Pure Appl. Chem., Vol. 79, No. 11, pp. 2013–2030, 2007.
doi:10.1351/pac200779112013

Controlled ring-opening polymerization of lactide by group 3 metal complexes*

Abderramane Amgoune, Christophe M. Thomas†, and Jean-François Carpentier‡

Sciences Chimiques de Rennes, UMR 6226 CNRS Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

Abstract: In this review, attention is focused on the use of group 3 metal complexes for the ring-opening polymerization (ROP) of lactide to give polylactides (PLAs). Synthesis of PLAs has been studied intensively due to their biocompatible and biodegradable properties and their potential applications in medical and agricultural fields. ROP of lactide, a cyclic diester of lactic acid, provides PLA. This review includes our recent research results and implications in developing new amino-bis(phenolate) group 3 initiators for the synthesis of polyesters.

Keywords: polymerization; catalysis; green chemistry; lanthanides; polylactides.

INTRODUCTION

A variety of metal alkoxides have been used as initiators and catalysts for the ring-opening polymerization (ROP) of lactide (LA) [1–3]. However, examples of group 3 metal complexes for the synthesis of polylactides (PLAs) remain rare [3]. The first example of LA polymerization by Ln (Ln = lanthanides + group 3 metals) alkoxide complexes was reported by McLain and Drysdale in 1991 [4], with a complex formulated as "$Y(OCH_2CH_2NMe_2)_3$", which was shown to polymerize LA in a rapid and controlled fashion [5]. Based on this report, several lanthanide systems were investigated for the ROP of LA [6]. Feijen then evaluated "yttrium isopropoxide" for the polymerization of *L*-LA [6a]. In fact, "yttrium isopropoxide" is a pentanuclear cluster with a central μ-oxo oxygen and bridging and terminal isopropoxide ligands, i.e., $Y_5(\mu\text{-}O)(O\textit{i}Pr)_{13}$ (**1**) [7]. Complex **1** exhibits high activity for the polymerization of *L*-LA in dichloromethane at room temperature. End-group analysis revealed that only PLAs terminated with isopropyl esters are formed, and kinetic measurements showed that the average number of active sites is 2.6. Thus, it was concluded that all isopropoxide groups initiate the polymerization in a living fashion [6a]. Polymerization of *rac*-LA using different lanthanide oxo alkoxide clusters $Ln_5(\mu\text{-}O)(O\textit{i}Pr)_{13}$ (Ln = Y, La, Sm, Yb) was also reported [6d]. All clusters were evaluated in the same conditions, and lanthanum oxo isopropoxide was found to be the most reactive initiator. However, significant transesterification reactions are generated with this compound. In the case of Y, Sm, and Yb initiators, narrow polydispersities (PDIs) are observed, even for high conversions. These initiators showed also some activity for the ROP of lactones such as β-butyrolactone and δ-valerolactone [6d]. In order to prevent aggregation phenomena, trivalent yttrium and lanthanum alkoxides "$Ln(OR)_3$" (R = *i*Pr, *n*Bu) were prepared in situ by exchange reaction between bulky phenolates and isopropyl- or

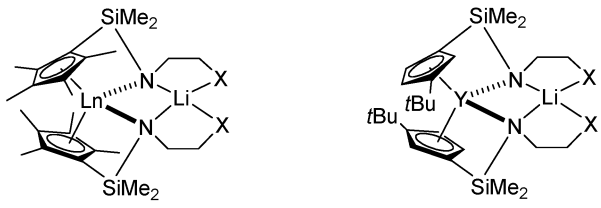
Pure Appl. Chem.* **79, 1831–2100. An issue of reviews and research papers based on lectures presented at the 1st International IUPAC Conference on Green–Sustainable Chemistry, held in Dresden, Germany, 10–15 September 2006.

†E-mail: christophe.thomas@univ-rennes1.fr

‡Corresponding author: Fax: (+33) 2 23 23 69 39; E-mail: jean-francois.carpentier@univ-rennes1.fr

n-butyl alcohol for the polymerization of *L*-LA [6a,6b]. The rate of polymerization with these initiators is several orders of magnitude higher than that observed with the commercial yttrium oxo isopropoxide. Evidence for a three-step coordination-insertion mechanism was provided by ^{1}H and ^{13}C NMR spectroscopy of the reaction products of each step. The dimeric yttrium complex $[Y(OCH_2CH_2O^iPr)_3]_2$ also proved to be a more convenient initiator than clusters, combining high activities and narrow PDIs up to high conversions with three growing species per metallic centers [6c]. However, prolongation of the polymerization after complete conversion led to broadening of PDIs due to the occurrence of transesterification reactions.

