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Comparative study of ring-opening polymerization of L-lactide and ε-caprolactone using zirconium hexadentate bis(aminophenolate) complexes as catalysts†

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A series of zirconium bis(aminophenolate) complexes as catalysts for the ring opening polymerization of L-lactide (LA) and ε-caprolactone (CL) were investigated. Ligands bearing various chelating groups have a profound influence on the catalysis results. Among them, the thiophen-2-yl methyl group showed the greatest activity while the pyridine-2-yl methyl group showed the worst performance with regard to the rate of CL polymerization. However, the trend was reversed for the rate of LA polymerization. The kinetic results indicated a first-order dependency on [CL] and [LA]. However, the order of the catalyst concentration was different. Polymerization proceeded with second-order dependence on [$L^{OMe}Zr(OBn)_2$] for CL but with first-order dependence on [$L^{OMe}Zr(OBn)_2$] for LA.

Introduction

Poly(lactide) (PLA), poly(ε-caprolactone) (PCL), and their copolymers are applied in a wide range of fields[1] due to their biodegradability, biocompatibility, and permeability. The most common method used for the synthesis of PLA and PCL is ring-opening polymerization (ROP). Most metal complexes[2] have been used as catalysts for the ROP of cycloesters. However, the use of catalysts of low cytotoxicity is essential for materials with medicinal applications. Zirconium complexes are also commonly used as catalysts for ROP due to the inexpensive precursors and high oxidation state associated with polyanionic ligands. Fig. 1 presents a series of multi-dentate ligands of zirconium complexes used for ROP of cycloesters.

Among these, salen,[3g] salan[3c,d] and salalen[3h,i] type (*i.e.* bis-(iminophenol)) ligands are the most commonly used due to the ease of diverse modification on the moiety between the two nitrogen atoms.[4] The previous studies usually involved up to three or four dentate ligands around the metal. Never has hexadentate ligand been applied to the synthesis of zirconium complex.

In 2010 and 2012, Sun[3e] and Okuda[3k] reported zirconium complexes with an eight-coordinate metal center that included two tetradentate ligands and two OSSO bis(phenolate) ligands, respectively, which demonstrated outstanding polymerization activity for *meso*-lactide. These findings inspired us to design a series $LZr(OR)_2$ complexes bearing hexadentate salan ligands for catalytic studies. ROP catalysis is favored by reducing the bond strength of Zr–OR bond which is usually strong due to the high oxidation state of Zr(IV) ion. Multi-dentate ligands can donate electrons to metal through coordination, thereby weakening the metal–alkoxide bond.[5] On the other hand, however, the pendant atoms on the hexadentate ligands is in direct competition with monomers which may result in a decreased polymerization rate. The difficulty is in identifying suitable pendant atoms that are capable of minimizing the competition with monomers by forming a labile coordination with Zr center. Herein, we report the syntheses of a series of hexadentate salan ligands, their associated kinetic studies, and their applications in ROP catalysis.

Results and discussion

Synthesis and characterization of Zr complexes

Arylaldehydes and ethyldiamine were condensed to produce diimines. Further reduction using $NaBH_4$ followed by reaction with 2,4-di-*tert*-butyl-6-(chloromethyl)phenol offered a series of hexadentate salan ligands. All ligands were reacted with two equivalents of *n*-butyllithium in THF to produce a moderate yield of lithium compounds. These lithium complexes were then reacted with $ZrCl_4$ to form zirconium dichloride

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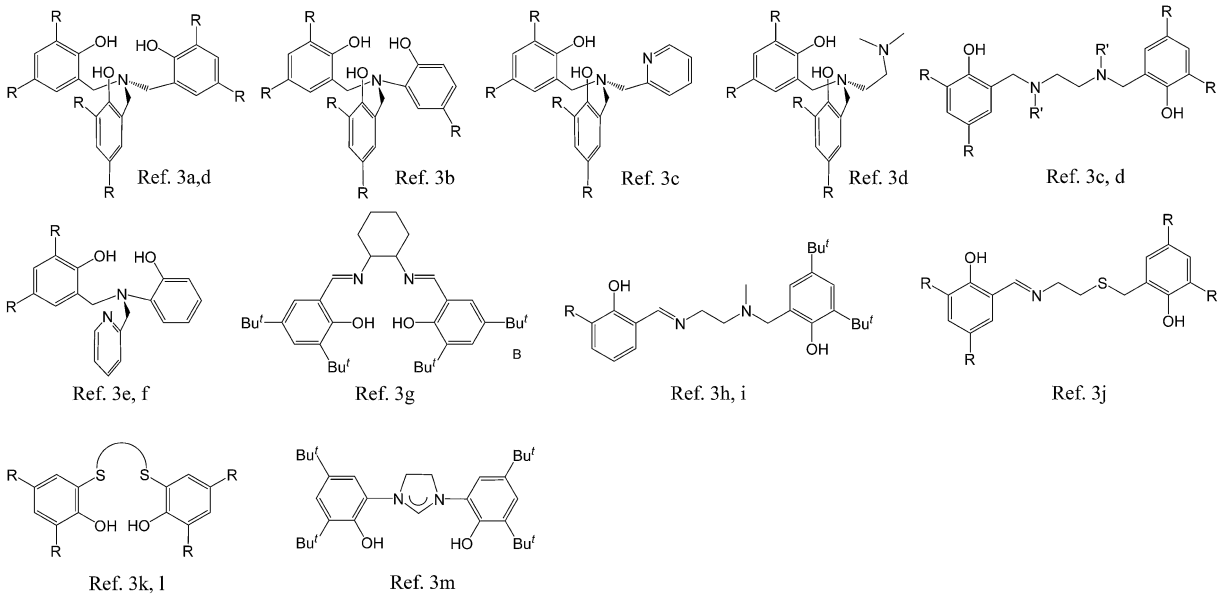

