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PAPER

Synthesis, characterization and catalytic activity of lithium and sodium iminophenoxide complexes towards ring-opening polymerization of L-lactide†

Wei-Yi Lu,[a,b] Mon-Wei Hsiao,[b] Sodio C. N. Hsu,[a] Wei-Te Peng,[a] Ya-Ju Chang,[a] Yu-Chi Tsou,[a] Ting-Yi Wu,[a] Yi-Chun Lai,[a] Yun Chen[a] and Hsuan-Ying Chen*[a]

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A series of lithium and sodium iminophenoxide complexes have been successfully synthesized and characterized by X-ray crystallography and investigated as catalysts for the ring opening polymerization of L-lactide. The nature and steric bulk of the ligands coordinated to the central metal ions greatly influence the catalytic properties. Complexes with bidenate ligands exhibit higher catalytic activity than tridentate counterparts because the third coordination atom contends with L-lactide, which decreases activity. Oxygen is the third atom in the tridentate ligand, providing stronger chelation ability with Li and Na than nitrogen or sulfur and occupies the space with which L-lactide is coordinated.

Introduction

The discovery of petrochemical plastic materials has made life easier and more convenient, but it has also led to environmental pollution. Polylactide (PLA) is a potential replacement material for petrochemical plastic due to its biodegradability, biocompatibility, and permeability. It is utilized in protein encapsulation and delivery, hydrogels, medical applications, drug delivery systems and development of microspheres. The main approach to synthesizing PLA involves ring-opening polymerization (ROP) using metal catalysts (*e.g.*, Al,[1] Mg,[2] Fe,[3] Sn,[4] Zn,[5] and lanthanide[6]). However, the metal residue in the polymers must be dealt with if it is to be used as a biomaterial. For this reason, alkali metal, such as Li[7] and Na[7l,m,8] complexes, have been researched extensively with regard to LA polymerization. In addition, their precursors are cheap and the synthesis simple.

Schiff base ligands are the most common due to their diversity and ease of preparation; their complexes have been widely used as catalysts in a wide range of applications.[9] As with Schiff base supported Al,[1n–x] Mg,[2j,k] Sn,[4d–g] and Zn[4h–m] complexes, their application in ROP has been thoroughly explored. However, Schiff base supported Li and Na complexes have not been previously reported in ROP of lactides. Hereby, this study describes the preparation of a series of Schiff base ligands (Chart 1) with aryl and alkyl imines to discuss the relationship between the coordination with various imines and the catalytic activity of L-lactide polymerization. The catalytic activity of Li and Na complexes with different substituents on the imine group of Schiff base ligands is discussed in detail.

Results and discussion

Synthesis and characterization of Li and Na complexes

All L^{1-6}–H ligands were prepared by refluxing a mixture of salicylaldehyde and alkylamine (or aniline) in toluene to remove water using a Dean–Stark apparatus. L^{1-6}–H reacted with a stoichiometric quantity of NaH and lithium *tert*-butoxide in THF to respectively produce a moderate yield of Li and Na compounds (Scheme 1). The formula and structure were confirmed by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray crystal analysis. The X-ray structure of **L^5Li** (Fig. 1) shows that the Li complex is the tetramer in nature, with the five-coordinate Li ions with a distorted trigonal bipyramidal geometry. The axial angle of O(1B)–Li–N(1) is 154.0(5)° and the equatorial angles of O(1)–Li–O(1C), O(1)–Li–S(1), and O(1C)–Li–S(1) are 92.0 (4), 143.6(5), and 123.3(4)°, respectively. The distances between

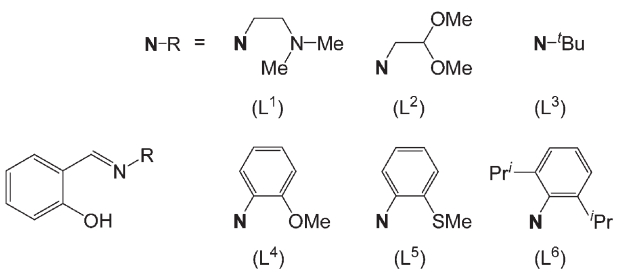
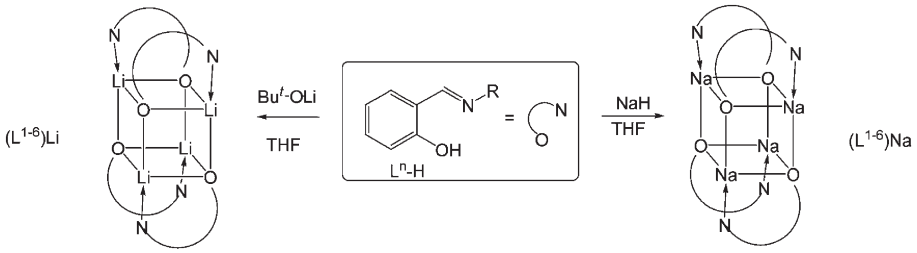


Chart 1

[a]*Department of Medicinal and Applied Chemistry, Kaohsiung Medical University, 100, Shih-Chuan 1st Road, Kaohsiung, 80708 Kaohsiung, Taiwan, R.O.C. E-mail: hchen@kmu.edu.tw*
[b]*Department of Chemistry, National Chung Hsing University, Taichung 402, Taiwan, R.O.C.*

†Electronic supplementary information (ESI) available: Table giving further details of the crystal structure determination, atomic coordinates and isotropic thermal parameters, bond lengths and angles, and anisotropic displacement parameters for **L^5Li** and **L^4Na**. CCDC reference numbers 848022 and 848023. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt12063a



Scheme 1 Preparation of compounds (L^{1-6})Li and (L^{1-6})Na.