Other homoleptic rare-earth derivatives of the general formula $Ln[N(SiHMe_2)_2)]_3(THF)_X$ proved to be very active for the polymerization of *rac*-LA at room temperature (450 equiv within 5 min) [8,9]. Even if these homoleptic systems have shown an unprecedented high efficiency for the polymerization of cyclic esters, several drawbacks such as complicated equilibria phenomena (aggregations, ligand exchange) and multiple nuclearities have limited the control of the polymerization. Efforts to obviate these problems focused on the use of supporting ligands designed to control the structure of the complexes and their polymerization reactivity. Based on the evolution of the group 3 and lanthanide organometallic chemistry, two types of complexes were independently studied: on one hand, organolanthanide metallocenes, which were earlier studied for the polymerization of cyclic esters [10], and on the other hand, lanthanide complexes supported by non-cyclopentadienyl ligands, which appeared later on [1]. However, except Okuda's bimetallic complexes **2** and **3** (Fig. 1), no Cp-based group 3 complexes have been reported to be active for the ROP of LA and those remain limited to the synthesis of polycaprolactone. Complexes **2** and **3** showed some activity for the controlled polymerization of *L*-LA to yield PLAs with high molecular weights and moderately narrow PDIs (M_w/M_n = PDI < 1.5) [12].



2a: Ln = Y, X = OMe
2b: Ln = Y, X = NMe_2
2c: Ln = Lu, X = OMe

3a: X = OMe
3b: X = NMe_2

Fig. 1 Heterobimetallic lanthanocene complexes.

In an attempt to enhance and control this reactivity, recent research efforts have been directed toward substitution of the cyclopentadienyl framework by other anionic ligand systems.

Group 3 complexes supported by bidentate ligands

One of the first alternatives to Cp donors to support group 3 derivatives was the aryl amidinate ligands. These ligands were used to prepare well-defined yttrium complexes **4–6** (Fig. 2) [9]. All these complexes were characterized by X-ray diffraction, which revealed their monomeric structures, and used for the ROP of LA [13]. Polymerizations are typically achieved quite rapidly at room temperature in tetrahydrofuran (THF). Complex **4** requires the addition of 1 equiv of benzyl alcohol (BnOH) to obtain reproducible reaction rates and narrower PDIs (PDI < 1.5). Benzyl ester end-group observed by ^{1}H NMR demonstrated that the phenolate ligand is substituted by benzyl alcohol prior to the monomer insertion. However, matrix-assisted laser desorption ionization/mass spectrometry (MALDI/MS) analyses suggested that polymeric species without benzyl end-group are also formed. The fastest polymerization was observed with **4**/BnOH system (1000 equiv, 25 °C, 1 h), while complexes **5** and **6** exhibit lower activities. In both cases, the nature of the initiating group was not determined. Arnold and

coworkers reported related studies using guanidinate ligands to prepare monomeric four-coordinate lanthanum complex **7** (Fig. 2) [14]. Polymerization of LA with **7** occurs with moderate control of the molecular weight for low monomer-to-catalyst ratio, but at higher ratios only low-molecular-weight polymers are obtained, suggesting significant transesterification reactions. Bochmann and coworkers recently described the synthesis and use for ROP of *rac*-LA of bis(allyl)-(diketiminate) lanthanide complexes **8a–d** (Fig. 2) [15]. The ROP of LA is shown to be slower than that of ε-CL but offers good control and gives polymers with narrow PDIs (PDI = 1.1) under mild conditions. More recently, the synthesis of yttrium complex **9**, which features a *N*-heterocyclic carbene ligand and may act as a bifunctional (i.e., via carbene and amido) initiator for the ROP of *rac*-LA, was reported (Fig. 2) [16]. This complex represents a very active (100 equiv within 2 min) and productive initiator leading to high-molecular-weight PLA with narrow PDIs.