Fig. 1 Multi-dentate ligands applied to the synthesis of zirconium complexes.

complexes. Subsequent reaction with sodium benzyl alkoxide gave zirconium dibenzyl alkoxide complexes (Fig. 2). The structures of the final complexes were confirmed according to their ^{1}H and ^{13}C NMR spectra, elemental analyses, and X-ray crystallographic analyses. The X-ray structure of $\mathbf{L^{Bn}Zr(OBn)_2}$ (Fig. 3) reveals that the zirconium complex is neutral, displaying two *cis* benzyl alkoxide and two *trans* phenolate groups (*α-cis* form). The axial angle of O(1)–Zr–O(1A) is 165.50(8)° and the equatorial angles between N(1)–Zr–N(1A), O(2)–Zr–N(1), and O(2)–Zr–O(2A) are 71.85(8), 91.87(6), and 105.88(9)°, respectively. The distances between the Zr atom and O(1), O(2), and N(1) are 2.0401(13), 1.9379(15), and 2.4684(17) Å, respectively, confirming that the structure is distorted from an ideal octahedral geometry. Moreover, the angles of C(24)–O(2)–Zr was 168.36(15)° with a strong π characteristic between zirconium and oxygen of benzyl alkoxide, which can be attributed to reduced bonding distance between the zirconium and oxygen of benzyl alkoxide. The X-ray structure of $\mathbf{L^{F}Zr(OBn)_2}$ (Fig. 4) and $\mathbf{L^{Th}Zr(OBn)_2}$ (Fig. 5) present a geometry similar to that of $\mathbf{L^{Bn}Zr(OBn)_2}$. In $\mathbf{L^{F}Zr(OBn)_2}$, the axial angles of O(1)–Zr–O(1A) is 165.64(15)° and the equatorial angles for N(1)–Zr–N(1A), O(2)–Zr–N(1), and O(2)–Zr–O(2A) are 72.28(14), 95.88(10), and 106.61(16)°, respectively. The distances between the Zr atom and O(1), O(2), and N(1) are 2.039(2), 1.942(2), and 2.472(3) Å, respectively, confirming that the structure was distorted from an ideal octahedral geometry. The angles of C(24)–O(2)–Zr is 168.8(3)°. In $\mathbf{L^{Th}Zr(OBn)_2}$, the axial angles of O(1)–Zr–O(1A) is 164.69(8)° and the equatorial angles for N(1)–Zr–N(1A), O(2)–Zr–N(1), and O(2)–Zr–O(2A) are 72.41(8), 91.56(6), and 105.84(9)°, respectively. The distances between the Zr atom and O(1), O(2),

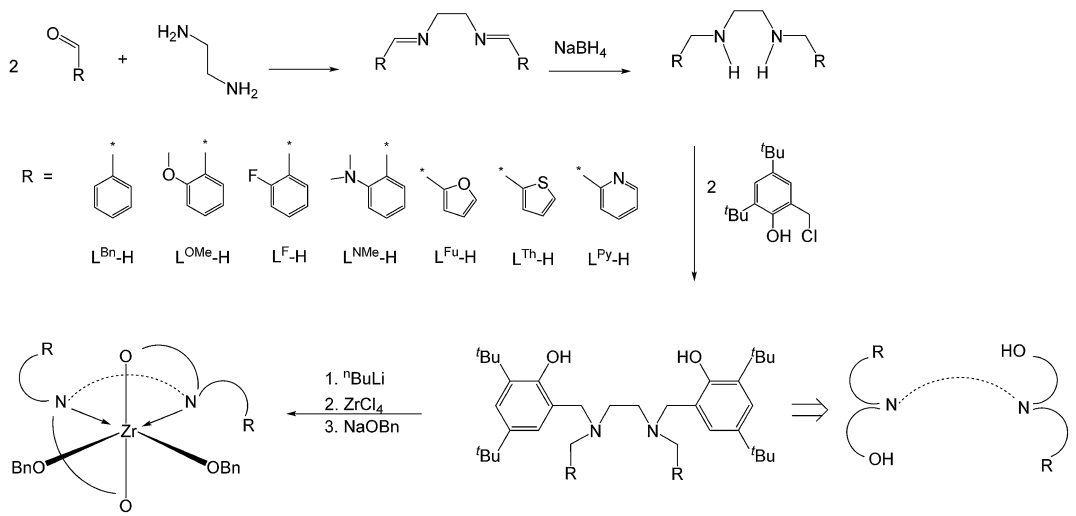

Fig. 2 Synthesis of bis(aminophenol) ligands and their Zr complexes.

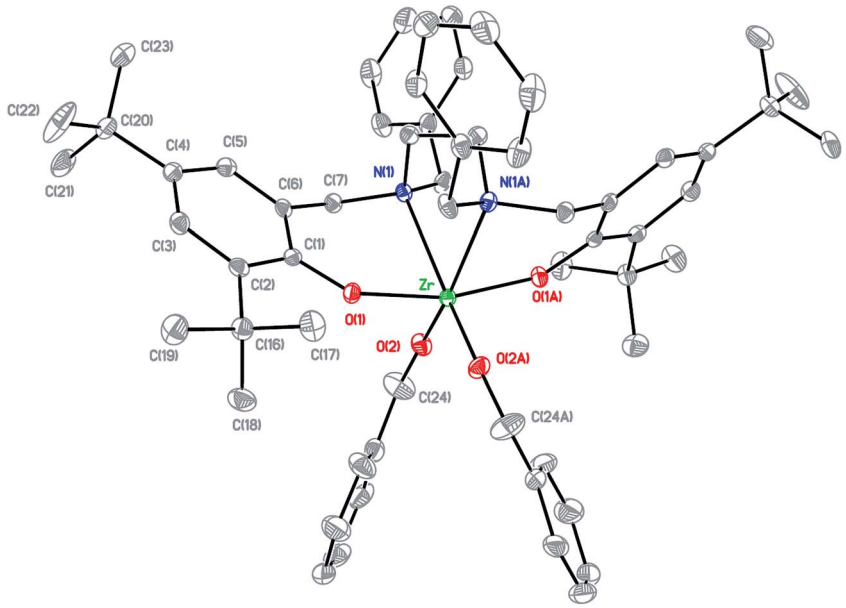

Fig. 3 Molecular structure of complex $L^{Bn}Zr(OBn)_2$ shown with 20% probability ellipsoids. CCDC deposition number: 1019663 (all of the hydrogen atoms were omitted for clarity).

