

Phenylimino-pyridine-phenolate Zinc Complexes for Polylactide Synthesis and Chemical Recycling to Monomers

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 Electronic Supplementary Information

Abstract Poly(L-lactide) (PLLA) is one of the best candidates as a bio-based plastic material for circular economy because of its biodegradability, sustainability, recyclability, and good thermal and mechanical properties. The industrial production of PLLA is mainly from tin(II) 2-ethylhexanoate [Sn(Oct)₂]-catalyzed ring-opening polymerization (ROP) of L-LA in melt and bulk conditions at high temperatures (150–200 °C). Despite the huge efforts devoted to the development of organometallics with low toxicity and many highly active catalysts under mild laboratory conditions, very few candidates can compete with Sn(Oct)₂ under industrially relevant conditions. Herein, we report novel zinc complexes bearing phenylimino-pyridine-phenolate ligands as efficient catalysts for L-LA polymerization under both mild and industrially relevant conditions, with a turnover frequency as high as 6200 h⁻¹. The best performing catalyst competed well with Sn(Oct)₂ under industrial conditions and afforded colorless and semicrystalline PLLA. In addition, preliminary depolymerization experiments suggested that the new catalysts can also be used for the chemical recycling of commercial PLLA directly to L-LA with high selectivity under bulk and melt conditions.

Keywords Polylactide; Organometallics; Ring-opening polymerization; Chemical recycling

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INTRODUCTION

Conventional petroleum-based polyolefins have long-term negative environmental impacts because of their non-degradability, and plastic pollution is now a global issue attracting urgent attention.^[1–5] Aliphatic polyesters, such as polylactide (PLA), poly(ϵ -caprolactone) (PCL), and poly(δ -valerolactone) (PVL), are promising alternatives to polyolefins because of their biocompatibility, biodegradability, and sustainability.^[6–11] PLA can be fully degraded by microorganisms into carbon dioxide and water, making it a widely recognized environmentally friendly material. In addition, PLA is well suited to a circular economy owing to the possibility of mechanical and chemical recycling.^[12–14] By the end of 2023, global demand for PLA is expected to reach 10.68 billion with a compound growth rate of 10.9%. The production of PLA is in high demand and has a significant potential for development.

Ring-opening polymerization (ROP) is currently the preferred method for synthesizing aliphatic polyesters compared to polycondensation. Careful control of the polymer

microstructure is key for tuning the material properties and requires the use of an appropriate catalyst.^[15,16] Tin(II) bis(2-ethylhexanoate) [Sn(Oct)₂] combined with an alcohol is the dominant industrial catalyst for PLA production.^[17] However, Sn(Oct)₂ is recognized as toxic, and the accumulation of Sn in the environment and body will cause great concerns. The focus of catalyst design has shifted toward the development of non-toxic and biocompatible organometallics.^[18–26] Zinc is an attractive metal for polyester synthesis because it is inexpensive, colorless, non-redox-active and non-toxic.^[27–29] The lack of toxicity is strongly desirable for biomedical applications.^[30]

Although many highly active zinc catalysts bearing β -diketiminate,^[31–34] amido-oxazolate,^[35,36] aminophenolate^[37,38] and other types of ligands^[39,40] have been developed, most of them address solution polymerizations that are typically performed at 25–100 °C. Only a few zinc complexes have been used in solventless polymerization at elevated temperatures. Ma *et al.* reported zinc complexes bearing chiral and achiral oxazolinyll/benzoxazolyl aminophenolate ligands that displayed high activities toward the ROP of *rac*-LA under the immortal melting conditions ([LA]:[Zn]:[*i*-PrOH]=10000–20000:1:100) but leading to PLAs with relatively low molecular weights (15.0–18.5 kDa).^[37] Pellecchia *et al.* reported that zinc complexes bearing (imidazole[1,5-*a*]pyrid-3-yl)phenolate lig-

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ands could promote technical grade unpurified *L*-LA polymerization under industrially relevant conditions with a monomer/catalyst feed ratio $[LA]:[Zn] = 3000:1$.^[41] Herres-Pawlis *et al.* found that the zinc guanidine catalysts can polymerize non-purified technical *rac*-LA and ϵ -CL in the melt at different monomer/initiator ratios with fast rate constants, high molar masses, and high yields in a short time, leading to colorless, transparent polymers (Scheme 1a)^[42]. Nonetheless, robust, thermally stable and protonic agent-tolerant zinc catalysts for industrial PLA production are still lacking.

The ligand backbone and coordination environment strongly affect the stability of the catalyst, tolerance to impurities, and subsequent polymerization behavior. In this study, we designed and synthesized zinc complexes bearing phenylimino-pyridine-phenolate ligands. These complexes could efficiently initiate *L*-LA polymerization under both mild (40 °C, in solution) and industrially relevant (150 °C, in the melt and bulk) conditions with low catalyst loading, affording colorless semi-crystalline poly(*L*-lactide) (PLLA) with high molecular weight. PLLA-diols (precursors for polyurethane) with a narrow distribution and tailored molecular weight could be readily prepared under industrial conditions using bifunctional alcohol as an initiator. In addition, the zinc complexes also catalyzed the ring-opening depolymerization of PLLA to afford *L*-LA monomer at 180 °C, suggesting that the new catalysts are suitable candidates for the chemical recycling of PLA.