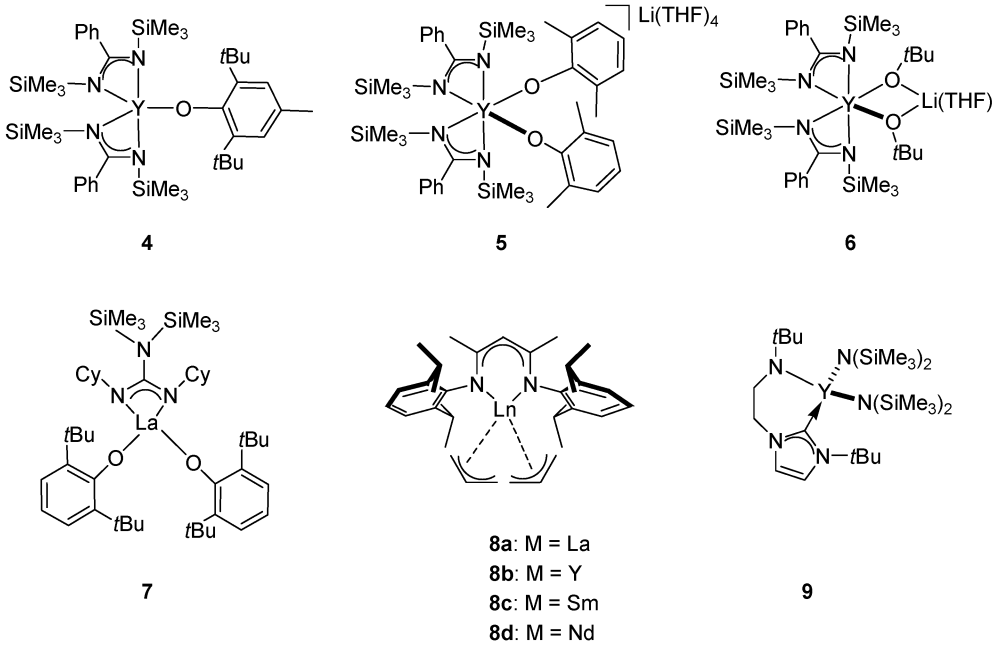
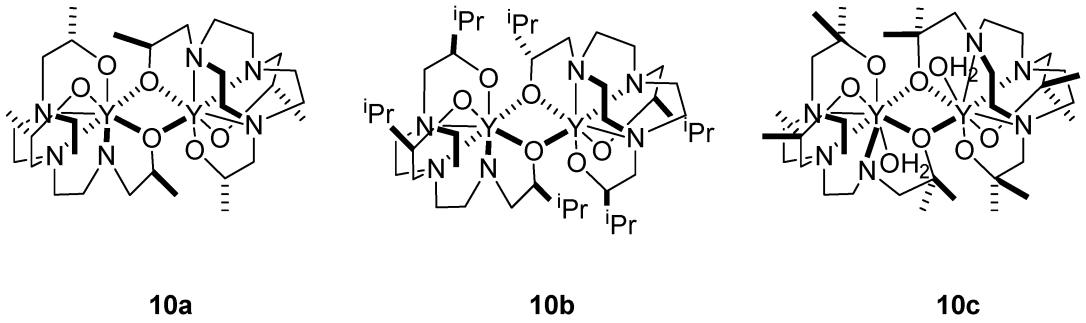


Fig. 2 Lanthanide and group 3 metal complexes supported by bidentate ligands.

Group 3 metal complexes supported by multidentate ligands

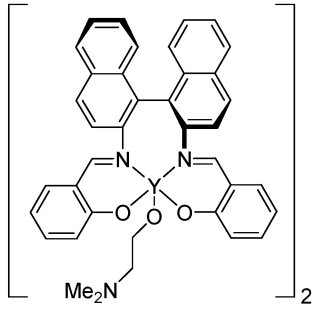
Since group 3 metals support large coordination numbers, several multidentate ligands such as amino-alkoxides, Schiff bases, and bis(phenolate)s were used to prepare discrete complexes. Hillmyer reported the synthesis of yttrium alkoxide complexes based on multidentate amino-alkoxide ligands **10a–c** (Fig. 3) [13,17,18]. X-ray analyses revealed the same dimeric structures for the series, the only major difference being the coordinated water in **10c**. The complexes are active for LA polymerization at room temperature (400 equiv within 24 h) with different rates (**10c** > **10b** > **10a**) and different controls (PDI from 1.55 to 2.20). The high activity of complex **10c** (1000 equiv, 30 min) was suspected to result from the presence of water. The nature of the initiating species is still uncertain with these complexes. However, subsequent treatment of complex **10a** with benzyl alcohol significantly improved its catalytic behavior and allowed the identification of benzyl ester end-groups.



10a **10b** **10c**

Fig. 3 Dinuclear yttrium complexes supported by multidentate amino-alkoxide ligands.

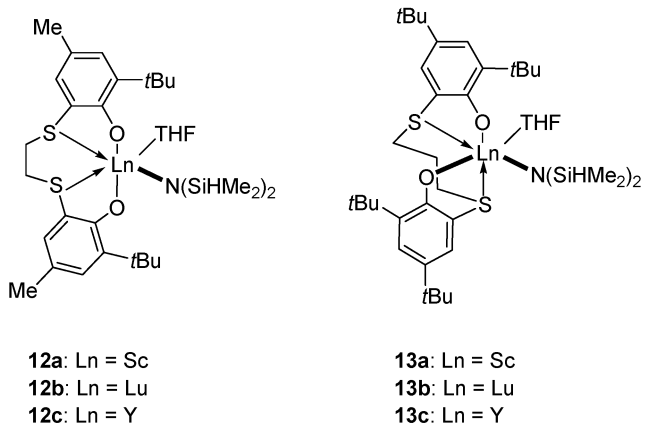
Using the same chiral Schiff-base ligand that enabled aluminum complexes to polymerize stereoselectively LA, Coates prepared yttrium alkoxide complex **11** (Fig. 4) [19]. This complex was shown to be dimeric in the solid state and revealed higher activity than the parent aluminum derivative for the polymerization of LA in toluene at 70 °C (100 equiv, 14 h with Y vs. 40 h with Al). However, unlike the analogous Al complex, complex **11** showed no stereoselectivity.



