analysis thus confirms that electronic factors predominate in the case of Cu while steric factor prevails for Zn.

It is interesting to note that Gibson *et al.* studied the effect of phenoxy substituents of aluminum salen type complexes on the rate and stereoselectivity of DL-Lactide polymerization.^[20] They found that electron-withdrawing groups attached to the phenoxy ring gave an increase in polymerization rate whereas bulky *ortho* substituents slowed down the polymerization. The latter, however, increased the isotacticity of the resulting PDLLA. Gibson *et al.* showed that the Al complexes adopt a five-coordinate trigonal bipyramidal geometry at the metal center. Thus steric factors due to the size of the *ortho* phenoxy substituent hinder the approach of the lactide monomer to the aluminum center.

Table 6. ¹³ C NMR characterization, [M] : [I] = 50, toluene 70 $^{\circ}$ C								
			Tetrad intensities (%)					
Complex	Conversion (%)	Time (h)	ssi	SSS	isi	iss	sis, sii, iis, iii	1
lsotactic ^[27,28]			0	0	25	0	75	
AI(O ⁱ Pr) ₃ ^[25]	75	16	0	0	30	0	70	-
HAPENAIOCH3 ^[26]	94	6	0	0	16	0	84	1.68
HAPENAIO ⁱ Pr ^[26]	96	4	0	8	16	3	73	1.7
Cu(4)	98	96	0	0	24	0	76	1.31
Cu(7)	86	68	0	0	27	0	73	1.54
Zn(1)	70	72	0	0	30	0	70	1.85
Zn(1)	94	96	0	0	30	0	70	2.28
Zn(4)	99	96	4	3.4	24	6.6	62	2.54

Table 7. PDLA syn	PDLA synthesized using $\mbox{Cu(4)}$ complex in toluene at 70 $^\circ\mbox{C}$						
Conversion (%) ([M] : [1]) / M_n^{SEC} (corrected) ^a							
25 (50)	1.25	5 800 (3 250)	0.6				
98 (50)	1.31	12 500(7 000)	1.0				
30 (75)	1.21	5 000 (2 800)	1.2				
47 (75)	1.19	13 145 (7 360)	0.7				
3 After and time a sum atter for the form (0.56 for A4 [30,31]							

^a After applying a correction factor of 0.56 for M_{n} .^{[3} ^b Number of active sites calculated using M_{n}^{SEC} .^[29]

Characterization of Polymers

Stereochemistry of polymers

The stereochemistry of the polymers was determined using ¹³C{¹H} spectroscopy. From the NMR spectra it can be concluded that predominantly isotactic polymers were obtained using the Cu and Zn complexes (Table 6), showing that the catalysts are stereoselective. This result can be correlated with the presence of bulky ortho phenoxy substituents as has also been reported by Gibson et al.^[20] for aluminum complexes. Cu complexes resulted

in polymers with higher isotactic content than those obtained from Zn complexes. It can be concluded that, while electronic factors affect the rate of polymerization, steric factors influence isotacticity of the polymers produced. It is also interesting to note that previously reported Zn complexes resulted in atactic PDLLAs.^[6,7]

Polymers obtained using complexes Cu(4), Cu(7) and Zn(1) as catalysts do not show the presence of the sss and ssi forbidden tetrads which indicate a low percentage of transesterification reactions even at high percentage conversion.[21-25] Complex Zn(4), which adopts a highly distorted tetrahedral structure, shows the presence of the forbidden tetrads. These results were compared with aluminum initiators synthesized by Bhaw-Luximon et al.^[25,26] (Table 6) and the degree of isotacticity was found to be between that of Al(OⁱPr)₃ and aluminum Schiff base initiators.

Molecular weight determination of the polymers

The molecular weights of the polymers were determined using ambient temperature size exclusion chromatography (SEC). This showed that the highest molecular weight polymers were obtained in the case where Zn(1) was used as initiator while narrower polydispersity index polymers were obtained with



Figure 9. SEC chromatograms of PDLLAs synthesized using (A) Zn and (B) Cu complexes in toluene at 70 $^{\circ}$ C at [M] : [I] = 50, [M] = 1M.



Figure 10. DSC chromatogram recorded for a PDLLA synthesized using Cu(4) at [M]: [I] = 75.



Figure 11. SEM image of PDLLA synthesized using (A) Cu(4) and (B) Cu(7).

copper complexes as initiators (Tables 6 and 7). The occurrence of transesterification reactions using zinc initiators was confirmed from SEC traces (Fig. 9), which showed the presence of low molar mass polymers. The values of the number average molecular weights as obtained from SEC (M_n^{SEC}) were further used to determine the number of active sites (*n*) for one of the complexes, **Cu(4)**, using eqn (3) in order to have a better insight into the mechanism of polymerization (Table 7).^[29] It was found that on average only one M–O bond was active in polymerization.

$$n = \% \text{conversion} \left[\frac{(\text{M/I}) \times \text{MM}(\text{DL-lactide})}{M_n^{\text{SEC}}} \right]$$
(3)

where n is the number of active sites; MM (DL-lactide) = molar mass of DL-lactide = 144 g mol^{-1} .

Thermal properties of polymers produced

The thermal properties of the polymers were studied using differential scanning calorimetry (DSC). PLLA with 100% L-content and PDLLA with completely racemic and random sequence have T_g at 62 and 45 °C respectively.^[32] DSC chromatograms of PDLLAs synthesized using copper and zinc complexes showed the presence of T_g in the range 53–59 and 54–54.5 °C. The range



of values obtained is directly related to the isotactic content of the polymers, as shown by Urayama *et al*.^[32] They showed that an increase in isotacticity brings about an increase in T_g . Indeed T_g determined here are higher than expected due to the higher isotactic content, indicating that the polymers contain stereoblocks. Cu complexes resulting in the higher isotactic content also gave PDLLA with higher T_g .

The high stereoregularity of the PDLLAs was confirmed by the presence of sharp melting points, $T_{\rm m}$ (130 °C), for polymers having isotactic content >70% (Fig. 10).^[33] The existence of a melting transition is due to the formation of sufficiently long stereosequences of D and L units. These stereoblocks give rise to stereocomplexes between the chains. Spassky *et al*.^[33–35] have previously observed $T_{\rm m}$ values in the range 125–150 °C for PDLLAs produced using aluminum Schiff base complexes as catalysts.

Polymer morphology

The morphology of the polymers produced were investigated using scanning electron microscopy (SEM). The SEM images of the purified PDLLAs were recorded. Different surface patterns were observed, namely microporous [using **Cu(4)**, Fig. 11A] and low roughness homogeneous surfaces [using **Cu(7)**, Fig. 11B]. Polymerization of DL-lactide has been successfully carried out using novel Cu and Zn salicyaldimine complexes. We have shown from X-ray data that the geometry of the complex influences the kinetics and microstructure of the polymer. It was found that the rate of polymerization was influenced by electronic factors for Cu complexes and steric factors for zinc complexes. Predominantly isotactic PDLLA was obtained which resulted in an increase of the glass transition temperature (T_g) and the presence of a melting point (T_m) for the polymers. Isotactic content was influenced by the bulkiness of ligands coordinated to the metal center.

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Supporting Information

CCDC 771676 and 771677 contain the supplementary crystallographic data for complexes **Cu(4)** and **Zn(4)**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or via e-mail: deposit@ccdc.cam.ac.uk. Tables S1–S3 are deposited as supporting information and can be found in the online version of this article.

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