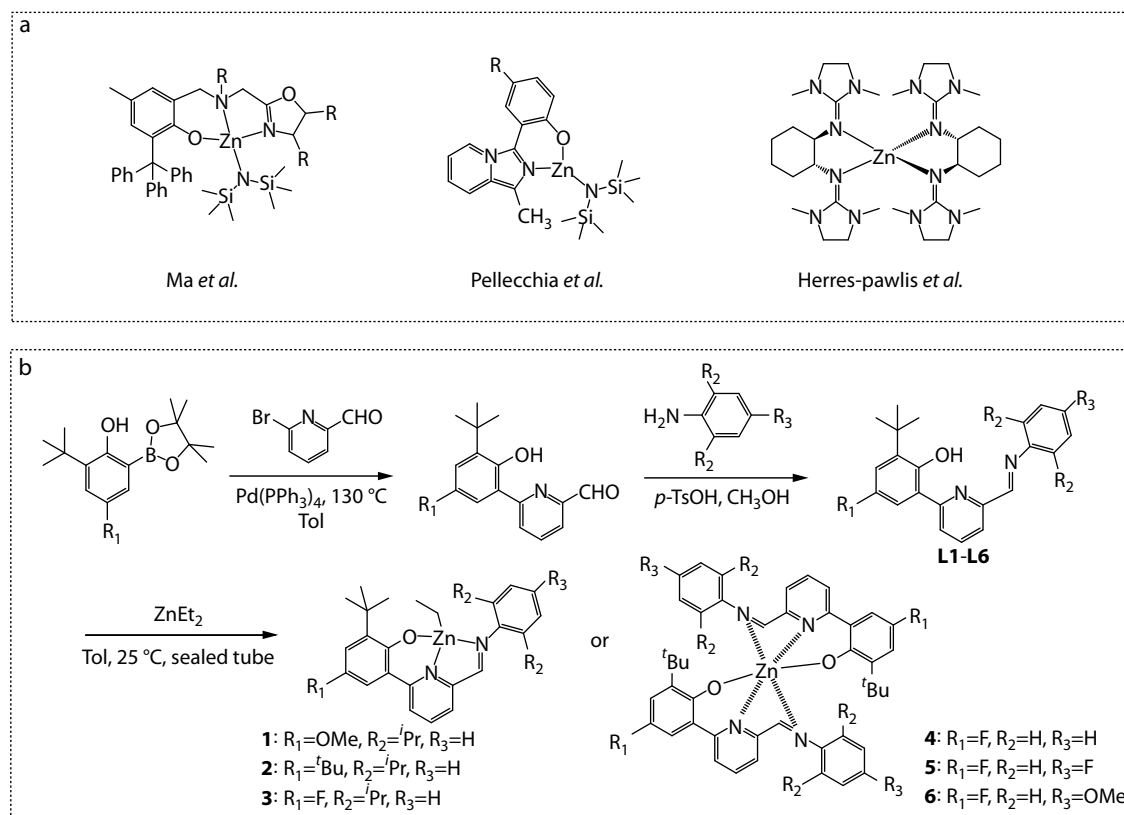
EXPERIMENTAL

Chemicals

Unless otherwise stated, all chemicals were used without further purification. All manipulations involving air- or water-sensitive compounds were conducted under nitrogen atmosphere in an Etelux Lab2000 glove box or using the standard Schlenk line technique. Phenol borates were synthesized by bromination of phenol and subsequent Suzuki-Miyaura reaction.^[43–45] The other reagents used in this work were purchased from Innoschem (Beijing, China). The *L*-LA for polymerization was purified by recrystallization from anhydrous ethyl acetate thrice. The purified monomers were stored in a nitrogen atmosphere.

Characterization

¹H-, ¹³C {¹H}, and ¹⁹F-NMR spectra were recorded on a Bruker Avance III spectrometer (400 MHz ¹H-NMR, 101 MHz ¹³C-NMR, and 376 MHz ¹⁹F-NMR) at room temperature using chloroform-d₁ (CDCl₃) or Benzene-d₆ as the solvent. Their internal standard shifts were at 7.16 ppm for ¹H-NMR (C₆D₆) or 0 ppm for ¹H-NMR (TMS) and at 128.06 ppm for ¹³C-NMR (C₆D₆), respectively. molecular weights and molecular weight distributions of copolymers were determined by GPC at 40 °C with a flow rate of 1.0 mL/min, using THF as the eluent on an Agilent PL-GPC 50 instrument coupled with a refractive index (RI) detector with respect to polystyrene (PS) standards. The columns included a PLgel guard 50 × 7.5 mm column, a PLgel mixed-B 300 × 7.5 mm column and a PLgel mixed-C 300 × 7.5 mm column. Samples for the GPC test were filtered through a 0.22 μm PTFE filter. Matrix-



Scheme 1 Typical zinc complexes used for *L*-LA polymerization under industrial conditions (a) and the zinc complexes bearing phenylimino-pyridine-phenolate ligands in this work (b).

assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the remnant polymer was performed on a Bruker Autoflex III mass spectrometer in linear, positive ion mode, using *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene] malonitrile (DCTB) and 2,5-dihydroxybenzoic acid (DHB) as the matrix, and THF as the solvent.

General Procedure for Ring-opening Polymerization of L-LA

In an Etelux glovebox, the accurate amount of zinc complexes (0.01 mmol, 1 equiv.), benzyl alcohol (0.01 mmol, 1 equiv.), L-LA (2.0 mmol, 100 equiv.), and toluene were added to an oven-dried tube equipped with a magnetic stirrer. The tube was sealed, removed from the glove box, and stirred at a predetermined temperature. After the prescribed time, a crude aliquot was withdrawn from the system using a pipette and monitored by ^1H -NMR spectroscopy in CDCl_3 to determine the monomer conversion. After the reaction was quenched, the reaction mixture was diluted with approximately 10 mL of dichloromethane, and then the mixture solution was dropped into 100 mL of stirring methanol. The products were precipitated and collected after the methanol was filtered. The obtained polymers were oven-dried under vacuum at 40 °C. L-LA polymerization under bulk and melt conditions was performed according to the procedure above, but no solvent was added during the polymerization stage.