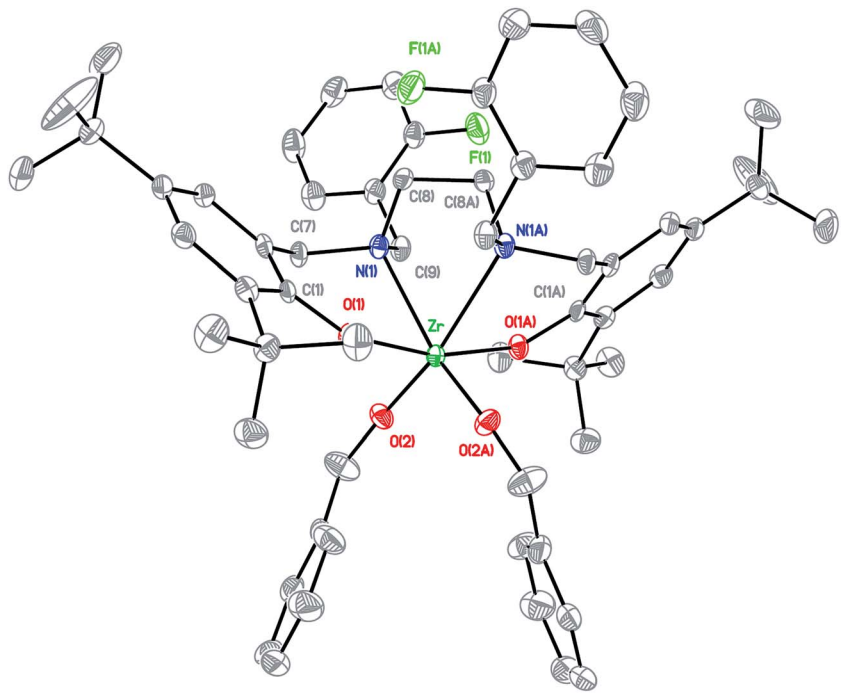

Fig. 4 Molecular structure of complex $L^{F}Zr(OBn)_2$ shown with 20% probability ellipsoids. CCDC deposition number: 1019661 (all of the hydrogen atoms were omitted for clarity).

and N(1) are 2.0408(14), 1.9391(14), and 2.4644(17) Å, respectively. Finally, the angles for C(22)–O(2)–Zr is 167.71(15)°.

Polymerization of ε-caprolactone and L-lactide

We investigated the polymerizations of ε-caprolactone (CL) and L-lactide (LA) using zirconium complexes as initiators in toluene under nitrogen at 100 °C (Table 1). In Table 1, entries 1–7 for CL polymerization ([CL]/[Cat.] = 200), $L^{F}Zr(OBn)_2$, $L^{Th}Zr(OBn)_2$, and $L^{Bn}Zr(OBn)_2$, (entries 1–3) showed greater activity than others and $L^{Py}Zr(OBn)_2$ (entry 7) was least efficient. Their ability of polymer control was efficient with a limited polydispersity index (PDI) (PDI = 1.09–1.21) and anticipated molecular weight when two benzyl alkoxide were used as initiators. As shown in Table 1 (entries 8–14) for LA polymerization ([LA]/[Cat.] = 200), $L^{Fu}Zr(OBn)_2$, $L^{OMe}Zr(OBn)_2$, and $L^{Py}Zr(OBn)_2$ (entries 8–10)

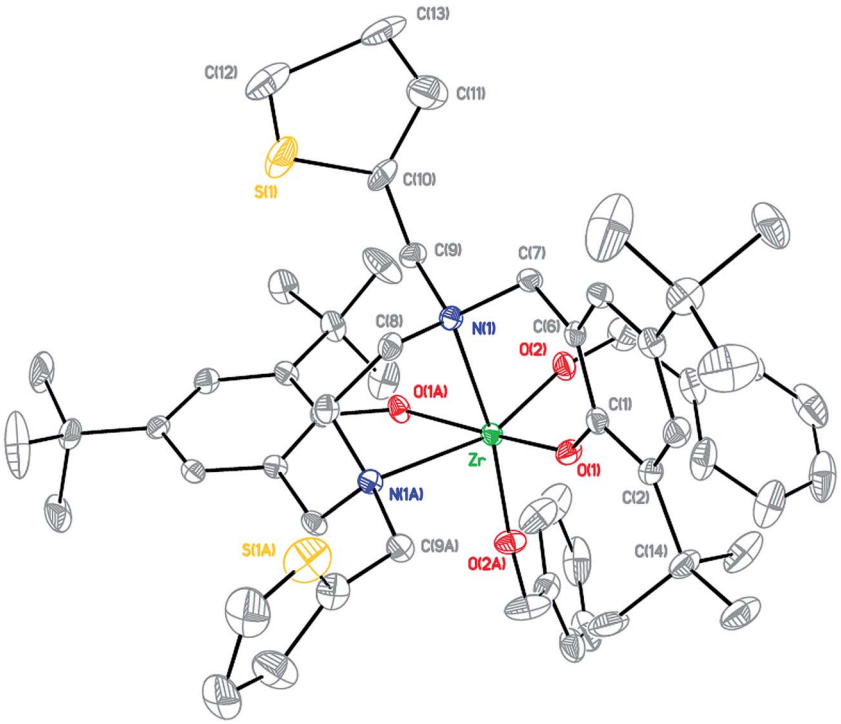

Fig. 5 Molecular structure of complex $L^{Th}Zr(OBn)_2$ shown with 20% probability ellipsoids. CCDC deposition number: 1019662 (all of the hydrogen atoms were omitted for clarity).

