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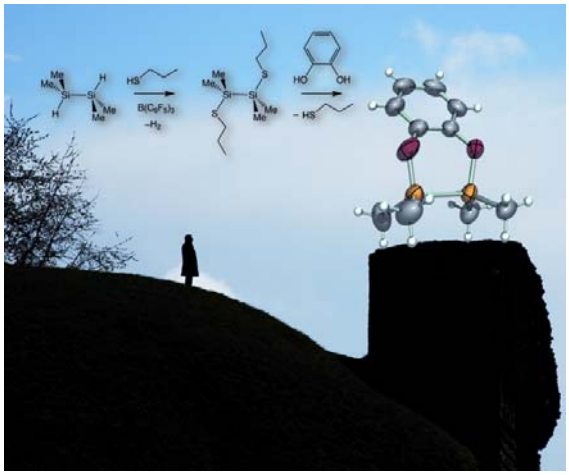

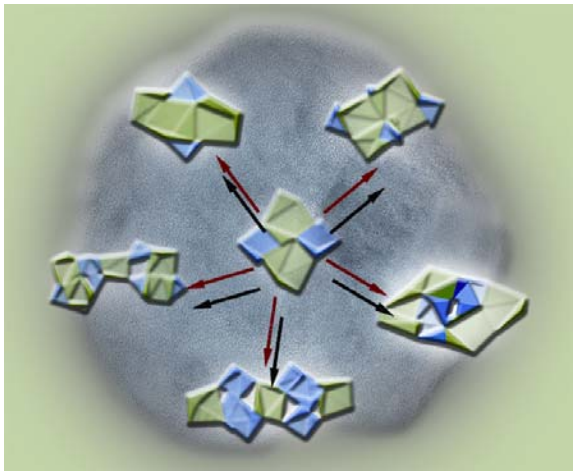

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Structural and catalytic studies of lithium complexes bearing pendant aminophenolate ligands†

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Lithium complexes bearing mono-anionic aminophenolate ligands are described. Reactions of ligand precursors $HON^{Me}Ph^{OMe}$, $HON^{Me}Ph^{SMe}$, $HON^{Me}C^{OMe}$ or $HON^{Me}C^{NMe2}$ [$HON^{Me}Ph^{OMe}$ = (2-$OMeC_6H_4$-CH_2)N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}Ph^{SMe}$= (2-SMe-$C_6H_4CH_2$)N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}C^{OMe}$ = ($MeOCH_2CH_2$)N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}C^{NMe2}$ = ($Me_2NCH_2CH_2$)N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$)] with 1.1–1.3 molar equivalents of ^{n}BuLi in diethyl ether solution afford ($LiON^{Me}Ph^{OMe}$)$_2$ (**3**), ($LiON^{Me}Ph^{SMe}$)$_2$ (**4**), ($LiON^{Me}C^{OMe}$)$_2$ (**5**) and ($LiON^{Me}C^{NMe2}$)$_2$ (**6**) as dinuclear lithium complexes. The BnOH adduct of **5**, (BnOH)($LiON^{Me}C^{OMe}$) (**7**), was prepared from the reaction of **5** and BnOH in diethyl ether solution. The molecular structures are reported for ligand precursor $HON^{Me}Ph^{SMe}$ and compounds **3–5** and **7**. These dinuclear lithium complexes show excellent catalytic activities toward the ring-opening polymerization of L-lactide in the presence of benzyl alcohol.

Introduction

There is an increasing interest in the development of catalysts/initiators for ring opening polymerization during the past decades. Indeed, a large diversity of metal complexes has been synthesized and these have been reviewed recently.[1] Among these studies, metal complexes bearing multidentate aminophenolate(s) ligands have been a focus of interest, mainly due to their excellent activities and great success in the preparation of the well-defined polyesters.[2–4] The steric and electronic effects of those versatile ligands can be easily programmed through variation of the substituents on the nitrogen atoms, many of which can be easily achieved *via* the Mannich condensation reaction. Most recently, some lithium complexes bearing bridged phenolates have been reported to be effective catalysts/initiators in the ring opening polymerization of cyclic esters.[3r,5] Their performances on both 'living' and 'immortal' properties also encourage us to examine the catalytic activities of lithium aminophenolate complexes toward ring opening polymerization reaction.

As part of our continuing interest in the development of novel catalysts/initiators for ring opening polymerization,[3b,d,r] we report here the synthesis and characterization of lithium complexes bearing the pendant amine-phenolate ligands. Their catalytic activities toward ring opening polymerization of L-lactide in the presence of benzyl alcohol are also presented.

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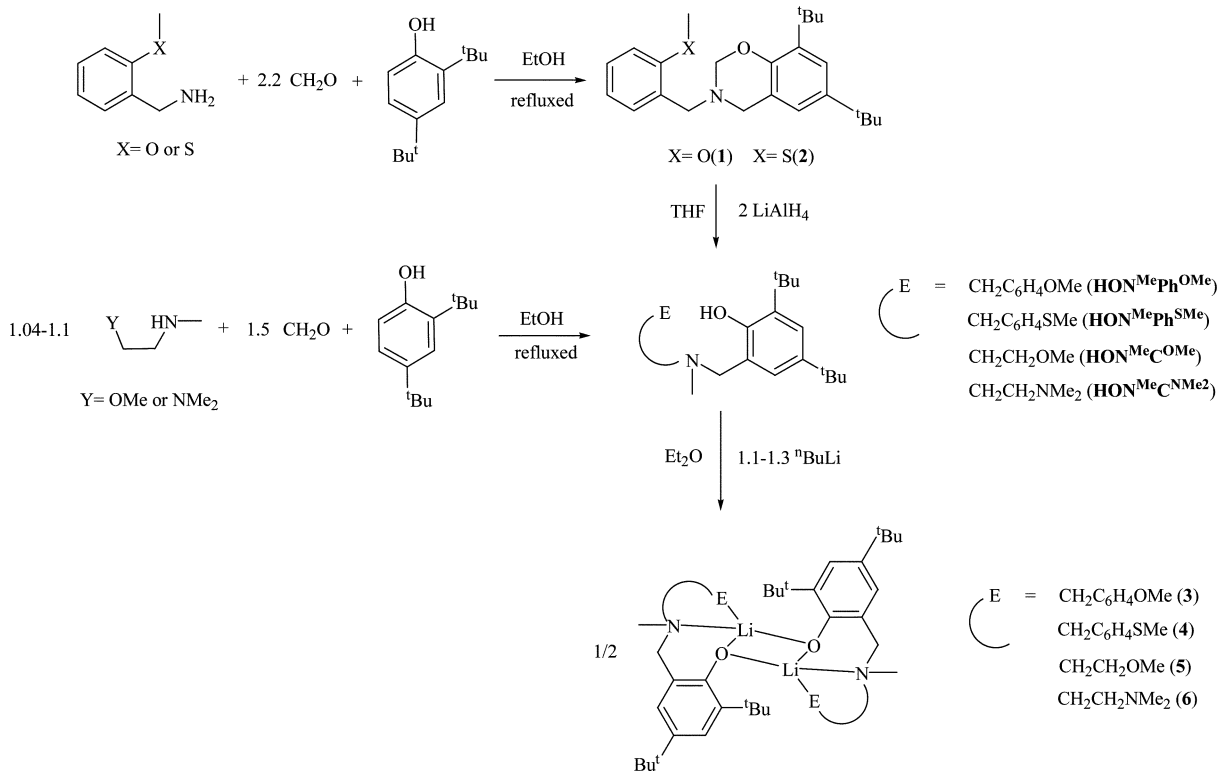
† Electronic supplementary information (ESI) available: Fig. S1: Molecular structure of $HON^{Me}PhS^{Me}$. Fig. S2: Homonuclear-decoupled methine ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of poly(L-lactide) synthesized at 26.5 °C for 5 min in CH_2Cl_2 using **6** as initiator. CCDC reference numbers 646484–646487. see DOI: 10.1039/b717370a

Results and discussion

Syntheses and characterization of lithium aminophenolate complexes

Ligand precursors $HON^{Me}Ph^{OMe}$, $HON^{Me}Ph^{SMe}$, $HON^{Me}C^{OMe}$ or $HON^{Me}C^{NMe2}$ [$HON^{Me}Ph^{OMe}$ = (2-OMe-$C_6H_4CH_2$)N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}Ph^{SMe}$= (2-SMe-$C_6H_4CH_2$)N(Me)-(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}C^{OMe}$ = $MeOCH_2CH_2$N-(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$); $HON^{Me}C^{NMe2}$ = Me_2NCH_2-CH_2N(Me)(CH_2-2-HO-3,5-$C_6H_2(^tBu)_2$)] are prepared from cyclization of 2-methoxybenzylamine or 2-methylthiobenzylamine with 2,4-di-*tert*-butylphenol and formaldehyde followed by the reduction of C-O bond with lithium aluminium hydride (for $HON^{Me}Ph^{OMe}$ and $HON^{Me}Ph^{SMe}$),[6] or from the condensation reaction of *N*-(2-methoxyethyl)methylamine or *N*,*N*,*N*′-trimethylethylenediamine with 2,4-di-*tert*-butylphenol and formaldehyde (for $HON^{Me}C^{OMe}$ and $HON^{Me}C^{NMe2}$),[4b] as shown in Scheme 1.