General Procedure for the Chemical Recycling of L-LA

Under N_2 atmosphere, PLLA (1000 equiv.) was added to an ampoule containing a zinc complex (1 equiv.), and polyethylene glycol (PEG; $M_n=2000$ Da, 1 equiv.) The PLLA, zinc complex, and PEG mixture were dissolved in a minimum amount of DCM (approximately 10.0 mL) before the solvent was removed under vacuum. An ice cold-finger was connected to the Schlenk and the reaction mixture was heated to 180 °C under vacuum. After 3 h, a white crystalline powder, which was determined to be L-lactide, was collected.

Synthesis of Ligands

2-(*tert*-Butyl)-6-(6-(((2,6-diisopropylphenyl)imino)methyl)pyridin-2-yl)-4-methoxyphenol (**L1**). 2-(*tert*-Butyl)-4-methoxy-6-(4,4,5,5-tetramethyl-1,3-dioxaborolyl)phenol (6.1 g, 0.02 mol) and 6-bromo-pyridine-2-carboxaldehyde (5.4 g, 0.03 mol) were weighed in a flask, and 60 mL of methanol and 30 mL of saturated sodium carbonate solution were added. A reflux device was connected to exhaust the dissolved oxygen in the suspension under a vacuum. Subsequently, nitrogen was introduced and 200 mL of $\text{Pd}(\text{PPh}_3)_4$ in a xylene solution (0.005 mol/L) was added. The solution was refluxed at 130 °C for 24 h. The solution was extracted with ethyl acetate and the oil phase in the upper layer was isolated. The phenol-carboxaldehyde intermediate was obtained by filtering and rotary evaporation after drying with anhydrous magnesium sulfate and then isolated by column chromatography with PE/EA (PE/EA=85/15) as the eluent. The phenol-carboxaldehyde intermediate 2.9 g (0.01 mol) was dissolved in methanol, 2.7 g (0.015 mol) of 2,6-diisopropylaniline and 6.0 mg (0.005 mol%) of *p*-toluenesulfonic acid were added. The solid product was filtered after stirring for 24 h at room temperature, washed with methanol, and finally dried under vacuum to obtain the yellowish-green solid **L1** in 80% yield.

^1H -NMR (400 MHz, benzene- d_6 , δ , ppm): 14.33 (s, 1H), 8.12

(s, 1H), 7.92 (d, $J=7.7$ Hz, 1H), 7.29 (d, $J=3.3$ Hz, 2H), 7.17 (m, 3H), 7.11 (d, $J=3.0$ Hz, 1H), 7.08 (t, $J=7.9$ Hz, 1H), 3.52 (s, 3H), 3.05 (hept, $J=6.9$ Hz, 2H), 1.70 (s, 9H), 1.16 (d, $J=6.8$ Hz, 12H).

^{13}C -NMR (101 MHz, Benzene- d_6 , δ , ppm): 161.57, 159.14, 154.20, 152.29, 151.13, 149.06, 140.34, 138.29, 137.28, 125.18, 123.53, 121.58, 118.68, 118.62, 117.71, 108.80, 55.49, 35.73, 29.79, 28.51, 23.46.

Elem. Anal. calculated for $\text{C}_{29}\text{H}_{36}\text{N}_2\text{O}_2$: C, 78.34; H, 8.16; N, 6.30. Found C, 78.48; H 8.25; N 6.17.

Free ligands **L2–L6** were synthesized from phenol borates according to the methods described above. The detailed procedures are described in the electronic supplementary information (ESI).

Synthesis of Zinc Complexes

Complex **1**. In an Etelux glovebox, the free ligand **L1** (0.44 g, 0.001 mol) was dissolved in ultra-dry toluene (2.0 mL). Then, the **L1**/toluene solution was slowly added to 1.5 mL of a ZnEt_2 /hexane solution (0.0015 mol, 1 mol/L) using a syringe. The flask was sealed and the mixture was stirred at room temperature. After 12 h, the solvent was removed under a vacuum. The crude products were re-dissolved in 2 mL ultra-dry toluene, and further addition of 4 mL of ultra-dry hexane into flask, the product was filtered to give complex **1** as yellow powder with 60% yield after three times from ultra-dry toluene/hexane mixture and vacuum drying.

^1H -NMR (400 MHz, Benzene- d_6 , δ , ppm): 7.45 (d, $J=3.3$ Hz, 1H), 7.34 (s, 1H), 7.13–7.06 (m, 4H), 6.95 (d, $J=3.3$ Hz, 1H), 6.82 (dd, $J=8.4$, 7.3 Hz, 1H), 6.27 (d, $J=7.3$ Hz, 1H), 3.60 (s, 3H), 3.14 (p, $J=6.8$ Hz, 2H), 1.83 (s, 9H), 1.41 (t, $J=8.1$ Hz, 3H), 1.30–1.09 (m, 12H), 0.52 (q, $J=8.1$ Hz, 2H).

^{13}C -NMR (101 MHz, Benzene- d_6 , δ , ppm): 163.72, 161.06, 149.08, 148.32, 145.47, 144.33, 140.12, 138.52, 136.41, 126.78, 124.24, 121.05, 121.87, 121.22, 120.91, 109.20, 55.76, 36.31, 30.42, 29.95, 28.58, 24.49, 23.03, 22.55, 13.42, –0.70.

Elem. Anal. calculated for $\text{C}_{31}\text{H}_{40}\text{N}_2\text{O}_2\text{Zn}$: C, 69.20; H, 7.49; N, 5.21. Found C, 68.89; H, 7.35; N, 5.16.

Complexes **2–6** were synthesized from the corresponding free ligands according to the methods described above; the detailed procedures and characterization are described in ESI.

