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Ring-opening polymerization of cyclic esters initiated by zirconium, titanium and yttrium complexes†

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A series of dinuclear zirconium $[LZr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**1–3**) as well as mononuclear titanium $[LTi(O^iPr)_2]$ (**4**), yttrium [LYCl] (**5**) and zirconium $[LZr(O^iPr)_2]$ (**6–7**) salen-type complexes (L = dianionic [ONNO]-tetradentate ancillary ligand) have been prepared and characterized. Dinuclear zirconium salen complexes $[LZr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**1–3**) have shown effective activity toward the ring opening polymerization of lactides and ε-caprolactone. However, mononuclear titanium, yttrium and zirconium complexes **4–7** are almost inactive for the ROP of L-lactide. Solvent-free bulk polymerization of L-lactide initiated by dinuclear zirconium complex **2** with a conversion >90% can be achieved within 10 min, yielding high molecular weight polylactide with low polydispersity index. Kinetic studies reveal the ROP of L-lactide initiated by dinuclear zirconium complex **3** has a first-order dependency on [LA].

Introduction

Due to their unique biocompatible and biodegradable properties, polyesters such as polylactides (PLAs) and poly(ε-caprolactone) (PCL) have been intensively used in many applications, ranging from packing to biomedical devices.[1] Polyesters can be prepared by direct polycondensation of acids or by ring-opening polymerization (ROP) of cyclic esters using a suitable homogeneous catalyst.[2] The most common and effective method for preparation of polyesters is ring-opening polymerization of lactides (LAs) and lactones using various metal complexes as catalysts/initiators. Over the past decades, numerous metal complexes supported by a variety of ligands have been used as catalysts/initiators for the ROP of cyclic esters.[3–8] Most of them show efficient activity in the ROP of cyclic esters in toluene or CH_2Cl_2. However, for environmental and biomedical purposes, the most desirable features of catalysts for lactides' polymerization are the compounds with high activity, low toxicity and the ability to produce high molecular weight polymers with low polydispersity in the absence of any organic solvent.

Because of their diverse forms and ease of preparation, many Schiff-base supported metal complexes have been widely used as catalysts in many applications.[9] Geometrically more rigid salen-type ligands are also readily prepared and their metal complexes are widely used in many applications such as organic syntheses,[10] and olefin polymerization.[11] Recently, metal salen complexes have been widely used in ring-opening polymerization. For instance, aluminum salen complexes have shown highly stereocatalytic activity toward the ROP of *rac*-lactide.[12] Group 4 metal salen complexes are also reported to be active in the ROP of cyclic esters. Recently, it has been reported that the activities of group 4 metal complexes in lactide polymerization are dramatically affected by the identity of the metal and the substituents of the ligands.[13] We report herein the preparation of a series of zirconium, titanium and yttrium salen-type complexes and their activities toward the ROP of lactides and ε-caprolactones.

Experimental section

General methods and materials

All manipulations were carried out under a dry nitrogen atmosphere. Solvents were dried by refluxing for at least 24 h over sodium/benzophenone (hexane, toluene, and tetrahydrofuran (THF)), phosphorus pentaoxide (CH_2Cl_2), or calcium hydride (benzyl alcohol). Deuterated solvents (Aldrich, Merck) were dried over molecular sieves. L-Lactide was purchased from the Bio Invigor Corporation and recrystallized from a toluene solution prior to use. Other regents were purchased from Aldrich or Acros and used without further purification.

Measurement

^1H and ^{13}C NMR spectra were recorded on a Varian Unity Inova-600 (600 MHz for ^1H and 150 MHz for ^{13}C) or a Varian

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Mercury-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS, toluene, or center line of $CHCl_3$. The GPC measurements were performed on a Jasco PU-2080 HPLC pump system equipped with a Jasco RI-2031 Plus detector using THF (HPLC grade) as an eluent. The chromatographic column was a Jordi 15022 column (250 mm) and the calibration curve was made by polystyrene standards to calculate M_n (GPC). 3,5-Bis(α,α-dimethylbenzyl)-2-hydroxybenzaldehyde and *N*,*N*′-3,5-bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-2,2-dimethyl-1,3-diamine (L^1H) were prepared according to the method described in the literature.[14]

Preparation of *N*,*N*′-3,5-bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-1,2-phenylenediamine (L^2H_2)

L^2H_2 was prepared according to the procedure of L^1H. Yield: 3.57 g (86%).^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 13.21 (s, O*H*, 2H), 8.18 (s, N=C*H*, 2H), 7.30–6.98 (m, Ar–*H*, 28H), 3.66 (s, $CH_2C(CH_3)_2CH_2$, 4H), 1.68 (s, CH_3, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 164.5 (Ar*C*=N), 157.9 (Ar*C*OH), 150.6, 150.3 (Ar*C*$C(CH_3)_2$), 142.4 (Ar*C*N–C), 139.8, 136.4 (Ar*C*-cumyl), 130.2, 128.6, 128.0, 127.7, 127.1, 126.7, 125.7, 125.6, 125.0 (Ar–*C*), 118.4 (Ar*C*C=N), 42.4, 42.4, 30.8, 29.3 ($C(CH_3)_2$) Anal. calcd for $C_{52}H_{56}N_2O_2$: C, 84.28; H, 7.62; N, 3.78%. Found: C, 84.40; H, 7.31; N, 3.47%.

Preparation of *N*,*N*′-3,5-bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-1,2-ethylenediamine (L^3H_2)

L^3H_2 was prepared according to the procedure of L^1H. Yield: 3.30 g (85%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 12.96 (s, O*H*, 2H), 8.42 (s, N=C*H*, 2H), 7.30–7.10 (m, Ar–*H*, 28H), 1.68 (s, CH_3, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.8 (Ar*C*=N), 157.6 (Ar*C*OH), 150.6, 150.5 (Ar*C*–$C(CH_3)_2$), 139.3, 135.9 (Ar*C*-cumyl), 129.0, 127.9, 127.7, 126.6, 125.5, 124.9 (Ar–*C*), 117.8 (Ar*C*C=N), 59.3 (NCH_2), 42.4, 42.0, 30.8, 29.3 ($C(CH_3)_2$). Anal. calcd for $C_{56}H_{56}N_2O_2$: C, 85.24; H, 7.15; N, 3.55%. Found: C, 85.40; H, 6.91; N, 3.07%.

General procedures for the preparation of $[LZr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$

A solution of $Zr(O^iPr)_4\cdot{}^iPrOH$ (4.00 mmol) in toluene (25 mL) was cooled to −78 °C and a solution of LH_2 (2.00 mmol) in toluene (25 mL) was then added slowly. After LH_2 was added, the mixture was stirred at 25 °C for 24 h. Volatile materials were removed under vacuum and the residue was recrystallized from toluene.

$[L^1Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (1)

Yield: 1.61 g (61%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.74 (s, N=C*H*, 1H), 7.25–7.13 (m, Ar–*H*, 12H), 7.04–6.92 (m, Ar–*H*, 12H), 4.42 (m, OC*H*$(CH_3)_2$), 4.06 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 2.87 (d, $CH_2C(CH_3)_2CH_2$, 4H, J = 9.6 Hz), 1.74–1.61 (m, $C(CH_3)_2$Ph, 12H), 1.29–1.17 (m, $C(CH_3)_2$, 12H), 0.92 (s, $C(CH_3)_2$, 3H), 0.85–0.76 (d, $C(CH_3)_2$, 6H), 0.50 (s, $C(CH_3)_2$, 3H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 166.3 (Ar*C*=N), 151.1, 151.0 (Ar*C*–O), 138.6, 137.8, 136.7, 131.6, 129.0, 128.2, 127.8, 127.6, 127.1, 126.7, 126.0, 125.3, 125.2, 124.2, 121.88 (Ar–*C*), 72.42, 71.9, 70.8, 70.6, 70.2, 69.0 ($C(CH_3)_2$), 42.4, 42.3, 42.2 ($C(CH_3)_2$Ph), 36.8, 30.8, 30.7 ($C(CH_3)_2$), 27.0, 26.8, 26.5, 26.4, 26.2, 26.1, 25.5, 24.3, 21.4 ($C(CH_3)_2$). Calc. for $C_{74}H_{96}N_2O_8Zr_2$: C, 66.52; H, 7.80; N, 2.13%. Found: C, 66.13; H, 8.70; N, 2.70%.