All the ligand precursors are characterized by NMR spectroscopy as well as microanalyses or by comparison with data reported in the literature.[4b] Crystals of $HON^{Me}Ph^{SMe}$ suitable for X-ray crystallographic analysis were grown from slow evaporation of hexane solution at room temperature. The molecular structure features a monomer without any intra- or inter- molecular hydrogen bonding, as shown in Fig. S1 (ESI†). This structure reveals a tertiary amine with potential to work as pendant aminophenolate ligand. Reactions of ligand precursors $HON^{Me}Ph^{OMe}$, $HON^{Me}Ph^{SMe}$, $HON^{Me}C^{OMe}$ or $HON^{Me}C^{NMe2}$ with 1.1–1.3 molar equivalents of ^{n}BuLi in diethyl ether afford ($LiON^{Me}Ph^{OMe}$)$_2$ (**3**), ($LiON^{Me}Ph^{SMe}$)$_2$ (**4**), ($LiON^{Me}C^{OMe}$)$_2$ (**5**) and ($LiON^{Me}C^{NMe2}$)$_2$ (**6**) as dinuclear lithium complexes. Due to the good solubility, the isolated yields (22–42%) are relatively lower for those dinuclear lithium complexes. Compounds **3–6** are characterized by NMR spectroscopy as well as microanalyses. Two sets of diastereotopic signals corresponding to the methylene protons of N–CH_2–aryl



Scheme 1

are found on the ^{1}H NMR spectra of **3** and **4** (2.42 and 4.08 ppm on ^{1}H NMR spectrum correlate to 56.1 ppm on ^{13}C{^{1}H} NMR spectrum, 2.82 and 4.37 ppm on ^{1}H NMR spectrum correlate to 64.1 ppm on ^{13}C{^{1}H} NMR spectrum for **3**; 2.59 and 4.15 ppm on ^{1}H NMR spectrum correlate to 58.4 ppm on ^{13}C{^{1}H} NMR spectrum, 2.83 and 4.31 ppm on ^{1}H NMR spectrum correlate to 63.6 ppm on ^{13}C{^{1}H} NMR spectrum for **4**). Due to the conformational flexibility of the aliphatic pendant groups, several sets of diastereotopic signals corresponding to the methylene protons of N–CH_2–aryl and N–(CH_2)$_2$–E are found on the ^{1}H NMR spectra of **5** and **6**. The ^{7}Li{^{1}H} NMR spectra of **3–6** in toluene-d_8 show singlet resonances at 2.64, 2.93, 2.37 and 2.40 ppm, respectively, indicating the single Li environment in solution. Crystals of **3–5** suitable for an X-ray determination were grown from concentrated hexane solution. The molecular structures of **3**, **4** and **5** exist as lithium-bridged dimers with a core planar Li–O–Li–O ring in each case and their molecular structure diagrams are depicted in Fig. 1–3.

Compound **3** can be described as a centrosymmetric dimer with a Li–O(1)–LiA–O(1A) planar core ring. Each of the lithium atoms is four-coordinate, which is bonded to one nitrogen atom of central amine, one oxygen atom of pendant functionality and two oxygen atoms of different phenolates. The planar core features two different Li–$O_{phenolates}$ distances of 1.863(3) and 1.910(3) Å with LiOLi and OLiO angles of 83.91(15) and 96.09(15)°. These data are in the range of the known distances and angles for dimeric lithium phenolate complexes.[7] The bond lengths of Li–O_{OMe} (Li–O(2A), 2.058(4) Å; Li(A)–O(2), 2.058(4) Å) are near the upper extremes of those (1.929–2.025 Å) found in literature.[8] The bond lengths of Li–N_{amine} (Li–N(0A), 2.101(3) Å; Li(A)–N, 2.101(3) Å) are within those (2.10(2)–2.332(8) Å) found in literature.[7c,9] Basically, compound **4** is quite similar to compound **3** with a different pendant group –SMe instead of –OMe for **3**. Each lithium atom is bonded to one nitrogen atom of the central amine, one sulfur atom of pendant functionality and two oxygen atoms of different phenolates. Similar to **3**, two lithium phenolates

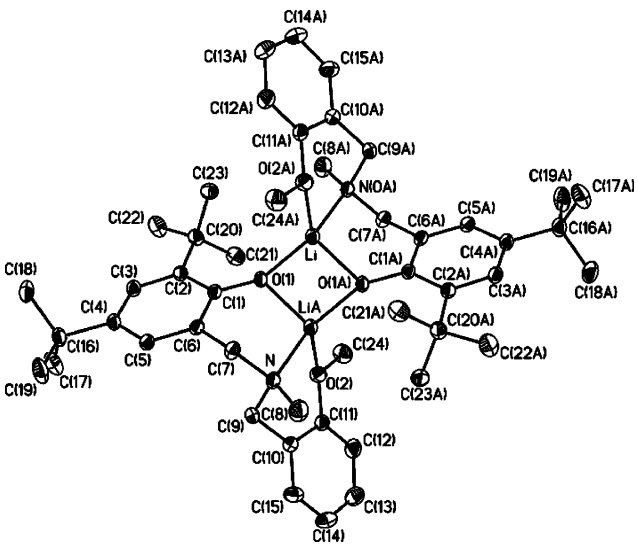


Fig. 1 Molecular structure of **3**. Selected bond lengths (Å) and bond angles (°): Li–O(1), 1.863(3); Li–O(1A), 1.910(3); Li–O(2A), 2.058(4); Li–N(0A), 2.101(3); Li(A)–O(1), 1.910(3); Li(A)–O(2), 2.058(4); Li(A)–N, 2.101(3); O(1)–Li–O(1A), 96.09(15); Li–O(1)–Li(A), 83.91(15). Hydrogen atoms omitted for clarity.

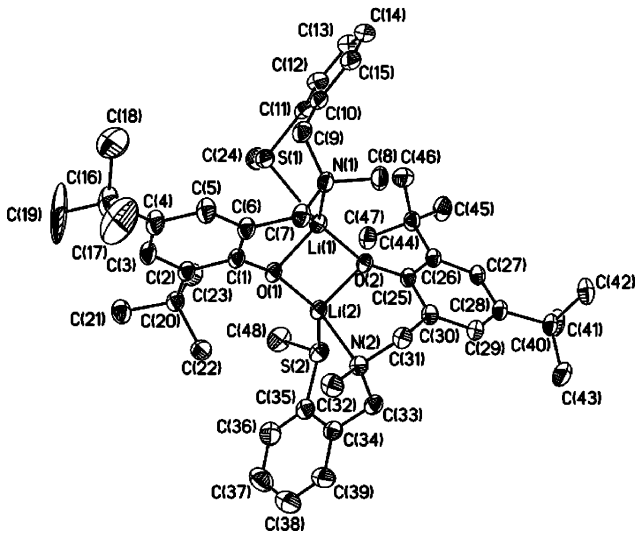


Fig. 2 Molecular structure of **4**. Selected bond lengths (Å) and bond angles (°): Li(1)–O(1), 1.894(4); Li(1)–O(2), 1.828(3); Li(1)–N(1), 2.059(4); Li(1)–S(1); 2.567(4); Li(2)–O(1), 1.809(3); Li(2)–O(2), 1.882(4); Li(2)–N(2), 2.058(4); Li(2)–S(2), 2.549(3); O(2)–Li(1)–O(1), 96.88(17); O(1)–Li(2)–O(2), 97.96(18); Li(2)–O(1)–Li(1), 82.48(16); Li(1)–O(2)–Li(2), 82.34(16). Hydrogen atoms omitted for clarity.

