

Neutral Metallocene Ester Enolate and Non-Metallocene Alkoxy Complexes of Zirconium for Catalytic Ring-Opening Polymerization of Cyclic Esters

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Four neutral zirconocene bis(ester enolate) and non-zirconocene bis(alkoxy) complexes have been employed for ring-opening polymerizations and chain transfer polymerizations of L-lactide (L-LA) and ϵ -caprolactone (ϵ -CL). All C_{2v} -, C_2 -, and C_s -ligated neutral zirconocene bis(ester enolate) complexes effectively polymerize ϵ -CL at 80 °C with high (>90%) initiator efficiencies. The C_s -ligated complex $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ (**1**) also promotes highly efficient polymerization of L-LA and is at least 100 times more reactive than the C_{2v} - and C_2 -ligated analogues. The L-LA polymerization by **1** exhibits living characteristics, producing PLA with quantitative isotacticity (no sign of monomer epimerization) and controlled molecular weight. This polymerization follows first-order kinetics with respect to both [L-LA] and [**1**], consistent with a monometallic, coordination–anionic propagation mechanism. The structurally characterized non-zirconocene bis(alkoxy) complex $[(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4)\text{N}(\text{CH}_2)_3\text{N}(2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_4)]\text{Zr}(\text{O}^i\text{Pr})_2[\text{O}=\text{C}(\text{NMe}_2)\text{CHMe}_2]$ (**2**) has been synthesized in quantitative yield from the reaction of the zirconium bis(amido) precursor with isopropyl isobutyrate. Complex **2** behaves as a single-site catalyst for polymerizations of both ϵ -CL and L-LA, unlike the comparative homoleptic zirconium tetraisopropoxy complex, which shows multisite behavior for the same processes. Both the zirconocene **1** and the non-zirconocene **2** catalyze efficient chain transfer polymerization in the presence of $^i\text{PrOH}$ as a chain transfer reagent (CTR) for the catalytic production of PLA and PCL, respectively; however, the metallocene system is more robust (in terms of ligand stability and maintaining the polymerization rate) toward an excess of a protic CTR than the present non-metallocene system.

Introduction

Ring-opening polymerization (ROP) of heterocyclic monomers via the coordination–anionic (also termed coordination–insertion) mechanism¹ is a leading polymerization technique to produce high-molecular-weight (MW) polymers typical of step-growth products, yet through the chain-growth mechanism (Scheme 1). A large number of metal complexes of various types have been extensively investigated as catalysts/initiators for the ROP of heterocyclic monomers, particularly cyclic esters (lactides such as L-LA and *rac*-LA; lactones such as ϵ -caprolactone, ϵ -CL),² largely due to the biodegradability and biocompatibility of the resulting lactide and lactone polymers (e.g., poly(lactide), PLA, and poly(ϵ -CL), PCL).³ These catalysts/initiators have encompassed organometallic or coordination complexes of main-group

elements, transition metals, and lanthanides, for controlled (over tacticity or MW) ROP polymerization of lactides⁴ and

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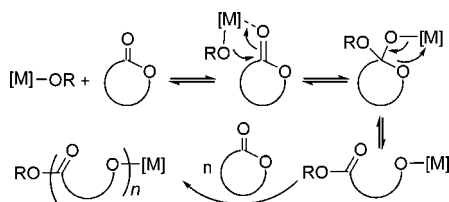
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Scheme 1



lactones.⁵ Relatively fewer reports have described studies on the catalytic ROP of cyclic esters using metal complexes in the presence of an excess of a chain transfer reagent (CTR).⁶

Group 4 non-metallocenes (non-Cp complexes) and metallocenes, typically in their cationic forms,⁷ are best known for their remarkable success in the production of revolutionary polyolefin materials through their catalyzed homogeneous, single-site, (co)polymerization of nonpolar vinyl monomers (α -olefins in particular).⁸ The polymerization of polar vinyl

monomers with such highly electron-deficient group 4 metallocene complexes is less known,⁹ despite their established high stereospecificity and degree of control for the polymerization of methacrylates¹⁰ and acrylamides.¹¹ On the other hand, coordination–anionic ROP of cyclic esters using group 4 *non-metallocene* complexes is well-known, thanks to extensive studies in this area (the metal and monomer used in each of the following examples selected for a brief overview are shown in parentheses for clarity). These catalysts/initiators are typical of those group 4 metal *alkoxides* (as initiating groups) supported by chiral phenoxyimine (Zr; *rac*-LA),¹² tris(phenoxy)amine (Zr, Hf; *rac*-LA),¹³ bis(β -ketoamidate) (Ti, Zr; *rac*-LA, ϵ -CL),¹⁴ bis(iminophenoxide) (“salen”) (Ti; *rac*-LA),¹⁵ N-heterocyclic carbene (Ti; *rac*-LA),¹⁶ bis(phenoxy)amine (Ti, Zr, Hf; *rac*-LA, L-LA, ϵ -CL),¹⁷ pyrrolylamine (Zr, Hf; ϵ -CL),¹⁸ tris(alkoxy or aryloxy) (Ti; *rac*-LA, L-LA),¹⁹ tris(alkoxy or aryloxy)amine (Ti; *rac*-LA, L-LA, ϵ -CL),²⁰ chalcogen-bridged chelating bis(aryloxy) (Ti; L-LA, ϵ -CL),²¹ and methylene-bridged bis(phenoxy) (Ti; ϵ -CL)²² ligands. In addition to alkoxides, bis(amido)titanium complexes supported by the chelating diaryloxy ligands have also been used for the ROP of L-LA and ϵ -CL.²³ Other catalysts included homoleptic group 4 alkoxide (Ti, Zr; L-LA, ϵ -CL)²⁴ and acetylacetonate (Zr; L-LA, ϵ -CL)²⁵ complexes as well as the titanium–organic framework derived from Ti(OⁱPr)₄ and 1,4-butanediol (L-LA and ϵ -CL).²⁶

Fewer reports have described the polymerization of ϵ -CL using group 4 *metallocene* complexes. Titanocene and zir-