Table 1 Polymerization of CL and LA using each of the Zr complexes as an initiator at 100 °C

Entry	Catalyst $\mathbf{LZr(OBn)_2}$	Time (h)	Conv[a]	$M_{n(Cal)}$[b]	$M_{n(NMR)}$[a]	$M_{n(GPC)}$[c]	PDI[c]
1[d]	L^F	4	99%	11 400	11 000	11 300	1.17
2[d]	L^{Th}	4	99%	10 600	11 800	11 200	1.12
3[d]	L^{Fu}	4	99%	11 400	10 900	15 600	1.18
4[d]	L^{Bn}	4	82%	9500	11 200	9300	1.09
5[d]	L^{NMe2}	4	74%	8500	11 200	9100	1.16
6[d]	L^{OMe}	4	54%	6300	10 400	9000	1.21
7[d]	L^{Py}	4	42%	4900	6700	4900	1.12
8[e]	L^{Fu}	48	89%	12 900	12 500	5200	1.42
9[e]	L^{OMe}	48	84%	9700	9600	8000	1.02
10[e]	L^{Py}	48	85%	9800	15 400	7300	1.12
11[e]	L^{NMe2}	48	75%	9600	9800	7500	1.07
12[e]	L^F	48	74%	8500	11 000	12 700	1.03
13[e]	L^{Bn}	48	69%	8000	8300	13 000	1.06
14[e]	L^{Th}	48	53%	7700	8400	10 400	1.03

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of monomer × $[monomer]_0/2[Cat]_0$ × conversion yield + Mw(OBn). [c] Obtained from GPC analysis and calibration based on the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58 for PLA and 0.56 for PCL. [d] Reaction condition: toluene (2 mL), [CL] = 5.0 M, [CL] : [Cat] = 200 : 1. [e] Reaction condition: toluene (2 mL), [LA] = 5.0 M, [LA] : [Cat] = 200 : 1.

showed the greater activity and $\mathbf{L^{Th}Zr(OBn)_2}$ (entry 14) was the least active catalyst. The $M_{n(NMR)}$ of PLA catalyzed using $\mathbf{L^{Fu}Zr(OBn)_2}$, $\mathbf{L^{Py}Zr(OBn)_2}$, and $\mathbf{L^{Bn}Zr(OBn)_2}$ was inconsistent with $M_{n(GPC)}$, perhaps due to the fact that transesterification was initiated by the catalysts for LA polymerization. Moreover, these Zr complexes appeared more active in the polymerization of CL than in the polymerization of LA. This trend is opposite to that of our previous findings related to Ti complexes.[4]

To elucidate the catalytic behavior of these zirconium complexes involved in the polymerization of CL and LA, we conducted kinetic studies to determine the k_{obs} (Table 2, Fig. S1 and S2, and Tables S1 andS2†). In Table 2, the trend of the activity of zirconium complexes with regard to polymerization in $CDCl_3$ are similar to the trends observed in the polymerization activity in Table 1. However, the zirconium complexes used for polymerization in CL and LA presented precisely the opposite results. For example, the order of CL polymerization is

Table 2 Kinetic study of polymerization of ε-caprolactone and L-lactide using each of the Zr complexes as an initiator in a sealed NMR tube in $CDCl_3$

Catalyst **LZr(OBn)$_2$**	$CDCl_3$			
	CL		LA	
Entry	k_{obs}	Ranking	k_{obs}	Ranking
L^{Th}	0.1162 (35)	1	0.0265 (12)	7
L^{F}	0.0989 (67)	2	0.0281 (17)	6
L^{Fu}	0.0916 (73)	3	0.3238 (153)	3
L^{Bn}	0.0662 (18)	4	0.0297 (15)	5
L^{NMe2}	0.0424 (16)	5	0.0337 (15)	4
L^{OMe}	0.0282 (10)	6	0.3264 (85)	2
L^{Py}	0.0202 (3)	7	1.1741 (363)	1

$\mathbf{L^{Th}Zr(OBn)_2}$ > $\mathbf{L^{F}Zr(OBn)_2}$ ≧ $\mathbf{L^{Fu}Zr(OBn)_2}$ > $\mathbf{L^{Bn}Zr(OBn)_2}$ > $\mathbf{L^{NMe2}Zr(OBn)_2}$ > $\mathbf{L^{OMe}Zr(OBn)_2}$ ≧ $\mathbf{L^{Py}Zr(OBn)_2}$, whereas the order of LA polymerization is $\mathbf{L^{Py}Zr(OBn)_2}$ > $\mathbf{L^{OMe}Zr(OBn)_2}$ > $\mathbf{L^{Fu}Zr(OBn)_2}$ > $\mathbf{L^{NMe2}Zr(OBn)_2}$ > $\mathbf{L^{Bn}Zr(OBn)_2}$ > $\mathbf{L^{F}Zr(OBn)_2}$ > $\mathbf{L^{Th}Zr(OBn)_2}$. The differences between CL and LA are that the size of LA exceeds that of CL and the dipole moment of CL exceeds that of LA. Nevertheless it is difficult to explain the results according to these properties of CL and LA.