RESULTS AND DISCUSSION

Catalyst Synthesis and Characterization

The phenylimino-pyridine-phenol ligands **L1–L6** and the corresponding zinc complexes **1–6** were prepared according to the synthetic routes shown in Scheme 1(b) (the detailed procedures are shown in the experimental section). The purity and identities of **L1–L6** were confirmed by ^1H -, ^{13}C -, ^{19}F -NMR (Figs. S1–S16 in ESI) and elemental analyses. The molecular structure of **L6** was further confirmed by single-crystal X-ray diffraction (Fig. S17 in ESI).

The structures of the zinc complexes were determined using the structures of **L1–L6**. Tetra-coordinate zinc complexes **1–3** were finally obtained using **L1–L3** with bulky 2,6-diisopropyl groups in the phenylimino moiety, and the structures were confirmed by ^1H - and ^{13}C -NMR (Fig. 1 and Figs. S18–S24 in ESI). As shown in Fig. 1(A), the resonance peak of the hydroxyl group on phenol disappeared after the formation of the zinc complex, which indicated the reaction between

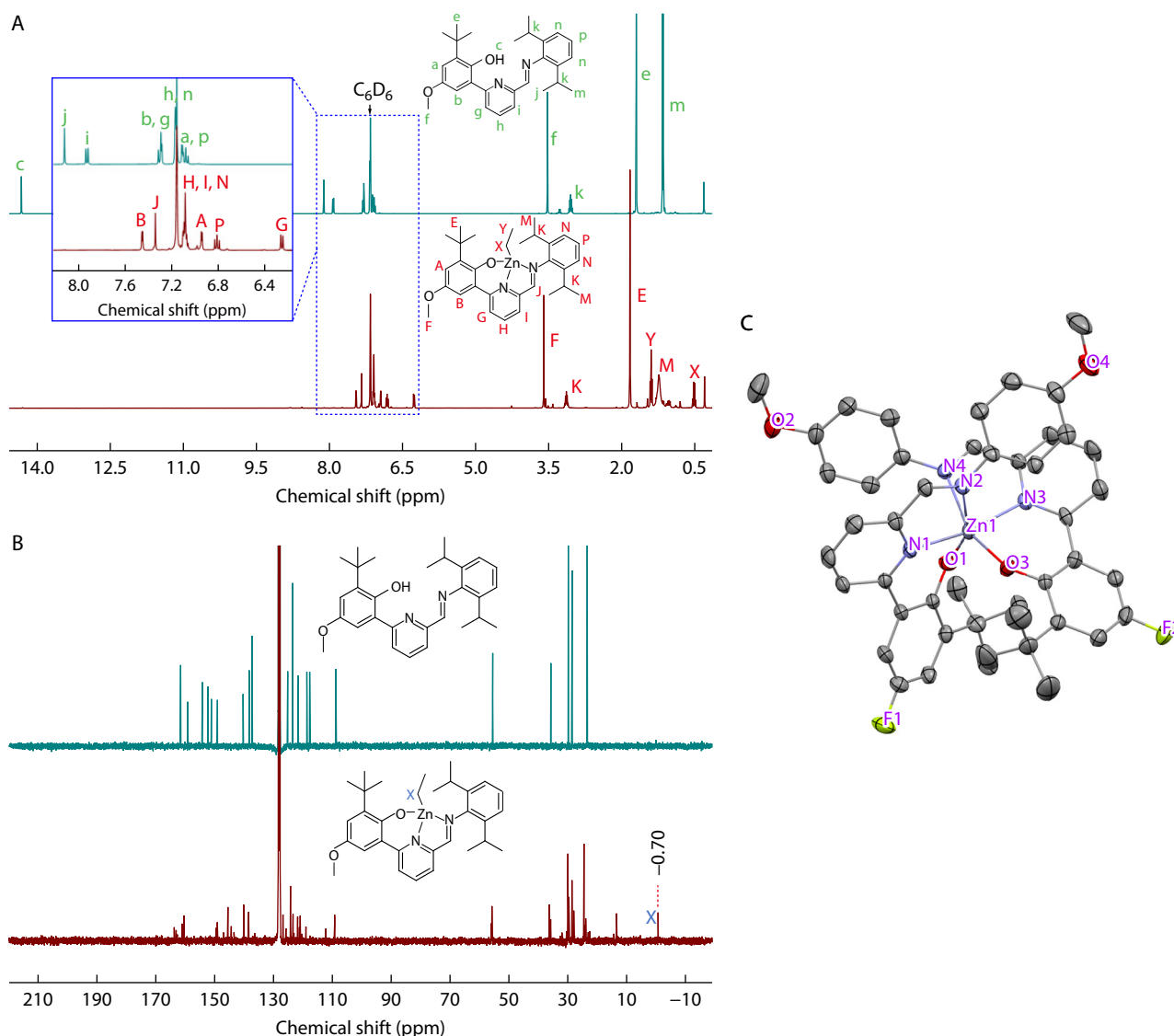


Fig. 1 Representative ^1H - and ^{13}C -NMR spectra of free ligand and zinc complex. (A) ^1H -NMR spectra of free ligand and zinc complex **1**; (B) ^{13}C -NMR spectra of **L1** and zinc complex **1**; (C) Molecular structure of complex **6**. The thermal ellipsoid is plotted at the 30% probability level. H atoms are omitted for clarity.

ZnEt_2 and the phenolic hydroxyl group. Meanwhile, we observed obvious signal shifts for the protons in the phenol rings, pyridine rings, and the phenylimino moiety. These results clearly indicate the formation of $\text{Zn}-\text{O}$ sigma and $\text{Zn}-\text{N}$ coordination bonds. The triple peaks at 1.40 ppm and quadruple peaks at 0.52 ppm were assigned to the methyl and methylene group respectively, and the ratio of integral area was calculated to be 3:2. In addition, a resonance peak at -0.70 ppm was observed in ^{13}C -NMR, also indicating the presence of a $\text{Zn}-\text{CH}_2\text{CH}_3$ bond (Fig. 1B).