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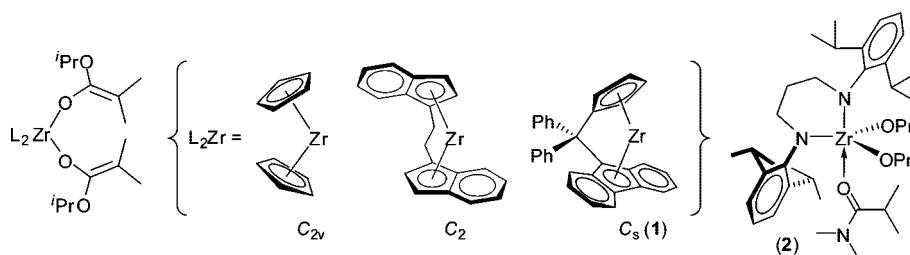
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Scheme 2



conocene alkyne complexes²⁷ as well as their bimetallic congeners formed with ^tBu₂AlH²⁸ were found active for the polymerization of ϵ -CL. Titanocene alkoxide species derived from the Cp₂TiCl-catalyzed radical ROP of epoxides can initiate controlled polymerization of ϵ -CL.²⁹ Half-sandwich (half-metallocene) dichlorotitanium alkoxides have been utilized to mediate controlled polymerization of ϵ -CL,³⁰ substituting the Cp ligand in half-titanocenes with the indenyl ligand resulted in significant (greater than an order of magnitude) ϵ -CL polymerization rate enhancement.³¹ Cationic zirconocene complexes such as [Cp₂ZrMe]⁺[B(C₆F₅)₄]⁻ and Cp₂ZrMe⁺MeB-(C₆F₅)₃⁻, which are derived from activation of the dimethyl complex with Ph₃CB(C₆F₅)₄ and B(C₆F₅)₃, respectively, are known to promote living polymerization of ϵ -CL; however, this occurs through a noncoordination, *cationic* mechanism.³²

The following three points readily become apparent on the basis of the above overview. *First*, there has been no report, to the best of our knowledge, on lactide polymerization using group 4 metallocenes, either in their neutral or cationic form. *Second*, there has been no study on the polymerization of lactide or ϵ -CL using group 4 non-metallocene complexes supported by a chelating diamide ligand. *Third*, as little has been studied on the catalytic ROP of cyclic esters using chain transfer polymerization strategies, there is a need for more research effort in this field devoted to the catalytic production of polymer chains. To address the above three points, we report in this contribution the first efficient lactide polymerization system catalyzed by group 4 metallocenes, especially Ph₂C(Cp)(Flu)Zr[OC(OⁱPr)=CMe₂]₂ (1) depicted in Scheme 2 (to point 1), the synthesis, structural characterization, and cyclic ester polymerization studies of the non-zirconocene bis(alkoxy) complex (BAIP)Zr(OⁱPr)₂[O=C(NMe₂)CHMe₂] (2, Scheme 2) supported by the chelating bulky aryl diamido ligand [(2,6-ⁱPr₂C₆H₄)N(CH₂)₃N(2,6-ⁱPr₂C₆H₄)] (BAIP)³³ (to point 2), and an investigation into the chain transfer polymerization characteristics of the zirconocene and non-zirconocene systems for catalytic polymer

chain production (to point 3). In addition to addressing the above three fundamentally important points, this study highlights the sharp differences between group 4 metallocene and non-metallocene catalysts in polymerization activity and, especially, converse behavior in their catalyzed chain transfer polymerization upon addition of an excess of isopropyl alcohol as a CTR.

Experimental Section

Materials, Reagents, and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, on a high-vacuum line, or in an argon-filled glovebox. NMR-scale reactions (typically on a 0.02 mmol scale) were conducted in Teflon-valve-sealed J. Young type NMR tubes. HPLC-grade organic solvents were first sparged extensively with nitrogen during filling of 20 L solvent reservoirs and then dried by passage through activated alumina (for Et₂O, THF, and CH₂Cl₂) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns. Benzene-*d*₆ and toluene-*d*₈ were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas CD₂Cl₂ and CDCl₃ were dried over activated Davison 4 Å molecular sieves. NMR spectra were recorded on either a Varian Inova 300 (FT 300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F) or a Varian Inova 400 spectrometer. Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe₄, whereas ¹⁹F NMR spectra were referenced to external CFCl₃. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

ϵ -Caprolactone (ϵ -CL), L-lactide (L-LA), and butylated hydroxytoluene (BHT-H, 2,6-di-*tert*-butyl-4-methylphenol) were purchased from Aldrich Chemical Co. ϵ -CL was first degassed and dried over CaH₂ overnight, followed by vacuum distillation, while L-LA was purified by sublimation. The purified monomers were stored in brown bottles inside a -30 °C glovebox freezer. BHT-H was recrystallized from hexanes prior to use. Isopropyl alcohol and isopropyl isobutyrate were purchased from TCI America and dried over CaH₂, followed by vacuum distillation. Literature procedures were employed for the preparation of the following ligand and complexes: Cp₂Zr[OC(OⁱPr)=CMe₂]₂ (Cp = η^5 -cyclopentadienyl),³⁴ *rac*-C₂H₄(Ind)₂Zr[OC(OⁱPr)=CMe₂]₂ (Ind = η^5 -indenyl),^{10e} Ph₂C(Cp)(Flu)Zr[OC(OⁱPr)=CMe₂]₂ (1, Flu = η^5 -fluorenyl),^{10a} (2,6-ⁱPr₂C₆H₄)HN(CH₂)₃NH(2,6-ⁱPr₂C₆H₄) ((BAIP)H₂),³³ (BAIP)ZrX₂(X = NMe₂, Cl),³³ [Zr(OⁱPr)₄(ⁱPrOH)]₂ (3),³⁵ and Cp₂Zr(OⁱPr)₂.³⁶

Synthesis of (BAIP)Zr(OⁱPr)₂[O=C(NMe₂)CHMe₂] (2). In an argon-filled glovebox, a 30 mL glass reactor was charged with (BAIP)Zr(NMe₂)₂ (0.223 g, 0.39 mmol) and 20 mL of hexanes. Neat Me₂CHC(=O)OⁱPr (0.102 g, 0.12 mL, 0.78 mmol) was added

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to this precooled ($-30\text{ }^{\circ}\text{C}$) and stirred solution via pipet. The resulting solution was gradually warmed to room temperature and stirred for 2 h, after which all volatiles were removed in vacuo to give 0.280 g (quantitative yield) of spectroscopically pure complex **2** as a colorless crystalline solid. The use of toluene as the reaction solvent gave a similar result. Anal. Calcd for $\text{C}_{39}\text{H}_{67}\text{N}_3\text{O}_3\text{Zr}$: C, 65.32; H, 9.42; N, 5.85. Found: C, 66.17; H, 9.23; N, 4.83. Crystallization from hexanes at $-30\text{ }^{\circ}\text{C}$ inside the freezer of the glovebox for 2 days afforded colorless single crystals, which were subsequently characterized by X-ray diffraction.

^1H NMR (C_7D_8 , $23\text{ }^{\circ}\text{C}$): δ 7.18–7.10 (m, 6H, Ar), 4.26 (sept, $J = 6.3\text{ Hz}$, 2H, OCHMe_2), 4.03 (sept, $J = 7.2\text{ Hz}$, 4H, ArCHMe_2), 3.56 (t, $J = 5.4\text{ Hz}$, 4H, NCH_2CH_2), 2.68 (pent, $J = 5.4\text{ Hz}$, 2H, NCH_2CH_2), 2.40 (s, 3H, NMe_2), 2.18 (sept, $J = 7.2\text{ Hz}$, 1H, CHMe_2), 2.14 (s, 3H, NMe_2), 1.41 (d, $J = 7.2\text{ Hz}$, 24H, ArCHMe_2), 1.03 (d, $J = 6.0\text{ Hz}$, 12H, OCHMe_2), 0.87 (d, $J = 7.2\text{ Hz}$, 6H, CHMe_2). $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , $23\text{ }^{\circ}\text{C}$): δ 176.85 ($\text{C}=\text{O}$), 145.50, 142.52, 128.33, 124.25, 123.83, and 123.71 (Ar), 71.40 (OCHMe_2), 58.40 (NCH_2CH_2), 50.62 (NMe_2), 36.30, 35.75, 32.51, 31.42, 30.58, 27.63, 27.07, 26.29, 25.28, 24.34, and 18.85 (NCH_2CH_2 , CHMe_2).