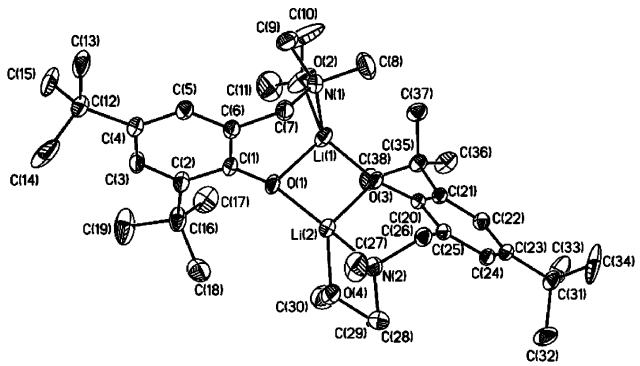


Fig. 3 Molecular structure of **5**. Selected bond lengths (Å) and bond angles (°): Li(1)–O(1), 1.922(5); Li(1)–O(2), 2.068(5); Li(1)–O(3), 1.823(5); Li(1)–N(1), 2.064(6); Li(2)–O(1), 1.856(5); Li(2)–O(3), 1.941(5); Li(2)–O(4), 2.022(5); Li(2)–N(2), 2.116(5); O(3)–Li(1)–O(1), 98.4(2); O(1)–Li(2)–O(3), 96.6(2); Li(2)–O(1)–Li(1), 82.1(2); Li(1)–O(3)–Li(2), 82.4(2). Hydrogen atoms omitted for clarity.

are bridged *via* Li–$O_{phenolate}$ bonds (1.828(3) and 1.809(3) Å) to form a planar core Li(1)–O(1)–Li(2)–O(2) ring with the angles subtended at oxygen atoms (82.48(16) and 82.34(16)°) narrower than those (96.88(17) and 97.96(18)°) at the lithium atoms. Unlike **3**, compound **4** is formed with two nitrogen atoms of amine above and two sulfur atoms of pendant functionality beneath the planar core ring. Bond lengths are similar to those discussed above with two Li–S_{SMe} bond lengths (2.567(4) and 2.549(3) Å) instead of Li–O_{OMe}. Bond lengths of Li–$O_{phenolates}$ (1.809(3)–1.894(4) Å) and Li–N_{amine} (2.059(4) and 2.058(4) Å) and bond angles of planar core Li–O–Li–O ring (O–Li–O, 96.88(17) and 97.96(18)°; Li–O–Li, 82.48(16) and 82.34(16)°) are similar to those discussed above for **3**. However, the geometric structures of **5** are similar to **4** with two nitrogen atoms of amine above and two oxygen atoms of pendant functionality beneath the planar core ring in each molecule.

Ring-opening polymerization of L-lactide catalyzed by 3–6 in the presence of benzyl alcohol

Several lithium phenolate complexes are known as efficient catalysts/initiators in the ring opening polymerization (ROP) of cyclic esters,[1e,f,3r] compounds **3–6** were expected to work as catalysts toward the ROP of L-lactide. Prescribed equivalent ratios on the catalyst (0.05 mmol), monomers and alcohol were employed in 10 mL solvent at 26.5 °C for the prescribed time. Representative results are collected in Table 1.

The results are solvent-dependent with CH_2Cl_2 being the best choice after several trials with toluene, THF and CH_2Cl_2 in the presence or absence of benzyl alcohol (BnOH). For the choice of initiator, we surveyed benzyl alcohol and isopropyl alcohol (IPA). Finally, we found that use of CH_2Cl_2 and benzyl alcohol leads to the best controlled behavior (entries 1–7). The same conditions were applied to examine the catalytic activity of **3**, **4** and **6**. After several trials (entries 8–10), compound **6** is the choice of the best catalyst among these dinuclear lithium complexes. Linear relationships between the number average molecular weights and the monomer-to-initiator ratio ($[M]_0/[I]_0$) demonstrated in Fig. 4 exhibit the 'living' character of the polymerization process (entries 10–14), however, the PDI values increase with monomer-to-initiator ratio. For the study of transesterification, compound **5** was chosen as candidate. Based on the data exhibited in Table 1 (entries 27–30), transesterification might occur in the later stages of ring opening polymerization.

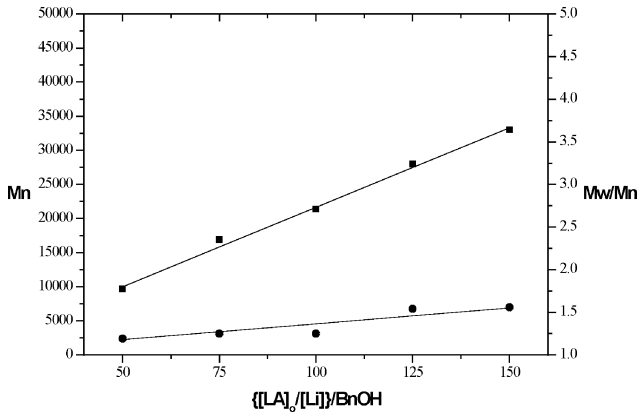


Fig. 4 Polymerization of L-lactide initiated by **6** and BnOH in CH_2Cl_2 at 26.5 °C.

This controlled behavior is further confirmed by the resumption experiments on **3–6** (entry 15 for **6**, entry 18 for **3**, entry 21 for **4**, and entry 24 for **5**). The 'immortal' character of **3–6** was examined using two or four equiv. ratios (relative to $[M]_0/[Li]_0$) of benzyl alcohol as the chain transfer agent (entries 16–17 for **6**; entries 19–20 for **3**; entries 22–23 for **4**; entries 25–26 for **5**). The number average molecular weights of the polymers created from these polymerization reactions became half or one to fourth of those found in the reactions with addition of one equiv. ratio of benzyl alcohol. Polymer produced by the '*in situ*' manner using L-lactide, lithium complex and BnOH on the ratios of 50 : 1 : 1 was used to examine the chain-end analysis. As shown in

Table 1 Ring-opening polymerization of L-lactides catalyzed by **3–7** at 26.5 °C[a]

Entry	Catalyst	{[M]$_0$/[Li]$_0$} : [BnOH]	t/min	M_n (obs.)[b]	M_n (calc.)[c]	Conv. (%)[d]	Yield (%)[e]	M_w/M_n[b]
1[f]	**5**	50 : 0	15	52000(30200)	5200	73	20	1.86
2[g]	**5**	50 : 0	15	9500(5500)	6100	84	42	35.64
3	**5**	50 : 0	15	41100(23800)	4900	68	41	1.89
4[f]	**5**	50 : 1	15	10700(6200)	6400	88	64	1.18
5[g]	**5**	50 : 1	15	3300(1900)	6900	94	77	2.87
6	**5**	50 : 1	15	12400(7200)	7000	95	81	1.14
7[h]	**5**	50 : 1	15	9600(5600)	3200	44	23	2.16
8	**3**	50 : 1	15	11000(6400)	6700	92	76	1.14
9	**4**	50 : 1	20	10100(5900)	6400	89	68	1.17
10	**6**	50 : 1	5	9700(5600)	6800	93	82	1.19
11	**6**	75 : 1	5	16900(9800)	10100	93	79	1.25
12	**6**	100 : 1	5	21400(12400)	13900	96	79	1.25
13	**6**	125 : 1	5	28000(16200)	17800	98	80	1.54
14	**6**	150 : 1	5	33000(19100)	20700	95	84	1.56
15	**6**	50(50)[i] : 1	5(5)	26100(15100)	13200	94(91)	72	1.30
16	**6**	100 : 2	5	10200(5900)	6300	86	75	1.15
17	**6**	200 : 4	5	13600(7900)	6600	90	88	1.11
18	**3**	50(50)[i] : 1	15(15)	30400(17600)	12800	89(88)	70	1.41
19	**3**	100 : 2	15	13500(7800)	7100	97	81	1.23
20	**3**	200 : 4	15	14100(8200)	7000	98	94	1.38
21	**4**	50(50)[i] : 1	25(25)	18000(10400)	12500	91(86)	77	1.26
22	**4**	100 : 2	20	13900(8100)	7000	96	85	1.22
23	**4**	200 : 4	20	13200(7700)	7100	97	88	1.32
24	**5**	50(50)[i] : 1	15(15)	23000(13300)	13900	96(96)	67	1.34
25	**5**	100 : 2	15	12900(7500)	6900	95	87	1.14
26	**5**	200 : 4	15	14000(8100)	7100	99	98	1.37
27	**5**	100 : 1	2	14200(8200)	6300	43	30	1.06
28	**5**	100 : 1	5	23100(13400)	10600	73	58	1.24
29	**5**	100 : 1	15	25100(14600)	13800	95	90	1.27
30	**5**	100 : 1	30	27600(16000)	13800	95	73	3.99
31	**7**	50 : 0	10	14100(8200)	6800	93	58	1.11
32	**7**	75 : 0	10	22500(13050)	10100	92	76	1.17
33	**7**	100 : 0	10	28600(16600)	13800	95	69	1.25
34	**7**	50(50)[i] : 0	10(10)	29100(16900)	12800	95(88)	66	1.30
35	**7**	100 : 1	10	15700(9100)	7200	98	76	1.17