Kinetic study of the polymerization of CL and LA catalyzed using $\mathbf{L^{OMe}Zr(OBn)_2}$

To rationalize our results related to the catalytic activity of these zirconium complexes in the polymerization of CL and LA, we conducted kinetic studies to establish the reaction order for monomer and catalysts. The experiments were performed using a ratio of $[M]_0/[\mathbf{L^{OMe}Zr(OBn)_2}]$ ($[CL] = 0.2$ M in 5 mL CH_2Cl_2 at room temperature and $[LA] = 1.25$ M in 1 mL $CDCl_3$ at 100 °C) as shown in Tables S5, S6 and Fig. S5–S8.† Preliminary results indicate a first-order dependency on monomer ([CL] or [LA]) (Fig. S5 and S7†). By plotting ln k_{obs} *vs.* ln $[\mathbf{L^{OMe}Zr(OBn)_2}]$, we obtained an order of 2.17 for $[\mathbf{L^{OMe}Zr(OBn)_2}]$, k_p (propagation) values of 0.0015 for CL polymerization (Fig. S6†). By plotting k_{obs} *vs.* $[\mathbf{L^{OMe}Zr(OBn)_2}]$ under the assumption that the order of $[\mathbf{L^{OMe}Zr(OBn)_2}]$ was 1, we obtained k_p values of 1.6632 for LA polymerization (Fig. S6†). The polymerization of CL and LA using $\mathbf{L^{OMe}Zr(OBn)_2}$ demonstrated the following rate law:

$$d[CL]/dt = 0.0015 \times [\mathbf{L^{OMe}Zr(O^{\textit{i}}Pr)_2}]^{2.17}[CL]^1$$

$$d[LA]/dt = 1.6632 \times [\mathbf{L^{OMe}Zr(O^{\textit{i}}Pr)_2}]^1[LA]^1$$

Formulating an appropriate mechanism to explain the polymerization of CL and LA in accordance with the above kinetic data was challenging. It was necessary to rationalize the mechanism on the basis of the results observed during the catalytic activity of zirconium complexes in the polymerization of CL and LA. The order of $[\mathbf{L^{OMe}Zr(OBn)_2}]$ is 2.17 for CL and 1 for LA. Therefore, one possible mechanism underlying CL polymerization would entail dinucleon[8] from $\mathbf{L^{OMe}Zr(OBn)_2}$ aggregation acting as the real active species. In LA polymerization, this would imply the mononuclear form of $\mathbf{L^{OMe}Zr(OBn)_2}$. In addition, CL and LA polymerizations using zirconium complexes as catalysts requires no induction period, unlike the previously reported case with titanium complexes.[4] One reason for this may be that the zirconium complexes with a six-coordinate metal center do not have to transform into other species in order to be coordinated with CL or LA since the maximum coordination number of Zr ion is eight.

Conclusions

This study synthesized a series of zirconium complexes bearing salan ligands to catalyze the polymerization of CL and LA. The polymerization rate of CL and LA showed opposing trends, according to the pendent group. Among the zirconium complexes, the thiophen-2-yl methyl group was most effective in enhancing the polymerization rate of CL, whereas the pyridine-2-ylmethyl group was most effective in polymerization of LA. Kinetic studies indicated a first-order dependency on [CL] and [LA] respectively. Polymerization proceeded with second-order dependence on $[\mathbf{L^{OMe}Zr(OBn)_2}]$ for CL but with first-order dependence on $[\mathbf{L^{OMe}Zr(OBn)_2}]$ for LA. These results revealed that the chelating groups influenced the polymerization activity of zirconium complexes. However, the effect of chelation differ between CL and LA polymerization.

Experimental section

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and treatment of all compounds. Solvents, ε-caprolactone, L-lactide, and deuterated solvents were purified prior to use. 2,4-Di-*tert*-butylphenol, sodium borohydride, formaldehyde (37 wt% sol. in water), triethylamine, thionyl chloride, ethylenediamine anhydrous, benzaldehyde, picolinaldehyde, 2-methoxybenzaldehyde, 2-fluorobenzaldehyde, thiophene-2-carbaldehyde, furan-2-carbaldehyde, titanium(IV) isopropoxide, sodium hydride, deuterated chloroform, L-lactide, and ε-caprolactone were purchased from Acros. Benzyl alcohol was purchased from Alfa. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN-O-RAPID instrument. GPC measurements were performed on a Jasco PU-2080 PLUS HPLC pump system equipped with a differential Jasco RI-2031 PLUS refractive index detector using THF (HPLC grade) as an eluent (flow rate 1.0 mL min^{-1}, at 40 °C). The chromatographic column was JORDI Gel DVB 103 Å, and the calibration curve was made by primary polystyrene standards to calculate $M_{n(GPC)}$. 2,4-Di-*tert*-butyl-6-(chloromethyl)phenol,[6] $\mathbf{L^{Bn}}$-$\mathbf{H_2}$,[4] $\mathbf{L^{OMe}}$-$\mathbf{H_2}$, $\mathbf{L^{F}}$-$\mathbf{H_2}$, $\mathbf{L^{Fu}}$-$\mathbf{H_2}$, $\mathbf{L^{Th}}$-$\mathbf{H_2}$, and 2-(dimethylamino)benzaldehyde[7] were prepared following literature procedures.

Synthesis of *N*,*N*′-bis(2-dimethylaminobenzyl)-*N*,*N*′-bis[(3,5-di-*tert*-butyl-2-hydroxyphenyl)-methylene]-1,2-diaminoethane (L^{NMe2}-H_2)