X-ray Crystallographic Analysis of 2. Single crystals of complex **2** were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at $120\text{ }^{\circ}\text{C}/10^{-6}$ Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker SMART CCD diffractometer. The structure was solved by direct methods and refined using the Bruker SHELXTL program library.³⁷ The structure was refined by full-matrix least squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. Selected crystallographic data for **2**: $\text{C}_{39}\text{H}_{67}\text{N}_3\text{O}_3\text{Zr}$, monoclinic, space group $P2_1/n$, $a = 18.422(2)\text{ \AA}$, $b = 23.949(2)\text{ \AA}$, $c = 18.896(2)\text{ \AA}$, $\beta = 101.982(1)^{\circ}$, $V = 8155.3(13)\text{ \AA}^3$, $Z = 8$, $D_{\text{calcd}} = 1.168\text{ Mg/m}^3$, $\text{GOF} = 1.094$, $R1 = 0.0498$ ($I > 2\sigma(I)$), $wR2 = 0.1379$.

General Procedures for Polymerizations Using Zirconocene Complexes. Polymerizations were performed either in 25 mL flame-dried Schlenk flasks interfaced to the dual-manifold Schlenk line for runs using an external temperature bath or in 20 mL glass reactors inside the argon-filled glovebox for ambient-temperature (ca. $25\text{ }^{\circ}\text{C}$) runs. A predetermined amount of a zirconocene complex such as **1** was first dissolved in 2 mL of toluene inside a glovebox, and the polymerization was started by rapid addition of the above solution via gastight syringe to a solution of L-LA (4.5 mmol) or ϵ -CL (4.5 mmol) in 3 mL of toluene with vigorous stirring at the pre-equilibrated bath temperature (on a Schlenk line). The amounts of monomers used were the same for all polymerizations, whereas the amount of the zirconocene was adjusted according to the $[\text{M}]/[\text{Zr}]$ ratio specified in the text. For chain transfer polymerizations, a predetermined amount of i -PrOH was mixed with the monomer in solution before addition of the catalyst. After the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried “wet” CDCl_3 stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ^1H NMR to obtain the monomer conversion data. The polymerization was immediately quenched after the removal of the last aliquot by addition of 1 mL of methanol, and the solvents were removed in vacuo. The polymer product was precipitated into 50 mL of methanol, stirred for 1 h, filtered, washed with methanol, and dried in a vacuum oven at $50\text{ }^{\circ}\text{C}$ overnight to a constant weight.

General Procedures for Polymerization Using Non-Zirconocene Complexes. In a typical ϵ -CL polymerization procedure, 22.5 μmol of the complex was first dissolved in 6 mL of toluene and ϵ -CL

(0.50 mL, $[\text{CL}]_0/[\text{Zr}]_0 = 200/1$) was added in 4 mL of toluene. For chain transfer polymerization, the monomer was premixed with a predetermined amount of i -PrOH. Polymerization of L-LA was performed in 25 mL Schlenk flasks on the Schlenk line at $80\text{ }^{\circ}\text{C}$. A Schlenk flask was placed in the glovebox, charged with L-LA (3.0 mmol) and 6 mL of toluene with or without 2-propanol, and subsequently interfaced on the Schlenk line. After the desired temperature was reached using an external temperature-controlled bath, 4 mL of the catalyst solution in toluene (15 μmol , $[\text{L-LA}]_0/[\text{Zr}]_0 = 200/1$) prepared in the glovebox was injected into the flask using a gastight syringe. The rest of the procedure is the same as that described above for the zirconocene complex.

Polymerization Kinetics. Kinetic experiments were carried out in a stirred glass reactor at ambient temperature ($\sim 25\text{ }^{\circ}\text{C}$) inside the glovebox for ϵ -CL polymerization or in flasks at $80\text{ }^{\circ}\text{C}$ on the Schlenk line for L-LA polymerization using stock solutions of the reagents and the procedures described in the literature.^{10d,38} Specifically, at appropriate time intervals, 0.2 mL aliquots were withdrawn from the reaction mixture using a syringe and quickly quenched into 1 mL vials containing 0.6 mL of undried “wet” CDCl_3 mixed with 250 ppm of BHT-H. The quenched aliquots were analyzed by ^1H NMR. For ϵ -CL polymerization, the ratio of $[\epsilon\text{-CL}]_0$ to $[\epsilon\text{-CL}]_t$ at a given time t , $[\text{CL}]_0/[\text{CL}]_t$, was determined by integration of the peaks for ϵ -CL (4.2 ppm for the OCH_2 signal) and PCL (4.0 ppm for the OCH_2 signal) according to the equation $[\epsilon\text{-CL}]_0/[\epsilon\text{-CL}]_t = (A_{4.2} + A_{4.0})/A_{4.2}$, where $A_{4.2}$ is the integral for the peak at 4.2 ppm and $A_{4.0}$ is the integral for the peak at 4.0 ppm. For L-LA polymerization, the $[\text{L-LA}]_0/[\text{L-LA}]_t$ ratio was determined by integration of the peaks for L-LA (4.8 ppm for the methine proton signal) and PLA (5.4 ppm for the methine proton signal) according to the equation $[\text{LLA}]_0/[\text{LLA}]_t = (A_{4.8} + A_{5.4})/A_{4.8}$. Apparent rate constants (k_{app}) were extracted from the slopes of the best-fit lines to the plots of $\ln([\text{M}]_0/[\text{M}]_t)$ vs time.

Polymer Characterizations. The polymer number-average molecular weight M_n and polydispersity index ($\text{PDI} = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at $40\text{ }^{\circ}\text{C}$ and a flow rate of 1.0 mL/min, with CHCl_3 as the eluent on a Waters University 1500 GPC instrument equipped with one PLgel 5 μm guard and three PLgel 5 μm mixed-C columns (Polymer Laboratories; linear range of molecular weight 200–2 000 000). The instrument was calibrated with 10 PMMA standards, and chromatograms were processed with Waters Empower software (version 2002). ^1H NMR spectra for the analysis of PCL and PLA microstructures³⁹ were recorded in CDCl_3 .