$[L^2Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$(2)

Yield: 1.77 g (67%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.92 (s, N=C*H*, 1H), 7.83 (s, N=C*H*, 1H), 7.24–7.22 (m, Ar–*H*, 5H), 7.18–7.10 (m, Ar–*H*, 10H), 7.07–7.06 (m, Ar–*H*, 3H), 6.93–6.92 (m, Ar–*H*, 3H), 6.89–6.88 (m, Ar–*H*, 2H), 6.83–6.82 (m, Ar–*H*, 1H), 6.79 (Ar–*H*, 1H), 6.63 (Ar–*H*, 1H), 4.53 (sept, OC*H*$(CH_3)_2$, 1H, J = 6.0 Hz), 4.41 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 4.11 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 3.47 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 1.88 (s, $C(CH_3)_2$, 3H), 1.62 (s, $C(CH_3)_2$, 9H), 1.46 (s, $C(CH_3)_2$, 6H), 1.24–1.19 (m, $C(CH_3)_2$, 18H), 1.10 (s, $C(CH_3)_2$, 6H), 0.95 (d, $C(CH_3)_2$, 3H, J = 6.0 Hz), 0.83 (d, $C(CH_3)_2$, 3H, J = 6.0 Hz), 0.75 (m, $C(CH_3)_2$, 3H, J = 6.0 Hz), 0.31 (m, $C(CH_3)_2$, 3H, J = 6.0 Hz), ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 169.5 (Ar*C*=N), 163.4, 162.9, 161.1 (Ar*C*–O), 151.0, 150.9, 150.4, 147.8, 146.5, 138.0, 137.64, 137.2, 136.5, 136.4, 134.0, 131.3, 131.0, 129.0, 128.2, 127.8, 127.7, 127.5, 127.4, 126.6, 126.5, 126.4, 126.0, 125.4, 125.2, 124.6, 122.2, 122.1, 120.0 (Ar–*C*), 71.7, 71.1, 70.4, 69.0, 68.7 ($C(CH_3)_2$), 42.6, 42.18, 41.82 ($C(CH_3)_2$), 31.9, 30.7, 30.5, 28.6, 28.0 ($C(CH_3)_2$), 26.9, 26.8, 26.7, 26.1, 24.2, 23.2 ($C(CH_3)_2$). Calc. for $C_{74}H_{96}N_2O_8Zr_2$: C, 67.13; H, 7.31; N, 2.12%. Found: C, 66.47; H, 8.26; N, 2.29%.

$[L^3Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (3)

Yield: 1.61 g (63%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 7.84 (s, N=C*H*, 2H), 7.33 (Ar–*H*, 2H), 7.26–7.21 (m, Ar–*H*, 7H), 7.17–7.12 (m, Ar–*H*, 7H), 7.04–7.02 (m, Ar–*H*, 4H), 6.93 (Ar–*H*, 4H), 4.45 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 4.10 (d, CH_2CH_2, 2H, J = 12 Hz), 3.91 (sept, OC*H*$(CH_3)_2$, 2H, J = 6.0 Hz), 3.83 (sept, OC*H*$(CH_3)_2$, 2H, J = 6 Hz), 3.48 (d, CH_2CH_2, 2H, J = 1.8 Hz), 2.00 (s, $C(CH_3)_2$, 6H), 1.67 (s, $C(CH_3)_2$, 9H), 1.49 (s, $C(CH_3)_2$, 3H), 1.24 (m, $C(CH_3)_2$, 12H), 0.99 (d, $C(CH_3)_2$, 6H, J = 6.6 Hz), 0.78 (d, $C(CH_3)_2$, 6H, J = 6.0 Hz), 0.66 (d, $C(CH_3)_2$, 6H, J = 6.6 Hz), 0.62 (m, $C(CH_3)_2$, 6H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ = 167.4 (Ar*C*=N), 160.9 (Ar*C*O), 151.5, 151.3, 137.9, 136.9, 131.6, 130.3, 129.0, 128.2, 127.8, 127.6, 126.7, 126.1, 125.8, 125.3, 125.2, 124.6, 121.6 (Ar–*C*), 70.8, 70.6, 69.7 ($C(CH_3)_2$), 63.6 (CH_2), 42.5 ($C(CH_3)_2$Ph), 33.4, 30.9, 30.8, 26.7 ($C(CH_3)_2$), 26.6, 26.5, 26.4, 26.0, 24.6, 24.3 ($C(CH_3)_2$). Anal. calcd for $C_{70}H_{96}N_2O_8Zr_2$: C, 66.00; H, 7.44; N, 2.20%. Found: C, 66.58; H, 7.58; N, 1.89%.

Preparation of $[L^3Ti(O^iPr)_2]$ (4)

A solution of L^3H_2 (1.48 g, 2.00 mmol) in THF (25 mL) was added slowly into a solution of $Ti(O^iPr)_4$ (0.57 g, 2.00 mmol) in THF (25 mL). The mixture was then refluxed under a N_2 atmosphere for 18 h and cooled to 0 °C. Hexane (25 mL) was added to the solution yielding a yellow solid. The solid was collected by filtration. Yield: 1.03 g (57%). ^{1}H NMR ($CDCl_3$, 600 MHz, ppm): δ 8.11 (s, N=C*H*, 2H), 7.32–7.02 (m, Ar–*H*, 24H), 3.76 (s, CH_2CH_2, 4H), 3.58 (m, OC*H*$(CH_3)_2$, 2H), 1.72 (s, PhC$(CH_3)_2$, 24H), 0.36 (m, OCH$(CH_3)_2$, 12H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 163.4, 163.1 (Ar*C*=N), 151.1, 151.0 (Ar*C*–O), 137.0,

136.8, 132.1, 129.6, 127.8, 127.6, 126.7, 126.0, 125.4, 124.6, 121.7 (Ar–*C*), 72.4 (*C*(CH_3)$_2$), 58.5, 42.7, 42.2 (*C*(CH_3)$_2$Ph), 30.8, 29.7 (C(*C*H_3)$_2$), 25.5 (O*C*H(CH_3)$_2$). Anal. calcd for $C_{58}H_{68}N_2O_4Ti$: C, 76.97; H, 7.57; N, 3.10%. Found: C, 77.12; H, 6.89; N, 2.99%.

Preparation of [L^2Na_2]

Sodium bis(trimethylsilyl)amide (0.81 g, 4.40 mmol) in THF (25 mL) was added slowly to an ice cold solution of *N*,*N*′-3,5-bis(α,α-dimethylbenzyl)-2-hydroxysalicylidene-1,2-benzenediamine (L^2H_2) (1.54 g, 2.00 mmol) in THF (25 mL). The mixture was stirred at 25 °C for 3 h and hexane (30 mL) was added yielding a yellow solid. The solid was filtered and dried under vacuum. Yield: 1.18 g (71%).

[L^2YCl] (5)

A mixture of [L^2Na_2] (0.83 g, 1.00 mmol) and YCl_3 (0.195 g, 1.00 mmol) in ice cold THF (25 mL) was stirred for 12 h during which the temperature was raised to 25 °C. The mixture was then filtered and the filtrate was dried under vacuum. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.35 (s, N=C*H*Ar, 2H), 7.34–7.13 (m, Ar*H*, 30H), 1.77 (s, C(CH_3)$_2$, 6H), 1.67 (s, C(CH_3)$_2$, 12H), 1.39 (s, C(CH_3)$_2$, 6H), ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 165.7 (Ar*C*=N), 163.6 (Ar*C*O), 151.6, 150.9 (Ar*C*C(CH_3)$_2$), 144.9 (Ar*C*N=C), 138.5 (Ar*C*-cumyl), 136.6 (Ar*C*-cumyl), 131.4, 129.0, 128.2, 128.0, 127.9, 127.4, 126.7, 126.2, 125.8, 125.4, 125.3, 124.8, 121.9 (Ar–*C*), 117.9 (Ar*C*C=N), 43.0, 42.2 (*C*(CH_3)$_2$), 32.2, 30.8 (C(*C*H_3)$_2$).

Synthesis of L^4H_2

A mixture of 4-benzoyl-3-methyl-1-phenyl-pyrazol-5(4H)-one (5.56 g, 20.0 mmol) and 2,2-dimethylpropane-1,3-diamine (1.2 mL, 10.0 mmol) was stirred in refluxing ethanol (30 mL) for 24 h. While stirring, a yellow precipitate was observed. The mixture was cooled to 25 °C and the resulting precipitate was collected by filtration and the solid was dried under vacuum. Yield: 5.16 (83%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ = 11.38 (s, O*H*, 2H), 7.99 (Ar–*H*, 2H), 7.46 (m, Ar–*H*, 6H), 7.40 (t, Ar–*H*, 4H), 7.22 (m, Ar–*H*, 4H), 7.15 (t, Ar–*H*, 2H), 3.02 (d, J = 6 Hz, NCH_2C(CH_3)$_2$, 4H), 1.45 (s, CH_3C=N, 6H), 1.06 (s, C(CH_3)$_2$, 6H), ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.0 (=*C*NH), 165.6 (*C*=O), 147.7, 139.0, 130.8, 130.5, 129.1, 128.7, 127.4, 124.3, 119.2 (Ar–*C*), 100.0 (C=*C*C), 51.9 (NHCH_2), 35.9 (*C*(CH_3)$_2$), 23.4 (C(*C*H_3)$_2$), 15.3 (C*C*H_3).

