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Stereoselective polymerization of *rac*-lactide catalyzed by zwitterionic calcium complexes†

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A reaction of heteroscorpionated ligands HL^1 and HL^2 (L^1 = $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh$, L^2 = $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh(2\text{-}OMe)$, Pz = pyrazole) with homoleptic calcium amide $Ca[N(SiMe_3)_2]_2(THF)_2$, respectively, afforded novel zwitterionic calcium complexes $L^1CaN(SiMe_3)_2(THF)$ (**1**) and $L^2CaN(SiMe_3)_2$ (**2**) through protolysis. **1** and **2** were characterized by NMR spectroscopy. The chemical shifts of the protons of pyrazole and phosphino phenyl within **1** are similar to those in complex **2**, while the chemical shift of phosphine in complex **2** (28.66 ppm) is a little higher than that in complex **1** (11.43 ppm). The structures of complexes **1** and **2** were determined by X-ray diffraction analysis. Both **1** and **2** adopt a distorted trigonal bipyramidal geometry. L^1 and L^2 chelate to the calcium ion through a κ^3 and κ^4 fashion, respectively. **1** and **2** were assayed towards the ROP of *rac*-lactide. Both of them catalyzed the polymerization in a controlled manner. With the increase of the feeding ratio of the monomer to catalyst, the molecular weights increased linearly. At 25 °C, these two calcium complexes catalyzed the ROP of *rac*-lactide to afford atactic polylactides. Surprisingly, at −75 °C, complex **1** gave a heterotactic sequence enriched polylactide (P_r = 0.84); in contrast, complex **2** produced an isotactic sequence enriched polymer. The reason behind was elucidated.

Introduction

Polylactide (PLA) has a wide range of applications in packaging, agriculture, medicine, pharmaceuticals, and the tissue engineering field due in part to its relatively facile production from renewable agricultural sources, and its biodegradability and biocompatibility.[1] Ring-opening polymerization (ROP) of lactide (LA) is a widely adopted manner to synthesize PLA. LA has three enantiomers L-LA, D-LA and *meso*-LA, thus producing PLA with various stereoisomers, such as poly(L-lactide) (PLLA), and poly(D-lactide) (PDLA).[2] Both PLLA and PDLA have a melting point at 170 °C, but they start to decompose at 200 °C,[3] leading to a narrow melt processing window. An interesting thermal property of PLA is that the melting temperature is raised to 230 °C upon stereo-complex formation of PLLA and PDLA.[4] This stereo-complex formation is an attractive technique to improve its thermal stability. But it has not been widely industrialized because of the low efficiency and high cost of D-LA manufacturing. Isoselective ROP of *rac*-LA (a 1 : 1 mixture of L-LA and D-LA) is considered to be another attractive approach to obtain a PLA stereo-complex. Much effort has been devoted to exploring efficient catalysts. Aluminum complexes ligated by salen ligands and their derivatives show impressive degrees of isoselective control, but suffer from low activities (taking days to reach completion) even at elevated temperatures (70–110 °C) as well as they need high initiator loadings (typically ~1 mol%).[5] Initiators based on other metals, such as Zn,[6] Mg,[7] In,[8] K,[9] group IV metals,[10] and rare-earth metals,[11] have been extensively studied, and some of them have displayed excellent stereo-control in the catalytic ROP of *rac*-LA. Nevertheless, only a few discrete isoselective catalysts with moderate to high activities have emerged recently.[8e,9d,11m,12] Thus, exploring new initiators which integrate excellent isoselectivity with high activity as well as high productivity toward the ROP of *rac*-LA is still a challenge.