[a] In 10 mL CH_2Cl_2. [Li]$_0$ = 0.01 M. [b] Obtained from GPC analysis and calibrated by polystyrene standard. Values in parentheses are the values obtained from GPC × 0.58.[10] [c] Calculated from [M(lactide) × ([M]$_0$/[Li]$_0$) × conversion yield/([BnOH]$_{eq}$)] + M(BnOH). [d] Obtained from ^{1}H NMR analysis. [e] Isolated yield. [f] In 10 mL toluene. [g] In 10 mL THF. [h] [BnOH] was replaced with [IPA]. [i] The values in parentheses are the second portion of monomers added after the polymerization of the first addition had gone to completion.

Fig. 5, peaks are almost the same as those found on the ^{1}H NMR spectra of polymers produced by lithium benzyl oxide initiators bearing bulky bis-phenolate ligands,[5a,c] and are assignable to the corresponding protons in the proposed structure.

Additionally, only one methine peak was found in the decoupled ^{1}H NMR spectrum of the products, as shown in Fig. S2 of ESI,† indicating that no significant racemization occurred during the polymerization of L-lactide initiated by the "*in situ*" manner.[11]

Mechanistic study for lithium amino phenolate complexes

In order to study the pathway of ROP of polyesters for the system discussed above, compound **5** and 2.2 molar equivalents of BnOH were mixed in diethyl ether solution to afford **7** as crystalline solid after slow evaporation of volatiles, as shown in Scheme 2.

Compound **7** is characterized by NMR spectroscopy as well as microanalyses. Similar to **5**, several sets of diastereotopic signals corresponding to the methylene protons of N–CH_2–aryl and N–(CH_2)$_2$–OMe are found on the ^{1}H NMR spectrum. A singlet resonance corresponding to the coordinated BnOH molecule (HOCH_2Ph) is found at 4.70 ppm on the ^{1}H NMR spectrum; however, with lower ratio compared to the integral intensities of

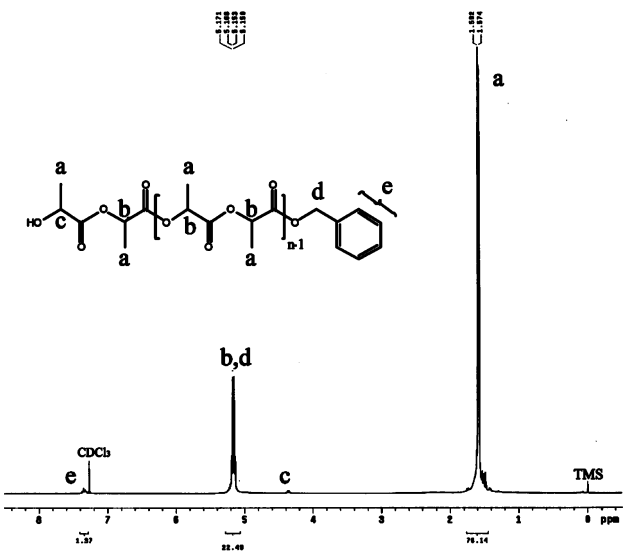
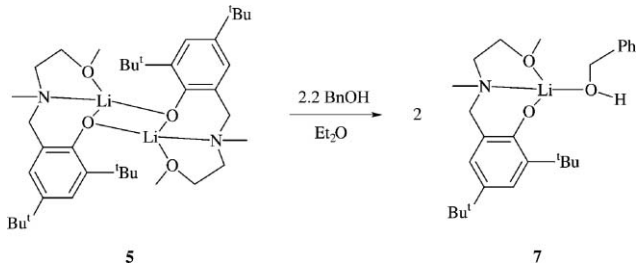


Fig. 5 ^{1}H NMR spectrum of PLA-50 initiated by **6** and BnOH in $CDCl_3$.

amino phenolate ligand at room temperature. A reasonable ratio is observed upon cooling to −60 °C. Therefore low-temperature

NMR data are reported for **7**. The molecular structure of **7** is depicted in Fig. 6.



Scheme 2

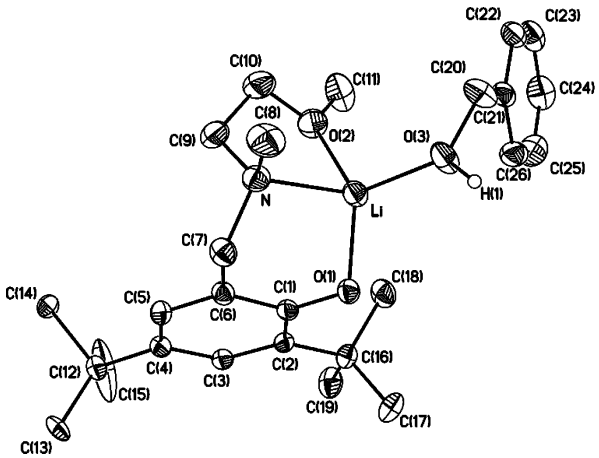


Fig. 6 Molecular structure of **7**. Selected bond lengths (Å) and bond angles (°): Li–O(1), 1.856(4); Li–O(2), 2.039(4); Li–O(3), 1.898(4); Li–N, 2.124(4); O(1)–Li–O(2), 126.6(2); O(1)–Li–O(3), 115.6(2); O(2)–Li–O(3), 110.4(2); O(1)–Li–N, 96.41(18); O(2)–Li–N, 83.05(16); O(3)–Li–N, 119.5(2). Only the hydrogen atom on the oxygen atom of BnOH is exhibited.

Compound **7** can be described as monomer–BnOH adduct with a four–coordinate lithium metal center bonded to one nitrogen atom of the central amine, one oxygen atom of pendant functionality, one oxygen atom of phenolate and one oxygen atom of BnOH. The bond distances of Li–N_{amine} (2.124(4) Å), Li–O_{OMe} (2.039(4) Å) and Li–$O_{phenolate}$ (1.856(4) Å) are similar to those discussed above. The bond distance of Li–O_{BnOH} (1.898(4) Å) is in the range of those (1.897(4) and 1.981(8) Å) found in the literature.[5c] Although only a mononuclear lithium complex is found in the unit cell, however, hydrogen bonding between the hydrogen atom of BnOH and oxygen atom of phenolate was expected. A dinuclear geometry is observed upon increasing the van der Waals radius of the hydrogen atom of BnOH up to 1.68 Å. Two molecules of **7** from different unit cells are bridged *via* intermolecular hydrogen bonds to form a dinuclear structure with a nearly linear O_{BnOH}–H–$O_{Phenolate}$ angle at 167°, as shown in Fig. 7.

The molecular structure of **7** reveals that neither ligand dissociation nor metal alkoxide formation could occur in the presence of added BnOH. The catalytic activity of **7** was examined and results are given in Table 1 (entries 31–35). Compound **7** shows both living and immortal properties in ROP. The reactivity of **7** and the properties of polymer produced by **7** are similar to

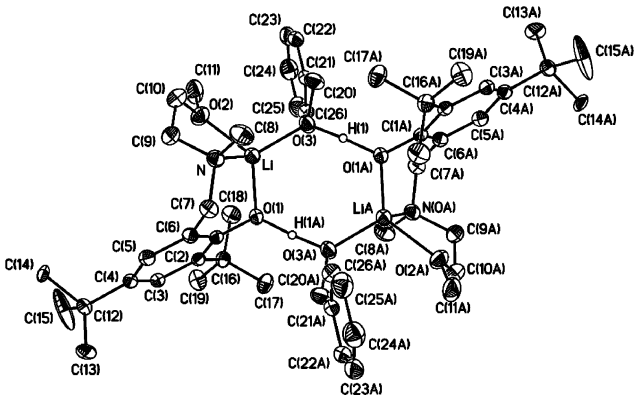


Fig. 7 Two symmetry related molecules of **7** bridged *via* intermolecular hydrogen bonds to form a dinuclear structure. Only the hydrogen atom on the oxygen atom of BnOH is shown.

those using the "*in situ*" route. The spectroscopic studies also demonstrate polymers prepared from those two conditions are capped with benzyl alkoxy groups, as shown in Fig. 8. However, poor stereocontrol was observed by using **5**/BnOH or **7** as initiating systems in ROP of *rac*-lactide ($[M]_0/[Li]_0 = 50$) with P_r values equal to 0.58 (for **5**/BnOH) and 0.60 (for **7**).