Synthesis of [$L^4Zr(O^iPr)_2$] (6)

A mixture of L^4H_2 (1.0 mmol, 0.622 g) and Zr(O^iPr)$_2$·^{i}PrOH (1.5 mmol, 0.58 g) was stirred in toluene (25 mL) at 60 °C for 12 h and was then cooled to 25 °C. The volatile materials were removed under vacuum giving a white powder. The solid was washed with hexane (30 mL) and then filtered. The resulting precipitate was then dried *in vacuo* to give a white solid. Yield: 0.55 g (67%). ^{1}H NMR (−40 °C, $CDCl_3$, ppm): δ 8.02 (2H, Ar–*H*), 7.69 (2H, Ar–*H*), 7.56–7.44 (m. 6H, Ar–*H*), 7.37 (t, 2H, Ar–*H*), 7.30–7.18 (m, 5H, Ar–*H*), 6.86–6.79 (m, 3H, Ar–*H*), 4.50 (sept, J = 6 Hz, C*H*(CH_3)$_2$, 1H), 4.16 (sept, J = 6 Hz, C*H*(CH_3)$_2$ 1H), 4.08 (d, J = 12 Hz, CH_2C(CH_3)$_2$, 1H), 3.74 (d, J = 12.8 Hz, CH_2C(CH_3)$_2$, 1H), 3.47 (d, J = 12 Hz, CH_2C(CH_3)$_2$, 1H), 3.27 (d, J = 12.8 Hz, CH_2C(CH_3)$_2$, 1H), 1.38 (s, 3H, C(CH_3)$_2$), 1.32 (s, 3H, C(CH_3)$_2$), 1.33–1.29 (m, 6H, OC(CH_3)$_3$), 0.95–0.89 (two doublet, J_1 = 6.0 Hz, J_2 = 7.2 Hz, OC(CH_3)$_3$, 6H), 0.75 (s, 3H, CH_3C=N), 0.61 (s, 3H, CH_3C=N). Anal. calcd for $C_{45}H_{50}N_6O_4Zr$: C, 65.11; H, 6.07; N, 10.12%. Found: C, 65.78; H, 6.05; N, 9.91%.

Syntheses L^5H_2

A mixture of 4-benzoyl-1-(4-chlorophenyl)-3-methyl-pyrazol-5(4H)-one (6.24 g, 20.0 mmol) and 2,2-dimethylpropane-1,3-diamine (1.2 mL, 10.0 mmol) was stirred in refluxing ethanol (30 mL) for 24 h. While stirring, a yellow precipitate was observed. The mixture was cooled to 25 °C and the resulting precipitate was collected by filtration and the solid was dried under vacuum. Yield: 4.97 (72%). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 11.30 (s, O*H*, 2H), 7.96 (Ar–*H*, 4H), 7.48 (m, Ar–*H*, 6H), 7.35 (m, Ar–*H*, 4H), 7.20 (m, Ar–*H*, 4H), 3.03 (d, J = 5.6 Hz, NCH_2C(CH_3)$_2$, 4H), 1.42 (s, CH_3C=N, 6H), 1.05 (s, C(CH_3)$_2$, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 166.0 (=*C*NH), 165.7 (*C*=O), 148.0, 137.6, 130.7, 130.6, 129.2, 129.1, 128.7, 127.4, 120.1 (Ar*C*), 99.9 (C=*C*C), 52.0 (NH*C*H_2), 35.9 (*C*(CH_3)$_2$), 23.4 (C(*C*H_3)$_2$), 15.3 (C*C*H_3). Anal. calcd for $C_{39}H_{36}Cl_2N_6O_2$: C, 67.72; H, 5.25; N, 12.15%. Found: C, 67.16; H, 4.61; N, 11.50%.

Synthesis of [$L^5Zr(O^iPr)_2$] (7)

A mixture of L^5H_2 (1.0 mmol, 0.692 g) and Zr(O^iPr)$_2$·^{i}PrOH (1.5 mmol, 0.58 g) was stirred in toluene (25 mL) at 60 °C for 12 h and was then cooled to 25 °C. The volatile materials were removed under vacuum giving a white powder. The solid was washed with hexane (30 mL) and then filtered. The resulting precipitate was then dried *in vacuo* to give a white solid. Yield: 0.67 g (75%). ^{1}H NMR (−40 °C, $CDCl_3$, 400 MHz, ppm): δ 7.95 (Ar–*H*, 2H), 7.56–7.46 (m, Ar–*H*, 8H), 7.24–7.20 (m, Ar–*H*, 6H), 6.85 (Ar–*H*, 2H), 4.47 (sept, J = 6 Hz, C*H*(CH_3)$_2$, 1H), 4.12 (sept, J = 5.2 Hz, C*H*(CH_3)$_2$, 1H), 4.04 (d, J = 12 Hz, CH_2C(CH_3)$_2$, 1H), 3.75 (d, J = 13.6 Hz, CH_2C(CH_3)$_2$, 1H), 3.51 (d, J = 12 Hz, CH_2C(CH_3)$_2$, 1H), 3.29 (d, J = 13.6 Hz, CH_2C(CH_3)$_2$, 1H), 1.37 (s, C(CH_3)$_2$, 3H), 1.35 (s, C(CH_3)$_2$, 3H), 1.33–1.30 (m, OCH(CH_3)$_2$, 6H), 0.90–0.86 (m, OCH(CH_3)$_2$, 6H), 0.78 (s, CH_3C=N, 3H), 0.62 (s, CH_3C=N, 3H). Anal. calcd for $C_{45}H_{48}Cl_2N_6O_4Zr$: C, 60.12; H, 5.38; N, 9.35%. Found: C, 59.94; H, 5.20; N, 8.97%.

Typical general procedures for polymerization of ε-caprolactone

A typical polymerization procedure was exemplified by the synthesis of PCL-50 (the number 50 indicates the designed [LA]$_0$/[complex]$_0$) initiated by **1** at room temperature. The conversion of polymerization was analyzed by ^{1}H NMR spectroscopic studies. Complex **1** (0.066 g, 0.05 mmol) was added to a solution of ε-caprolactone (0.28 mL, 2.5 mmol) in toluene (5.0 mL). The mixture was stirred at 80 °C for 5 min and was then quenched by the addition of isopropyl alcohol (IPA) (1.0 mL). The polymer was precipitated by pouring the

above mixture into *n*-hexane (20 mL) to give a white solid. Yield: 0.46 g (80%).

Typical general procedures for polymerization of lactides

A typical polymerization procedure was exemplified by the synthesis of PLLA-50 (the number 50 indicates the designed $[LA]_0/[complex]_0$) initiated by **1** at room temperature. The conversion of polymerization was analyzed by ^{1}H NMR spectroscopic studies. Complex **1** (0.066 g, 0.05 mmol) was added to a solution of L-lactide (0.36 g, 2.5 mmol) in toluene (5.0 mL). The mixture was stirred at 100 °C for 10 min and was then quenched by the addition of IPA (1.0 mL). The polymer was precipitated by pouring the above mixture into *n*-hexane (20 mL) to give a white crystalline solid. Yield: 0.62 g (85%).

Kinetic studies of the polymerization of lactides

Procedures for the kinetic studies were exemplified by the synthesis of PLLA-50 (the number 50 indicates the designed $[LA]_0/[complex]_0$) initiated by **3** at room temperature. The conversion of polymerization was analyzed by ^{1}H NMR spectroscopic studies. Complex **3** ($[\mathbf{3}]_0 = 1, 2, 3, 4$ mM) was added to a solution of L-lactide (0.05 M) in toluene (1.0 mL). The mixture was stirred at 100 °C for 5 min. The conversion yield of PLLA was monitored after every minute by ^{1}H NMR spectroscopic studies.