A mixture of ethylenediamine (6.01 g, 100 mmol) and 2-(dimethylamino)benzaldehyde (24.80 g, 200 mmol) was refluxed for one day in ethanol (150 mL). The reaction solution was cooled down in ice bath and sodium borohydride (7.57 g, 200 mmol) was transferred to the solution slowly. After 1 h, the solution was refluxed again for a day. Volatile materials were removed under vacuum to yield yellow oil. The oil was dissolved in CH_2Cl_2 (200 mL) and the solution was washed with water (2/200 mL). After solvent removal under reduced pressure, white powder was obtained. The white powder was set with 2,4-di-*tert*-butyl-6-(chloromethyl)phenol (53.55 g, 210 mmol) and NEt_3 (28 mL, 200 mmol) in 400 mL ethanol and refluxed for one month. Volatile materials were removed under vacuum to yield yellow oil. The oil was dissolved in CH_2Cl_2 (200 mL) and the solution was washed with water (2/200 mL) and several drops of HCl (37%). The yellow oil was obtained when CH_2Cl_2 was removed and ethanol (250 mL) was added to dissolve the oil. The white powder was obtained and filtered after 10 day at −20 °C. Yield: 48.84 g (64%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.84 (2H, s, ArO*H*), 7.23–6.78 (12H, m, Ar*H*), 3.60 (4H, s, NCH_2PhN$(CH_3)_2$), 3.59 (4H, s, NCH_2Ar), 2.63 (4H, s, NCH_2CH_2N), 2.50 (12H, PhN(C$H_3)_2$), 1.39 (18H, s, ArC(C$H_3)_3$), 1.24 (18H, s, ArC(C$H_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 154.08, 153.58, 140.18, 135.36, 131.77, 130.91, 128.17, 123.50, 123.48, 122.68, 121.41, 119.57 (Ar), 58.98 (N*C*H$_2$PhN$(CH_3)_2$), 53.74 (N*C*H$_2$Ar), 50.32 (N*C*H$_2$*C*H$_2$N), 45.16 (PhN(*C*H$_3)_2$), 34.81 (Ar*C*$(CH_3)_3$), 34.06 (Ar*C*$(CH_3)_3$), 31.70 (ArC(*C*H$_3)_3$), 29.55 (ArC(*C*H$_3)_3$). Elemental analysis ($C_{50}H_{74}N_4O_2$) found: N, 7.55%; C, 78.39%; H, 9.44%. Anal. calcd: N, 7.34%; C, 78.69%; H, 9.77%. ESI-MS(+) *m*/*z* calcd = 763.15. Found: 763.49.

Synthesis of *N*,*N*′-bis(pyridin-2-methylbenzyl)-*N*,*N*′-bis[(3,5-di-*tert*-butyl-2-hydroxyphenyl)-methylene]-1,2-diaminoethane (L^{Py}-H_2)

Synthetic procedures were similar to that of L^{NMe2}-H_2 except pyridine-2-methylbenzaldehyde was used in place of 2-(dimethylamino)benzaldehyde. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 10.46 (2H, s, ArO*H*), 8.50 (2H, d, J = 4.8 Hz, PyrH), 7.59–6.79 (10H, m, Ar*H*, Pyr*H*), 3.70 (8H, s, NCH_2Pyr), 3.59 (4H, s, NCH_2Ar), 2.81 (4H, s, NCH_2CH_2N), 1.39 (18H, s, ArC(C$H_3)_3$), 1.25 (18H, s, ArC(C$H_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 157.47, 153.82, 149.01, 140.53, 136.52, 135.60, 123.92, 123.62, 122.98, 122.26, 121.17 (Ar), 59.43 (N*C*H$_2$Pyr), 59.01 (N*C*H$_2$Ar), 50.47 (N*C*H$_2$*C*H$_2$N), 34.85 (Ar*C*$(CH_3)_3$), 34.09 (Ar*C*$(CH_3)_3$), 31.67 (ArC(*C*H$_3)_3$), 29.56 (ArC(*C*H$_3)_3$). Elemental analysis ($C_{44}H_{62}N_4O_2$) found: N, 3.21%; C, 77.59%; H, 9.29%. Anal. calcd: N, 8.25%; C, 77.83%; H, 9.20%. ESI-MS(+) *m*/*z* calcd = 678.49. Found: 679.31.

Synthesis of $L^{Bn}Zr(OBn)_2$

A mixture of L^{Bn}-H_2 (6.77 g, 10 mmol) and n-butyllithium (8.00 mL, 2.5 M) in THF (40 mL) was stirred for 3 h. Volatile materials were removed under vacuum and then zirconium(IV) chloride (2.29 g 10 mmol) dissolved in THF (40 mL) was added. After stirring for one day, the mixture was reacted with sodium benzyl alkoxide that was synthesized from sodium hydride (0.48 g, 20 mmol) and benzyl alcohol (2.16 g, 20 mmol) for another day. Volatile materials were removed under vacuum again and toluene (20 mL) was added to form a suspension. The sodium and lithium salts were removed by filtration and yellow powder was obtained under vacuum. It was washed with hexane (30 mL) to afford final product as light yellow powder. Yield: 6.17 g (63%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.44–6.01 (24H, m, Ar*H*), 5.29 (4H, s, OCH_2Ph), 4.22 (2H, dd, J = 14.2 Hz, NCH_2Ph), 4.06 (2H, dd, J = 13.4 Hz, NCH_2Ar), 4.22 (2H, dd, J = 14.2 Hz, NCH_2Ph), 3.91 (2H, dd, J = 14.2 Hz, NCH_2Ph), 3.32 (2H, dd, J = 13.4 Hz, NCH_2Ar), 2.70 (2H, dd, J = 9.8 Hz, NCH_2CH_2N), 2.38 (2H, dd, J = 9.8 Hz, NCH_2CH_2N), 1.50 (18H, s, ArC(C$H_3)_3$), 1.26 (18H, s, ArC(C$H_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.04, 143.80, 138.89, 136.59, 132.35, 131.40, 128.17, 127.97, 126.44, 126.34, 126.22, 124.71, 124.05, 123.42 (Ar), 72.25 (OCH_2Ph), 59.13 (NCH_2Ar), 58.33 (NCH_2Ph), 45.93 (NCH_2CH_2N), 35.19 (Ar*C*$(CH_3)_3$), 34.13 (Ar*C*$(CH_3)_3$), 31.79 (ArC(*C*H$_3)_3$), 30.13 (ArC(*C*H$_3)_3$). Elemental analysis ($C_{61}H_{79}N_2O_4Zr$) found: N, 2.87%; C, 73.58%; H, 8.05%. Anal. calcd: N, 2.86%; C, 73.50%; H, 7.81%. Mp: 224 °C.