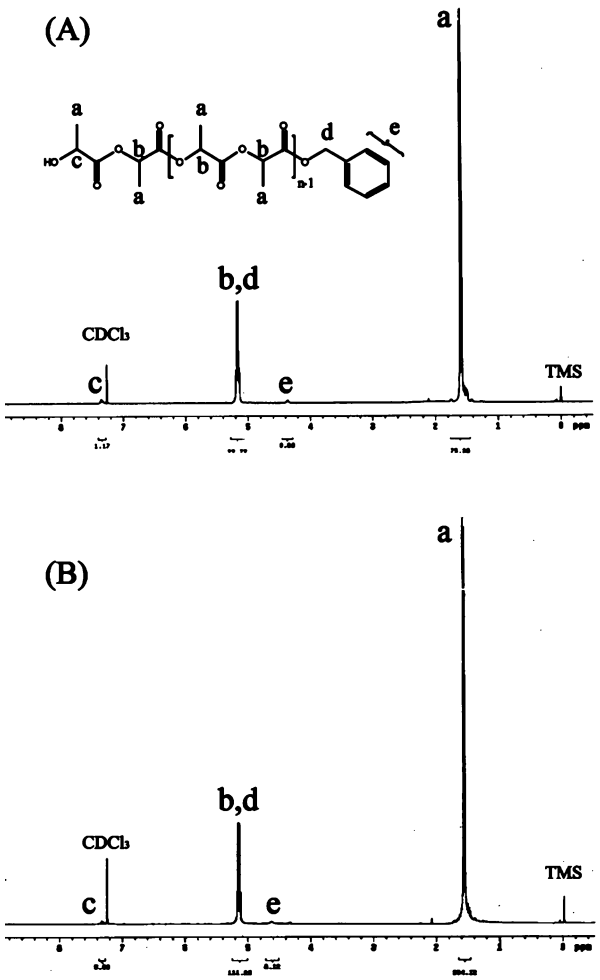
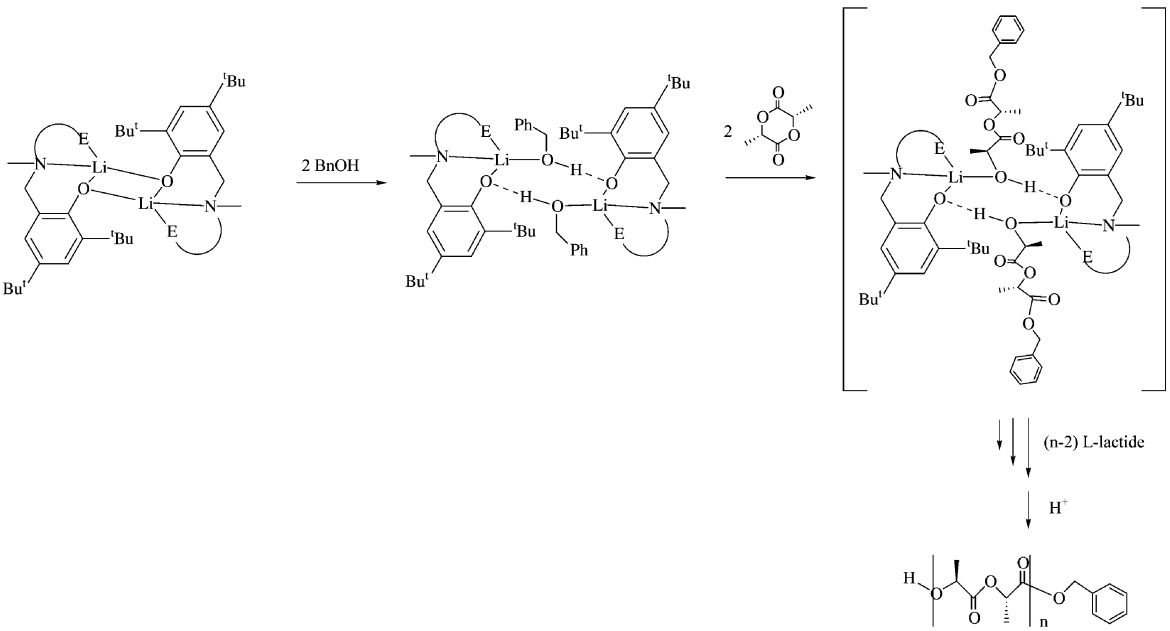


Fig. 8 ^{1}H NMR spectra of PLA-50 initiated by (A) **5**/BnOH or (B) **7** in $CDCl_3$.



Scheme 3

On the basis of these results, the alcohol initiator could be activated by the metal center first, followed by the insertion of the benzyl alkoxy group to the carbonyl group of L-lactide leading to ring opening polymerization, as shown in Scheme 3.

In conclusion, several dinuclear lithium complexes (**3–6**) supported by pendant aminophenolate ligands have been prepared and fully characterized. They all demonstrate efficient activity in catalyzing ring opening polymerization of L-lactide in the presence of benzyl alcohol at 26.5 °C with both living-controlled and immortal characters. Among them, the complex bearing amino phenolate with pendant amino functionality seems to exhibit better catalytic activity than those with pendant methoxy or thioether functionalities. The solid-state and catalytic studies of the monomer–BnOH adduct **7** reveal that the mechanism for the preparation of polyesters can be proposed in terms of the alcohol initiator being activated by the metal center first, followed by insertion of benzyl alkoxy group to the carbonyl group of L-lactide leading to ring opening polymerization for this lithium amino phenolate system.

Experimental

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Ethanol (95%) was used as received. Deuterated solvents were dried over molecular sieves.

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on a Varian Mercury-400 (400 MHz) or a Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. ^{7}Li{^{1}H} NMR spectra were referenced externally to LiCl in DMSO-d_6 at δ 0. Elemental analyses were performed by Elementar Vario ELIV instrument. The GPC measurements were performed in THF at 35 °C with a Waters 1515 isocratic HPLC pump, a Waters 2414 refractive index detector, and Waters Styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

2,4-Di-*tert*-butylphenol (Acros), 2-methoxybenzylamine (98%, Lancaster), *N*-(2-methoxyethyl)methylamine (TCI), formaldehyde (Union, 24 wt%) and anhydrous magnesium sulfate (99%, Showa) were used as received. Benzyl alcohol was dried over anhydrous magnesium sulfate and distilled before use. L-Lactide was recrystallized from toluene prior to use. ^{n}BuLi (2.5 M in hexane, Acros) was used as supplied. 2-Methylthiobenzylamine[12] and 2,4-di-*tert*-butyl-6-{[(2′-dimethylaminoethyl)methylamino]methyl}phenol ($HON^{Me}C^{NMe2}$) were prepared according to previously reported procedures.[4b]