11

Fig. 4 Yttrium complex **11**.

One important class of ligand which recently attracted much interest for the synthesis of single-site complexes, is constituted by bis(phenolate) ligands. Okuda reported the synthesis of several rare-earth complexes supported by dichalcogen-bridged bis(phenolate) ligands **12a–c** and **13a–c** for the polymerization of *L*-LA (Fig. 5) [8,20]. These complexes have been prepared by simple ligand exchange from $Ln[N(SiHMe_2)_2]_3(THF)_x$, and were isolated as monomeric complexes. All these complexes showed activity for the controlled polymerization of *L*-LA at room temperature in THF. The ancillary ligand was demonstrated to have a strong beneficial effect, the corresponding precursors $Ln[N(SiHMe_2)_2]_3(THF)_x$ being less active and showing lower control over the polymerization. In general, the less hindered the metal center, the higher the activity for ROP of *L*-LA. The best results have been obtained with the amido-lutetium complex **12b** that features an ethylene backbone (300 equiv, few minutes). The resulting polymers exhibited relatively narrow PDIs (PDI ~ 1.2); however, no amide or alkoxide end-groups could be observed. Investigations on the kinetics and mechanism of the polymerization confirmed this assumption [20]. Indeed, ^{1}H NMR and MALDI/TOF/MS (matrix-assisted laser desorption ionization with time-of-flight mass spectrometry) analyses of the polymers obtained by ROP of *L*-LA with complexes **12b**,**c–13c** suggested a coordination-insertion mechanism involving the amido ligand as the initiating group. However, the polymerization was shown not to be well controlled (PDI ~ 1.8). On the contrary, when these complexes are reacted with an excess of isopropanol, the in situ gen-



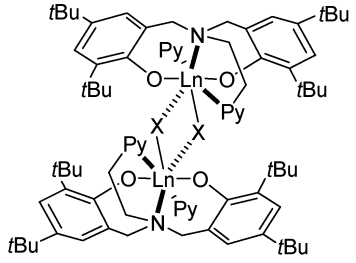
12a: Ln = Sc
12b: Ln = Lu
12c: Ln = Y

13a: Ln = Sc
13b: Ln = Lu
13c: Ln = Y

Fig. 5 Lanthanide complexes supported by dichalcogen-bridged ligands.

erated alkoxides were found to initiate very efficiently the living polymerization of *L*-LA, demonstrating the importance of the initiating group in the polymerization process.

Inspired by the work of Guillaume with metallocene borohydride complexes [21], Mountford and coworkers recently used a diamino-bis(phenolate) ligand to prepare new lanthanide borohydride complexes **14** for the polymerization of *rac*-LA (Fig. 6) [22]. The X-ray structure of the lanthanum derivative revealed a dimeric species with bridging borohydrides. These complexes proved to be efficient initiators for the ROP of *rac*-LA. The best control was achieved by using the samarium derivative, while yttrium complex was found to favor heterotactic polymerization of *rac*-LA (P_r = 87 %). The authors proposed a mechanism occurring via insertion of the monomer into the metal-borohydride bond by analogy with the results of Guillaume [21]. However, no experimental evidences were brought.



14
(Ln = Y, Nd, Sm)
($X = BH_4$)

Fig. 6 Lanthanide amino-bis(phenolate) complexes.

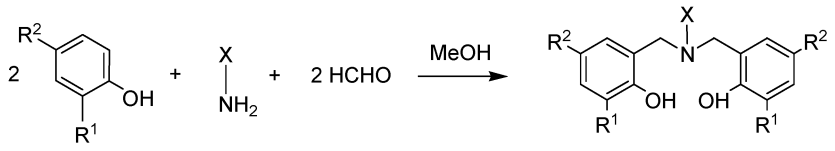
To summarize, several research groups took advantage of group 3 metal complexes which represent promising systems for the ROP of cyclic esters. Polymers of relatively high-molecular-weight and narrow PDIs are formed. Detrimental side-reactions such as macrocycle formation, transesterification, and racemization are often negligible. From our side, we decided about five years ago to investigate such type of complexes with the overall goal of optimizing the activities and the control of the polymerization.