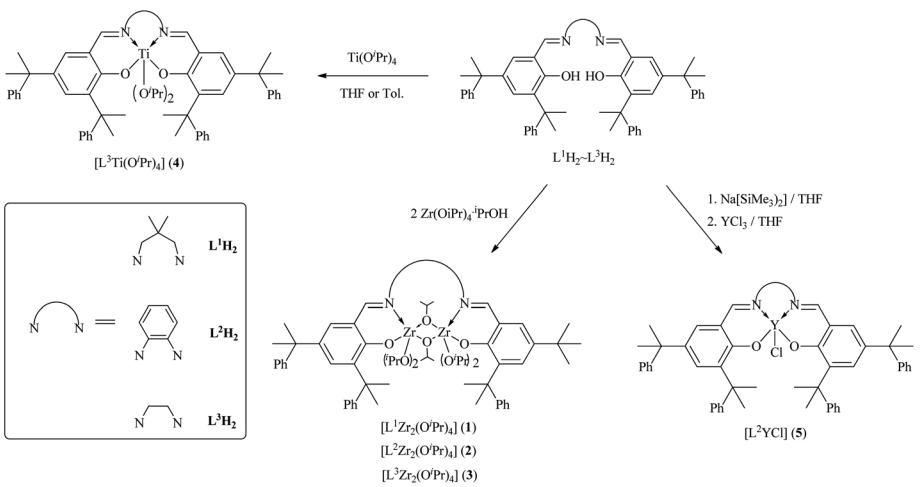
X-ray crystallographic studies

Single crystals suitable for X-ray single crystal structure determination were obtained from slowly cooling a toluene solution (complex **3**) or from a toluene/hexane solution (complex **6**). Suitable crystals were immersed with FOMBLIN®Y under a nitrogen atmosphere and mounted on an Oxford Gemini S diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The absorption correction was based on the symmetry equivalent reflections using SADABS program.[15] The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[16] All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for the H atoms.

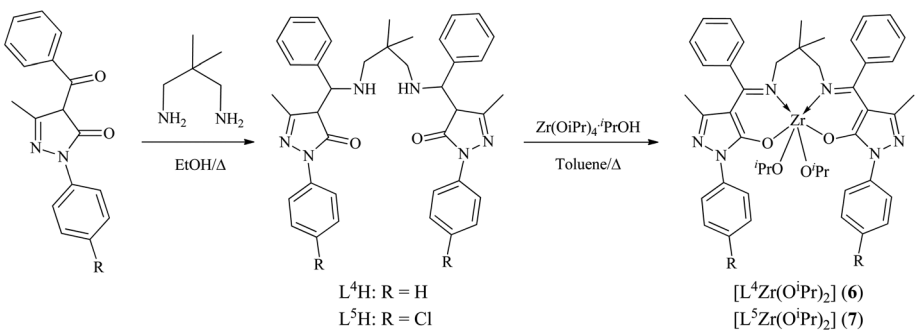
Results and discussion

Synthesis and structural characterization

The reactions of a series of sterically bulky salen ligands (L^1H_2-L^3H_2) with two equiv. of $[Zr(O^iPr)_4 \cdot HO^iPr]$ yield dinuclear zirconium complexes $[L^1Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**1**), $[L^2Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**2**) and $[L^3Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**3**), respectively (Scheme 1).



Scheme 1 Preparation of complexes **1–5**.



Scheme 2 Preparation of complexes **6–7**.

It is worth noting that no mononuclear species [LZr(O^{i}Pr)$_2$] was observed even though the reaction of L^{1}H$_2$-L^{3}H$_2$ with a stoichiometric amount of Zr(O^{i}Pr)$_4$·HO^{i}Pr was carried out. Instead, only bimetallic zirconium complexes **1–3** were obtained. However, L^{3}H$_2$ reacts with one equiv. of Ti(O^{i}Pr)$_4$ giving a mononuclear titanium complex [L^{2}Ti(O^{i}Pr)$_2$] (**4**). Furthermore, treatment of L^{2}H$_2$ with a stoichiometric amount of Na[N(SiMe$_3$)$_2$] in tetrahydrofuran (THF), followed by the addition of YCl$_3$ produces a mononuclear yttrium complex [L^{2}YCl] (**5**). The reaction of 4-benzoyl-3-methyl-1-(4-R-phenyl-pyrazol-5(4H)-one (R = H or Cl)) with 2,2-dimethylpropane-1,3-diamine produces less sterically bulky salen-like ligands L^{4}H$_2$ and L^{5}H$_2$, respectively. Further reaction of L^{4}H$_2$ and L^{5}H$_2$ with a stoichiometric amount of [Zr(O^{i}Pr)$_4$·HO^{i}Pr] gives mononuclear zirconium complexes [L^{4}Zr(O^{i}Pr)$_2$] (**6**) and [L^{5}Zr(O^{i}Pr)$_2$] (**7**), respectively (Scheme 2). All of these complexes have been characterized according to the

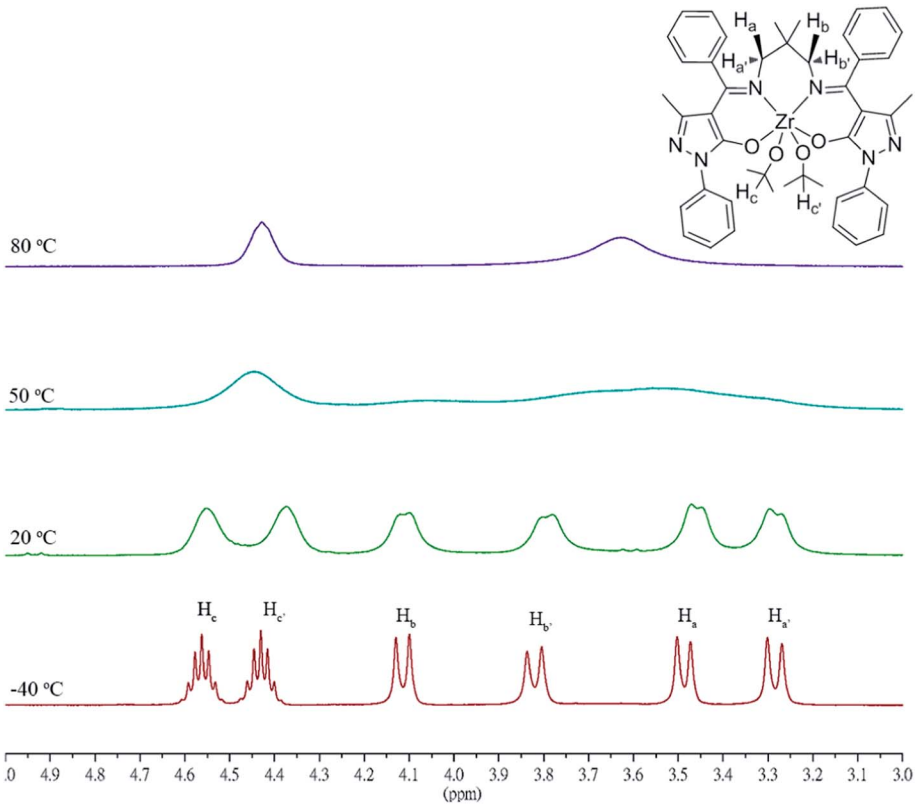


Fig. 1 Variable temperature dependent ^{1}H NMR spectra of **6**.

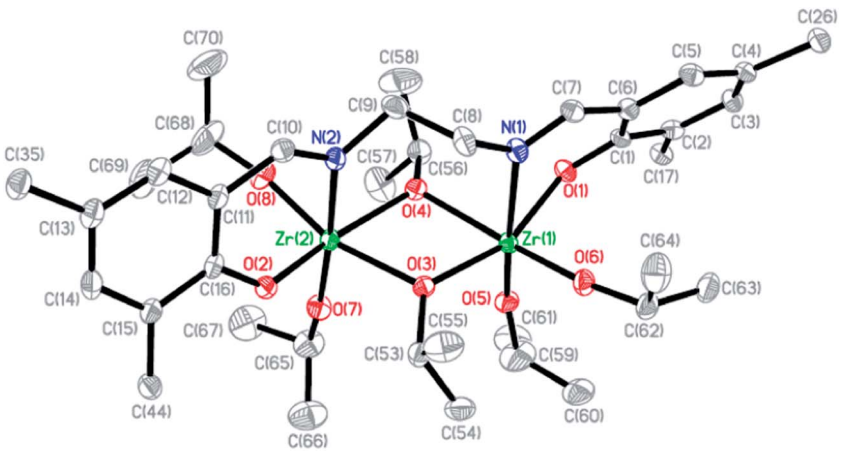


Fig. 2 Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. The methyl carbon of the *tert*-butyl groups and all H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): Zr1–O1 2.067(2), Zr1–O3 2.146(2), Zr1–O4 2.205(2), Zr1–O5 1.936(2), Zr1–O6 1.930(2), Zr1–N1 2.422(2), Zr2–O2 2.068(2), Zr2–O3 2.200(2), Zr2–O4 2.148(2), Zr2–O7 1.925(2), Zr2–O8 1.937(2), Zr2–N2 2.427(2); O1–Zr1–O3 158.2(1), O4–Zr1–O6 161.8(3), N1–Zr1–O5 171.9(1), O2–Zr2–O4 157.4(1), O3–Zr2–O8 163.0(1), N2–Zr2–O7 171.6(1).