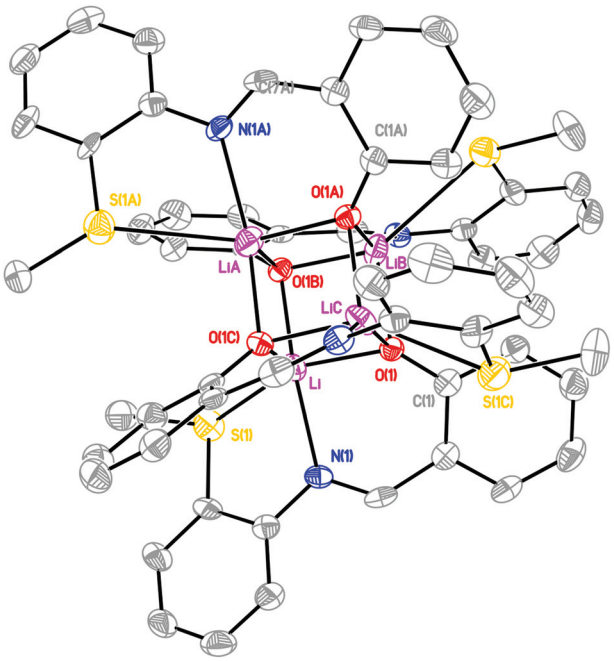


Fig. 1 Molecular structure of complex $\mathbf{L^5Li}$ as 20% ellipsoids (all of the hydrogen atoms were omitted for clarity).

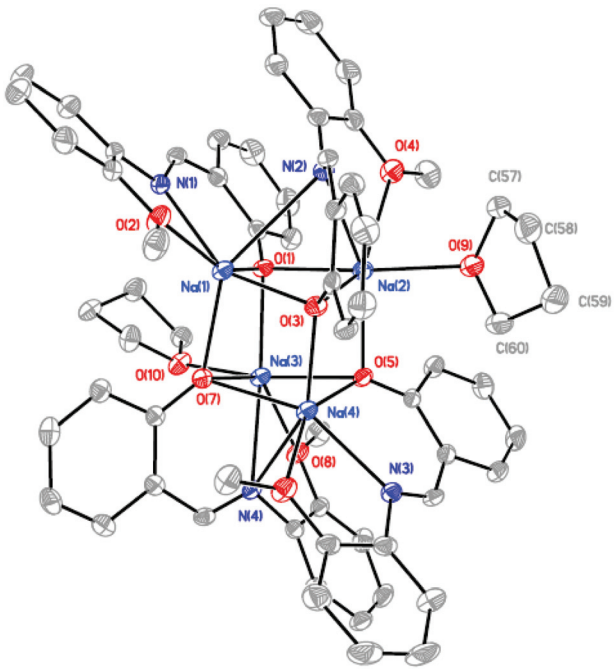


Fig. 2 Molecular structure of complex $\mathbf{L^4Na}$ as 20% ellipsoids (all of the hydrogen atoms were omitted for clarity).

the Li atom and O(1), O(1B), O(1C), S(1) and N(1) are 1.932 (10), 1.979(10), 1.995(10), 2.825(10) and 2.160(10) Å, respectively, confirming the distortion of the structure from an ideal trigonal bipyramidal topology. The X-ray structure of $\mathbf{L^4Na}$ (Fig. 2) shows that Na complex is also tetrameric in nature, comprising a six-coordinate Na ion with a distorted octahedral geometry. Na atoms have two coordination forms. First, it can be seen to have as a five-coordinate cubic structure (Fig. 2(a)), such as $\mathbf{L^5Li}$ in Fig. 1; however, the coordination number of Na is more than Li because the Na atom is larger. Therefore, an empty space surrounds the Na coordinated by THF and the two N atoms of the imine group bridge to another Na (Fig. 2(b)). The axial angles of O(2)–Na(1)–O(1) and O(1)–Na(2)–O(9) are 150.05(9) and 170.54(9), respectively. The equatorial angles between N(2)–Na(1)–N(1), O(3)–Na(1)–N(2), O(3)–Na(1)–O(7), O(7)–Na(1)–N(1), O(4)–Na(2)–N(2), N(2)–Na(2)–O(3), O(3)–Na(2)–O(5), and O(5)–Na(2)–O(4) are 84.71(8), 65.42(7), 86.45(7), 124.52(9), 65.29(8), 72.40(8), 85.03(7), and 137.93 (8)°, respectively. The distances between the Na(1) atom and O(1), N(1), O(2), O(3), O(7) and N(2) are 2.239(2), 2.383(2), 2.338(2), 2.328(2), 2.308(2), and 2.897(3) Å, respectively. The distances between the Na(2) atom and O(3), N(2), O(4), O(5), O(1) and O(9) are 2.364(2), 2.482(3), 2.428(2), 2.332(2), 2.428(2), and 2.362(2) Å, respectively, confirming the distortion of the structure from an ideal octahedral topology. From the report in the literature,[11] the study of alkali Schiff base complexes was rare and there are two forms of the tetramer of cubic form and the dimer of quadrilateral form. The Li and Na complexes in this paper are all tetramer of cubic form (Fig. 3).