Six-coordinate complexes **4–6** were formed when **L4–L6** were used as ligands, as evidenced by the absence of resonance peaks of the ethyl group in ^1H - and ^{13}C -NMR spectra (Figs. S25–S33 in ESI). The molecular structure of complex **6** was further confirmed using single-crystal X-ray diffraction (Fig. 1C). This clearly indicated that the zinc center was coordinated by the N, N, and O atoms from two separate ligands,

and the six-coordinate zinc complex adopted a distorted octahedral geometry. The formation of homoleptic complexes was probably ascribed to the lower steric hindrance around the phenylimino moiety in **L4–L6**.

Catalyst Evaluation in Solution Polymerization

Initially, we evaluated the catalyst performance toward *L*-LA polymerization in toluene at 40°C and investigated the structure-property relationship (Table 1). With a feed ratio $[\text{L-LA}]:[\text{Cat}]:[\text{BnOH}]=100:0.8:1$, complex **1** with the -OMe group at the *para*-position of phenolate moiety converted 55% of *L*-LA within 30 min, and the turnover frequency was calculated to be 138 h^{-1} (entry 1, Table 1). *In situ* ^1H -NMR experiment suggested that complex **3** could react with BnOH to form LZnOBn species (Fig. S34 in ESI), and the polymerization followed “coordination-insertion” mechanism. Substituting -OMe with -*i*Bu (complex **2**) slightly increased the catalytic activity ($\text{TOF}=140\text{ h}^{-1}$, entry 2, Table 1), and introducing an electron-withdrawing fluo-

rine atom (complex **3**) further increased the catalytic activity ($\text{TOF}=183\text{ h}^{-1}$, entry 3, Table 1). We hypothesized that the electron-withdrawing group would increase the Lewis acidity of the metal center and thus facilitate monomer activation. For the phenylimino moieties, both electronic and steric effects would affect the catalytic activity. *In situ* $^1\text{H-NMR}$ experiment suggested that complex **3** could react with BnOH to form LZnOBn species (Fig. S34 in ESI), and the polymerization followed “coordination-insertion” mechanism.

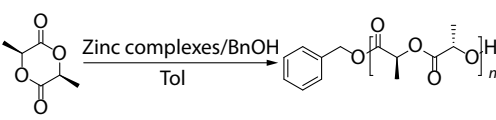
In the presence of BnOH , six-coordinate complexes **4–6** could efficiently promote *L*-LA polymerization. Complex **4** with a phenyl ring, showed a much higher catalytic activity than complex **3** (entries 3 and 4, Table 1), probably because the small steric group in the phenylimino group decreased the bulkiness around the metal center and facilitated monomer coordination. Introducing an electron-withdrawing fluorine at the para-position of anilido (complex **5**) decreased the catalytic activity, but we observed increased activity by introducing an electron-donating $-\text{OMe}$ group

(complex **6**) (entries 5 and 6, Table 1). Here, we envisioned that the higher Lewis acidity of complex **5** led to stronger Zn-alkoxide interactions, which disfavored the nucleophilic attack of the alkoxide on the activated monomer. PLLA with a high molecular weight and narrow distribution was easily prepared by increasing the monomer/catalyst feed ratio (entry 7, Table 1).

To understand the mechanism of polymerization catalyzed by complexes **4–6** in the presence of BnOH , complex **6** was treated with 2 equiv. of BnOH in C_6D_6 and the mixture was further analyzed by $^1\text{H-NMR}$ (Fig. S35 in ESI). Some free ligands dissociated during the addition of alcohol. Based on previous reports of homoleptic Zn analogs for ROP catalysts,^[46,47] we deduced that a binuclear active species was formed from complex **6**, accompanied by dissociation of a ligand in the presence of BnOH (Scheme 2). Finally, the ROPs proceeded via a “coordination-insertion” mechanism.

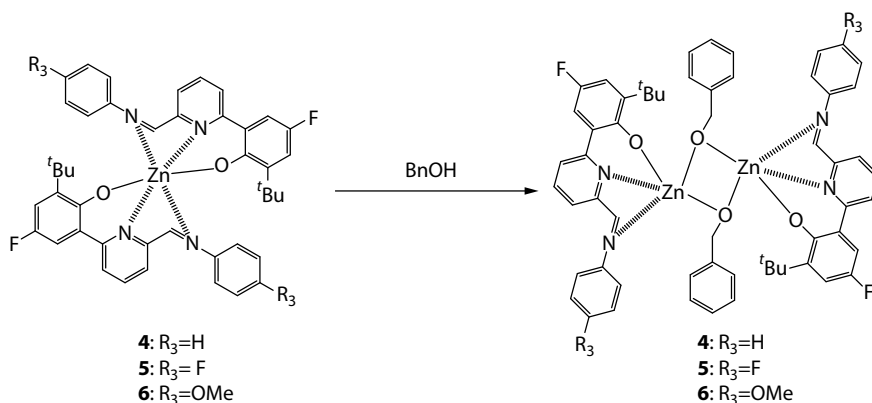
All zinc complexes **1–6** show a high degree of control in *L*-LA solution polymerization, as indicated by the close theoreti-

Table 1 *L*-LA polymerization by zinc complexes.