Recently, Kol [23] reported the syntheses of different amino-bis(phenolate) group 4 metal complexes and demonstrated the high activities and living abilities of these complexes in α-olefin polymerization [24]. Contrary to their group 4 analogs, examples of group 3 metal complexes supported by amino-bis(phenolate) ligands are still rare [25]. For all these reasons, we anticipated that well-defined

amino-bis(phenolate) group 3 metal complexes would be of interest in order to achieve stereocontrolled ROP of chiral cyclic esters.

RESULTS AND DISCUSSION

We synthesized amino-bis(phenolate) ligands H_2L by a double Mannich condensation [26] of the corresponding substituted phenol, formaldehyde, and amino-ether, diamine, or methylamine in methanol (Scheme 1) and we obtained a series of amino-bis(phenol)s **15–22** by varying the nature of the *ortho*-substituent and side arm (Fig. 7) [27].



R^1 = Me, *t*Bu, adamantyl, cumyl
R^2 = Me, *t*Bu, cumyl
X = CH_2CH_2OMe, $CH_2CH_2NMe_2$, CH_3

Scheme 1 Synthesis of amino-bis(phenol)s.

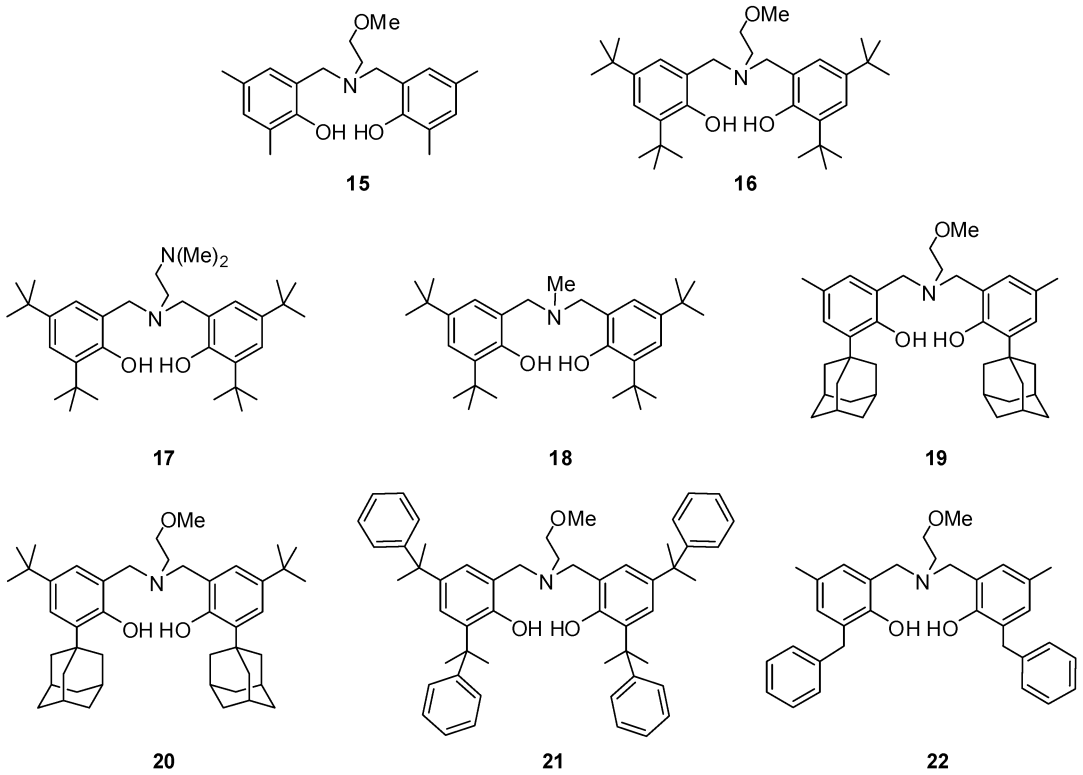
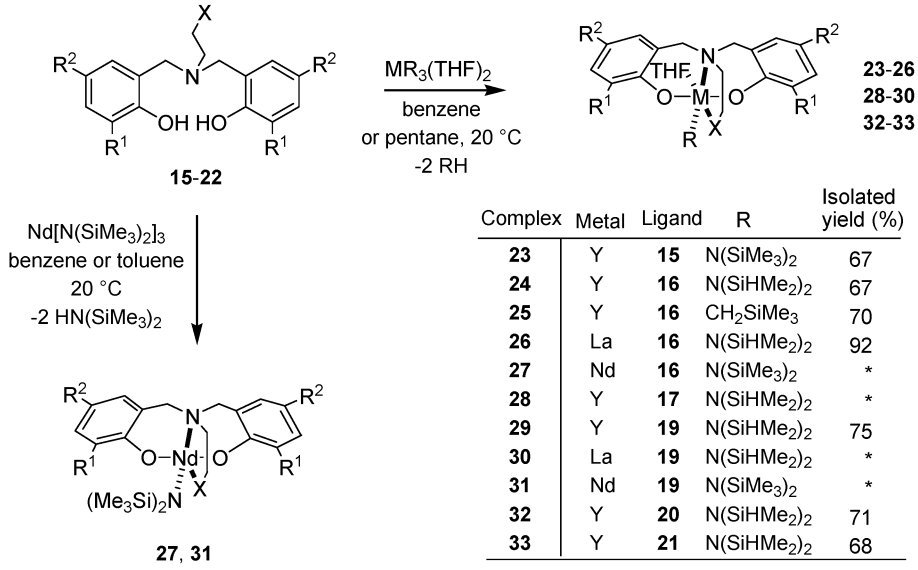


Fig. 7 Amino-bis(phenolate) ligands screened.