Polymerization of L-lactide

Polymerizations of L-lactide using all of the Li and Na complexes with BnOH as an initiator in THF were investigated under nitrogen at 25 °C (Table 1). As seen in entries 1–6 of Table 1, Li complexes demonstrated different degrees of catalytic activity with different ligands. Only the polymerization of $\mathbf{L^6Li}$ was completed within 36 min and the reactivity order of Li catalysts is $\mathbf{L^6Li} > \mathbf{L^3Li} > \mathbf{L^5Li} > \mathbf{L^1Li} > \mathbf{L^4Li} > \mathbf{L^2Li}$. However, polymers catalyzed by high catalytic Li complexes showed broad polydispersity (entries 3 and 6). It is possible that the extra

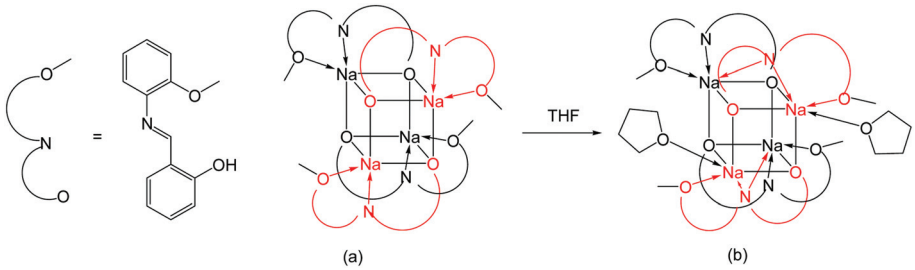


Fig. 3 Illustration of $\mathbf{L^4Na}$ X-ray structure.

Table 1 Polymerizations of L-lactide using each of the Li and Na complexes with BnOH as an initiator at 25 °C

Entry	Catalyst	Time (min)	Conv. (%)[a]	Mn_{Cal}[b]	Mn_{NMR}[a]	Mn_{GPC}[c]	PDI[c]
1[d]	L^1Li	90	52	7600	4200	4700	1.16
2[d]	L^2Li	90	45	3300	3600	6400	1.29
3[d]	L^3Li	40	88	6500	16 700	16 200	1.46
4[d]	L^4Li	90	10	830	2400	2100	1.14
5[d]	L^5Li	90	76	5600	1400	10 000	1.33
6[d]	L^6Li	36	90	6600	2300	15 200	1.31
7[e]	L^1Na	1	95	13 700	15 900	14 200	1.44
8[e]	L^2Na	1	91	13 200	5200	9000	1.82
9[e]	L^3Na	0.5	99	14 400	23 000	13 400	1.68
10[e]	L^4Na	40	93	13 500	3700	9000	1.21
11[e]	L^5Na	2	94	13 700	3600	12 000	1.48
12[e]	L^6Na	1	99	14 400	4700	13 100	1.58
13[f]	L^1Na	15	92	26 500	9800	16 000	1.50
14[f]	L^2Na	130	86	25 000	15 700	13 400	1.37
15[f]	L^3Na	2	99	28 600	27 700	23 200	1.36
16[f]	L^4Na	27.5 h	70	20 300	7300	11 800	1.18
17[f]	L^5Na	90	82	23 900	17 200	14 400	1.38
18[f]	L^6Na	15	88	25 400	16 000	15 500	1.51
19[g]	L^1Na	4	94%	13 700	11 000	8500	1.42
20[g]	L^2Na	3	99%	14 400	14 300	8300	1.49
21[g]	L^4Na	6.5	86%	12 500	12 700	7800	1.26
22[g]	L^5Na	2	99%	14 400	6400	8000	1.47
23[g]	L^6Na	4	99%	14 400	13 600	8100	1.34

[a] Obtained from ^{1}H NMR analysis. [b] Calculated from the molecular weight of LA × $[LA]_0/[BnOH]_0$ × conversion yield + Mw(BnOH). [c] Obtained from GPC analysis and calibrated using the polystyrene standard. Values in parentheses are the values obtained from GPC times 0.58. [d] Reaction condition: toluene (10 mL), [LA] = 0.5 M, [LA] : [BnOH] : [Cat] = 100 : 1 : 0.25. [e] Reaction condition: THF (10 mL), [LA] = 0.5 M, [LA] : [BnOH] : [Cat] = 100 : 1 : 0.25. [f] Reaction condition: THF (10 mL), [LA] = 1 M, [LA] : [BnOH] : [Cat] = 200 : 1 : 0.125. [g] Reaction condition: toluene (10 mL), [LA] = 0.5 M, [LA] : [BnOH] : [Cat] = 100 : 1 : 0.25. L^3Na is insoluble in toluene.

donating group of ligands, such as L^1, L^2, L^4, and L^5, coordinates with Li to prevent the transesterification but decreases reactivity by competing with L-lactide. According to the polymerization data, the order of bond strength is Li–O > Li–N > Li–S. As seen in entries 7–12 of Table 1, Na complexes demonstrated efficient activity in the polymerization of L-lactide and all other complexes, except $\mathbf{L^4Na}$ (conv. = 93% in 40 min, PDI = 1.21) went to completion within 2 min. This means that the bond between the Na and phenylmethylether group of $\mathbf{L^4}$ is strong and L-lactide has to coordinate with Na in competition with the phenylmethylether group. Although other Na complexes demonstrated notable activity, the polydispersity of the polymers was broad. To overcome this problem, the ratio ([LA] : [BnOH] : [Cat] = 200 : 1 : 0.125, [LA] = 1 M) was used in entries 13–18. The polydispersity of the polymer narrowed but the reaction time increased 15–130 times that of the original. The reaction time of LA polymerization by $\mathbf{L^4Na}$ extended to 27.5 h with PDI = 1.18. The reactivity order of Na catalysts is $\mathbf{L^3Na}$ > $\mathbf{L^1Na}$ ≥ $\mathbf{L^6Na}$ > $\mathbf{L^5Na}$ > $\mathbf{L^2Na}$ > $\mathbf{L^4Na}$. The catalytic order of Na complexes is different than those of Li complexes, possibly because the order of bond strength is Na–O > Na–S > Na–N. Polymerization using Na complexes in toluene were also studied in entries 19–23. The Na complexes still demonstrated efficient activity and the polymerization went to completion within 6.5 min; however, the catalytic time of $\mathbf{L^4Na}$ decreased to 6.5 min. Compared with THF, these polymers had the property that Mn_{GPC} was smaller than Mn_{NMR}. This means that transesterification occurs frequently in toluene. The ^{1}H NMR spectrum of PLLA prepared by $\mathbf{L^4Li}$ (entry 4) showed that one benzyl group and hydroxy chain ends with an integral ratio of 5 : 2 between Ha and Hd, suggesting that initiation occurred through the insertion of the BnOH into L-lactide (Fig. 4). The results show that the catalytic activity of Na complexes is faster than that of Li complexes, which exactly matches the results in previous studies. The general explanation is that the size of Na exceeds that of Li, which increases the ability of LA coordination with