Results and Discussion

Polymerizations of L-LA and ϵ -CL by Zirconocene Bis(ester enolate) Complexes. In this study we chose L-LA over *rac*-LA for a simple reason: high-purity (99.9%) L-LA is currently produced on a large industrial scale from L-lactic acid derived from fermentation of biorenewable raw materials such as corn⁴⁰ and the prices for L-LA and *rac*-LA are about the same (a rare case where a racemic substance is not any cheaper than its enantiopure isomer), thus possessing no economical advantage for polymerization of *rac*-LA over L-LA as far as the production of isotactic PLA is concerned.

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We initially screened the L-LA polymerization using cationic zirconocene alkyl or alkoxy complexes of various ligation, including $\text{Cp}_2\text{ZrMe}^+\text{MeE}(\text{C}_6\text{F}_5)_3^-$ ($\text{E} = \text{B}, \text{Al}$), $\text{Cp}_2\text{Zr}(\text{OMe})^+\text{MeB}(\text{C}_6\text{F}_5)_3^-$, $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{ZrMe}^+\text{MeE}(\text{C}_6\text{F}_5)_3^-$, and $\text{rac-Me}_2\text{Si}(\text{Ind})_2\text{Zr}^{2+}[\text{MeAl}(\text{C}_6\text{F}_5)_3^-]_2$, and found that all were inactive. Next, we turned our attention to *neutral* metallocene *bis(ester enolate)* complexes, as we reasoned that the ester enolate ligand, being a strong nucleophile, could initiate the lactide polymerization. Indeed, the C_{2v} -ligated achiral zirconocene *bis(ester enolate)* complex $\text{Cp}_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ exhibits some activity for L-LA polymerization with a $[\text{L-LA}]/[\text{Zr}]$ ratio of 200 in toluene at 80 °C, although achieving only 7% monomer conversion in 26 h and producing PLA with a low MW of $M_n = 5.29 \times 10^3$ and narrow MW distribution (MWD) of PDI = 1.12 (the calculated initiator efficiency, I^* , is 41%). Similarly, C_2 -ligated chiral $\text{rac-C}_2\text{H}_4(\text{Ind})_2\text{-Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ is only marginally active for L-LA polymerization ($[\text{L-LA}]/[\text{Zr}] = 200$) in toluene at 80 °C, achieving only 7% monomer conversion in 18 h; the resulting PLA also has a low MW of $M_n = 4.38 \times 10^3$ and narrow MWD of PDI = 1.15 ($I^* = 49\%$). Excitingly, the C_s -ligated complex $\text{Ph}_2\text{C}(\text{Cp})(\text{Flu})\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ (**1**) is substantially more active (with >100-fold rate enhancement) under the same conditions (toluene, 80 °C) and can also achieve high monomer conversions. This interesting finding prompted us to investigate the L-LA polymerization by complex **1** in more detail, the results of which are summarized in Table 1.

The polymerization in a low $[\text{L-LA}]/[\text{Zr}]$ ratio of 50 exhibits living characteristics. A plot of the PLA M_n vs monomer conversion gave a linear relationship ($R^2 = 0.997$), whereas the MWD remains narrow for all conversions (PDI = 1.18–1.25) (Figure 1). The calculated initiator efficiency I^* values (based on one chain produced per Zr center) range from 92% to 102% for conversions below 46%, implying that only one of the two enolate ligands is used for chain initiation. As monomer conversion gets higher, the I^* value goes higher (up to 115% at 92% conversion), suggesting either a small degree of chain transfer occurring at the late stage of polymerization or the possibility of a small percentage of initiation by the second enolate ligand at Zr.

Variations of the $[\text{L-LA}]/[\text{Zr}]$ ratio to 70, 100, 135, and 200 still afforded generally well-behaved polymerization (Table 1), although in some cases the I^* values become somewhat higher due to longer reaction times. The PLA produced from all the $[\text{L-LA}]/[\text{Zr}]$ ratios is 100% isotactic (Figure 2), and there is no sign of epimerization at the NMR detection limit.

The polymerization by **1** follows strictly first-order kinetics with respect to monomer concentration for all five $[\text{L-LA}]/[\text{Zr}]$ ratios investigated (Figure 3). A double-logarithm plot (Figure 4) of the apparent rate constants (k_{app}), obtained from the slopes of the best-fit lines to the plots of $\ln([\text{L-LA}]_0/[\text{L-LA}])$ vs time, as a function of $\ln [\text{Zr}]$, was fit to a straight line ($R^2 = 0.995$) of slope 0.9(1). The kinetic order with respect to $[\text{Zr}]$, given by this slope, reveals that propagation is also approximately first order in $[\text{Zr}]$, thus consistent with the *monometallic*, coordination–anionic propagation mechanism depicted in Scheme 1.

We also investigated characteristics of ϵ -CL polymerization by these three metallocene *bis(ester enolate)* complexes, the selected results of which are summarized in Table 2. $\text{Cp}_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ exhibits no activity for ϵ -CL polymerization in toluene at ambient temperature but good activity in toluene at 80 °C with an $[\epsilon\text{-CL}]/[\text{Zr}]$ ratio of 200, achieving 89% monomer conversion in 8 h and producing PCL with a medium MW of $M_n = 2.26 \times 10^4$ and PDI = 1.48 (run 2). The

Table 1. L-LA Polymerization Results by Zirconocene *Bis(ester enolate)* **1**^a

[Zr] (mmol/L)	[L-LA] ₀ / [Zr] ₀	time (min)	conversn (%)	10 ³ <i>M</i> _n ^b (g/mol)	PDI ^b (<i>M</i> _w / <i>M</i> _n)	<i>I</i> ^{*c} (%)
18.0	50	11	31	2.58	1.18	92
		15	36	2.82	1.21	97
		20	46	3.38	1.22	102
		25	53	3.73	1.23	106
		35	64	4.34	1.23	109
		50	76	5.07	1.24	110
		80	86	5.76	1.24	110
		105	92	5.86	1.25	115
12.9	70	10	19	2.03	1.26	101
		15	27	2.96	1.27	97
		20	34	3.31	1.26	107
		30	45	4.03	1.33	116
		45	58	4.64	1.32	128
		60	68	6.12	1.23	114
		100	83	7.17	1.28	118
		151	91	7.93	1.22	117
9.02	100	15	24	3.07	1.28	117
		20	30	4.21	1.25	106
		35	47	6.38	1.22	108
		45	56	6.51	1.26	126
		65	68	7.95	1.22	125
		90	77	9.14	1.21	123
		130	85	9.90	1.28	125
6.68	135	5	10	2.61	1.21	80
		10	21	4.38	1.25	96
		20	31	5.99	1.26	103
		30	48	9.36	1.23	101
		50	60	9.97	1.21	118
		70	77	12.9	1.21	117
		113	84	14.9	1.18	111
		150	90	15.4	1.15	115
		210	93	16.9	1.12	108
4.51	200	5	5	1.97	1.05	80
		10	8	2.50	1.14	97
		20	17	3.90	1.28	129
		30	24	4.80	1.26	147
		50	49	11.0	1.15	128
		70	61	15.8	1.14	112
		110	71	15.6	1.14	132
		150	75	16.8	1.14	129
		285	84	20.5	1.14	118