Preparations

6,8-Di-*tert*-butyl-3-[2-(methoxy)benzyl]-3,4-dihydro-2*H*-1,3-benzoxazine (1). 2,4-Di-*tert*-butylphenol (2.06 g, 10 mmol), 2-methoxybenzylamine (1.30 ml, 10 mmol), and formaldehyde (2.3 ml, 20 mmol) were dissolved in ethanol (30 ml). The solution was heated at reflux for 72 h and then cooled to room temperature. All the volatiles were removed under reduced pressure. The crude product was washed with 15 ml ethanol to afford a white powder. Yield, 3.44 g, 93.4%. ^{1}H NMR (600 MHz): δ 1.28 (s, 9H, Ar-C-(CH_3)$_3$), 1.40 (s, 9H, Ar-C-(CH_3)$_3$), 3.82 (s, 3H, OCH_3), 3.92, 4.06, 4.85 (three singlets, 6H, one for N(CH_2)Ar^{OMe}, one for N(CH_2)O, one for N(CH_2)Ar^{OH}), 6.79 (d, 1H, C$_6H_2$, J = 3.0 Hz), 6.89 (d, 1H, CH–Ph, J = 8.4 Hz), 6.95 (t, 1H, CH–Ph, J = 7.8 Hz), 7.16 (d, 1H, C$_6H_2$, J = 2.4 Hz), 7.27 (m, 1H, CH–Ph), 7.34 (m, 1H, CH–Ph). ^{13}C{^{1}H} NMR (150 MHz): δ 29.7 (s, Ar-C-(CH_3)$_3$), 31.6 (s, Ar-C-(CH_3)$_3$), 34.2 (s, Ar-*C*-(CH$_3$)$_3$), 34.9 (s, Ar-*C*-(CH$_3$)$_3$), 50.0 (s, *C*H$_2$), 51.2 (s, *C*H$_2$), 55.5 (s, O*C*H$_3$), 81.0 (s. *C*H$_2$), 110.5, 120.3, 121.8, 122.0, 128.5, 130.8 (s, *C*H-Ph), 119.1, 126.5, 136.5, 141.9, 150.6, 158.0 (s, *tert-C*). Anal. Calc. for $C_{24}H_{33}NO_2$: C, 78.43; H, 9.05; N, 3.81. Found: C, 78.19; H, 8.89; N, 3.55%.

6,8-Di-*tert*-butyl-3-[2-(methylthio)benzyl]-3,4-dihydro-2*H*-1,3-benzothiazine (2). 2,4-Di-*tert*-butylphenol (2.06 g, 10 mmol), 2-methythiobenzylamine (1.57 g, 10 mmol), and formaldehyde (2.3 ml, 20 mmol) were dissolved in ethanol (30 ml). The solution was heated at reflux for 72 h and then cooled to room temperature. All the volatiles were removed under reduced pressure. The crude product was washed with 10 ml ethanol to afford a white powder. Yield, 2.6 g, 67%. ^{1}H NMR (600 MHz): δ 1.29 (s, 9H, Ar-C-(CH_3)$_3$), 1.42 (s, 9H, Ar-C-(CH_3)$_3$), 2.48 (s, 3H, SCH_3), 3.98, 4.06 (two broads, 4H, one for N(CH_2)O, one for N(CH_2)Ar$^{tert\text{-}Butyl}$), 4.84 (s, 2H, N(CH_2)Ar^{SMe}), 6.81 (d, 1H, C$_6H_2$, J = 2.4 Hz), 7.14 (t, 1H, CH–Ph, J = 7.8 Hz), 7.19 (d, 1H, C$_6H_2$, J = 1.8 Hz), 7.26–7.32 (overlap, 3H, CH–Ph). ^{13}C{^{1}H} NMR (150 MHz): δ 15.7 (s, SCH$_3$), 29.6 (s, Ar-C-(CH_3)$_3$), 31.5 (s, Ar-C-(CH_3)$_3$), 34.2 (s, Ar-*C*-(CH$_3$)$_3$), 34.9 (s, Ar-*C*-(CH$_3$)$_3$), 50.9 (s, *C*H$_2$), 53.7 (s, *C*H$_2$), 80.6 (s, N(*C*H$_2$)Ar^{SMe}), 122.0, 124.5, 125.3, 128.1, 130.1 (s, *C*H-Ph), 118.8, 135.9, 136.6, 139.2, 142.1, 150.5 (s, *tert-C*). Anal. Calc. for $C_{24}H_{33}NOS$: C, 75.15; H, 8.67; N, 3.65. Found: C, 75.11; H, 8.80; N, 3.69%.

2,4-Di-*tert*-butyl-6-{[(2-methoxybenzyl)methylamino]methyl}-phenol (HON^{Me}Ph^{OMe}). To a flask containing LiAlH$_4$ (0.38 g, 10 mmol) and 15 ml THF, a solution containing **1** (1.84 g, 5 mmol) in 15 ml THF was added dropwise at 0 °C. After 7 h of stirring, the resulting mixture was quenched with deionized water, followed by extraction with ether to afford a yellow crystalline solid. Yield, 1.51 g, 81.6%. ^{1}H NMR (600 MHz): δ 1.28 (s, 9H, Ar-C-(CH_3)$_3$), 1.42 (s, 9H, Ar-C-(CH_3)$_3$), 2.17 (s, 3H, NCH_3), 3.65, 3.72 (two br, 4H, one for N(CH_2)Ar^{OMe}, one for N(CH_2)Ar^{OH}), 3.87 (s, 3H, OCH_3), 6.84 (d, 1H, C$_6H_2$, J = 2.4 Hz), 6.89 (d, 1H, CH–Ph, J = 8.4 Hz), 6.92 (t, 1H, CH–Ph, J = 7.2 Hz), 7.19 (d, 1H, C$_6H_2$, J = 2.4 Hz), 7.23 (m, 1H, CH–Ph), 7.27 (m, 1H, CH–Ph), 11.16 (br, 1H, OH). ^{13}C{^{1}H} NMR (150 MHz): δ 29.6 (s, Ar-C-(CH_3)$_3$), 31.7 (s, Ar-C-(CH_3)$_3$), 34.1 (s, Ar-*C*-(CH$_3$)$_3$), 34.9 (s, Ar-*C*-(CH$_3$)$_3$), 40.7 (s, NCH$_3$), 55.1 (s, OCH$_3$), 56.2 (s, *C*H$_2$), 61.8 (s, *C*H$_2$), 110.4, 120.2, 122.6, 123.3, 128.9, 131.3 (s, *C*H-Ph), 121.6, 125.4, 135.3, 140.0, 154.5, 158.2 (s, *tert-C*). Anal. Calc. for $C_{24}H_{35}NO_2$: C, 78.00; H, 9.55; N, 3.79. Found: C, 77.74; H, 9.05; N, 3.77%.

2,4-Di-*tert*-butyl-6-{[(2-methylthiobenzyl)methylamino]methyl}-phenol (HON^{Me}Ph^{SMe}). To a flask containing LiAlH$_4$ (0.12 g, 3.0 mmol) and 15 ml THF, a solution containing **2** (0.57 g, 1.5 mmol) in 15 ml THF was added dropwise at 0 °C. After 7 h of stirring, the resulting mixture was quenched with deionized water, followed by extraction with ether to afford a yellow crystalline solid. Yield, 0.37 g, 65.5%. Crystals suitable for X-ray crystallographic analysis were grown from slow evaporation of hexane solution at room temperature. ^{1}H NMR (600 MHz): δ 1.28 (s, 9H, Ar-C-(CH_3)$_3$), 1.42 (s, 9H, Ar-C-(CH_3)$_3$), 2.22 (s, 3H, NCH_3), 2.48 (s, 3H, SCH_3), 3.69, 3.75 (two singlets, 4H, one for N(CH_2)Ar^{OMe}, one for N(CH_2)Ar^{OH}), 6.86 (s, 1H, C$_6H_2$), 7.14 (m, 1H, CH–Ph), 7.20 (s, 1H, C$_6H_2$), 7.25 (m, 2H, CH–Ph), 7.30 (d, 1H, CH–Ph, J = 7.2 Hz), 11.61 (br, 1H, OH). ^{13}C{^{1}H} NMR (150 MHz): δ 16.1 (s, SCH$_3$), 29.6 (s, Ar-C-(CH_3)$_3$), 31.7 (s, Ar-C-(CH$_3$)$_3$), 34.1 (s, Ar-*C*-(CH$_3$)$_3$), 34.8 (s, Ar-*C*-(CH$_3$)$_3$), 41.1 (s, NCH$_3$), 58.8 (s, *C*H$_2$), 62.0 (s, *C*H$_2$), 122.8, 123.5, 125.0, 126.0, 128.1, 130.2 (s, *C*H-Ph), 121.4, 135.36, 135.38, 138.6, 140.4, 154.1 (s, *tert-C*). Anal. Calc. for $C_{24}H_{35}NOS$: C, 74.75; H, 9.15; N, 3.63. Found: C, 74.77; H, 8.94; N, 3.57%.