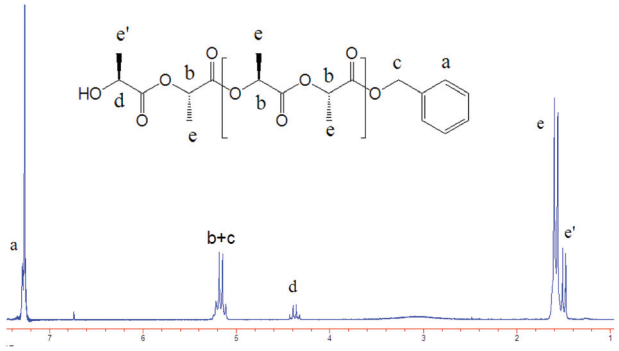


Fig. 4 ^{1}H NMR spectrum of PLLA (polymerization by L^{4}Li, entry 4).

the metal. A survey of the recent literature on LA polymerization using Li and Na complexes is shown in Fig. 5 and 6. Fig. 5 shows that the catalytic activity order is Li aminophenolate[7i,j] > Li iminophenolate > Li bisphenolate[7b,c,d,m] > Li bissulfonamidate[7l] > Li bispyrazol-1-ylacetamidinate.[7h] The results show that Li complexes with a phenol group as the ligands display high catalytic activity in LA polymerization. A nitrogen atom from the amino or imino group can improve the reactivity by regulating the coordination number, the geometry, and the valence electrons. The polymerization time using Li benzenesulfonamidate and di-pyrazol-1-yl-acetamidinate complex extended to 2.5 h and 36 h (110 °C), respectively. Fig. 6 shows that Na complexes exhibit catalytic ability six to eighteen times greater than that of Li complexes and Na phenolate complexes have better activity than Na benzenesulfonamidate complexes. With the regulation of nitrogen on the imine group, Na iminophenolate complexes demonstrate activity superior to other Na complexes described in the literature.

Conclusions

This study synthesized a series of iminophenol ligands (L$^{1-6}$–H) and their lithium and sodium complexes. These complexes showed that they are the tetramer of cubic form with the five-coordinate for Li and six-coordinate for Na complexes. By adjusting the coordination number and size of the imino group, the activity of the system altered the polymerization of LA. Generally, by changing coordination number of the ligands from 3 to 2, the degree of activity dramatically increases. The third coordination atom contends with L-lactide and decreases activity. However this effect also protects the active center against transesterification and increases the catalytic control of the polymer polydispersity. Oxygen is the third atom in the tridentate ligand, such as L^{2}–H and L^{4}–H, providing stronger chelation ability than nitrogen or sulfur, and preventing the coordination of L-lactide with the metal.

Experimental

General

Standard Schlenk techniques and a N_2-filled glovebox were used throughout the isolation and handling of all the compounds. Solvents, L-lactide, and deuterated solvents were purified prior to use. Salicylaldehyde, *N*,*N*-dimethylethylenediamine, sodium hydride, *tert*-butylamine, *o*-anisidine, 2-(methylthio)aniline, and 2,6-diisopropylaniline were purchased from Alfa. 2,2-Dimethoxyethylamine, benzyl alcohol and lithium *tert*-butoxide were purchased from Aldrich. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Gemini2000-200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometer with chemical shifts given in ppm from the internal TMS or center line of $CDCl_3$. Microanalyses were performed using a Heraeus CHN–O–RAPID instrument. The gel permeation chromatography (GPC) measurements were performed on a Waters 1515 Isotratic HPLC pump system equipped with a differential Waters 2414 refractive index detector using THF (HPLC grade) as the eluent. The chromatographic column was a Water Styragel Column (HR4E), and the calibration curve was made by polystyrene standards to calculate Mn(GPC). L^{1}–H,[5h] L^{3}–H,[10] L^{4}–H,[10] and L^{6}–H[10] were prepared by acid-catalyzed condensation following literature procedures.

Synthesis of 2-((*E*)-(2,2-dimethoxyethylimino)methyl)phenol (L^{2}–H)

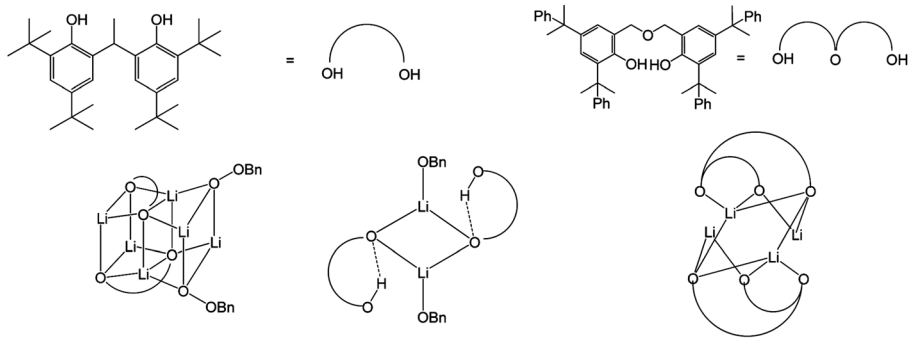
A mixture of 2,2-dimethoxyethanamine (5.26 g, 50 mmol) and 2-hydroxybenzaldehyde (6.11 g, 500 mmol) in toluene (20 mL), was refluxed with a Dean–Stark condenser for 12 h. Volatile materials were removed under vacuum to give dark yellow powder. Yield: 10.22 g (90%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.26 (1H, s, C*H*=N), 7.163–7.271, 6.76–6.90, (4H, m, ArH), 4.53 (1H, t, J = 5.6 Hz, $CH_2CH(OCH_3)_2$), 3.66 (2H, d, J = 5.6 Hz, CH=NCH_2), 3.33 ppm (6H, s, $CH_2CH(OCH_3)_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 167.01 (*C*=N), 160.02 (*C*OH), 132.40, 132.34, 131.38, 118.53, 110.94 (Ar), 103.50 ($CH_2CH(OCH_3)_2$), 61.417 ($CH_2CH(OCH_3)_2$), 54.32 (OCH_3). Anal. Calcd (found) for $C_{11}H_{15}NO_3$ (209.26): C, 63.14 (62.99); H, 7.23 (7.46); N, 6.69 (6.90)%.