^a All polymerizations were carried out in flame-dried Schlenk flasks (5 mL toluene solution) on a Schlenk line using an external temperature-control bath set at 80 °C. ^b Number-average molecular weight (*M*_n) and polydispersity index (PDI) determined by GPC relative to PMMA standards. ^c Initiator efficiency (I^*) = $M_n(\text{calcd})/M_n(\text{exptl})$, where $M_n(\text{calcd}) = \text{MW}(\text{M}) \times [\text{M}]/[\text{I}] \times \text{conversion} (\%) + \text{MW}(\text{chain-end groups})$.

calculated I^* is 91%, suggesting again that only one of the two ester enolate groups was used to initiate the polymerization. The C_2 -ligated chiral $\text{rac-C}_2\text{H}_4(\text{Ind})_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ is quite active even at ambient temperature, achieving 98% monomer conversion in 9 h with an $[\epsilon\text{-CL}]/[\text{Zr}]$ ratio of 100. The same polymerization but with an $[\epsilon\text{-CL}]/[\text{Zr}]$ ratio of 200 in toluene at 80 °C gelled in less than 30 min and gave 100% monomer conversion upon quenching in 7 h ($M_n = 2.43 \times 10^4$, PDI = 1.48, $I^* = 95\%$, run 4). The C_s -ligated complex **1** is more active than $\text{Cp}_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$ but less active than $\text{rac-C}_2\text{H}_4(\text{Ind})_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$, achieving 88% monomer conversion at ambient temperature after 19 h (run 5 vs runs 1 and 3). This activity trend in ϵ -CL polymerization is different from that observed for the L-LA polymerization, where the C_s -ligated complex **1** is at least 100 times more reactive than the other two (vide supra). It is important to note here that all three zirconocene *bis(ester enolate)* complexes employed for poly-

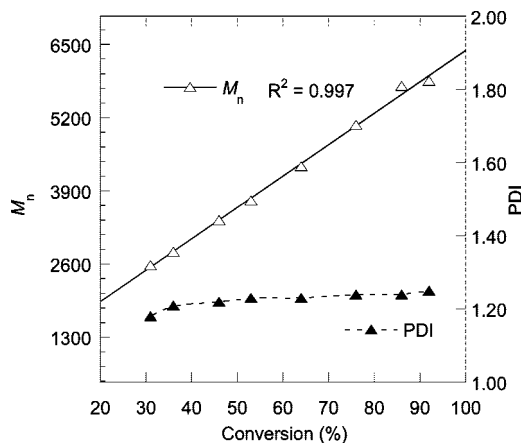


Figure 1. Plot of M_n and PDI of PLA by **1** vs monomer conversion. Conditions: $[MMA]_0/[1]_0 = 50$, toluene, 80 °C.

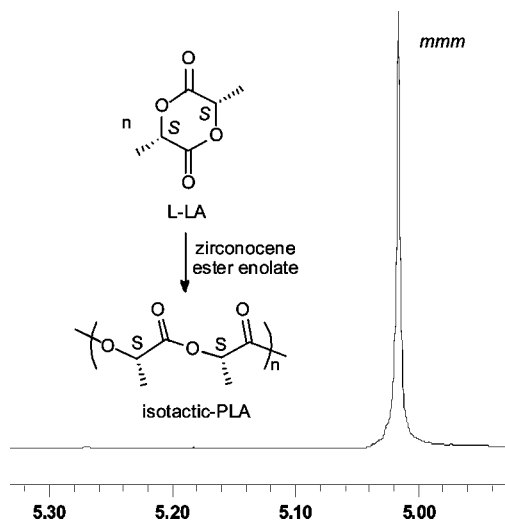


Figure 2. Homonuclear decoupled ^1H NMR of the methine region of isotactic-PLA produced by **1**.

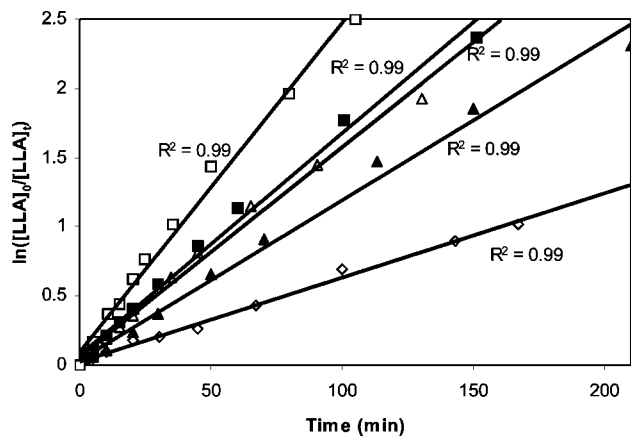


Figure 3. Semilogarithmic plots of $\ln\{[L\text{-}LA]_0/[L\text{-}LA]_t\}$ vs time for the polymerization of L-LA by **1** in toluene at 80 °C. Conditions: $[L\text{-}LA]_0 = 0.90$ M, $[1]_0 = 18.0$ mM ($\square$), 12.9 mM ($\blacksquare$), 9.02 mM ($\triangle$), 6.68 mM ($\blacktriangle$), 4.51 mM ($\diamond$).

merizations here are stable (with no evidence for decomposition by NMR) in toluene solutions at 80 °C up to 20 h.

Synthesis and Structure of the Non-Zirconocene Bis(isopropoxide) 2. Comparative studies of metallocene vs non-metallocene zirconium bis(ester enolate) complexes in the

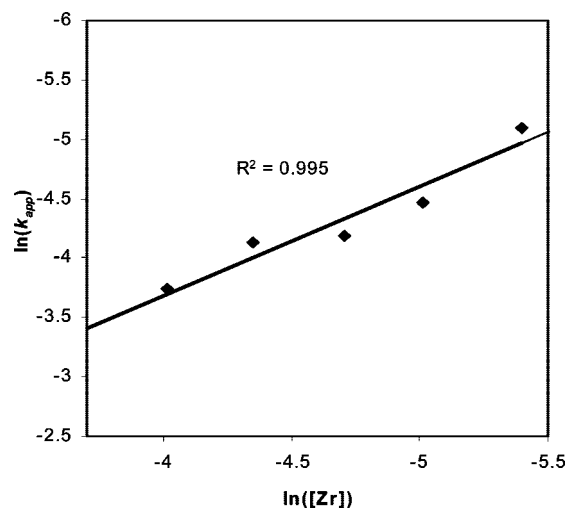


Figure 4. Plot of $\ln k_{\text{app}}$ vs $\ln [Zr]$ for the L-LA polymerization by complex **1** in toluene at 80 °C.