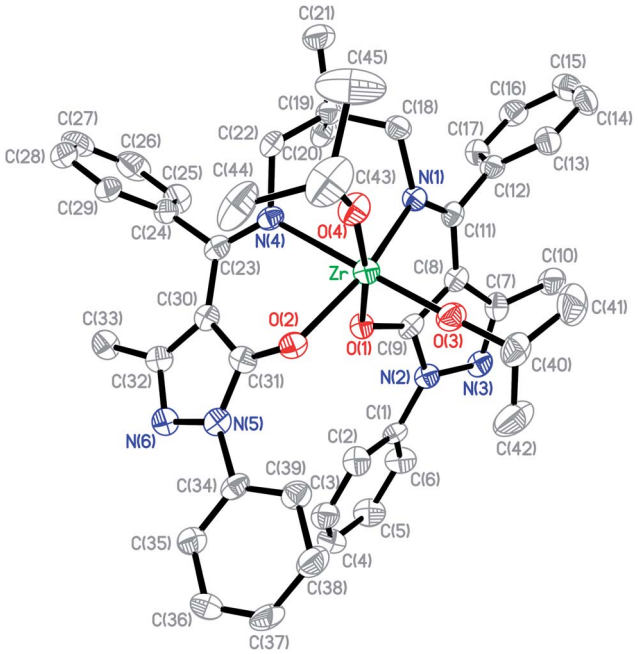


Fig. 3 Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level and H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg.): Zr–O1 2.187(4), Zr–O2 2.088(4), Zr–O3 1.930(4), Zr–O4 1.932(4), Zr–N1 2.272(5), Zr–N4 2.374(5); O1–Zr–O4 168.7(2), O2–Zr–N1 153.7(2), O3–Zr–N4 172.9(2), C40–O3–Zr 175.6(4), C43–O4–Zr 159.7(5).

integration ratio of protons in the salen-type ligand and isopropoxyl group from ^{1}H NMR spectra as well as elemental analysis. The molecular structures of complexes **3** and **6** were further verified by X-ray structural studies. It is interesting to note that variable temperature dependent ^{1}H NMR spectra (Fig. 1) of **6** reveal two inequivalent –O^{i}Pr groups at low temperature with two multiplets for methine protons (4.56 and 4.46 ppm). All of the four methylene protons are also inequivalent as four resonance doublets (4.11, 3.83, 3.50, and 3.29 ppm) were observed. However, they merge into one peak each for both methine (4.42 ppm) and methylene (3.58 ppm) protons at temperature >60 °C indicating fluxionality of this complex.

Crystals of $[L^3Zr(O^iPr)_2]_2[(\mu\text{-}O^iPr)_2]$ (**3**) were obtained from slow cooling a toluene solution. The Oak Ridge Thermal Ellipsoid Plot (ORTEP) of the solid state molecular structure of **1** is shown in Fig. 2. The X-ray structure of **3** indicates that the complex is dinuclear in the solid state, resembling the zirconium salen complexes reported by Chakraborty *et al.*[17] Each Zr center adopts a distorted octahedral geometry bridging through two –O^{i}Pr moieties. The two N centers from the salen ligand are coordinated to two different Zr centers. All bond lengths and angles are in agreement with similar zirconium complexes reported in the literature.[17,18] Crystals suitable for X-ray structure studies of compound $[L^4Zr(O^iPr)_2]$ (**6**) were obtained from slow diffusion of hexane in a toluene solution and the solid state structure of complex **6** is shown in Fig. 3. The solid structure indicates that complex **6** is mononuclear with a distorted octahedral Zr center and two –O^{i}Pr moieties are inequivalent, which is consistent with the result observed in the solution.

Ring-opening polymerization of lactides

Ring-opening polymerization of L-lactide (L-LA) initiated by complexes **1–7** was systematically studied as shown in Table 1. Experimental results reveal that dinuclear zirconium complex **1** is an effective initiator for the ROP of L-lactide in toluene at 100 °C. The conversion can reach over 90% within 10 min in the $[LA]_0/[complex]_0$ ratio ranging from 50 to 300 (Table 1, entries

Table 1 Ring opening polymerization of L-lactide[a]

Entry	Complex	$[LA]_0/[complex]_0$	Time (min)	Conv.[b] (%)	M_n[b] (NMR)	M_n[c] (obsd)	PDI[d]
1	**1**	50/1	10	94	1100	3000 (1700)	1.14
2	**1**	100/1	10	91	2600	5000 (2900)	1.14
3	**1**	150/1	10	93	4100	7700 (4300)	1.20
4	**1**	200/1	10	92	6300	11 000 (6400)	1.20
5	**1**	300/1	10	93	9000	16 000 (9300)	1.17
6[e]	**1**	50/1	10	93	1000	2600 (1500)	1.15
7	**2**	50/1	10	91	1900	3600 (2100)	1.19
8	**2**	100/1	10	94	3500	6500 (3800)	1.18
9	**2**	150/1	10	93	4700	8700 (5100)	1.17
10	**2**	200/1	10	93	6300	10 800 (6200)	1.21
11	**2**	300/1	10	92	8900	16 000 (9300)	1.13
12	**3**	100/1	10	72	2900	5600 (3200)	1.14
13	**3**	100/1	15	91	4000	7400 (4300)	1.13
14	**3**	150/1	15	93	7000	12 000 (7000)	1.18
15	**3**	200/1	15	92	8100	15 200 (8800)	1.10
16	**3**	300/1	15	96	11 400	20 000 (12 000)	1.19
17	**4**	100/1	420	<1%	—	—	—
18[f]	**5**	100/1	96	<1%	—	—	—
19	**6**	100/1	10	<1%	—	—	—
20	**7**	100/1	10	<1%	—	—	—

[a] Reaction conditions: 100 °C, toluene (5.0 mL), $[complex]_0$ = 5.0 mM. [b] Obtained from the ^{1}H NMR analysis. [c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[19] [d] Obtained from GPC. [e] Use unpurified L-Lactide. [f] 80 °C.

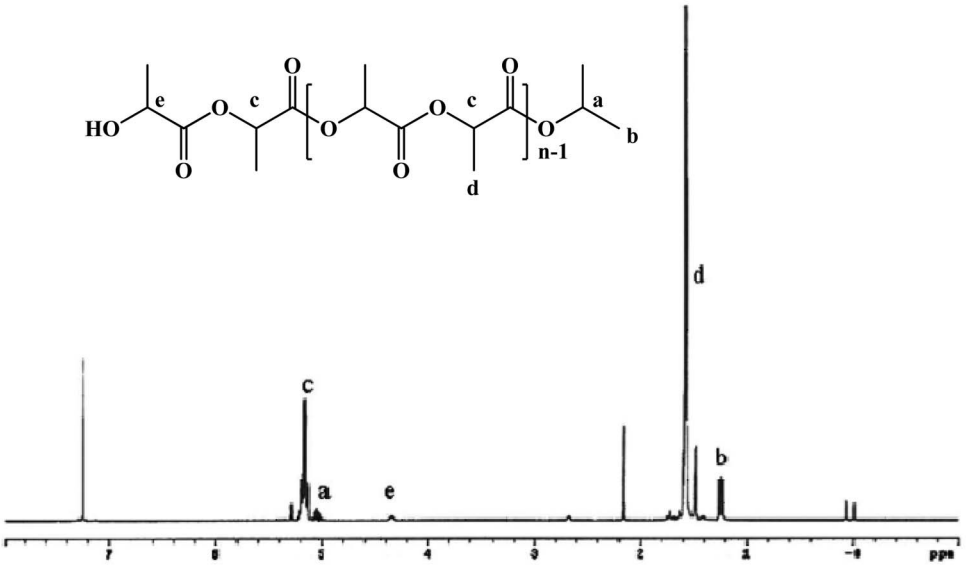


Fig. 4 ^{1}H NMR spectrum of PLLA-50 (50 indicates $[LA]_0/[\mathbf{1}]_0 = 50$).

Table 2 Ring-opening polymerization of *rac*-LA[a]

Entry	Complex	Conv.[b] (%)	Solvent	M_n[b] (NMR)	M_n[c] (obsd)	PDI[d]	P_r[e]
1	**1**	93	Toluene	3200	6800 (3900)	1.23	0.64
2	**2**	90	Toluene	3000	6000 (3500)	1.17	0.62
3	**3**	92	Toluene	3000	6100 (3500)	1.21	0.55
4[f]	**1**	91	Toluene	3100	6200 (3600)	1.19	0.65
5[f]	**1**	82	THF	2800	5400 (3100)	1.24	0.64
6[g]	**1**	93	Toluene	2700	6100 (3500)	1.23	0.54

[a] Reaction conditions: $[rac\text{-LA}]_0/[\text{complex}]_0 = 100/1$, 100 °C, solvent (5.0 mL), $[\text{complex}]_0 = 5$ mM for 10 min. [b] Obtained from the ^{1}H NMR analysis. [c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[19] [d] Obtained from GPC. [e] P_r is the probability of racemic linkages between monomer units and is determined from the methine region of the homonuclear decoupled ^{1}H NMR spectrum: $[mmm] = [2(1 - P_r)^2 + P_r(1 - P_r)]/2$; $[mrm] = [P_r^2 + P_r(1 - P_r)]/2$; $[mmr] = [rmm] = [P_r(1 - P_r)]/2$; $[rmr] = P_r^2/2$. [f] Reaction conditions: 80 °C, 50 min. [g] Reaction conditions: 50 °C, 24 h.