Entry ^a	Cat.	<i>t</i> (s)	Conv. ^b (%)	TOF ^c (h^{-1})	$M_{n,\text{calc}}$ ^d (kDa)	$M_{n,\text{GPC}}$ ^e (kDa)	$\bar{D}$ ^e
1	1	1800	55	138	8.0	8.9	1.06
2	2	1800	56	140	8.2	12.1	1.06
3	3	1800	73	183	10.6	10.6	1.05
4	4	60	60	4500	8.8	11.4	1.09
5	5	60	55	4125	8.0	9.6	1.07
6	6	60	70	5250	10.2	11.7	1.08
7 ^f	6	360	80	5000	57.8	70.0	1.09

^a Unless otherwise stated, *L*-LA polymerization was performed in toluene at $40\text{ }^\circ\text{C}$, $[\text{L-LA}]:[\text{Cat}]:[\text{BnOH}]=100:0.8:1$, $[\text{L-LA}]=0.5\text{ mol/L}$; ^b Monomer conversion was determined by $^1\text{H-NMR}$ spectroscopy; ^c Turnover frequency; ^d $M_{n,\text{calc}} = 144.14 \times ([\text{L-LA}]_0/[\text{BnOH}]_0) \times \text{conv. (\%)} + 108.13$; ^e Determined by gel permeation chromatography in THF using polystyrene standards and corrected by a coefficient of 0.58; ^f $[\text{L-LA}]:[\text{Cat}]:[\text{BnOH}]=500:0.8:1$.



Scheme 2 Formation of binuclear active species via reaction of complexes **4–6** with BnOH .

cal and experimental number-averaged molecular weights, as well as narrow polydispersity indices. The molecular weights also increased linearly with monomer conversion, and the molecular weight distribution remained monomodal and narrow (Fig. 2a). These results suggest that *L*-LA polymerization catalyzed by zinc complexes proceeds in a controlled manner. The polymerization kinetics were further studied to correlate the polymerization rate with the monomer and catalyst concentration. When the monomer concentration was kept constant, but the catalyst concentration was varied, the slope of the $\ln[k]$ versus $\ln[\text{Cat}]$ plot was approximately 1 (Fig. 2b). Therefore, the *L*-LA polymerization exhibited a first-order dependence on the catalyst concentration. In addition, the plot of $\ln([M]_0/[M])$ versus time exhibited a linear relationship, suggesting *L*-LA polymerization also exhibited first-order dependence on monomer concentration (Fig. 2c). Analysis of the polymers by MALDI-TOF mass spectrometry showed the presence of the BnO/H end group (Fig. 2d), in line with polymerization occurring *via* a well-known coordination-insertion mechanism.

Ring-opening Polymerization of Cyclic Esters in Melt and Bulk Conditions

Having clarified the structure-activity relationship in solution polymerization, *L*-LA polymerization was further conducted at elevated temperatures without any solvents to evaluate the cat-

alytic performance of the zinc catalysts under industrially relevant conditions. Complexes **1–6** were both active toward *L*-LA bulk polymerization at 150 °C, and the structure-activity relationships under melt and bulk conditions were the same as those in solution polymerization. The introduction of electron-withdrawing groups at the para-position of the phenolic moiety gradually increased the catalytic activity due to the increased Lewis acidity of the zinc center (**3** > **2** > **1**) (entries 1–3, Table 2). Reducing the steric hindrance around the phenylimino moiety (complexes **3** and **4**) significantly increased catalytic activity (entries 3, 4, Table 2). The introduction of an electron-withdrawing fluorine at the para-position of phenylimino (complex **5**) decreased the catalytic activity, but electron-donating groups (complex **6**) increased the catalytic activity (entries 5, 6, Table 2). It was noted that the experimental molecular weights approximated the theoretical values under a feed ratio of $[\text{L-LA}]:[\text{Cat}]:[\text{BnOH}]=1000:1:1$ and the polydispersity indices were ≤ 1.50 , suggesting that the zinc complexes still exhibited a high degree of control over *L*-LA polymerization under melt and bulk conditions.

L-LA bulk polymerization proceeded smoothly at higher monomer/catalyst feed ratios (entries 7, 8, Table 2). Polymerization slowed with increasing monomer/catalyst ratio because of the decreased catalyst concentration. The molecular weights of the resultant PLLAs did not increase significantly at