Calcium is non-toxic, biocompatible and inexpensive. However, the development of calcium chemistry was impeded by the fact that the heteroleptic complexes Ca–Nu (Nu = nucleophilic group) readily decompose during deleterious

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† Electronic supplementary information (ESI) available: ^1H, ^{31}P, ^{13}C NMR spectra of complexes **1–2**; the GPC traces and DSC curves of the afforded polymers; the crystallographic data and structure refinement details for complexes **1–2**; the optimized structures and the free energy of the O atom of the methoxy group coordinated/dissociated with the central metal. CCDC 2034134 (**2**) and 2034135 (**1**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0py01397h

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Schlenk-type equilibria to generate the poorly reactive and ill-defined homoleptic species. This issue has been preliminarily addressed by employing sterically demanding multi-dentate ligands, such as tris(pyrazolyl)borates,[13] aminotrop(on)iminates,[14] β-diketiminates,[15] bis- or tris-(imidazolin-2-ylidene-1-yl)borate,[16] and phenolate.[17] Well-defined heteroleptic calcium complexes have displayed remarkable catalysis in the ROP of bio-resourced cyclic esters, but except for a report by Panda *et al.*, who reported that bis-phosphinimino-chalcogen amide and aminophosphine borane ligated homoleptic calcium complexes exhibited high iso-selectivity, with P_m values of 0.78–0.87;[18] there are rare examples of calcium complexes being used in the isoselective ROP of *rac*-lactide in the literature.

Herein, we prepared two heteroleptic calcium complexes **1** and **2** *via* a reaction of iminophosphine heteroscorpionate ligands $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh$ (HL^1), $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh(2\text{-}OMe)$ (HL^2) with homoleptic calcium amide, $Ca[N(SiMe_3)_2]_2(THF)_2$, respectively (Scheme 1). Their catalytic behaviors towards the ROP of *rac*-LA were assayed. Both of them showed high activity toward the ROP of *rac*-LA, but no stereoselectivity at 25 °C. Surprisingly, at low temperature, complexes **1** and **2** respectively showed heteroselectivity (P_r = 0.84) and isoselectivity (P_m = 0.78). The reason behind was elucidated.

Results and discussion

Synthesis and characterization of calcium complexes 1–2

Recently, our group demonstrated that iminophosphine ligated achiral heteroscorpionate zwitterionic rare-earth metal bisalkyl complexes showed high heteroselectivity (P_r = 0.89) towards the ROP of *rac*-lactide,[19] whilst the corresponding zinc silylamido and benzyloxy complexes exhibited isoselectivity (P_m = 0.85).[20] These diametrical results intrigued us to employ the iminophosphine heteroscorpionate ligand $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh$ (HL^1) to prepare a calcium complex. Treatment of HL^1 with 1.05 equiv. of $Ca[N(SiMe_3)_2]_2(THF)_2$ in THF at 25 °C for 5 h afforded a pale yellow solution. Most of the solvent was removed under vacuum. Then several drops of hexane were added. The mixture was stored at −30 °C to give colorless crystals. The product was firstly analyzed by ^1H NMR spectroscopy. The disappearance of the singlet at 6.84 ppm assigned to the methine proton of HL^1 suggested that the protolysis reaction occurred to generate a carbanion which gave a doublet resonance at 58.83 ppm with J = 154.2 Hz in the ^{13}C NMR spectrum (Fig. S1†).[20] The ratio of the integral intensity of resonance at 5.40 ppm to that at 0.55 ppm, respectively, derivated from the protons of 4-H of pyrazole and methyl protons of the amide groups, is 1 : 9, indicating the formation of the heteroleptic calcium amide **1** (Fig. S2†). The resonances at 3.71 ppm and 1.43 ppm are attributed to the protons of THF, suggesting the coordination of THF which is unwanted. HL^2 $(3,5\text{-}Me_2Pz)_2CHP(Ph)_2NPh(2\text{-}OMe)$ containing an additional dentate was selected. By following a similar procedure to synthesize complex **1**, complex **2** was isolated. As expected, there are no resonances assigned to THF. Compared to that in HL^2 (3.12 ppm), the resonance of methoxyl protons shifts downfield (3.98 ppm), suggesting that the methoxyl group coordinates to the metal center (Fig. S3†). The chemical shifts of the protons of pyrazole and phosphino phenyl are similar to those in complex **1**. While the chemical shift of phosphine in complex **2** (28.66 ppm) (Fig. S4†) is a little higher than that in complex **1** (11.43 ppm) (Fig. S5†).