2,4-Di-*tert*-butyl-6-{[(2-methoxyethyl)methylamino]methyl}-phenol (HON^{Me}C^{OMe}). To a flask containing 2,4-di-*tert*-butylphenol (4.12 g, 20 mmol), MgSO$_4$ (3 g, 25 mmol), *N*-(2-methoxyethyl)methylamine (2.14 ml, 20 mmol) and formaldehyde (2.74 ml, 20 mmol), 30 ml ethanol was added. The solution was heated at reflux for 5 days and then cooled to room temperature. The reaction mixture was filtered and the volatiles were removed under reduced pressure to afford a yellow oil. Yield, 5.5 g, 88%. ^{1}H NMR (600 MHz): δ 1.28 (s, 9H, Ar-C-(CH_3)$_3$), 1.42 (s, 9H, Ar-C-(CH_3)$_3$), 2.36 (s, 3H, NCH_3), 2.68 (t, 2H, N-(CH_2)$_2$-OMe, J = 5.4 Hz), 3.33 (s, 3H, OCH_3), 3.54 (t, 2H, N-(CH_2)$_2$-OMe, J = 6.0 Hz), 3.71 (s, 2H, N–CH_2-Ar), 6.82 (d, 2H, C$_6H_2$, J = 2.4 Hz), 7.21 (d, 2H, C$_6H_2$, J = 2.4 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 29.6 (s, Ar-C-(CH_3)$_3$), 31.7 (s, Ar-C-(CH_3)$_3$), 34.1 (s, Ar-*C*-(CH$_3$)$_3$), 34.8 (s, Ar-*C*-(CH$_3$)$_3$), 42.0 (s, NCH$_3$), 55.5 (s, N-(*C*H$_2$)$_2$-OMe), 58.7 (s, OCH$_3$), 62.2 (s, N-(*C*H$_2$)$_2$-OMe), 70.3 (s, N-*C*H$_2$-Ar), 122.8, 123.3 (s, *C*H-Ph), 121.3, 135.6, 140.3, 154.3 (s, *tert-C*). Anal. Calc. for $C_{19}H_{33}NO_2$: C, 74.22; H, 10.82; N, 4.56. Found: C, 74.26; H, 10.92; N, 4.38%.

(LiON^{Me}Ph^{OMe})$_2$ (3). To a solution of HON^{Me}Ph^{OMe} (1.24 g, 3.36 mmol) in 20 ml Et$_2$O, 1.48 ml *n*-BuLi (2.5 M in hexane, 3.7 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and reacted for 6 h. The resulting mixture was filtered and the filtrate was pumped to dryness. The residue was washed with 20 ml hexane to afford a white powder. Yield, 0.55 g, 22%. Crystals suitable for X-ray crystallographic analysis were grown from concentrated hexane solution at −24 °C. ^{1}H NMR (600 MHz): δ 1.24 (s, 18H, two Ar-C-(CH_3)$_3$), 1.30 (s, 18H, two Ar-C-(CH_3)$_3$), 2.02 (s, 6H, NCH_3), 2.42 (d, 2H, N–CH_2-Ar, J = 12.6 Hz), 2.82 (d, 2H, N–CH_2-Ar, J = 11.4 Hz), 3.95 (s, 6H, OCH_3), 4.08 (d, 2H, N–CH_2-Ar, J = 12.6 Hz), 4.37 (d, 2H, N–CH_2-Ar, J = 10.8 Hz), 6.85 (d, 2H, C$_6H_2$, J = 3.0 Hz), 6.89 (t, 2H, CH–Ph, J = 7.2 Hz), 6.94 (d, 2H, CH–Ph, J = 7.8 Hz), 7.05 (m, 2H, CH–Ph), 7.10 (d, 2H, C$_6H_2$, J = 3.0 Hz), 7.24 (m, 2H, CH–Ph). ^{13}C{^{1}H} NMR (150 MHz): δ 30.1 (s, Ar-C-(CH_3)$_3$), 32.0 (s, Ar-C-(CH_3)$_3$), 33.7 (s, Ar-*C*-(CH$_3$)$_3$), 35.1 (s, Ar-*C*-(CH$_3$)$_3$), 43.0 (s, NCH$_3$), 56.1 (s, N-*C*H$_2$-Ar), 57.34 (s, OCH$_3$), 64.1 (s N-*C*H$_2$-Ar), 113.1, 121.9, 123.2, 126.9, 128.7, 131.6 (s, *C*H-Ph), 123.9, 127.6, 132.5, 135.9, 156.7, 164.2 (s, *tert-C*). ^{7}Li{^{1}H} NMR (233 MHz, 0.3M in toluene-d_8): δ 2.64. Anal. Calc. for $C_{48}H_{68}Li_2N_2O_4$: C, 76.77; H, 9.13; N, 3.73. Found: C, 76.12; H, 9.31; N, 4.25%.

(LiON^{Me}Ph^{SMe})$_2$ (4). To a solution of HON^{Me}Ph^{SMe} (1.64 g, 4.3 mmol) in 20 ml Et$_2$O, 1.87 ml *n*-BuLi (2.5 M in hexane, 4.68 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 23 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 5 ml hexane to afford a white powder. Yield, 0.954 g, 28.7%. Crystals suitable for X-ray crystallographic analysis were grown from concentrated hexane solution at room temperature. ^{1}H NMR (600 MHz): δ 1.20 (s, 18H, two Ar-C-(CH_3)$_3$), 1.24 (s, 18H, two Ar-C-(CH_3)$_3$), 2.12 (s, 6H, NCH_3), 2.23 (s, 6H, SCH_3), 2.59 (d, 2H, N–CH_2–Ar, J = 12.6 Hz), 2.83 (d, 2H, N–CH_2-Ar, J = 11.4 Hz), 4.15 (d, 2H, N–CH_2–Ar, J = 12.6 Hz), 4.31 (d, 2H, N–CH_2–Ar, J = 10.8 Hz), 6.89 (d, 2H, C$_6H_2$, J = 3.0 Hz), 7.04–7.11 (m, 8H (2H for C$_6H_2$, 6H for CH–Ph)), 7.23 (m, 2H, CH–Ph). ^{13}C{^{1}H} NMR (150 MHz): δ 14.0 (s, SCH$_3$), 29.4 (s, Ar-C-(CH_3)$_3$), 32.0 (s, Ar-C-(CH_3)$_3$), 33.7 (s, Ar-*C*-(CH$_3$)$_3$), 34.8 (s, Ar-*C*-(CH$_3$)$_3$), 43.6 (s, NCH$_3$), 58.4 (s, N-*C*H$_2$-Ar), 63.6

(s N-CH_2-Ar), 123.2, 125.0, 125.3, 126.7, 128.3, 131.9 (s, *C*H-Ph), 123.5, 132.8, 135.6, 135.8, 136.0, 163.7 (s, *tert-C*). ^{7}Li{^{1}H} NMR (233 MHz, 0.15 M in toluene-d_8): δ 2.93. Anal. Calc. for $C_{48}H_{68}Li_2N_2O_2S_2$: C, 73.62; H, 8.75; N, 3.58. Found: C, 73.95; H, 8.59; N, 3.74%.

(LiON^{Me}C^{OMe})$_2$ (5). To a solution of HON^{Me}C^{OMe} (11.5 g, 37.4 mmol) in 50 ml Et_2O, 19.4 ml *n*-BuLi (2.5 M in hexane, 48.5 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 18 h of stirring, the volatiles were removed under reduced pressure. The residue was washed with 30 ml hexane to afford white powder. Yield, 8.07 g, 34.5%. Crystals suitable for X-ray crystallographic analysis were grown from concentrated hexane solution at room temperature. ^{1}H NMR (600 MHz): δ 1.28 (s, 18H, Ar-C-(CH_3)$_3$), 1.42 (s, 18H, Ar-C-(CH_3)$_3$), 2.34 (s, 6H, NCH_3), 3.14 (s, 6H, OCH_3), 2.23, 2.74, 2.86, 2.93, 3.32, 4.13 (six br (two for N–CH_2-Ar, four for N-(CH_2)$_2$-OMe), 12H (4H for N–CH_2-Ar, 8H for N-(CH_2)$_2$-OMe)), 6.85 (d, 2H, C$_6H_2$, J = 2.4 Hz), 7.17 (d, 2H, C$_6H_2$, J = 2.4 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 29.7 (s, Ar-C-(CH_3)$_3$), 32.0 (s, Ar-C-(CH_3)$_3$), 33.7 (s, Ar-*C*-(CH$_3$)$_3$), 35.0 (s, Ar-*C*-(CH$_3$)$_3$), 45.3 (s, NCH_3), 58.8 (s, OCH_3), 53.5, 63.5, 70.0 (s, CH_2), 123.1, 126.0 (s, *C*H-Ph), 124.7, 132.3, 136.1, 164.5 (s, *tert-C*). ^{7}Li{^{1}H} NMR (233 MHz, 0.3M in toluene-d_8): δ 2.37. Anal. Calc. for $C_{38}H_{64}Li_2N_2O_4$: C, 72.81; H, 10.29; N, 4.47. Found: C, 73.23; H, 9.67; N, 4.61%.