Table 3 Bulk polymerization of L-lactide initiated by complex **2**[a]

Entry	$[LA]_0/[\mathbf{2}]$	Time (min)	Conv.[b] (%)	M_n[b] (NMR.)	M_n[c] (obsd)	PDI[d]
1	100/1	10	91	5000	9700 (5600)	1.37
2	200/1	10	93	18 000	19 000 (11 300)	1.32
3	1000/1	10	93	45 900	80 600 (46 700)	1.39
4	6000/1	15	95	94 100	164 000 (95 000)	1.31

[a] Reaction conditions: 140 °C, $[\text{complex}]_0 = 5.0$ mM. [b] Obtained from the ^{1}H NMR analysis. [c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58.[19] [d] Obtained from GPC.

1–5). The linear relationship between M_n *versus* $[LA]_0/[\text{complex}]_0$ and low polydispersity indexes (PDIs) indicate a good controlled manner and "living" character for the polymerization process. The ^{1}H NMR spectrum of PLLA-50 reveals that the polymer chain is end-capped with an isopropyl ester and a hydroxyl group (Fig. 4). Based on these results, it is believed that the polymerization proceeds *via* the "coordination–insertion" mechanism and there are only two $-O^iPr$ groups that are active in the polymerization. Furthermore, complex **1** is also active toward unpurified L-lactide (entry 6). Complex **2** shows similar activity to that of complex **1** with the process occuring in a controlled manner (entries 7–11). However, the activity of **3** is somewhat lower than that of **1** and **2** with a conversion of L-LA of 72% within 10 min (entry 12). The conversion can reach >90% within 15 min (entries 13–16). In contrast, the mononuclear titanium complex **4** and yttrium complex **5** are inactive towards the ROP of L-lactide (entries 17–18) with the conversion <10% after several hours. It is also worth noting that the activity of

Table 4 Ring opening polymerization of ε-caprolactone (ε-CL)[a]

Entry	Complex	[ε-CL]$_0$/[complex]	Time (min)	Conv.[b] (%)	M_n[b] (NMR.)	M_n[c] (obsd)	PDI[d]
1	**1**	50/1	5	94	3700	6900 (3900)	1.14
2	**1**	100/1	5	94	5600	10 800 (6000)	1.16
3	**1**	150/1	5	95	7100	12 900 (7200)	1.15
4	**1**	200/1	5	95	7500	14 300 (8000)	1.15
5[e]	**1**	200/1	15	87	6600	12 500 (7000)	1.15
6	**2**	100/1	5	95	5500	10 500 (5900)	1.10
7	**3**	100/1	20	88	5700	11 000 (6200)	1.21
8	**4**	100/1	90	6	—	—	—
9	**4**	100/1	420	73	7000	12 900 (7200)	1.38
10	**5**	100/1	32	86	—	35 700 (20 000)	1.18

[a] Reaction conditions: 80 °C, toluene (5.0 mL), [complex]$_0$ = 5 mM. [b] Obtained from the ^{1}H NMR analysis. [c] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC times 0.56.[19] [d] Obtained from GPC. [e] Reaction conditions: 60 °C.

mononuclear pyrazolonato zirconium complexes **6–7** in the ROP of L-LA is also low with the conversion <1% within 12 min. Complexes **1–3** are also active in the polymerization of *rac*-lactide in toluene with the conversion >90% within 10 min (Table 2, entries 1–3). However, the selectivity is poor with P_r = 0.64 for **1** and P_r = 0.62 for **2**, which are somewhat higher than that of **3** (P_r = 0.55). For environmental protection purposes, metal complexes that can polymerize L-lactide in the absence of solvent are of great interest. It is interesting to note that complex **2** showed great activity in the solvent-free bulk polymerization of L-lactide with the conversion >90% within 15 min, yielding a polymer with high molecular weight (M_n = 5600–95 000) and low PDI (PDI < 1.40) (Table 3).

Ring-opening polymerization of ε-caprolactone

Ring-opening polymerization (ROP) of ε-caprolactone (ε-CL) initiated by complexes **1–7** was also studied (Table 4). Experimental results indicate that the dinuclear complex **1** is highly active in the polymerization of ε-CL with the conversion >90% within 5 min at 80 °C (entries 1–4). However, it requires 15 min to reach 86% conversion when the temperature is decreased to 60 °C (entry 5). The activity of complex **1** in ε-CL polymerization (80 °C, 5 min) is higher than the activity in LA polymerization (100 °C, 10 min). The plot of M_n *versus* ([M]$_0$/[complex]$_0$) exhibits a linear relationship for ROP of ε-CL, indicating the "living" character of the polymerization process. Similarly, the activity of **2** (entry 6) in ε-CL polymerization is comparable with that of **1**, and the activity of **3** (entry 7) is somewhat lower that of **1** and **2**. Unlike in the ROP of LA, mononuclear titanium and yttrium complexes are also active initiators in ROP of ε-CL, with the conversion of 73% for **4** (entry 9, Table 4) in 420 min and 86% for **5** in 32 min (entry 10, Table 4).

Kinetic studies of the ring-opening polymerization of L-lactide

The kinetic studies of complex **3** were performed in toluene at 100 °C. Conversion of L-lactide with time in the presence of different concentration of complex **3** ([**3**]$_0$ = 1, 2, 3, 4 mM) was monitored by ^{1}H NMR spectroscopic studies. The plots of ln([LA]$_0$/[LA]$_t$) *versus* time were linear indicating the polymerization rate has a first-order dependency on L-lactide (Fig. 5a). Thus, the rate law of polymerization can be written as $-d[LA]/dt = k_{obs}[LA]$, where $k_{obs} = k_{app}[\mathbf{3}]^x$. The reaction order of [**3**] can be obtained by the plotting of ln k_{obs} *versus* ln[**3**]. The slope reveals that the polymerization rate is $-d[LA]/dt = k_{app}[LA][\mathbf{3}]^{1.5}$, where the rate constant k_{app} = 4.95 mol^{-2} L^2 s^{-1} based on the intercept of the fitted line in Fig. 5b.