The molecular structures of complexes **1** and **2** were determined by X-ray diffraction analysis (Fig. 1). The details of the structural and refinement parameters are given in Table S1.† The heteroscorpionate ligand HL^1 facially chelates to the calcium ion through one nitrogen atom of phosphino imine and the two nitrogen atoms of the pyrazole rings in a κ^3 mode. The atoms of C(1), P(1), N(5) and Ca(1) are almost coplanar with the amino phenyl. The THF molecule and amido group locate in the two sides of the above plane. In contrast, in complex **2**, the heteroscorpionate ligand HL^2 chelates to the

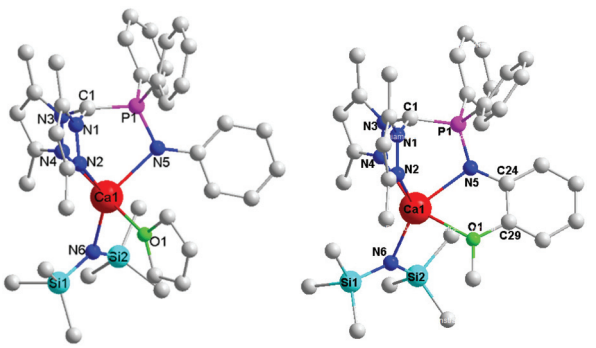
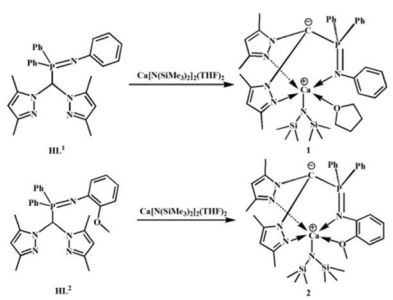


Fig. 1 The crystal structures of complexes **1** (left) and **2** (right). All the hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (deg): complex **1**: Ca(1)–N(2) 2.494, Ca(1)–N(4) 2.498, Ca(1)–N(5) 2.421, Ca(1)–N(6) 2.331, Ca(1)–O(1) 2.438, Ca(1)···C(1) 3.160, N(5)–P(1) 1.635, C(1)–N(1) 1.432, C(1)–N(3) 1.423, C(1)–P(1) 1.726, N(4)–Ca(1)–N(5) 90.19, N(5)–Ca(1)–O(1) 89.73, N(2)–Ca(1)–N(5) 88.33, N(5)–Ca(1)–N(6) 134.53, N(2)–Ca(1)–N(6) 137.07, P(1)–N(5)–Ca(1) 107.14, N(1)–C(1)–N(3) 114.99, N(1)–C(1)–P(1) 117.29, N(3)–C(1)–P(1) 118.05; complex **2**: Ca(1)–N(2) 2.479, Ca(1)–N(4) 2.445, Ca(1)–N(5) 2.391, Ca(1)–N(6) 2.313, Ca(1)–O(1) 2.450, Ca(1)···C(1) 3.230, N(5)–P(1) 1.608, C(1)–N(1) 1.439, C(1)–N(3) 1.425, C(1)–P(1) 1.734, N(2)–Ca(1)–N(4) 83.89, N(2)–Ca(1)–N(5) 84.20, O(1)–Ca(1)–N(5) 65.49, N(5)–Ca(1)–N(4) 88.74, N(5)–Ca(1)–N(6) 142.82, N(2)–Ca(1)–N(6) 131.55, P(1)–N(5)–Ca(1) 110.44, N(1)–C(1)–N(3) 115.10, N(1)–C(1)–P(1) 114.83, N(3)–C(1)–P(1) 116.50.



Scheme 1 Synthesis of heteroscorpionate calcium complexes **1–2**.

calcium ion through N(2), N(4), N(5) and O(1) in a κ^4 fashion. The dihedral angle of the four member ring composed by Ca(1), N(5), C(24) and C(29) is 13.31°, suggesting that the amino phenyl deviates from the plane composed by C(1), P(1), N(5) and Ca(1) owing to the coordination of the methoxyl group. In addition, the rigidity derived from the methoxyl coordination results in the angle of O(1)–Ca(1)–N(5) (65.49°) being much smaller than that in complex **1** (89.73°) and the distance between Ca(1) and C(1) (3.230 Å) being longer than that in complex **1** (3.160 Å). Apparently, the distance between the carbanion atom C(1) and the central calcium ion Ca(1) is beyond the normal range of the Ca–C bond, indicating that the complex is a zwitterion with one negative charge that resides on C(1) and a positive charge on Ca(1).