Lanthanide complexes are conveniently prepared by the amine or alkane elimination method; this reaction involves the protonolysis of two of the bulky amido or carbyl ligands in the homoleptic precursor by the relatively acidic amino-bis(phenol)s [28]. Group 3 precursors $MR_3(THF)_2$ [M = Y, La; R = CH_2SiMe_3, $N(SiMe_3)_2$, $N(SiHMe_2)_2$] and $Nd[N(SiMe_3)_2]_3$ were reacted with one equivalent of the neutral bis(phenol)s H_2L **15–22** in toluene, benzene, or pentane, at room temperature, to give the corresponding complexes **23–33** (Scheme 2).

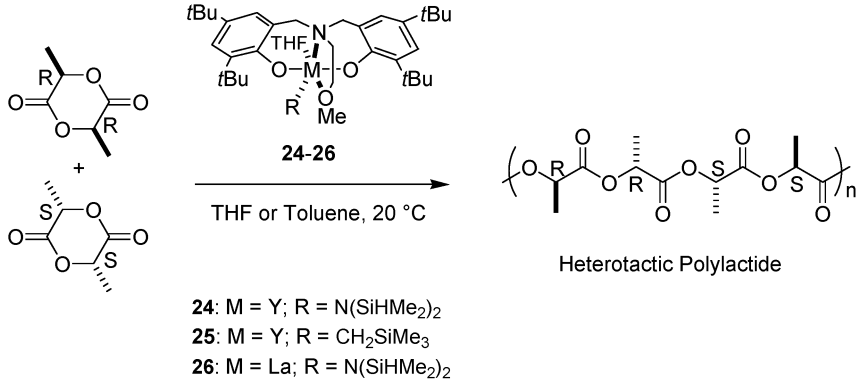


Complex	Metal	Ligand	R	Isolated yield (%)
23	Y	**15**	$N(SiMe_3)_2$	67
24	Y	**16**	$N(SiHMe_2)_2$	67
25	Y	**16**	CH_2SiMe_3	70
26	La	**16**	$N(SiHMe_2)_2$	92
27	Nd	**16**	$N(SiMe_3)_2$	*
28	Y	**17**	$N(SiHMe_2)_2$	*
29	Y	**19**	$N(SiHMe_2)_2$	75
30	La	**19**	$N(SiHMe_2)_2$	*
31	Nd	**19**	$N(SiMe_3)_2$	*
32	Y	**20**	$N(SiHMe_2)_2$	71
33	Y	**21**	$N(SiHMe_2)_2$	68

(*) small scale synthesis

Scheme 2 Synthesis of [amino-bis(phenolate)]lanthanide complexes.

We first investigated the yttrium and lanthanum complexes **24–26** for the ROP of *rac*-LA (Scheme 3). Polymerization of *rac*-LA with yttrium complexes **24** and **25** proceeds rapidly at room temperature, equally in toluene and THF solvents in terms of activity. Complete conversions of the monomer to PLA are achieved within 1 h for monomer-to-yttrium ratios up to 500. Representative results are summarized in Table 1.



Scheme 3 Synthesis of heterotactic PLAs.

Table 1 ROP of *rac*-LA in THF promoted by **24–26**.[a]

Entry	Initiator [I]	[LA]/[I] ratio	Solvent	$M_{n,calc}$[b] (g mol^{-1})	M_n[c] (g mol^{-1})	M_w/M_n[c]	P_r[d]
1	**24**	100	Toluene	14 400	19 100	1.66	0.60
2	**24**	100	THF	14 400	15 500	1.33	0.80
3	**24**	200	THF	28 800	39 900	1.32	0.80
4	**24**	300	THF	43 200	56 200	1.25	0.80
5	**24**	500	THF	72 100	87 000	1.24	0.80
6	**25**	100	THF	14 400	19 000	1.28	0.80
7	**25**	100	Toluene	14 400	19 300	1.47	0.60
8	**26**	100	THF	14 400	18 400	1.34	0.64

[a]All reactions performed with [*rac*-LA] = 0.44 *M* at 20 °C in THF in 1 h (reaction time was not optimized); conversion > 97 % as determined by integration of the methyl resonances of LA and PLA.
[b]$M_{n,calc}$ of PLA calculated from the conversion of LA: $M_{n,calc} = 144.00 \times ([LA]/[I]) \times$ conversion of LA.
[c]M_n and M_w/M_n of PLA determined by SEC-RI using polystyrene standards.
[d]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.