Synthesis of 2-((*E*)-(2-(methylthio)phenylimino)methyl)phenol (L^{5}–H)

Using a method similar to that for L^{2}–H. Yield: 11.90 g (90%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.64 (1H, s, C*H*=N), 7.36–7.28, 7.21–7.10, 7.01–6.83, (8H, m, ArH), 2.41 ppm (3H, s, SCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 161.43 (*C*=N), 160.03 (*C*OH), 144.06 ($CSCH_3$), 134.76, 133.09, 132.17, 127.32, 125.06, 124.70, 119.05, 118.88, 117.12, 116.20 (Ar), 14.52 (SCH_3). Anal. Calcd (found) for $C_{14}H_{13}NOS$ (243.35): C, 69.11 (67.73); H, 5.39 (5.44); N, 5.76 (6.41)%.

Synthesis of L^{1}Li

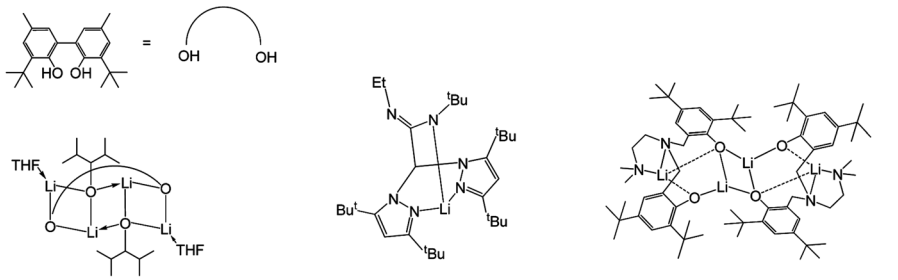
A mixture of L^{1}–H (1.92 g, 10 mmol) and lithium *tert*-butoxide (0.80 g, 10 mmol) in THF (10 mL), was stirred for 12 h. Volatile materials were removed under vacuum to give white powder and then it was washed with hexane (20 mL) and white powder was obtained after filtration. Yield: 1.78 g (66%). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.06 (1H, s, C*H*=N), 7.12–7.05, 6.61–6.47, (4H, m, ArH), 3.27 (2H, br, $NCH_2CH_2N(CH_3)_2$), 2.14 (2H, br, $NCH_2CH_2N(CH_3)_2$), 1.95 (6H, s, $N(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 167.85 (*C*=N), 166.92 (*C*OH), 135.06, 132.14,



Ref. 7b
25 °C, CH_2Cl_2, M = *L*-LA
[M] / [Cat] = 150, [Cat] = 5 mM
reaction time = 1 hr, conv. > 99 %
Mn_{GPC} = 22100, PDI = 1.43,

Ref. 7d
25 °C, CH_2Cl_2, M = *L*-LA
[M] / [Cat] = 50, [Cat] = 5 mM
reaction time = 1 hr, conv. > 99 %
Mn_{GPC} = 15900, PDI = 1.16,

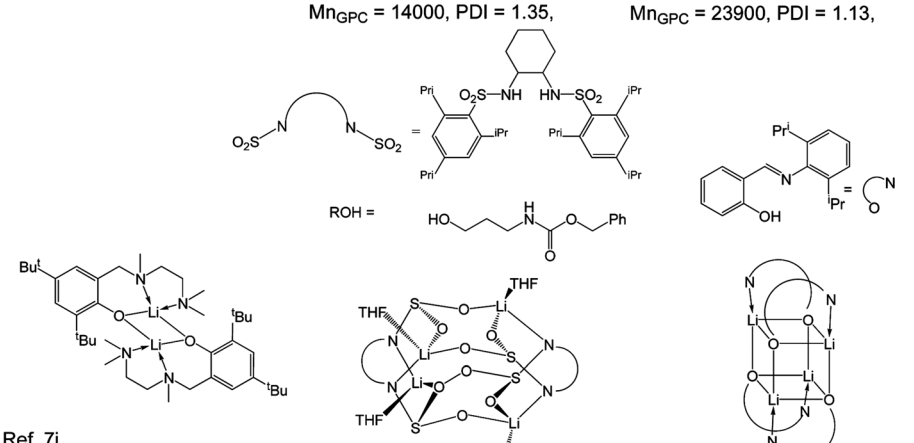
Ref. 7m
20 °C, CH_2Cl_2, M = *L*-LA
[M] / [Cat] / [BnOH]= 200 / 1 / 2,
[Cat] = 0.25 mM, conv. = 93 %
reaction time = 50 min,
Mn_{GPC} = 25900, PDI = 1.06,



Ref. 7c
25 °C, CH_2Cl_2, M = *rac*-LA
[M] / [Cat] = 200, [Cat] = 6 mM
reaction time = 1 hr, conv. > 99 %
Mn_{GPC} = 16000, PDI = 1.72,