Ring-opening polymerization of *rac*-LA initiated by calcium complexes 1 and 2

Complex **1** as a single-component catalyst was initially assayed towards the ROP of *rac*-lactide at 25 °C. At a feeding ratio of $[LA]_0:[Ca]_0 = 200:1$, the monomer conversion reached 89% within 1 min (Table 1, entry 1). The molecular weight of the afforded polymer is 3.10×10^4, a little higher than the theory value, and the molecular weight distribution is 1.5. According to the homonuclear decoupled ^{1}H NMR spectrum, the P_r value is 0.40, suggesting the formation of atactic PLA. Doubling the monomer feeding but keeping the monomer concentration as a constant, 97% conversion of the monomer was achieved within 5 min (Table 1, entry 2). The molecular weight of the corresponding polymer is 5.93×10^4, nearly twice higher than that of the former one, while the molecular weight distribution is still relatively narrow. A further increase in the feeding of *rac*-LA is necessary for achieving high conversion to prolong the polymerization time (Table 1, entries 3–5). The molecular weights of the afforded polymers increase linearly with the feeding ratio, suggesting that the polymerization proceeds in a controlled manner.[21] Noteworthy is that the heteroselectivity slightly increases. This might be attributed to the decreasing polymerization rate. To confirm this hypothesis, the polymerization was carried out at 0 °C (Table 1, entry 6). The P_r value of the afforded polymer is 45%, 5% higher than that afforded at 25 °C. This inspired us to further lower the polymerization temperature. With the temperature decreasing from −20 °C to −75 °C, the P_r value increases from 0.56 to 0.84 (Table 1, entries 7–9). The molecular weights of polymers afforded at various temperatures are close to their corresponding theory values. Complex **1** was one of few calcium complexes that exhibited high hetero-selectivity.[13]

The catalytic behavior of complex **2** was also examined at various feeding ratios of monomer to catalyst and polymerization temperatures. The results are summarized in Table 2.

Table 1 ROP of *rac*-LA catalyzed by calcium complex **1**[a]

Entry	$[LA]_0/[\mathbf{1}]_0$	T_p (°C)	T (min)	Conv.[b] (%)	$M_{n,calcd}$ (10^4)[c]	$M_{n,exp}$ (10^4)[d]	M_w/M_n[d]	P_r[e]
1	200/1	25	1	89	2.56	3.10	1.5	0.40
2	400/1	25	5	97	5.59	5.93	1.4	0.42
3	800/1	25	5	63	7.26	6.32	1.6	0.43
4	800/1	25	20	96	11.07	9.17	1.6	0.43
5	1600/1	25	60	96	22.14	16.20	1.5	0.45
6	200/1	0	8	89	2.56	2.81	1.5	0.45
7	200/1	−20	20	83	2.36	2.62	1.4	0.56
8	200/1	−40	120	98	2.82	3.80	1.6	0.67
9	200/1	−75	540	79	2.28	2.89	1.4	0.84

[a] Conditions: **1**: 10 μmol, $[LA]_0$ = 0.8 M, solvent: THF. [b] Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd} = [LA]_0/[Cat]_0 \times 144.13 \times$ conv. (%). [d] Determined by GPC in THF at 40 °C against the polystyrene standard, M_n using a correcting factor for polylactides (0.58).[22] [e] Determined from the relative intensity of the tetrad signals of the methine region in the homonuclear decoupled ^{1}H NMR spectra. $P_r = 2I_1/(I_2 + I_1)$, while $I_1 = \delta$ 5.20–5.23 ppm (rmr, rmm) and $I_2 = \delta$ 5.13–5.20 ppm (mmr, mmm, mrm).[23]

Table 2 ROP of *rac*-LA initiated by calcium complex **2**[a]