polymerization of L-LA and ϵ -CL require the synthesis of non-zirconocene bis(ester enolate) complexes. Attempts to synthesize an ester enolate complex of zirconium supported by the diamido ligand BAIP³³ (point 2, vide supra) involved reactions of zirconium precursors, including $(\text{BAIP})\text{ZrCl}_2$, $(\text{BAIP})\text{Zr}(\text{OTf})_2$, and $(\text{BAIP})\text{ZrMe}(\text{OTf})$, with $\text{Me}_2\text{C}=\text{C}(\text{O}^i\text{Pr})\text{OLi}$, all of which led to either decomposition of the starting reagents or formation of unidentifiable product mixtures. Interestingly, treatment of $(\text{BAIP})\text{Zr}(\text{NMe}_2)_2$ with isopropyl isobutyrate (IPIB) at ambient temperature led to a facile reaction, affording a single, crystalline product in quantitative yield. The spectroscopic data (see the Experimental Section) indicate that the product is a zirconium bis(isopropoxy) complex, $(\text{BAIP})\text{Zr}(\text{O}^i\text{Pr})_2[\text{O}=\text{C}(\text{NMe}_2)\text{CHMe}_2]$ (**2**; Scheme 3). Two possible paths leading to the formation of **2** are depicted in Scheme 3. Path **A** follows a classic mechanism of ester nucleophilic substitution catalyzed by the Lewis acidic Zr center, while path **B** proceeds with a plausible aminolysis which leads to an unstable bis(ester enolate) intermediate, followed by its decomposition involving isopropoxide abstraction by the electron-deficient zirconium center, with concomitant elimination of a ketene which is subsequently trapped by the amine eliminated in the prior aminolysis step, forming 2 equiv of *N,N*-dimethyl isobutyramide (IBA, 1 equiv is free and subsequently removed during workup, while the other 1 equiv is coordinated to Zr). As all experiments intended to detect the bis(enolate) and other transient species associated with path **B** even at low temperatures or by using bulky *tert*-butyl isobutyrate and the more stable amide enolate precursor IBA did not yield any positive evidence, we concluded that the reaction proceeds most likely via path **A**.

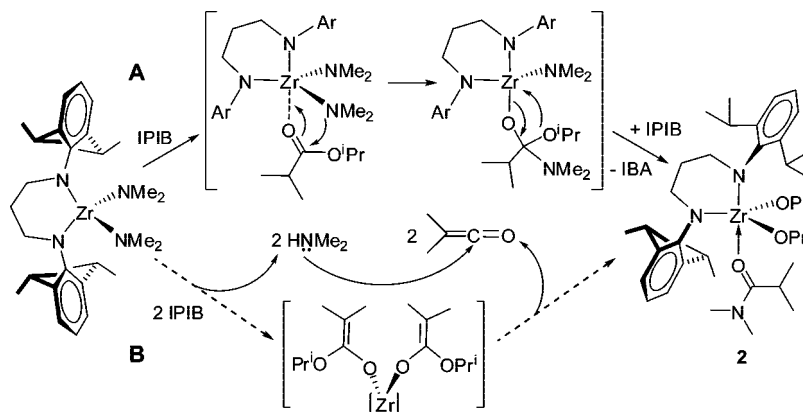
The single-crystal structure of $(\text{BAIP})\text{Zr}(\text{O}^i\text{Pr})_2[\text{O}=\text{C}(\text{NMe}_2)\text{CHMe}_2]$ (**2**) is shown in Figure 5. This complex features a five-coordinate zirconium center in a distorted-trigonal-bipyramidal geometry, with one amido nitrogen and the isobutyramide oxygen atoms occupying approximately axial positions ($\text{N}(1)\text{-Zr-O}(3) = 175.45(7)^\circ$) and the other amido nitrogen and two isopropoxy oxygen atoms occupying approximately equatorial positions (the sum of the angles around the Zr in a trigonal arrangement for the three equatorial ligands is 358.60°). The two $\text{Zr-N}(\text{amido})$ bond lengths are identical ($\text{Zr-N}(1) = 2.101(2)$ Å, $\text{Zr-N}(2) = 2.102(2)$ Å) and are the same as those found in a related five-coordinate chelating diamido zirconium dimethyl complex.⁴¹ On the other hand, the dative Zr-O bond ($\text{Zr-O}(3) = 2.273(2)$ Å) is considerably

Table 2. Selected Results of ϵ -CL Polymerization by Zirconocene Bis(ester enolate) Complexes^a

run no.	cat. (ligand)	$[\epsilon\text{-CL}]/[\text{Zr}]$	temp (°C)	time (h)	conversn (%)	$10^4 M_n$ (g/mol)	PDI (M_w/M_n)	I^* (%)
1	Cp ₂	100	25	8	0			
2	Cp ₂	200	80	8	89	2.26	1.48	91
3	<i>rac</i> -EBI	100	25	9	98			
4	<i>rac</i> -EBI	200	80	7	100	2.43	1.48	95
5	Ph ₂ C(Cp)(Flu)	200	25	19	88	1.64	1.67	122

^a Carried out in 5 mL of toluene at the indicated temperatures. See the footnotes in Table 1 for definitions of the abbreviations.

Scheme 3



longer than the other two covalent Zr–O bonds (Zr–O(1) = 1.945(2) Å, Zr–O(2) = 1.971(2) Å) in **2**. The sums of the angles around the N(1), N(2), and N(3) nitrogens are 359.8, 360.0, and 360.0°, respectively, for the sp²-hybridized, trigonal-planar nitrogen centers.

Polymerization of L-LA and ϵ -CL by the Non-Zirconocene Bis(alkoxy) Complex **2.** Complex **2** exhibits negligible activity for L-LA polymerization in toluene at 25 °C; however, at 80 °C with a [L-LA]/[Zr] ratio of 200, 76% monomer conversion was achieved in 6 h, producing isotactic PLA (no epimerization)

with $M_n = 2.09 \times 10^4$ and PDI = 1.35; the calculated I^* is 105%, suggesting only one of two isopropoxy groups was used to initiate the polymerization. The comparable zirconium tetraisopropoxy complex [Zr(OⁱPr)₄(ⁱPrOH)]₂ (**3**) is also quite active for L-LA polymerization, even at 25 °C, achieving 95% monomer conversion in 4 h with a [L-LA]/[Zr] ratio of 200. However, the resulting PLA exhibits a *bimodal* MWD and an initiator efficiency of greater than 250%, indicative of the multisite nature of complex **3**. These results highlight the importance of supporting ligands around the metal center for rendering its single-site nature in this polymerization catalysis.