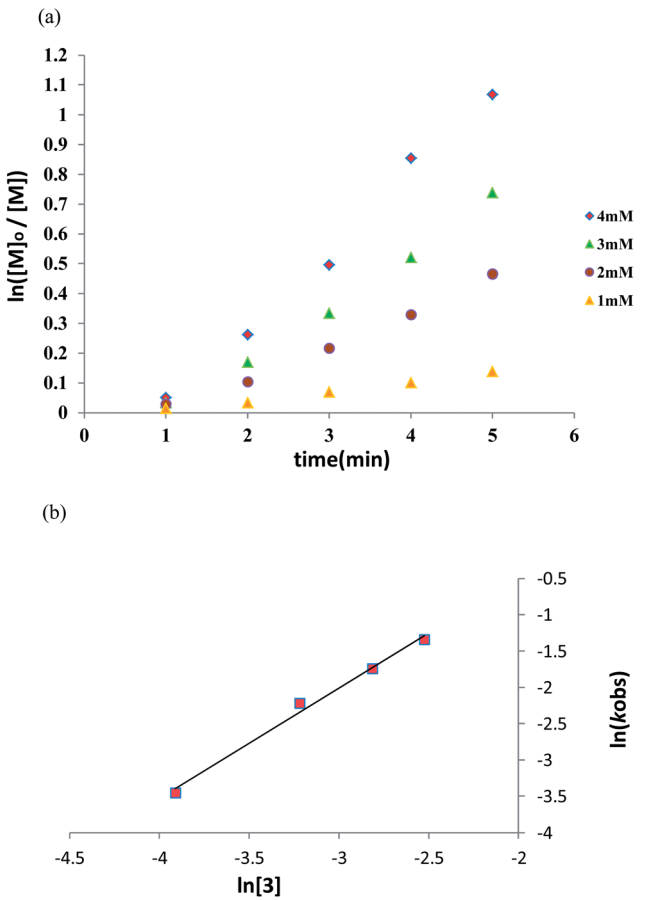
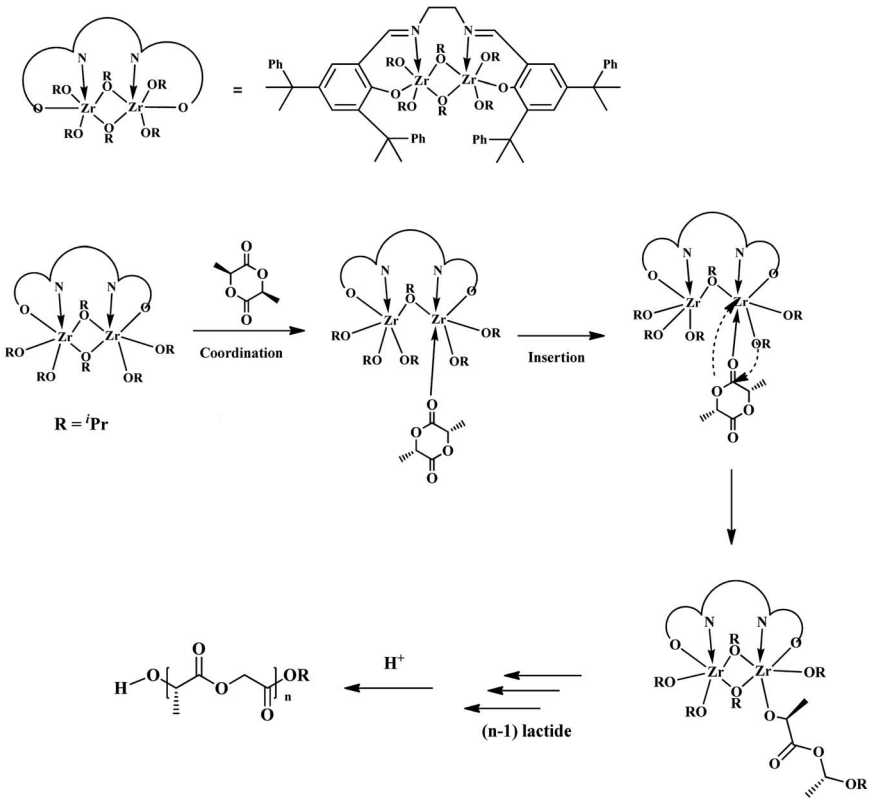


Fig. 5 (a) ln([M]$_0$/[M]) *versus* time plot, demonstrating the first-order dependence for L-lactide polymerizations catalyzed by complex **3** in toluene at 100 °C with different concentrations of **3** ([**3**]$_0$ = 1, 2, 3, 4 mM in toluene at 100 °C, [LA]$_0$ = 0.05 M). (b) Linear plot of ln k_{obs} *versus* ln[**3**] for the polymerization of L-lactide (toluene, 100 °C, [LA]$_0$ = 0.05 M).



Scheme 3 Proposed mechanism for the ROP of L-lactide initiated by complex **3**.

Proposed mechanism for the polymerization of L-lactide

Based on the molecular structure and kinetic study results of zirconium complex **3**, it is believed that the polymerization proceeds by the dissociation of the bridging isopropoxide and the coordination of L-lactide giving intermediate **A** (Scheme 3). Following the insertion of Zr-O^{i}Pr into the L-lactide, intermediate **B** is obtained.

Conclusion

A series of dinuclear zirconium complexes and mononuclear titanium, yttrium and zirconium complexes supporting salen-type ligands have been prepared and characterized. Dinuclear zirconium salen complexes $[LZr(O^{i}Pr)_2]_2[(\mu\text{-}O^{i}Pr)_2]$ (**1–3**) have shown effective activity toward the ring opening polymerization of lactides and ε-caprolactone. Bulk polymerization of L-lactide initiated by **2** with high molecular weight PLLA (M_n(obsd) = 95 000 g mol^{-1} after correction) can be achieved within 15 min.

Acknowledgements

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References

1 (*a*) M. Vert, S. M. Li, G. Spenlehauer and P. Guerin, *J. Mater. Sci.: Mater. Med.*, 1992, **3**, 432–446; (*b*) W. C. Puelacher, D. Mooney, R. Langer, J. Upton, J. P. Vacanti and C. A. Vacanti, *Biomaterials*, 1994, **15**, 774–778; (*c*) E. Chiellini and R. Solaro, *Adv. Mater.*, 1996, **8**, 305–313; (*d*) B. Jeong, Y. H. Bae, D. S. Lee and S. W. Kim, *Nature*, 1997, **388**, 860–862; (*e*) R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807; (*f*) R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, **12**, 1841–1846; (*g*) R. Auras, B. Harte and S. Selke, *Macromol. Biosci.*, 2004, **4**, 835–864.

2 (*a*) A. P. Gupta and V. Kumar, *Eur. Polym. J.*, 2007, **43**(10), 4053; (*b*) S. Inkinen, M. Hakkarainen, A. C. Albertsson and A. Sodergard, *Biomacromolecules*, 2011, **12**, 523.

3 For reviews: (*a*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *J. Chem. Soc., Dalton Trans.*, 2001, 2215–2224; (*b*) D. A. Atwood and M. J. Harvey, *Chem. Rev.*, 2001, **101**, 37–52; (*c*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147–6176; (*d*) J. Wu, T.-L. Yu, C.-T. Chen and C.-C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602–626; (*e*) K. M. Stridsberg, M. Ryner and A.-C. Albertsson, *Adv. Polym. Sci.*, 2002, **157**, 41–52; (*f*) R. H. Platel, L. M. Hodgson and C. K. Williams, *Polym. Rev.*, 2008, **48**, 11–63; (*g*) C. Wheaton, P. Hayes and B. Ireland, *Dalton Trans.*, 2009, (25), 4832–4846; (*h*)

D. Samuel, N. Mickael, K. Evgeny and J.-F. Carpentier, *Coord. Chem. Rev.*, 2013, **257**, 1869–1886.

4 Examples of group 1 and 2 metals: (*a*) B.-T. Ko and C.-C. Lin, *J. Am. Chem. Soc.*, 2001, **123**, 7973–7977; (*b*) C. A. Huang and C. T. Chen, *Dalton Trans.*, 2007, 5561–5566; (*c*) H.-Y. Chen, J. Zhang, C.-C. Lin, J. H. Reibenspies and S. A. Miller, *Green Chem.*, 2007, **9**, 1038; (*d*) W. Clegg, M. G. Davidson, D. V. Graham, G. Griffen, M. D. Jones, A. R. Kennedy, C. T. O'Hara, L. Russo and C. M. Thomson, *Dalton Trans.*, 2008, 1295–1301; (*e*) Y. Huang, Y.-H. Tsai, W.-C. Hung, C.-S. Lin, W. Wang, J.-H. Huang, S. Dutta and C.-C. Lin, *Inorg. Chem.*, 2010, **49**, 9416–9425; (*f*) B. Calvo, M. G. Davidson and D. García-Vivó, *Inorg. Chem.*, 2011, **50**, 3589–3595; (*g*) X. Xu, X. Pan, S. Tang, X. Lv, L. Li, J. Wu and X. Zhao, *Inorg. Chem. Commun.*, 2013, **29**, 89–93; (*h*) R. K. Dean, A. M. Reckling, H. Chen, L. N. Dawe, C. M. Schneider and C. M. Kozak, *Dalton Trans.*, 2013, **42**, 3504–3520; (*i*) M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold and K. Phomphrai, *J. Am. Chem. Soc.*, 2000, **122**, 11845–11854; (*j*) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2001, **123**, 3229–3238; (*k*) M. S. Hill and P. B. Hitchcock, *Chem. Commun.*, 2003, 1758–1759; (*l*) M. Westerhausen, M. Gärtner, R. Fischer and J. Langer, *Angew. Chem., Int. Ed.*, 2007, **46**, 1950–1956; (*m*) J. D. Smith, *Angew. Chem., Int. Ed.*, 2009, **48**, 6597–6599; (*n*) S. Harder, *Chem. Rev.*, 2010, **110**, 3852–3876; (*o*) R. A. Collins, J. Unruangsri and P. Mountford, *Dalton Trans.*, 2013, **42**, 759–769; (*p*) M.-W. Hsiao and C.-C. Lin, *Dalton Trans.*, 2013, **42**, 2041–2051; (*q*) H.-J. Chuang, H.-L. Chen, J.-L. Ye, Z.-Y. Chen, P.-L. Huang, T.-T. Liao, T.-E. Tsai and C.-C. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 696–707.