Entry	$[LA]_0/[\mathbf{2}]_0$	T_p (°C)	T (min)	Conv.[b] (%)	$M_{n,calcd}$ (10^4)[c]	$M_{n,exp}$ (10^4)[d]	M_w/M_n[d]	P_m[e]
1	200/1	25	2	77	2.22	1.35	2.2	0.56
2	400/1	25	5	97	5.59	5.58	1.3	0.55
3	1200/1	25	40	97	16.78	13.23	1.6	0.54
4	1600/1	25	60	96	22.14	18.15	1.6	0.55
5	200/1	0	8	98	2.82	1.76	2.1	0.58
6	200/1	−20	20	88	2.54	1.75	2.0	0.65
7	200/1	−40	120	86	2.48	2.09	1.8	0.72
8	200/1	−75	540	62	1.79	1.69	1.8	0.78

[a] Conditions: **2**: 10 μmol, $[LA]_0$ = 0.8 M, solvent: THF. [b] Determined by ^{1}H NMR spectroscopy. [c] $M_{n,calcd} = [LA]_0/[Cat]_0 \times 144.13 \times$ conv. (%). [d] Determined by GPC in THF at 40 °C against the polystyrene standard, M_n using a correcting factor for polylactides (0.58).[22] [e] Determined from the relative intensity of the tetrad signals of the methine region in the homonuclear decoupled ^{1}H NMR spectra. $P_m = (I_2 - I_1)/(I_2 + I_1)$, while $I_1 = \delta$ 5.20–5.23 ppm (rmr, rmm) and $I_2 = \delta$ 5.13–5.20 ppm (mmr, mmm, mrm).[23]

With the increase of the feeding ratio, the molecular weights of the afforded polymers increase linearly, and the molecular weight distributions are relatively narrow (Table 2, entries 1–4), indicating that **2** also catalyzed the ROP of *rac*-lactide in a controlled manner. At 25 °C, **2** catalyzed the ROP of *rac*-lactide to generate atactic polylactide with a P_m value of *ca.* 0.55. The polymerization was carried out at 0 °C to produce polylactide with a P_m value of 0.58 (Table 2, entry 5). Surprisingly, on further decreasing the polymerization temperature from −20 °C to −40 °C, the P_m value gradually enhanced from 0.65 to 0.72 (Table 2, entries 6 and 7). The P_m value could reach as high as 0.78 at −75 °C (Table 2, entry 8), however, no melting temperature was detected in the second run through DSC analysis.[24] Although Panda *et al.* recently reported calcium complexes stabilized by the bis-phosphinimino-chalcogen amide ligand and aminophosphine borane ligand[18] catalyzed ROP of *rac*-lactide to give polylactide with the highest P_m value of 0.87, this is the first heteroleptic calcium complex that exhibited high isotactic selectivity. Thus, the reason behind was investigated.

The difference between **1** and **2** is that there is an additional coordination side arm in **2**, leading to the asymmetry of the molecular structure of **2** (Fig. 1), suggesting that the coordination of the side arm should be the key factor to determine the iso-selectivity. As the iso-selectivity was significantly affected by the temperature, complex **2** was investigated *via* the variable-temperature ^{1}H NMR technique (Fig. 2). The protons of the methoxyl group give a sharp singlet at 4.06 ppm at 25 °C. This signal shifts to 4.00 ppm but still remains narrow at 0 °C. From −20 °C to −80 °C, the singlet attributed to methoxyl protons continues to shift upfield, but becomes broad gradually. Meanwhile, the multiplet assigned to the *ortho* protons of diphenylphosphine also becomes wide even flat. In contrast, the resonances derived from amino phenyl protons have no obvious change. This could be explained by the fluxional behavior of complex **2** due to the swing of the amino phenyl group as the Gibbs free energy of methoxyl dissociation is 9 kcal mol^{-1} (Fig. S6 and 7†).[25] With the decrease of the temperature, the rate of the swing becomes slow. **2** could stay at a certain state long enough for the monomers with the same chirality continuous insertion, giving isotactic sequence enriched polylactide.