Polymerization of ϵ -CL by **2** proceeds rapidly in toluene at 25 °C in an $[\epsilon\text{-CL}]_0/[\mathbf{2}]_0$ ratio of 200, which showed first-order kinetics with respect to monomer concentration (Figure 6) and achieved quantitative monomer conversion in 2 h. All polymers produced at various monomer conversions exhibit *unimodal* and

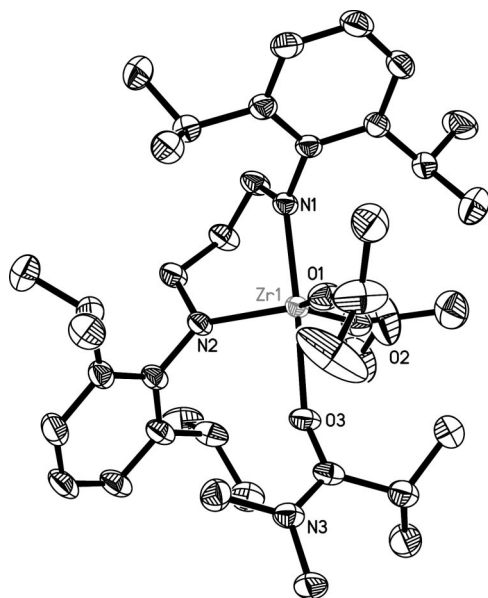


Figure 5. Molecular structure of (BAIP)Zr(OⁱPr)₂[O=C(NMe₂)CHMe₂] (**2**). Selected bond lengths (Å) and angles (deg): Zr–N(1) = 2.101(2), Zr–N(2) = 2.102(2), Zr–O(1) = 1.945(2), Zr–O(2) = 1.971(2), Zr–O(3) = 2.273(2); N(1)–Zr–O(3) = 175.45(7), N(1)–Zr–N(2) = 90.66(7), O(1)–Zr–O(2) = 125.42(8), O(2)–Zr–O(3) = 87.24(7), N(1)–Zr–O(1) = 93.71(7).

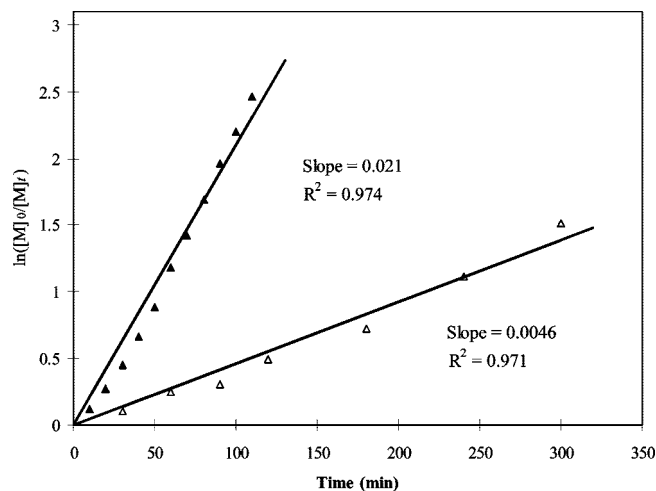
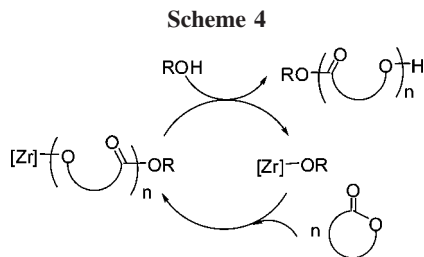


Figure 6. First-order plots of $\ln([M]_0/[M]_t)$ ($M = \epsilon\text{-CL}$) vs time for the polymerization of $\epsilon\text{-CL}$ by **2** in 10 mL of solvent at 25 °C. Conditions: $[\epsilon\text{-CL}]_0 = 0.450$ M, $[\mathbf{2}]_0 = 2.25$ mM, with a $[\epsilon\text{-CL}]_0/[\mathbf{2}]_0$ ratio of 200, in toluene ($\blacktriangle$) and CH₂Cl₂ ($\triangle$).



narrow MWDs in the range of PDI = 1.05–1.30, indicative of the single-site nature of this catalyst in ϵ -CL polymerization. Unexpectedly, the same polymerization in the polar, noncoordinating solvent CH_2Cl_2 is approximately 4.5 times slower than that in toluene. As complex **2** is stable in CH_2Cl_2 (no spectroscopic changes observed for a CD_2Cl_2 solution of **2** at room temperature for at least 3 days), the reduced polymerization rate in CH_2Cl_2 may suggest that this polar solvent stabilizes the ground-state structure more than the transition-state structure associated with this ring-opening polymerization reaction.

The comparative zirconium isopropoxy complex **3** exhibits much lower activity than complex **2** for ϵ -CL polymerization in toluene at 25 °C, achieving 100% monomer conversion only after 24 h (vs 2 h by complex **2**) with a $[\epsilon\text{-CL}]/[\text{Zr}]$ ratio of 200. More important, the resulting PCL by **3** shows a *trimodal* MWD, and the polymerization gave an initiator efficiency I^* of greater than 450%, again indicative of the multisite nature of complex **3**.

Chain Transfer Polymerization Catalyzed by Zirconocene Complex 1 and Non-Zirconocene Complex 2. To render a catalytic production of polymer chains in the present coordination–anionic polymerization catalyzed by zirconium complexes, a suitable CTR added externally must effectively cleave the growing polymer chain from the active metal center, and the resulting new species containing the nucleophilic part of the CTR moiety (typically in its deprotonated, anionic form) must efficiently reinitiate the polymerization (Scheme 4). The control experiment with $\text{Cp}_2\text{Zr}(\text{O}^i\text{Pr})_2$, which showed that it exhibits activity for L-LA polymerization in toluene at 80 °C similar to that of $\text{Cp}_2\text{Zr}[\text{OC}(\text{O}^i\text{Pr})=\text{CMe}_2]_2$, suggests that $^i\text{PrOH}$ be a suitable CTR. Accordingly, to ascertain if $^i\text{PrOH}$ is indeed a suitable CTR for promoting efficient chain transfer, we varied the $[^i\text{PrOH}]/[\text{monomer}]$ ratio and examined the changes in polymerization activity and the resulting polymer M_n for the L-LA polymerization by complex **1** and for the ϵ -CL polymerization by complex **2**. Table 3 summarizes the selected results.

Indeed, addition of $^i\text{PrOH}$ effected chain transfer polymerization for both polymerization systems, as evidenced by a gradual decrease in M_n (thus increased initiator efficiency of >100% for the catalytic production of polymer chains) as an increase in the amount of $^i\text{PrOH}$ added (runs 1–7, Table 3).

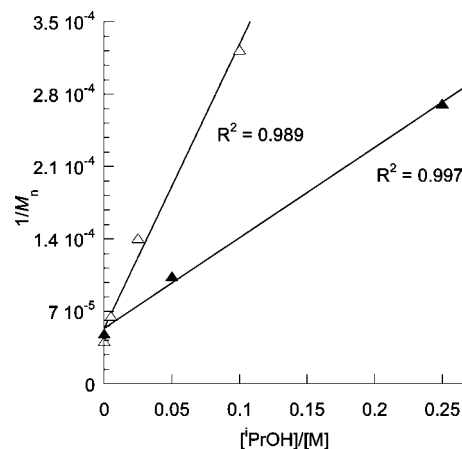


Figure 7. Plots of $1/M_n$ vs $[^i\text{PrOH}]/[\text{M}]$ for chain transfer polymerization of L-LA by complex **1** (▲) and of ϵ -CL by complex **2** (Δ).