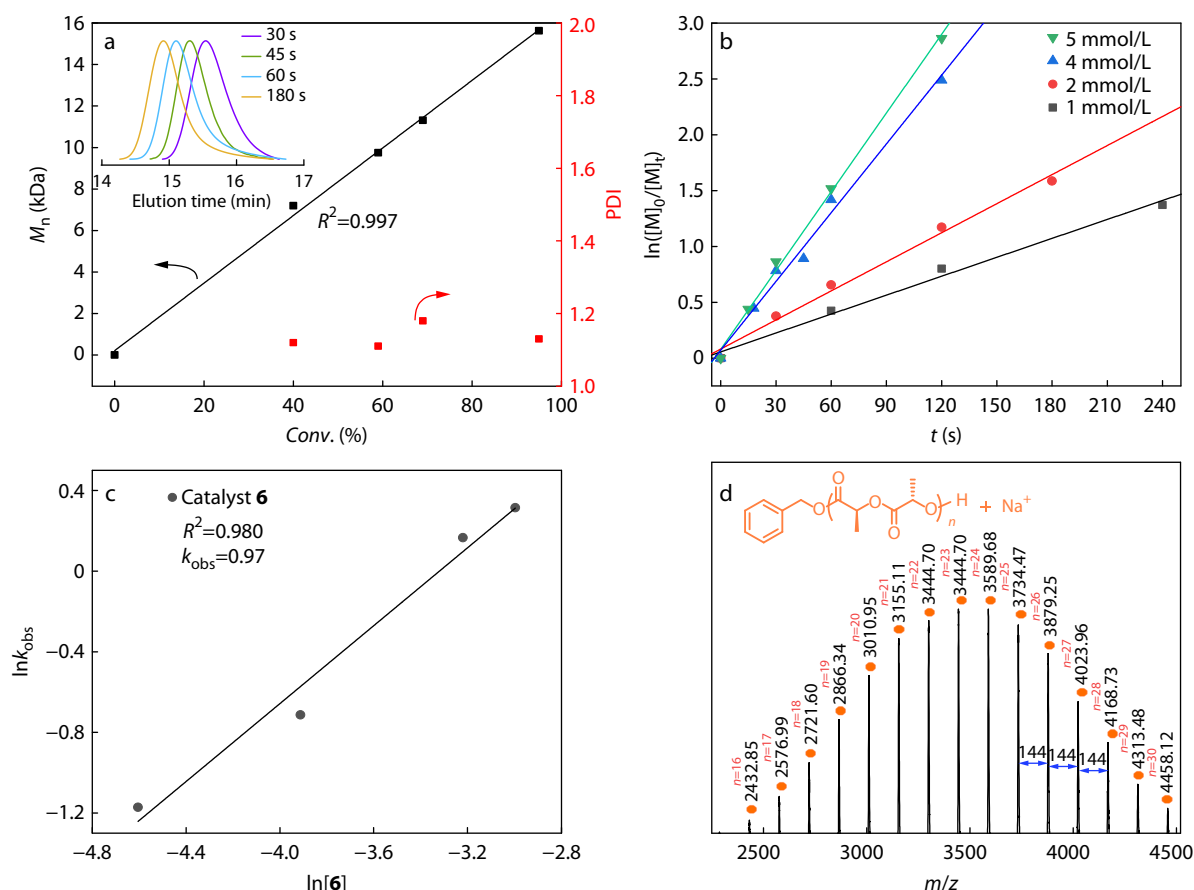


Fig. 2 (a) Dependence of $M_{n,\text{GPC}}$ and $\bar{D}$ on *L*-LA conversion. Inset: GPC traces of PLLA; (b) Double logarithmic plot of $\ln k_{\text{obs}}$ versus $\ln[\text{6}]$, suggesting the *L*-LA polymerizations exhibited first-order dependence on catalyst concentration; (c) Kinetic plot for *L*-LA polymerization using **6** as catalyst ($[\text{L-LA}]:[\text{Zn}]:[\text{BnOH}]=100:1:1$, in toluene, 40 °C); (d) MALDI-TOF mass spectrum of PLLA.

Table 2 ROP of L-LA under industrial conditions.

Entry ^a	Cat.	[L-LA]:[Cat.]:BnOH	<i>t</i> (h)	Conv. ^b (%)	TOF ^c (h ^{−1})	<i>M</i> _{n,calc} ^d (kDa)	<i>M</i> _{n,GPC} ^e (kDa)	<i>Đ</i> ^e
1	1	1000:1:1	0.3	93	3100	134.2	114.3	1.38
2	2	1000:1:1	0.3	95	3160	137.0	105.1	1.50
3	3	1000:1:1	0.3	96	3200	138.5	107.4	1.44
4	4	1000:1:1	0.2	92	4600	132.7	109.2	1.42
5	5	1000:1:1	0.2	90	4500	129.8	118.4	1.40
6	6	1000:1:1	0.15	93	6200	134.2	114.3	1.38
7	6	3000:1:1	0.45	92	6130	397.9	116.2	1.46
8	6	5000:1:1	1.0	93	4650	670.4	149.9	1.25
9	Sn(Oct) ₂	1000:1:1	0.25	97	3880	139.9	98.7	1.52

^a Unless otherwise stated, L-LA polymerization was performed in bulk and melt without solvents. *T* = 150 °C; ^b Determined using ¹H-NMR spectroscopy; ^c Turnover frequency. ^d $M_{n,calc} = 144.14 \times ([L-LA]_0/[BnOH]_0) \times \text{conv.} (\%) + 108.13$; ^e Determined by gel permeation chromatography in THF using polystyrene standards and corrected by a coefficient of 0.58.

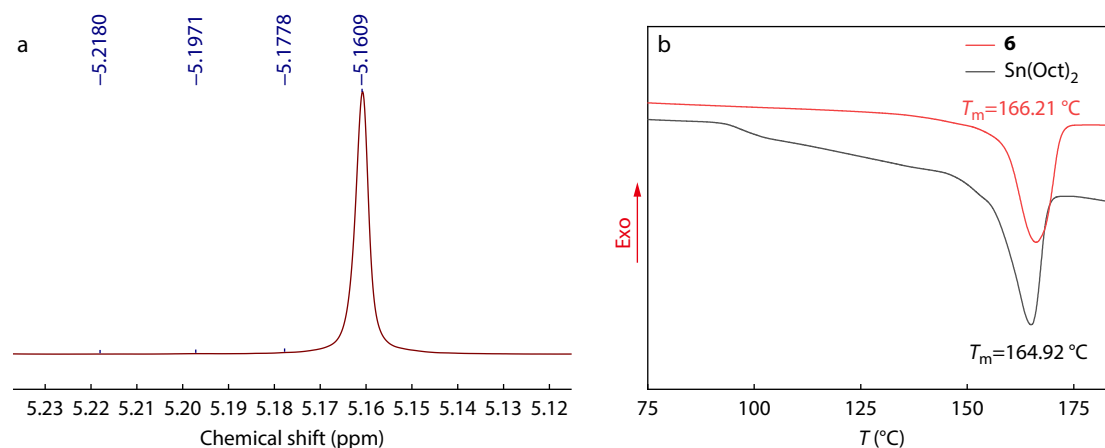


Fig. 3 (a) Homonuclear decoupled ¹H-NMR of PLLA obtained by complex **6**; (b) DSC thermograms of the PLLA obtained by complex **6** and Sn(Oct)₂, respectively.