A ^{1}H NMR monitoring for the polymerization of 100 equiv of *rac*-LA with **24** in THF at 0 °C indicated turnover frequencies up to 300 h^{-1} (26 % conversion after 5 min; 50 % after 10 min). As evidenced by the linear relationship between the monomer-to-metal ratio and number-average molecular masses (M_n) (Fig. 8), a good control of polymerization is achieved with this system, even at a catalyst loading of 0.2 % that yielded M_n as high as 87 000 g/mol. The experimental (uncorrected) M_n values were only slightly higher (ca. 15–20 %) from the calculated values. This control of the polymerization, as well as a single type of reaction site, is also supported by the relatively low PDI, with M_w/M_n values ranging from 1.25 to 1.35. These values are somewhat higher than those expected for a purely living polymerization ($M_w/M_n < 1.1$), and suggest that either transesterification takes place to a small extent and/or the initiation step is not very fast with respect to propagation, i.e., the k_p/k_i ratio is not ultimately favorable.

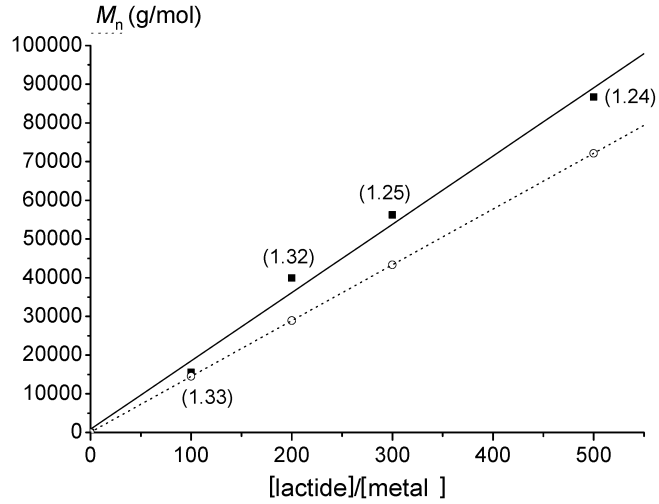


Fig. 8 Plot of Mn vs. monomer-to-yttrium ratio for *rac*-LA polymerization with **11** in THF at 20 °C for 1 h (yield of PLA > 97%): ■ M_n (GPC; polystyrene standards), ○: M_n (theory).

Furthermore, the homonuclear decoupled ^{1}H NMR spectrum of the methine region of the PLA samples derived from **24** and **25** in THF at room temperature is consistent with the formation of chains that are most predominantly heterotactic. The peaks are assigned to the appropriate tetrads in accordance with the correlations established in the literature [29,30]. Both amido- and alkyl-yttrium complexes **24** and **25** lead to the same P_r value, which is consistent with initiation of polymerization by the R (amido or alkyl) group and assistance of the [{ONOO}Ln] fragment on stereocontrol [31]. This hypothesis is supported by the results obtained with the La complex **26**. Although **26** initiates the ROP of *rac*-LA with similar activity, control of molecular weights and PDIs to **24** and **25** (Table 1, entry 8), the level of heterotacticity is significantly lower (P_r = 0.64). We assume that this change may reflect the direct influence of the metal center, i.e., via its ionic radius, or its indirect influence on the overall conformation of the [{ONOO}Ln] fragment. The strong influence of the solvent on the level of stereoselectivity is also noteworthy, with a neat decrease (P_r = 0.60) observed when the polymerization is carried out in toluene instead of THF.

Based on other reports that evidenced the influence of both the nature of the metal center and the ligand architecture on the stereocontrol of the polymerization [31], these promising results prompted us to further study this system by investigating the effect of changes to the metal center and the substituents of the amino-bis(phenolate) ligand on the polymerization behavior. We evaluated all the prepared complexes to first observe the possible influence of the complex modifications on the activity. All amido and carbyl complexes **23–33** are active initiators for the controlled ROP of *rac*-LA under mild conditions. Representative polymerization data are summarized in Table 2. Polymerization proceeds equally with all complexes at room temperature within 1 h; we observed complete conversion of *rac*-LA to PLA for monomer-to-initiator ratios up to 500. All the polymers produced have narrow PDIs and number-average molecular masses (M_n) values close to the theoretical ones (calculated on the assumption that each silylamide or carbyl group initiates the polymerization).