However, two major differences exist between the two polymerization processes. First, for the L-LA polymerization by complex **1**, addition of the CTR did not noticeably affect the polymerization rate (runs 1–3), implying that the relative rate constants for propagation (k_p) and reinitiation (k_{ri}) by the $\text{Zr}-\text{O}^i\text{Pr}$ moiety (derived from the $\text{Zr}-\text{PLA}$ chain cleavage by $^i\text{PrOH}$) is about the same ($k_p \approx k_{ri}$); thus, the observed decrease in M_n while the same polymerization rate is more or less maintained upon addition of the CTR can be characterized as a “normal chain transfer” polymerization.⁴² On the other hand, the ϵ -CL polymerization by complex **2** experienced a large decrease in the polymerization rate as the amount of $^i\text{PrOH}$ added increases (runs 4–7). This observation may be indicative of ineffective reinitiation (i.e., $k_{ri} < k_p$), but this appears unlikely, because the $\text{Zr}-\text{O}^i\text{Pr}$ moiety resulting from chain transfer is essentially identical with the $\text{Zr}-\text{OR}$ ($\text{Zr}-\text{PCL}$) propagation species. Alternatively, catalyst deactivation by $^i\text{PrOH}$ is responsible for the drop in the polymerization rate, which was verified by the NMR-scale reaction showing that an excess of $^i\text{PrOH}$ indeed decomposes catalyst **2** to the neutral ligand and $[\text{Zr}(\text{O}^i\text{Pr})_4(^i\text{PrOH})_2]$ (**3**). As complex **3** exhibits substantially lower activity than **2** in ϵ -CL polymerization and also produces multimodal PCL in the presence or absence of $^i\text{PrOH}$, it is a reasonable assumption that the polymer product (all with unimodal MWD) for the current **2** + $^i\text{PrOH}$ chain transfer polymerization system contains no to negligible contribution from **3**, the catalyst **2** decomposition product in the presence of $^i\text{PrOH}$. In comparison, the metallocene system is more robust in the presence of a protic CTR.

The second major difference between these two polymerization systems is in their chain transfer constants. A plot of $1/M_n$ vs the $[^i\text{PrOH}]/[\text{M}]$ ratio gives a linear relationship for

Table 3. Chain Transfer Polymerization Results Using $^i\text{PrOH}$ as a Chain Transfer Reagent^a

run no.	cat. (amt (mM))	monomer (M)	$[^i\text{PrOH}]/[\text{Zr}]$	$[^i\text{PrOH}]/[\text{M}]$	time (h)	conversion ^b (%)	$10^3 M_n^c$ (g/mol)	PDI ^c (M_w/M_n)	I^*d (%)
1	1 (4.51)	L-LA	0	0	5	84	20.5	1.14	118
2	1 (4.51)	L-LA	10	0.05	6	100	9.59	1.30	302
3	1 (4.51)	L-LA	50	0.25	6	100	3.69	1.30	785
4	2 (2.25)	ϵ -CL	0	0	2	100	24.2	1.29	95
5	2 (2.25)	ϵ -CL	1	0.005	5	100	15.2	1.42	151
6	2 (2.25)	ϵ -CL	5	0.025	11	99	7.10	1.11	320
7	2 (2.25)	ϵ -CL	20	0.10	48	94	3.10	1.22	694

^a L-LA polymerizations were carried out in 5 mL of toluene at 80 °C, and ϵ -CL polymerizations were carried out in 10 mL of toluene at 25 °C; $[\text{M}]/[\text{Zr}] = 200$ for all runs. ^b Monomer conversion determined by ^1H NMR. ^c M_n and PDI determined by GPC relative to PMMA standards. ^d Initiator efficiency (I^*) as defined in Table 1.

both systems (Figure 7), the slope of which corresponds to the chain transfer constant (C_{tr}): that is, the ratio of rate constants of chain transfer to propagation, $C_{tr} = k_{tr}/k_p$.⁴² Accordingly, C_{tr} ($\times 10^4$) values for the L-LA polymerization by complex **1** and the ϵ -CL polymerization by complex **2** are estimated to be 8.74 and 27.4, respectively. These results indicate that chain transfer processes are much more efficient for the ϵ -CL polymerization by complex **2** than for the L-LA polymerization by complex **1**, while the ratio k_p/k_{tr} is much smaller for the former system (3.65×10^2) than for the latter (1.14×10^3).

Conclusions

Neutral C_{2v} -, C_2 -, and C_s -ligated zirconocene bis(ester enolate) complexes effectively polymerize ϵ -CL in toluene at 80 °C with high initiator efficiencies based on one chain per metal initiation. In the polymerization of L-LA, there are large activity differences among these three types of zirconocenes, with the C_s -ligated complex **1** exhibiting markedly higher activity (greater than an order of magnitude) than the C_{2v} - and C_2 -ligated complexes. Additionally, the L-LA polymerization by **1** is well-behaved and characteristic of living. The PLA produced is 100% isotactic, and there is no sign of epimerization. This polymerization follows first-order kinetics with respect to both monomer and catalyst concentrations. Overall, all evidence obtained from the current study points to a conclusion that the polymerization of L-LA by the zirconocene bis(ester enolate) **1** is well-behaved and proceeds with a monometallic, coordination–anionic propagation mechanism.

Attempts to synthesize non-zirconocene bis(ester enolate) complexes for comparative polymerization studies led to isolation of the structurally characterized zirconium bis(isopropoxy) complex **2** in quantitative yield from the reaction of the zirconium bis(amido) precursor with isopropyl isobutyrate. This route utilizes a Zr-catalyzed ester nucleophilic substitution

reaction and is unique in terms of its synthetic utility and high-yielding synthesis. The bis(isopropoxy) complex **2** supported by the chelating bulky aryl amido ligand behaves as a single-site catalyst for polymerizations of both ϵ -CL and L-LA, whereas the comparative homoleptic zirconium tetrakisopropoxy complex **3** shows multisite behavior for the same polymerizations.

Both the zirconocene **1** and non-zirconocene **2** catalyze efficient chain transfer polymerization in the presence of i PrOH as CTR for the catalytic production of PLA and PCL, respectively, but they do exhibit two major differences. First, while complex **1** catalyzes the “normal chain transfer” L-LA polymerization without loss in the polymerization rate upon increasing [CTR], complex **2** experiences a large decrease in the ϵ -CL polymerization rate as [CTR] is increased, reflecting a certain instability of the non-Cp-based ligand present in complex **2** under the protic reaction conditions. Second, the chain transfer process is much more efficient for the ϵ -CL polymerization by **2** than for the L-LA polymerization by **1**, as reflected by their estimated chain transfer constants C_{tr} ($\times 10^4$) of 27.4 and 8.74, respectively.

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Supporting Information Available: A CIF file giving crystallographic data for **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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