To further investigate the microstructures of isotactic PLAs obtained in this work, the tetrad signal of a typical PLA sample obtained by **2** was analyzed *via* homonuclear decoupled ^{1}H NMR spectroscopy. As depicted in Fig. 3, the resonance assigned to mmm tetrad splits, suggesting that the length of the isotactic sequence is not long, thus leading to no T_m being detected. The absence of resonance assigned to rmr tetrad excludes the existence of *–RRRRSSRRRR–*/*–SSSSRRSSSS–* sequences derived from single insertion stereo errors. In contrast, the intensity ratio of rmm : mmr : mrm is near 1 : 1 : 1, indicating that the polymer main chain is essentially stereo blocky (*e.g. –RRRRRSSSSSS–*). Hence, it is conceivable that the mechanism of isoselectivity achieved by complex **2** is the chain end control.

To provide further insight into the mechanism, an oligomer M_n = 2900 g mol^{-1} was synthesized and characterized by ^{1}H NMR spectroscopy and matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The MALDI-TOF mass spectrum (Fig. 4) consisted of two series of molecular ion peaks. One series is corresponding to linear PLA with -N(SiMe$_3$)$_2$ as chain ends which were corroborated from the ^{1}H NMR spectrum of the oligomer, where the resonance at 0.16 ppm was assigned to the methyl protons of the N(SiMe$_3$)$_2$ group (Fig. S8†). The other series is corresponding to [LA]$_n$, suggesting the existence of cyclic PLA with no chain ends. According to the literature,[26] the formation of the cyclic polymers might be *via* intramolecular backbiting.

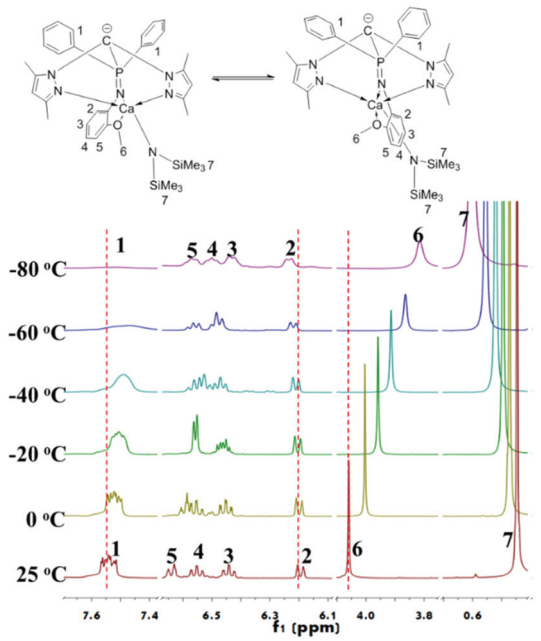


Fig. 2 Variable-temperature ^{1}H-NMR spectra (toluene-d_8, 400 MHz) showing the phenyl and OCH_3 regions of the complex **2**.

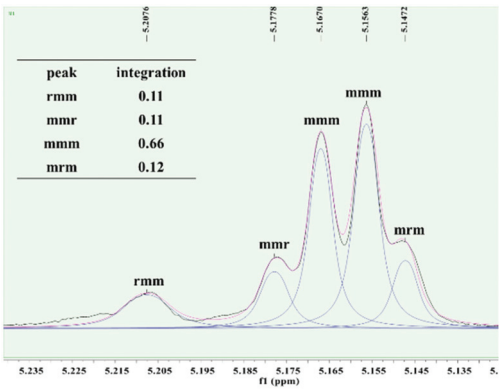


Fig. 3 Methine region of the homonuclear-decoupled ^{1}H NMR spectrum of the resulting PLA (Table 2, entry 8).