5 For group 3 metals: (*a*) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra and J. Feijen, *Macromolecules*, 1996, **29**, 3332–3333; (*b*) B. M. Chamberlain, Y. Sun, J. R. Hagadorn, E. W. Hemmesch, V. G. Young, Jr, M. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 1999, **32**, 2400–2402; (*c*) T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 1999, **121**, 4072–4073; (*d*) A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chem. – Eur. J.*, 2005, **12**, 169–179; (*e*) C. Bakewell, T. P. Cao, N. Long, X. F. Le Goff, A. Auffrant and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 20577–20580; (*f*) M. Mazzeo, R. Tramontano, M. Lamberti, A. Pilone, S. Milione and C. Pellecchia, *Dalton Trans.*, 2013, **42**, 9338–9351; (*g*) J. Qiu, M. Lu, Y. Yao, Y. Zhang, Y. Wang and Q. Shen, *Dalton Trans.*, 2013, **42**, 10179–10189.

6 For group 4 metals: (*a*) Y. Kim, P. N. Kapoor and J. G. Verkade, *Inorg. Chem.*, 2002, **41**, 4834; (*b*) B. Lian, L. Toupet and J.-F. Carpentier, *Chem. – Eur. J.*, 2004, **10**, 4301–4307; (*c*) A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2006, 887–889; (*d*) N. Marquet, E. Kirillov, T. Roisnel, A. Razavi and J.-F. Carpentier, *Organometallics*, 2009, **28**, 606–620; (*e*) A. L. Zelikoff, J. Kopilov, I. Goldberg, G. W. Coates and M. Kol, *Chem. Commun.*, 2009, 6804–6806; (*f*) B. J. Jeffery, E. L. Whitelaw, D. Garcia-Vivo, J. A. Stewart, M. F. Mahon, M. G. Davidson and M. D. Jones, *Chem. Commun.*, 2011, **47**, 12328–12330; (*g*) E. Kirillov, N. Marquet, M. Bader, A. Razavi, V. Belia, F. Hampel, T. Roisnel, J. A. Gladysz and J.-F. Carpentier, *Organometallics*, 2011, **30**, 263–272; (*h*) T. K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, 2011, **50**, 2720–2722; (*i*) C. Romain, B. Heinrich, S. B. Laponnaz and S. Dagorne, *Chem. Commun.*, 2012, **48**, 2213–2215; (*j*) L.-C. Liang, S.-T. Lin, C.-C. Chien and M.-T. Chen, *Dalton Trans.*, 2013, **42**, 9286–9293.

7 For group 13 metals: (*a*) B.-T. Ko and C.-C. Lin, *Macromolecules*, 1999, **32**, 8296; (*b*) M. H. Chisholm, C.-C. Lin, J. C. Gallucci and B.-T. Ko, *Dalton Trans.*, 2003, 406; (*c*) R. C. Yu, C. H. Hung, J. H. Huang, H. Y. Lee and J. T. Chen, *Inorg. Chem.*, 2002, **41**, 6450; (*d*) A. Alaaeddine, T. Roisnel, C. M. Thomas and J.-F. Carpentier, *Adv. Synth. Catal.*, 2008, 350; (*e*) M. P. F. Pepels, M. Bouyahyi, A. Heise and R. Duchateau, *Macromolecules*, 2013, **46**, 4324–4334; (*f*) V. Balasanthiran, M. H. Chisholm, C. B. Durr and J. C. Gallucci, *Dalton Trans.*, 2013, **42**, 11234–11241.

8 For other metals: (*a*) B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, *Dalton Trans.*, 2001, 2215–2224; (*b*) E. Barnea, D. Moradove, J.-C. Berthet, M. Ephritikhine and M. S. Eisen, *Organometallics*, 2006, **25**, 320; (*c*) E. Rabinovich, S. Aharonovich, M. Botoshansky and M. S. Eisen, *Dalton Trans.*, 2010, **39**, 6667–6676; (*d*) P. J. Dijkstra, H. Du and J. Feijen, *Polym. Chem.*, 2011, **2**, 520–527; (*e*) C. E. Hayes, Y. Sarazin, M. J. Katz, J.-F. Carpentier and D. B. Leznoff, *Organometallics*, 2013, **32**, 1183–1192.

9 (*a*) J. F. Larrow and E. N. Jacobsen, *Top. Organomet. Chem.*, 2004, **6**, 123–152; (*b*) N. S. Venkataramanan, G. Kuppuraj and S. Rajagopai, *Coord. Chem. Rev.*, 2005, **249**, 1249.

10 (*a*) S. R. Doctrow, K. Huffman, C. B. Marcus, G. Tocco, E. Malfroy, C. A. Adinolfi, H. Kruk, K. Baker, N. Lazarowych, J. Mascarenhas and B. Malfroy, *J. Med. Chem.*, 2002, **45**, 4549–4558; (*b*) K. Pamin, G. Pozzi, E. Tabor, W. Bukowski and J. Połtowicz, *Catal. Commun.*, 2013, **39**, 102–105; (*c*) K. Balaraman, R. Vasanthan and V. Kesavan, *Tetrahedron*, 2013, **69**, 6162–6169; (*d*) Y. Noritake, N. Umezawa, N. Kato and T. Higuchi, *Inorg. Chem.*, 2013, **52**, 3653–3662.

11 (*a*) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs and D. A. Bansleben, *Science*, 2000, **287**, 460–462; (*b*) E. Y. Tshuva, I. Goldberg and M. Kol, *J. Am. Chem. Soc.*, 2000, **122**, 10706–10707; (*c*) J. Huang, B. Lian, L. Yong and Y. Qian, *Inorg. Chem. Commun.*, 2001, **4**, 392–394; (*d*) V. Busico, R. Cipullo, N. Friederich, S. Ronca and M. Toguru, *Macromolecules*, 2003, **36**, 3806–3808; (*e*) V. Busico, R. Cipullo, N. Friederich, S. Ronca, G. Talarico, M. Toguru and B. Wang, *Macromolecules*, 2004, **37**, 8201–8203; (*f*) A. Yeori, I. Goldberg, M. Szuster and M. Kol, *J. Am. Chem. Soc.*, 2006, **128**, 13062–13063; (*g*) J.-L. Huang, B. Lian, L. Yong and Y.-L. Qian, *Chin. J. Chem.*, 2004, **22**, 577–584; (*h*) M. Strianese, M. Lamberti, M. Mazzeo, C. Tedesco and C. Pellecchia, *J. Mol. Catal. A: Chem.*, 2006, **258**, 284–291;

(*i*) M. Bialek and A. Pietruszka, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**(23), 6693–6703.

12 (*a*) C. P. Radano, G. L. Baker and M. R. Smith, *J. Am. Chem. Soc.*, 2000, **122**, 1552–1553; (*b*) Z. Zhong, P. J. Digkstra and J. Feijen, *Angew. Chem., Int. Ed.*, 2002, **41**, 4510–4513; (*c*) P. Hormnirun, E. L. Marshall, V. C. Gibson, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2004, **126**, 2688–2689; (*d*) P. Hormnirun, E. L. Marshall, V. C. Gibson, R. I. Pugh and A. White, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 15343–15348; (*e*) N. Nomura, R. Ishii, Y. Yamamoto and T. Kondo, *Chem. – Eur. J.*, 2007, **13**, 4433–4451; (*f*) X. Pang, H. Du, X. Chen, X. Wang and X. Jing, *Chem. – Eur. J.*, 2008, **14**, 3126–3136; (*g*) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen and J. Feijen, *Chem. – Eur. J.*, 2009, **15**, 9836–9845; (*h*) H.-L. Chen, S. Dutta, P.-Y. Huang and C.-C. Lin, *Organometallics*, 2012, **31**, 2016–2025.

13 S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783–4790.

14 H.-J. Chuang, Y.-C. Su, B. T. Ko and C.-C. Lin, *Inorg. Chem. Commun.*, 2012, **18**, 38–42.

15 G. M. Sheldrick, *SADABS: Siemens Area Detector Absorption Correction Softwares*, University of Gottingen, Gottingen, Germany, 1998.

16 G. M. Sheldrick, *SHELXTL-Plus, NT Crystallographic System, release 5.1; Bruker Analytical X-ray Systems*, Madison, WI, 1998.

17 T. K. Saha, V. Ramkumar and D. Chakraborty, *Inorg. Chem.*, 2011, **50**, 2720–2722.

18 (*a*) S. Gendler, S. Segal, I. Goldberg, Z. Gold Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250–7257; (*b*) A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698–704.

19 Values in parenthesis is M_n(GPC) times 0.58 for polylactide and 0.56 for ε-caprolactone (*a*) J. Baran, A. Duda, A. Kowalski, R. Szymanski and S. Penczek, *Macromol. Rapid Commun.*, 1997, **18**, 325–333; (*b*) T. Biela, A. Duda and S. Penczek, *Macromol. Symp.*, 2002, **183**, 1–10; (*c*) M. Save, M. Schappacher and A. Soum, *Macromol. Chem. Phys.*, 2002, **203**, 889–899.