Synthesis of $L^{OMe}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except L^{OMe}-H_2 was used in place of L^{Bn}-H_2. Yield: 8.84 g (85%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.47–6.62 (22H, m, Ar*H*), 5.34 (4H, s, OCH_2Ph), 4.45 (2H, dd, J = 13.8 Hz, NCH_2PhOMe), 4.27 (2H, dd, J = 13.0 Hz, NCH_2Ar), 3.97 (2H, dd, J = 13.8 Hz, NCH_2PhOMe), 3.39 (2H, dd, J = 13.0 Hz, NCH_2Ar), 3.22 (6H, s, NCH_2PhOCH_3), 3.15 (2H, dd, J = 9.2 Hz, NCH_2CH_2N), 1.96 (2H, dd, J = 9.2 Hz, NCH_2CH_2N), 1.48 (18H, s, ArC(C$H_3)_3$), 1.22 (18H, s, ArC(C$H_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 189.86, 159.36, 157.96, 144.21, 138.34, 136.61, 134.85, 129.72, 127.86, 126.19, 125.98, 124.65, 123.95, 123.65, 120.77, 120.36, 120.25, 111.46 (Ar), 71.96 (OCH_2Ph), 59.35 (NCH_2PhOMe), 55.32 (OCH_3), 51.43 (NCH_2-PhOMe), 45.22 (NCH_2CH_2N), 35.13 (Ar*C*$(CH_3)_3$), 34.08 (Ar*C*$(CH_3)_3$), 31.84 (ArC(*C*H$_3)_3$), 30.10 (ArC(*C*H$_3)_3$). Elemental analysis ($C_{63}H_{83}N_2O_6Zr$) found: N, 2.95%; C, 72.03%; H, 7.80%. Anal. calcd: N, 2.69%; C, 71.57%; H, 7.75%. Mp: 207 °C.

Synthesis of $L^{F}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except L^{F}-H_2 was used in place of L^{Bn}-H_2. Yield: 7.01 g (69%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.43–6.60 (22H, m, Ar*H*), 5.31 (4H, s, OCH_2Ph), 4.31 (2H, dd, J = 10.0 Hz, OCH_2PhF), 4.21 (2H, dd, J = 13.0 Hz, NCH_2Ar), 4.15 (2H, dd, J = 10.0 Hz, NCH_2PhF), 3.22 (2H, dd, J = 13.0 Hz, NCH_2Ar), 2.96 (2H, dd, J = 10.6 Hz, NCH_2CH_2N), 2.24 (2H, dd, J = 10.6 Hz, NCH_2CH_2N), 1.50 (18H, s, ArC(C$H_3)_3$), 1.24 (18H, s, ArC(C$H_3)_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 157.68, 143.79, 138.90, 136.90, 136.45, 134.84, 130.56, 130.39, 127.92, 126.34, 126.16, 124.78, 123.91, 123.15, 118.95, 118.60, 116.90, 115.63 (Ar), 72.21 (OCH_2Ph), 59.27 (NCH_2PhF), 51.20 (NCH_2PhF), 45.73 (NCH_2CH_2N), 35.11 (Ar*C*$(CH_3)_3$), 34.08 (Ar*C*$(CH_3)_3$), 31.73 (ArC(*C*H$_3)_3$), 30.09 (ArC(*C*H$_3)_3$). Elemental

analysis ($C_{61}H_{77}N_2F_2O_4Zr$) found: N, 2.60%; C, 71.13%; H, 7.35%. Anal. calcd: N, 2.76%; C, 70.90%; H, 7.34%. Mp: 218 °C.

Synthesis of $L^{NMe2}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except L^{NMe2}-H_2 was used in place of L^{Bn}-H_2. Yield: 8.74 g (82%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48–6.58 (22H, m, Ar*H*), 5.36 (4H, s, OCH_2Ph), 4.52 (2H, dd, J = 14.0 Hz, NCH_2PhNMe$_2$), 4.22 (2H, dd, J = 12.8 Hz, NCH_2Ar), 3.97 (2H, dd, J = 14.0 Hz, NCH_2-PhNMe$_2$), 3.39 (2H, dd, J = 12.8 Hz, NCH_2Ar), 3.15 (2H, dd, J = 9.2 Hz, NCH_2CH_2N), 1.98 (12H, s, NCH_2PhN(CH_3)$_2$), 1.96 (2H, dd, J = 9.2 Hz, NCH_2CH_2N), 1.48 (18H, s, ArC(CH_3)$_3$), 1.22 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 157.94, 155.74, 144.22, 138.53, 136.40, 135.29, 129.40, 127.87, 127.20, 126.21, 126.07, 126.03, 124.94, 124.24, 123.65, 123.59, 120.93 (Ar, Ph), 71.99 (O*C*H$_2$Ph), 58.95 (N*C*H$_2$ BnN(CH$_3$)$_2$), 52.25 (N*C*H$_2$ Ar), 44.78 (NCH$_2$*C*H$_2$N), 44.46 (BnN(*C*H$_3$)$_2$),35.16 (Ar*C*(CH$_3$)$_3$), 34.07 (Ar*C*(CH$_3$)$_3$), 31.82 (ArC(*C*H$_3$)$_3$), 30.08 (ArC(*C*H$_3$)$_3$). Elemental analysis ($C_{65}H_{89}N_4O_4Zr$) found: N, 3.57%; C, 72.27%; H, 7.84%. Anal. calcd: N, 5.25%; C, 72.07%; H, 8.13%. Mp: 178 °C.