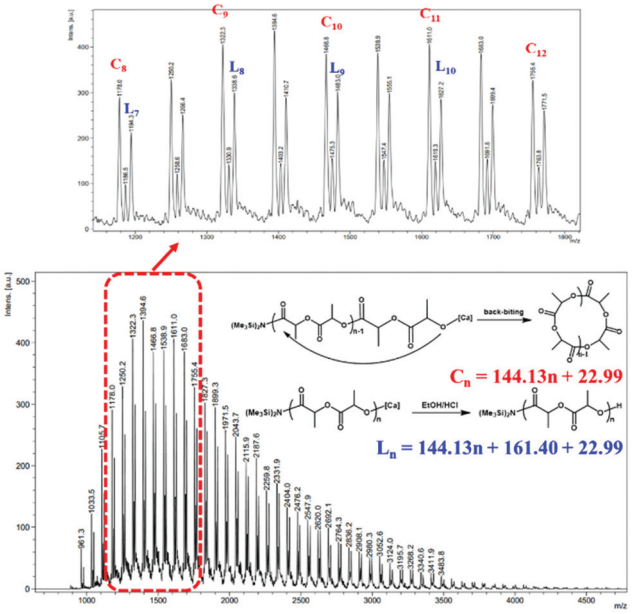


Fig. 4 MALDI-TOF mass spectrum (major population: Na^+) of the PLA sample ($M_{n,GPC}$ = 2900 g mol^{-1}, M_w/M_n = 1.88) prepared with catalyst **1** (C(cyclic) = 144.13n + 22.99, L(linear) = 144.13n + 161.40 + 22.99, where n is the degree of polymerization, M_{LA} = 144.13 g mol^{-1}, $M_{NH(SiMe3)2}$ = 161.40 g mol^{-1}, M_{Na} = 22.99 g mol^{-1}).

Conclusions

Novel zwitterionic calcium complexes **1** and **2** were synthesized *via* treatment of heteroscorpionated iminophosphine ligands HL^1 and HL^2 with calcium amide, respectively. Compared to L^1, L^2 has an additional methoxyl group at the *ortho* position of the imino phenyl ring. Thus, L^1 coordinates to the calcium center in a κ^3 fashion, while L^2 chelates to the metal center in a κ^4 mode. The additional coordination side arm leads to the asymmetry of the structure of **2**. Both **1** and **2** could catalyze the ring-opening polymerization of *rac*-lactide in a controlled manner to give atactic polylactide at 25 °C. While with the temperature decrease of polymerization catalyzed by **1**, the content of the heterotactic sequence with the polylactide increased. At −75 °C, the P_r value reached 0.84. In contrast, the coordination side arm in **2** resulted in iso-selectivity towards the ROP of *rac*-lactide. The iso-selectivity of **2** increased with the decrease of the swing rate of the side arm. At −75 °C, the P_m value reached 0.78. The mechanism of isoselectivity achieved by complex **2** is the chain end control. The existence of a cyclic polymer indicated the occurrence of intramolecular backbiting during the polymerization. These interesting results will shed new light on designing catalyst precursors for specifically selective polymerization.

Experimental section

General procedures

All reactions were carried out under a dry nitrogen atmosphere using Schlenk techniques or in a glovebox filled with dry nitrogen. Hexane was purified using an SPS Braun system. THF was dried by distillation over sodium with benzophenone as the indicator under a nitrogen atmosphere and was stored over freshly cut sodium in a glovebox. Calcium iodide was purchased from Aldrich and stored in a glove box. Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ can be prepared *via* salt metathesis involving treatment of metal halides with alkali metal amides.[27] HL^1 and HL^2 were synthesized according to previous literatures.[19,28] *rac*-LA was recrystallized with dry ethyl acetate three times. Glassware and flasks used in the polymerization were dried in an oven at 115 °C for 14 h and exposed to a vacuum-nitrogen cycle three times. The molecular weights and the molecular weight distributions of the polymers were measured using a TOSOH HLC 8220 GPC instrument at 40 °C with THF as the eluent against the polystyrene standard. Complexes for NMR spectroscopy measurements were prepared in a glovebox by the use of a NMR tube sealed with paraffin film. ^{1}H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC).

X-ray crystallographic study

A crystal for X-ray analysis was obtained as described in the following preparations. The crystal was manipulated in a glovebox. Data collection was performed at −86.5 °C using a Bruker SMART APEX diffractometer with a CCD area detector and graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of the crystal class and unit-cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using the SHELXTL program.

ROP of *rac*-LA

Polymerizations of *rac*-LA were carried out in a 25 mL flask under a nitrogen atmosphere. A typical procedure was described as follows: a solution of complex **1** (10 μmol) in THF (2 mL) was added to a stirred solution of *rac*-LA (4 mmol) in THF (3 mL). The polymerization took place immediately at 25 °C. The system became viscous in 5 min. Then it was quenched by adding several drops of acidified ethanol, and a small sample of the viscous solution was separated for the measurement of conversion by ^{1}H NMR. Then polymers were precipitated with abundant ethanol, collected and dried at 40 °C for 24 h *in vacuo*. The molecular weights and molecular weight distributions of the resulting polymers were determined by GPC. The tacticity of the PLA was calculated according to the methine region homonuclear decoupled ^{1}H NMR spectrum.