Ref. 7h
110 °C, toluene, M = *L*-LA
[M] / [Cat] = 100, Cat. = 90 μmol
[Cat] = no mention.
reaction time = 36 hr, conv. = 92 %
Mn_{GPC} = 14000, PDI = 1.35,

Ref. 7i
26.5 °C, CH_2Cl_2, M = *L*-LA
[M] / [Cat] / [BnOH] = 100 / 1 / 1,
[Cat] = 10 mM, conv. = 92 %
reaction time = 15 min,
Mn_{GPC} = 23900, PDI = 1.13,



Ref. 7j
26.5 °C, CH_2Cl_2, M = *L*-LA
[M] / [Cat] / [BnOH] = 100 / 1 / 1,
[Cat] = 10 mM, conv. = 96 %
reaction time = 5 min,
Mn_{GPC} = 21400, PDI = 1.25,

Ref. 7l
28 °C, toluene, M = *L*-LA
[M] / [Cat] / [ROH] = 100 / 1 / 1,
[Cat] = 6.25 mM, yield = 90 %
reaction time = 2.5 hr,
Mn_{GPC} = 14600, PDI = 1.07,

This work
25 °C, THF, M = *L*-LA
[M] / [Cat] / [BnOH] = 100 / 1 / 1,
[Cat] = 1.25 mM, conv. = 90 %
reaction time = 36 min,
Mn_{GPC} = 26200, PDI = 1.31,

Fig. 5 A survey of the recent literature sources on LA polymerization using Li complexes.

122.71, 113.24, (Ar), 59.88 ($NCH_2CH_2N(CH_3)_2$), 58.70 ($NCH_2CH_2N(CH_3)_2$), 45.33 ($NCH_2CH_2N(CH_3)_2$). Anal. Calcd (found) for $C_{11}H_{15}N_2OLi$ (198.19): C, 66.66 (66.26); H, 7.63 (7.53); N, 14.13 (14.58)%. Mp: 162 °C.

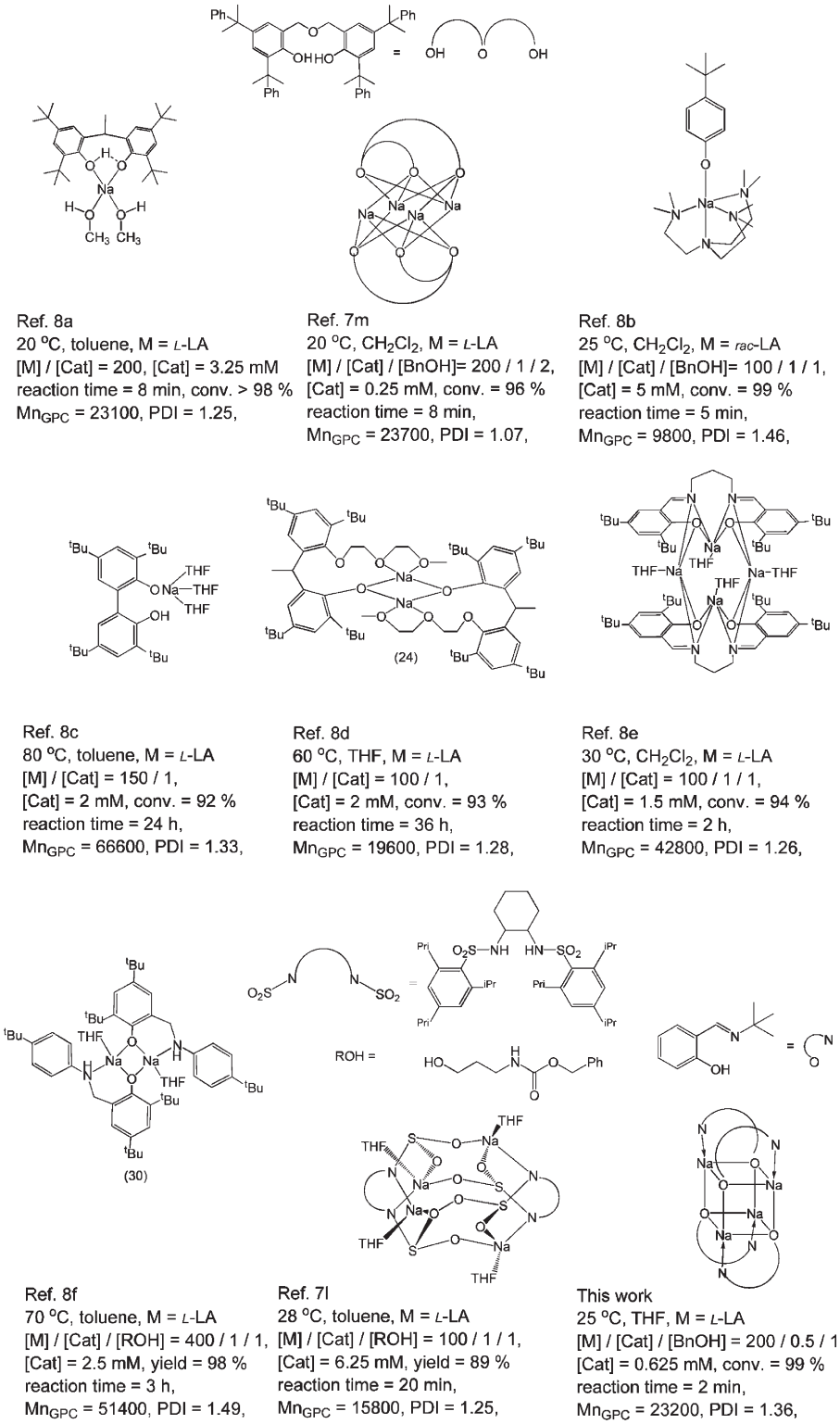


Fig. 6 A survey of the recent literature sources on LA polymerization using Na complexes.