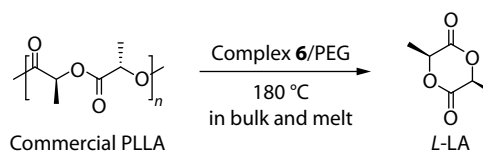
high monomer-catalyst feed ratios. We supposed that the dosage of trace protonic impurities (such as water and residual lactic acid) also increased at high monomer loading, and the severe chain transfer reaction would reduce the molecular weight. Under the same conditions, complex **6** exhibited a much higher catalytic activity than Sn(Oct)₂, producing PLLA with a higher molecular weight and narrow distribution (entries 6 and 9, Table 2). The *P_m* value of the resultant PLLA by complex **6** determined by homonuclear decoupled ¹H-NMR, was approximately 0.976 (Fig. 3a), and the melting temperature (*T_m*, 166.21 °C) was comparable to that of the polymer sample obtained by Sn(Oct)₂ (Fig. 3b). These results suggest that there was no obvious epimerization side reaction in the bulk polymerization using complex **6** as the catalyst. Thus, zinc complexes could serve as alternatives to Sn(Oct)₂ for industrial PLA production.

Chemical Recycling of Commercial Poly(L-lactide) to L-Lactide by Zinc Complexes

One attractive feature of PLLA is that it is well suited for a circular economy owing to the possibility of mechanical and chemical recycling.^[48–51] Life cycle analyses of PLLA production reveal that approximately 80% of the process energy input occurs from the plant to production of L-LA, with 30% being required for the transformation of lactic acid to L-LA.^[49] Therefore, the chemical recycling of PLLA directly to L-LA is important to minimize waste and energy input. However, the chemical recycling of PLLA to L-LA tends to be hindered by side reactions, includ-

ing the epimerization of L-LA to meso-Lactide and its operation under harsh conditions.^[52–54]

Given the good thermostability of the zinc complexes and no obvious epimerization side reactions under bulk polymerization, complex **6** was further used for the depolymerization of commercial PLLA to L-LA under bulk and melt conditions (Scheme 3), according to the methods reported by Williams.^[55] A combination of complex **6** with poly(ethylene glycol) (PEG) was used as a catalytic system for the chemical recycling of PLLA. With a 0.1 mol% of zinc catalyst loading (PLLA:Zn=1000:1), ca. 94.3% of PLLA was depolymerized within 3 h (TOF=314 h^{−1}) at 180 °C under vacuum. ¹H-NMR and DSC analyses suggested that the depolymerization product was mainly L-LA using commercial L-LA and *rac*-LA as references (A and B, Fig. 4). The depolymerization products were further analyzed using high-performance liquid chromatography equipped with chiral columns (Fig. S36 in ESI). It is indicated that the content of L-LA in crude product was up to 98.55%, suggesting a negligible epimerization side reaction



Scheme 3 Chemical recycling of commercial poly(L-lactide) to L-lactide by zinc complexes.

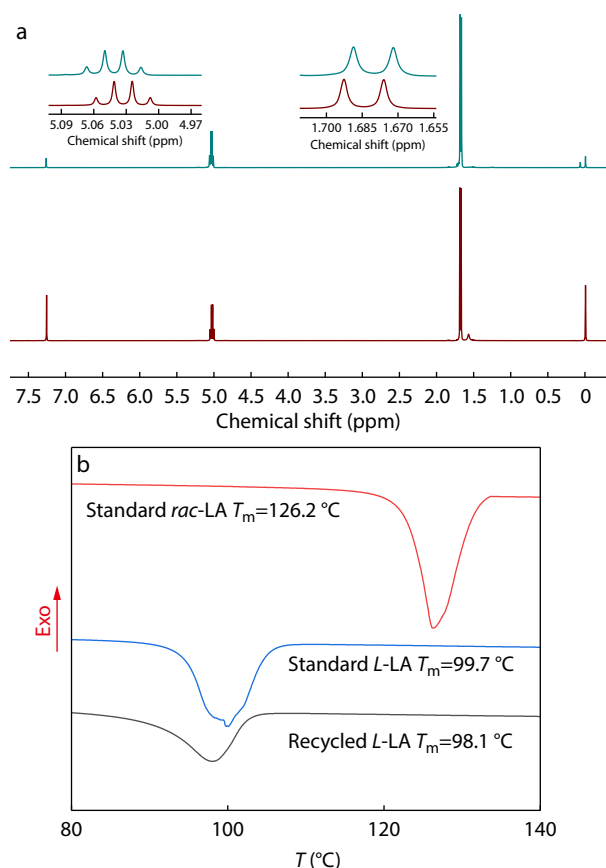


Fig. 4 (a) ¹H-NMR spectra of the recycled and standard L-LA; (b) DSC thermograms of the standard *rac*-LA, standard L-LA and recycled L-LA.

during depolymerization and that PLLA could be chemically recycled to L-LA with high selectivity by the novel zinc complexes.

CONCLUSIONS

Phenylimino-pyridine-phenolate zinc complexes proved to be promising alternatives to $\text{Sn}(\text{Oct})_2$ for L-LA polymerization. The catalytic activity is affected by the electronic and steric effects of the substituents. The introduction of electron-donating groups at the para-position of the phenolic moiety decreases the catalytic activity because of the decreased Lewis acidity of the metal center. Reducing the steric hindrance around the anilido moiety significantly increased the catalytic activity, and introducing electron-donating $-\text{OMe}$ further increased the catalytic activity. These novel zinc complexes showed good thermostability and could mediate L-LA polymerization under industrially relevant conditions (in the melt and bulk). There was no epimerization side reaction under bulk and melt conditions, and semicrystalline PLLA could be obtained. Finally, the preliminary depolymerization of commercial isotactic PLLA samples in bulk and melt directly afforded L-LA with high activity and selectivity.

Conflict of Interests

The authors declare no interest conflict.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-025-3263-4>.

Data Availability Statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request. Author contact information: binwang@tju.edu.cn (B.W.).

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