Synthesis of the calcium complexes

Synthesis of calcium complex 1. Under a nitrogen atmosphere, a THF (10 mL) solution of ligand HL^1 (0.4796 g, 1 mmol) was added to a stirred solution of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (0.5282 g, 1.05 mmol) in THF (8 mL) at 25 °C.

During the addition, the color of the solution changed gradually from colorless to pale yellow. The reaction mixture was stirred at 25 °C for 5 h and then concentrated approximately to 1 mL and several drops of hexane were added. Colorless crystals deposited at the bottom of the flask from the solution under −30 °C after one day. Yield: 70%. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 7.72–7.67 (m, 4H, Ph–*H*), 7.00 (m, 8H, Ph–*H*), 6.85 (d, 2H, Ph–*H*), 6.60 (t, 1H, Ph–*H*), 5.40 (s, 2H, Pz–*H*), 3.71 (m, 12H, *THF*), 2.29 (s, 6H, Pz–CH_3), 1.84 (s, 6H, Pz–CH_3), 1.43 (m, 12H, *THF*), 0.55 ppm (s, 18H, Si–*Me*$_3$); ^{31}P NMR (C_6D_6, 162 MHz, 25 °C): δ 11.43 ppm; ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 151.88, 151.81, 148.44 (C^3 or C^5), 145.38, 145.31, 132.96, 132.88, 130.72, 130.60, 129.60, 128.67, 128.14, 122.55, 122.37, 117.84 (Ph), 104.79 (C4), 68.36 (THF), 58.83 (d, J = 154.2 Hz, P–*C*), 25.72 (*THF*), 14.49 (Pz–*C*H$_3$), 12.05 (Pz–*C*H$_3$), 6.16 ppm (Si–*C*H$_3$). Anal. calcd for $C_{39}H_{55}CaN_6OPSi_2$: C, 62.44; H, 7.41; N, 11.21. Found: C, 62.38; H, 7.34; N, 11.26.

Synthesis of calcium complex 2. Complex **2** was synthesized using the same method as complex **1** with ligand HL^2. Yield: 73%. ^{1}H NMR (C_6D_6, 400 MHz, 25 °C): δ 7.54–7.49 (m, 4H, Ph–*H*), 6.95 (m, 6H, Ph–*H*), 6.60 (d, 1H, Ph–*H*), 6.53 (t, 1H, Ph–*H*), 6.42 (t, 1H, Ph–*H*), 6.19 (d, 1H, Ph–*H*), 5.41 (s, 2H, Pz–*H*), 3.98 (s, 3H, –OC*H*$_3$), 2.33 (s, 6H, Pz–CC*H*$_3$), 1.86 (s, 6H, Pz–CC*H*$_3$), 0.44 (s, 18H, Si–C*H*$_3$); ^{31}P (C_6D_6, 162 MHz, 25 °C): δ 28.66 ppm; ^{13}C NMR (C_6D_6, 100 MHz, 25 °C): δ 152.26, 152.09, 148.27 (C^3 or C^5), 146.17, 146.10, 141.26, 141.16, 132.78, 132.70, 130.93, 130.07, 129.05, 128.20, 122.61, 117.61, 109.91 (*Ph*), 104.51 (C^4), 60.66 (d, J = 141.1 Hz, P–*C*), 14.58 (Pz–*C*Me$_3$), 12.05 (Pz–*C*Me$_3$), 5.86 ppm (Si–*C*H$_3$). Anal. calcd for $C_{36}H_{50}CaN_6OPSi_2$: C, 60.89; H, 7.11; N, 11.84. Found: C, 60.83; H, 7.09; N, 11.74.

Author contributions

N. Liu and D. Liu performed the experiments. B. Liu and D. Cui conceived and designed the experiments. All authors discussed the results and commented on the manuscript. N. Liu and D. Liu contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

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