Synthesis of L^{2}Li

Using a method similar to that for L^{1}Li. Yield: 1.97 g (68%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.97 (1H, s, C*H*═N), 7.08–7.04 (2H, m, ArH), 6.64 (1H, d, J = 8.4 Hz, ArH), 6.46 (1H, t, J = 7.4 Hz, ArH), 4.11 (1H, br, CH$_2$C*H*(OCH$_3$)$_2$), 3.10 (2H, br, CH═NC*H*$_2$), 3.03 ppm (6H, s, CH$_2$CH(OC*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 50 MHz): δ 167.32 (*C*OH), 160.65 (*C*═N), 134.78, 131.99, 123.39, 122.07, 112.72 (Ar), 103.15 (CH$_2$*C*H(OCH$_3$)$_2$), 62.71 (*C*H$_2$CH(OCH$_3$)$_2$), 53.80 (O*C*H$_3$). Anal. Calcd (found)

for $C_{11}H_{14}NO_3Li$ (215.17): C, 61.40 (60.94); H, 6.56 (6.48); N, 6.51 (6.25)%. Mp: 180 °C.

Synthesis of L^3Li

Using a method similar to that for L^1Li. Yield: 1.46 g (57%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.09 (1H, s, C*H*═N), 7.17–7.04 (2H, m, ArH), 6.54 (2H, t, J = 6.8 Hz, ArH), 0.99 ppm (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 166.77 (*C*OH), 163.16 (*C*═N), 138.70, 131.67, 128.74, 123.18, 118.60 (Ar), 29.81 (C(CH_3)$_3$). Anal. Calcd (found) for $C_{11}H_{14}NOLi$ (183.18): C, 72.13 (70.06); H, 7.70 (7.90); N, 7.65 (6.90)%. Mp > 300 °C.

Synthesis of L^4Li

Using a method similar to that for L^1Li. Yield: 1.88 g (61%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.17 (1H, s, C*H*═N), 7.08 (1H, br, ArH), 6.92–6.81 (3H, m, ArH), 6.75 (1H, d, J = 7.6 Hz, ArH), 6.53 (1H, d, J = 8.2 Hz, ArH), 6.38 (1H, d, J = 6.3 Hz, ArH), 6.14 (1H, t, J = 7.2 Hz, ArH), 3.93 ppm (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 172.62 (*C*OH), 160.72 (*C*═N), 152.70, 139.05, 134.99, 131.40, 126.03, 123.24, 122.81, 120.49, 115.44, 112.60, 110.19 (Ar), 55.04 (O*C*H$_3$). Anal. Calcd (found) for $C_{14}H_{12}NO_2Li$ (233.19): C, 72.11 (72.13); H, 5.19 (5.38); N, 6.01 (5.90)%. Mp > 300 °C.

Synthesis of L^5Li

Using a method similar to that for L^1Li. Yield: 2.16 g (67%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.05 (1H, s, C*H*═N), 6.99–6.94, 6.71–6.57, (6H, m, ArH), 6.37 (1H, d, J = 8.6 Hz, ArH), 6.25 (1H, t, J = 7.0 Hz, ArH), 1.94 ppm (3H, s, SCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 168.85 (*C*OH), 165.98 (*C*═N), 150.92 (*C*SCH$_3$), 135.60, 132.67, 132.01, 126.12, 126.00, 125.21, 123.63, 122.64, 119.06, 113.24, (Ar), 15.51 (S*C*H$_3$). Anal. Calcd (found) for $C_{14}H_{12}NOSLi$ (249.26): C, 67.46 (66.90); H, 4.85 (5.36); N, 5.62 (5.39)%. Mp: 224 °C.

Synthesis of L^6Li

Using a method similar to that for L^1Li. Yield: 2.16 g (67%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.86 (1H, s, C*H*═N), 7.07–6.93, 6.54–6.47, (7H, m, ArH), 6.37 (1H, d, J = 8.6 Hz, ArH), 2.43 (2H, m, C*H*(CH$_3$)$_2$), 0.84, 0.44 ppm (12H, s, J = 6.6 Hz, CH(CH_3)$_2$)). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.34 (*C*OH), 170.46 (*C*═N), 150.66, 139.11, 138.18, 134.34, 124.43, 123.39, 122.14, 122.01, 112.93 (Ar), 28.12 (CH(*C*H$_3$)$_2$), 25.27, 22.48 (*C*H(CH$_3$)$_2$). Anal. Calcd (found) for $C_{19}H_{22}NOLi$ (287.19): C, 79.42 (77.86); H, 7.72 (8.09); N, 4.89 (5.15) %. Mp: >300 °C.

Synthesis of L^1Na

A mixture of L^1–H (3.85 g, 20 mmol) and sodium hydride (0.48 g, 20 mmol) in THF (20 mL), was stirred for 12 h. Volatile materials were removed under vacuum to give white powder and then it was washed with hexane (50 mL) and white powder was obtained after filtration. Yield: 3.27 g (75%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.16 (1H, s, C*H*═N), 7.06–6.94, 6.41–6.28, (4H, m, ArH), 3.38 (2H, br, NCH_2CH$_2$N(CH$_3$)$_2$), 2.19 (2H, br, NCH$_2$CH_2N(CH$_3$)$_2$), 1.72 (6H, s, N(CH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 172.02 (*C*OH), 166.24 (*C*═N), 135.97, 131.40, 123.28, 123.05, 110.40 (Ar), 61.05 (N*C*H$_2$CH$_2$N(CH$_3$)$_2$), 58.61 (NCH$_2$*C*H$_2$N(CH$_3$)$_2$), 44.73 (NCH$_2$CH$_2$N(*C*H$_3$)$_2$). Anal. Calcd (found) for $C_{11}H_{15}N_2ONa$ (214.27): C, 61.67 (61.79); H, 7.06 (7.62); N, 13.08 (12.79)%. Mp: 288 °C.