(LiON^{Me}C^{NMe2})$_2$ (6). To a solution of HON^{Me}C^{NMe2} (2.0 g, 6.24 mmol) in 30 ml Et_2O, 2.75 ml *n*-BuLi (2.5M in hexane, 6.87 mmol) was added dropwise at 0 °C. The reaction mixture was warmed to room temperature and reacted overnight. After 21 h of stirring, the reaction mixture was filtered and the volatiles were removed under reduced pressure to afford a white powder. Yield, 1.71 g, 42.0%. ^{1}H NMR (600 MHz): δ 1.27 (s, 18H, Ar-C-(CH_3)$_3$), 1.44 (s, 18H, Ar-C-(CH_3)$_3$), 1.65 (m, 2H, N-(CH_2)$_2$-NMe$_2$), 1.88 (m, 14H; 12H for N-(CH_3)$_2$, 2H for N-(CH_2)$_2$-NMe$_2$), 2.27 (s, 6H, N-CH_3), 2.42 (m, 2H, N-(CH_2)$_2$-NMe$_2$), 2.82 (m, 2H, N-(CH_2)$_2$-NMe$_2$), 2.86 (d, 2H, N–CH_2-Ar, J = 10.8 Hz), 4.18 (d, 2H, N–CH_2-Ar, J = 10.8 Hz), 6.83 (d, 2H, C$_6H_2$, J = 3 Hz), 7.13 (d, 2H, C$_6H_2$, J = 3 Hz). ^{13}C{^{1}H} NMR (150 MHz): δ 30.1 (s, Ar-C-(CH_3)$_3$), 32.0 (s, Ar-C-(CH_3)$_3$), 33.7 (s, Ar-*C*-(CH$_3$)$_3$), 35.4 (s, Ar-*C*-(CH$_3$)$_3$), 44.7 (s, N-CH_3), 46.2 (s, N(CH_3)$_2$), 49.7 (s, N-(CH_2)$_2$-NMe$_2$), 58.3 (s, N-(CH_2)$_2$-NMe$_2$), 62.7 (s, N-CH_2-Ar), 123.0 (s, *C*H-Ph), 127.0 (s, *C*H-Ph), 124.6, 132.3, 136.2, 165.1 (s, *tert-C*). ^{7}Li{^{1}H} NMR (233 MHz, 0.3M in toluene-d_8): δ 2.40. Anal. Calc. for $C_{40}H_{70}Li_2N_4O_2$: C, 73.58; H, 10.81; N, 8.58. Found: C, 73.66; H, 10.68; N, 8.72%.

(BnOH)LiON^{Me}C^{OMe} (7). To a solution of **5**(0.319 g, 0.509 mmol) in 15 ml Et_2O, benzyl alcohol (0.110 g, 1.02 mmol) was added at room temperature. All the volatiles were removed under slow evaporation to afford a colorless crystalline solid. Yield, 0.404 g, 94.0%. ^{1}H NMR (600 MHz, −60 °C): δ 1.28 (s, 9H, Ar-C-(CH_3)$_3$), 1.42 (s, 9H, Ar-C-(CH_3)$_3$), 2.23, 2.75, 2.83, 3.35 (four br for N-(CH_2)$_2$-OMe), 4H), 2.35 (s, 3H, NCH_3), 2.93 (d, 1H, N–CH_2-Ar, J = 11.4 Hz), 3.17 (s, 3H, OCH_3), 4.12 (d, 1H, N–CH_2-Ar, J = 10.2 Hz), 4.72 (s, 2H, HO–CH_2-Ph), 6.89 (d, 1H, C$_6H_2$, J = 2.4 Hz), 7.16 (d, 1H, C$_6H_2$, J = 2.4 Hz), 7.35–7.44 (m, 5H, HO–CH$_2$-*Ph*). ^{13}C{^{1}H} NMR (150 MHz, −60 °C): δ 29.2 (s, Ar-C-(CH_3)$_3$), 31.8 (s, Ar-C-(CH_3)$_3$), 33.6 (s, Ar-*C*-(CH$_3$)$_3$), 34.9 (s, Ar-*C*-(CH$_3$)$_3$), 45.2 (s, NCH_3), 58.9 (s, OCH_3), 65.0 (s, O-CH_2-Ph), 52.9, 63.1, 69.6 (s, CH_2), 122.8, 125.9, 126.9, 127.5, 128.4 (s, *C*H-Ph), 124.6, 131.7, 135.4, 140.4, 164.1 (s, *tert-C*). ^{7}Li{^{1}H} NMR (233 MHz, 0.3M in toluene-d_8): δ −2.62. Anal. Calc. for $C_{26}H_{40}LiNO_3$: C, 74.08; H, 9.56; N, 3.32. Found: C, 74.65; H, 9.51; N, 3.25%.

Polymerization studies. Typically, to a flask containing a prescribed amount of L-lactide and catalyst (0.05 mmol for **3–6**; 0.1 mmol for **7**) was added a solution (10 ml in CH_2Cl_2) containing a prescribed amount of benzyl alcohol. The reaction mixture was stirred at 26.5 °C for the prescribed time. After the reaction was quenched by the addition of 10 ml acetic acid solution (0.35 M), the resulting mixture was poured into 50 ml *n*-heptane to precipitate

Table 2 Summary of crystal data for compounds HON^{Me}Ph^{SMe}, **3–5** and **7**

	HON^{Me}Ph^{SMe}	**3**	**4**	**5**	**7**
Formula	$C_{24}H_{35}NOS$	$C_{48}H_{68}Li_2N_2O_4$	$C_{48}H_{68}Li_2N_2O_2S_2$	$C_{38}H_{64}Li_2N_2O_4$	$C_{26}H_{40}LiNO_3$
M_r	385.59	750.92	783.04	626.79	421.53
T/K	293(2)	293(2)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
a/Å	14.4226(12)	9.6656(8)	12.726(2)	18.434(3)	10.3335(10)
b/Å	9.8356(9)	10.6883(9)	13.834(2)	17.666(3)	10.6740(11)
c/Å	17.4956(15)	10.9810(9)	18.762(3)	12.896(2)	12.8376(13)
α/°	90	96.694(2)	72.370(3)	90	99.290(2)
β/°	108.763(2)	90.990(2)	72.813(4)	105.790(4)	90.890(2)
γ/°	90	92.233(2)	65.937(3)	90	112.650(2)
V/Å^3	2349.9(4)	1125.57(16)	2817.7(9)	4041.2(12)	1284.9(2)
Z	4	1	2	4	2
D_c/Mg m^{-3}	1.090	1.108	0.923	1.030	1.089
μ(Mo-Kα)/mm^{-1}	0.150	0.068	0.125	0.064	0.069
Reflections collected	12881	6425	15649	45212	7371
No. of parameters	244	253	532	455	284
Indep. reflns (R_{int})	4594 (0.0299)	4358 (0.0381)	10729 (0.0185)	7913 (0.0635)	4984 (0.0189)
Final R indices R_1[a], wR_2[a]	0.0504, 0.1483	0.0746, 0.2144	0.0625, 0.1710	0.0668, 0.1773	0.0644, 0.1918
R indices (all data)	0.0766, 0.1658	0.0892, 0.2336	0.0924, 0.1893	0.1381, 0.2160	0.0969, 0.2149
GoF[b]	1.036	0.996	1.140	1.154	1.199

[a] $R_1 = [\sum|F_o| - |F_c|]/\sum|F_o|]$; $wR_2 = [\sum w(F_o - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$; $w = 0.10$. [b] GoF $= [\sum w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

PLL (poly-L-lactide). Crude products were recrystallized from THF–hexane and dried *in vacuo* up to a constant weight.

Crystal structure data

Crystals were grown from slow evaporation of diluted solution (hexane for $HON^{Me}Ph^{SMe}$, diethyl ether for **7**) or concentrated hexane solution (**3–5**), and isolated by filtration. Suitable crystals of **3**, **4**, **5** or **7** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. 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 was confirmed using the structure solution. The structure was solved by direct methods using a 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. Some details of the data collection and refinement are given in Table 2.

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For crystallographic data in CIF or other electronic format see DOI: 10.1039/b717370a

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