Synthesis of $L^{Py}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except L^{Py}-H_2 was used in place of L^{Bn}-H_2. Yield: 7.27 g (74%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.03 (Pyr*H*), 7.60–6.60 (20H, m, Ar*H*), 5.46 (4H, d, J = 4 Hz, OCH_2Ph), 4.61 (2H, dd, J = 14.8 Hz, NCH_2Py), 4.38 (2H, dd, J = 13.2 Hz, NCH_2Ar), 3.57 (2H, dd, J = 14.8 Hz, NCH_2Py), 3.43 (2H, dd, J = 13.2 Hz, NCH_2Ar), 3.11 (2H, dd, J = 13.2 Hz, NCH_2CH_2N), 2.40 (2H, dd, J = 13.2 Hz, NCH_2CH_2N), 1.29 (18H, s, ArC(CH_3)$_3$), 1.24 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 156.57, 150.54, 145.58, 138.48, 137.10, 136.80, 127.63, 127.60, 126.34, 126.23, 126.13, 125.51, 125.45, 124.74, 123.83, 123.25, 122.43 (Ar, Pyr), 71.18 (O*C*H$_2$Ph), 59.85 (N*C*H$_2$Pyr), 50.29 (N*C*H$_2$Ar), 48.24 (NC*H*$_2$*C*H$_2$N), 34.80 (Ar*C*(CH$_3$)$_3$), 34.02 (Ar*C*(CH$_3$)$_3$), 30.52 (ArC(*C*H$_3$)$_3$), 29.81 (ArC(*C*H$_3$)$_3$). Elemental analysis ($C_{59}H_{77}N_4O_4Zr$) found: 5.60%; C, 69.60%; H, 8.03%. Anal. calcd: N, 5.70%; C, 70.91%; H, 7.59%. Mp: 168 °C.

Synthesis of $L^{Th}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except L^{Th}-H_2 was used in place of L^{Bn}-H_2. Yield: 6.84 g (69%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.36–7.15 (14H, m, Ar*H*), 6.89–6.58 (6H, m, Thio*H*), 5.21 (4H, s, OCH_2Ph), 4.46 (2H, dd, J = 15.8 Hz, NCH_2Th), 4.22 (2H, dd, J = 15.8 Hz, NCH_2Th), 4.03 (2H, dd, J = 13.0 Hz, NCH_2Ar), 3.77 (2H, dd, J = 14.8 Hz, NCH_2CH_2N), 3.55 (2H, dd, J = 13.2 Hz, NCH_2Ar), 2.71 (2H, dd, J = 13.2 Hz, NCH_2CH_2N), 1.50 (18H, s, ArC(CH_3)$_3$), 1.28 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 158.15, 143.51, 139.06, 136.58, 133.09, 130.88, 127.98, 126.96, 126.89, 126.43, 126.29, 124.88, 124.16, 123.18 (Ar), 72.28 (O*C*H$_2$Ph), 58.68 (N*C*H$_2$Th), 52.39 (N*C*H$_2$Ar), 47.08 (NC*H*$_2$*C*H$_2$N), 35.17 (Ar*C*(CH$_3$)$_3$), 34.16 (Ar*C*(CH$_3$)$_3$), 31.81 (ArC(*C*H$_3$)$_3$), 30.11 (ArC(*C*H$_3$)$_3$). Elemental analysis ($C_{57}H_{75}N_2O_4S_2Zr$) found: 2.74%; C, 67.73%; H, 6.95%. Anal. calcd: N, 2.82%; C, 67.77%; H, 7.31%. Mp: 174 °C.

Synthesis of $L^{Fu}Zr(OBn)_2$

Synthetic procedures were similar to that for $L^{Bn}Zr(OBn)_2$ except except L^{Fu}-H_2 was used in place of L^{Bn}-H_2. Yield: 3.45 g (36%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.37–7.14 (14H, m, Ar*H*), 6.70, 6.32, 6.03 (6H, m, Fu*H*), 5.20 (4H, s, OCH_2Ph), 4.26 (2H, dd, J = 15.8 Hz, NCH_2Fu), 4.06 (2H, dd, J = 13.2 Hz, NCH_2Ar), 4.00 (2H, dd, J = 15.8 Hz, NCH_2Fu), 3.45 (2H, dd, J = 13.2 Hz, NCH_2Ar), 2.84 (2H, dd, J = 10.2 Hz, NCH_2CH_2N), 2.45 (2H, dd, J = 10.2 Hz, NCH_2CH_2N), 1.50 (18H, s, ArC(CH_3)$_3$), 1.29 (18H, s, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 157.85, 148.18, 143.60, 143.29, 138.90, 136.52, 127.92, 126.30, 126.17, 124.88, 123.94, 123.15, 112.71, 110.32 (Ar, Ph, Furan), 72.13 (O*C*H$_2$Ph), 59.37 (N*C*H$_2$-Furan), 50.24 (N*C*H$_2$ Ar), 46.81 (NCH$_2$*C*H$_2$N), 35.14 (Ar*C*(CH$_3$)$_3$), 34.13 (Ar*C*(CH$_3$)$_3$), 31.79 (ArC(*C*H$_3$)$_3$), 30.06 (ArC(*C*H$_3$)$_3$). Elemental analysis ($C_{57}H_{75}N_2O_6Zr$) found: 2.76%; C, 69.91%; H, 7.74%. Anal. calcd: N, 2.92%; C, 70.03%; H, 7.56%. Mp: 122 °C.

General procedures for the polymerization of CL

A typical polymerization procedure was exemplified by the synthesis of entry 6 (Table 1) using complex $L^{OMe}Zr(OBn)_2$ as a catalyst. The polymerization conversion was analyzed by ^{1}H NMR spectroscopic studies. Toluene (2.0 mL) was added to a mixture of complex $L^{OMe}Zr(OBn)_2$ (0.05 mmol) and ε-caprolactone (1.14 g, 10 mmol) at 100 °C. After the solution was stirred for 4 h, the reaction was quenched by adding a drop of ethanol. Then the polymer was precipitated as white solid by pouring into *n*-hexane (30.0 mL). The white solid was redissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) added to give white crystalline solid. Yield: 0.62 g (54%).

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