Synthesis of L^2Na

Using a method similar to that for L^1Na. Yield: 3.12 g (67%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.09 (1H, s, C*H*═N), 7.06–6.98 (2H, m, ArH), 6.52 (1H, d, J = 9.0 Hz, ArH), 6.33 (1H, t, J = 7.4 Hz, ArH), 4.20 (1H, t, J = 4.8 Hz, CH$_2$C*H*(OCH$_3$)$_2$), 3.44 (2H, d, J = 4.8 Hz, CH═NCH_2), 3.01 ppm (6H, s, CH$_2$CH(OCH_3)$_2$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.29 (*C*OH), 167.56 (*C*═N), 135.47, 131.82, 124.23, 122.49, 111.11 (Ar), 103.55 (CH$_2$*C*H(OCH$_3$)$_2$), 61.98 (*C*H$_2$CH(OCH$_3$)$_2$), 53.42 (O*C*H$_3$). Anal. Calcd (found) for $C_{11}H_{14}NO_3Na$ (213.26): C, 57.14 (56.45); H, 6.10 (6.28); N, 6.06 (5.73)%. Mp: 188 °C.

Synthesis of L^3Na

Using a method similar to that for L^1Na. Yield: 2.6 g (54%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.06 (1H, s, C*H*═N), 7.13–7.07 (2H, m, ArH), 6.54–6.42 (2H, m, ArH), 0.96 ppm (9H, s, C(CH_3)$_3$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 169.96 (*C*OH), 163.51 (*C*═N), 136.91, 133.21, 123.40, 122.08, 112.11 (Ar), 29.67 (C(CH_3)$_3$). Anal. Calcd (found) for $C_{11}H_{14}NONa$ (199.26): C, 66.32 (63.86); H, 7.08 (7.12); N, 7.03 (7.78)%. Mp: 260 °C.

Synthesis of L^4Na

Using a method similar to that for L^1Na. Yield: 3.65 g (73%). ^1H NMR ($CDCl_3$, 200 MHz): δ 8.19 (1H, s, C*H*═N), 7.07–6.84 (5H, m, ArH), 6.62 (1H, d, J = 7.8 Hz, ArH), 6.45 (1H, d, J = 8.2 Hz, ArH), 6.27 (1H, t, J = 7.4 Hz, ArH), 3.35 ppm (3H, s, OCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.88 (*C*OH), 164.13 (*C*═N), 152.16, 141.37, 136.38, 132.77, 125.74, 123.07, 122.67, 121.31, 117.82, 111.60, 110.52 (Ar), 55.01 (O*C*H$_3$). Anal. Calcd (found) for $C_{14}H_{12}NO_2Na$ (249.28): C, 67.46 (66.66); H, 4.85 (5.36); N, 5.62 (5.55)%. Mp: 206 °C.

Synthesis of L^5Na

Using a method similar to that for L^1Na. Yield: 3.15 g (59%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.94 (1H, s, C*H*═N), 6.96, (5H, br, ArH), 6.75 (1H, br, ArH), 6.41 (1H, br, ArH), 6.25 (1H, br, ArH), 1.99 ppm (3H, s, SCH_3). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.75 (*C*OH), 166.87 (*C*═N), 151.87 (*C*SCH$_3$), 137.11, 133.00, 130.64, 126.16, 125.13, 123.22, 122.45, 119.12, 111.66, (Ar), 14.71 (S*C*H$_3$). Anal. Calcd (found) for $C_{14}H_{12}NOSNa$ (265.35): C, 63.38 (62.83); H, 4.56 (4.56); N, 5.28 (5.31)%. Mp: 244 °C.

Synthesis of L^6Na

Using a method similar to that for L^1Na. Yield: 3.03 g (50%). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.94 (1H, s, C*H*═N), 7.14–6.97, 6.47–6.40, (7H, m, ArH), 3.11, 2.54 (2H, br, C*H*$(CH_3)_2$), 1.26, 0.88, 0.49 ppm (12H, br, CH(CH_3)$_2$)). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 171.29 (*C*OH), 170.64 (*C*═N), 150.67, 139.14, 138.24, 134.47, 124.47, 123.69, 123.32, 122.10, 113.05 (Ar), 27.99 (CH(*C*H_3)$_2$), 25.89, 24.80, 23.30, 21.63 (*C*H$(CH_3)_2$). Anal. Calcd (found) for $C_{19}H_{22}NONa$ (303.41): C, 75.22 (75.65); H, 7.31 (6.90); N, 4.62 (4.03) %. Mp: 292 °C.

X-Ray crystallographic studies

Suitable crystals of complexes **L^5Li** and **L^4Na** were sealed in a thin-walled glass capillary under dry nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing width of 0.3° per frame. The absorption correction was based on the symmetry-equivalent reflections using the SADABS program. The space group determination was based on a check of the Laue symmetry and systematic absences and confirmed by using the structure solution. The structure was solved by a direct method using an SHELXTL package. 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 H atoms.

General procedures for the polymerization of L-lactides

A typical polymerization procedure was exemplified by the synthesis of entry 21 (Table 1) using complex **L^4Na** as a catalyst. The polymerization conversion was analyzed by ^1H NMR spectroscopic studies. Toluene (10.0 mL) was added to a mixture of complex **L^4Na** (0.0125 g, 0.0125 mmol) and L-lactide (0.72g, 5 mmol) at 25 °C. After the solution was stirred for 6.5 min, the reaction was quenched by adding a drop of ethanol, and the polymer was precipitated pouring into *n*-hexane (30.0 mL) to give a white solid. The white solid was dissolved in CH_2Cl_2 (5.0 mL) and then *n*-hexane (70.0 mL) was added to give a white crystalline solid. Yield: 0.68 g (94%).

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