Table 2 ROP of *rac*-LA in THF promoted by **23–33**.[a]

Entry	Initiator [I]	[LA]/[I] ratio	$M_{n,calc}$[b] (g mol^{-1})	M_n[c] (g mol^{-1})	M_w/M_n[c]	P_r[d]
1	**23**	200	28 800	36 000	1.25	0.56
2	**24**	100	14 400	15 500	1.33	0.80
3	**24**	300	43 200	56 200	1.25	0.80
4	**24**	500	72 100	87 000	1.24	0.80
5	**25**	100	14 400	19 000	1.28	0.80
6	**26**	100	14 400	20 400	1.34	0.65
7	**27**	200	28 800	38 500	1.28	0.49
8	**28**	100	14 400	20 900	1.17	0.60
9	**29**	200	28 800	48 000	1.22	0.80
10	**29**	100	14 400	17 300	1.07	0.80
11	**30**	200	28 800	39 400	1.29	0.55
12	**31**	100	14 400	22 000	1.18	0.62
13	**32**	200	28 800	37 800	1.22	0.80
14	**33**	100	14 400	26 300	1.19	0.90

[a]All reactions performed with [*rac*-LA] = 0.44 *M* at 20 °C in THF until completion as determined *by* integration of the methyl resonances of LA and PLA (reaction time: 10–60 min.).

[b]$M_{n,calc}$ of PLA calculated from the conversion of LA: $M_{n,calc}$ = 144.00 × ([LA]/[I]) × conversion LA.

[c]M_n and M_w/M_n of PLA determined by SEC-RI using polystyrene standards.

[d]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.

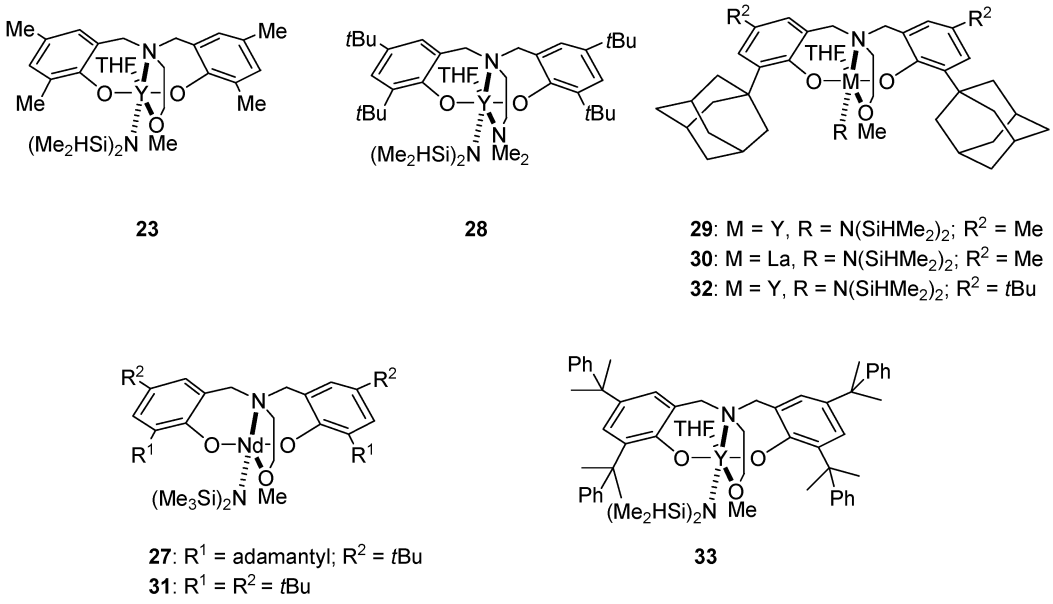
An important goal of this work was to study the asymmetric incorporation of *rac*-LA into the polymer backbone. For this purpose, we analyzed the PLA microstructures through inspection of the methine region of homonuclear decoupled ^{1}H NMR spectra. These analyses revealed that complexes **23**, **27–33** exert at room temperature a significant influence on the tacticity of the polymer formed, as the microstructure is moderately to highly heterotactic depending on the ligand architecture, the metal center, and the operating conditions.

Effect of the solvent on stereoselectivity

We first studied the influence of the solvent on stereochemistry with these systems. Indeed, polymerizations in THF were always found to be much more selective than those in toluene (65 % for toluene vs. 80 % for THF). In a recent paper, Rzepa and coworkers proposed by computational analysis that ROP of *rac*-LA initiated by a single-site β-diketiminate magnesium complex [HC{CMeN-2,6-^{i}Pr$_2$C$_6$H$_3$}$_2$]Mg(OMe)(THF) proceeds via two major transition states (TS1, TS2), with the highest-energy transition state dictating the stereochemistry of monomer insertion to give highly heterotactic PLAs [32]. The results suggested that the solvent plays a key role, serving to entropically balance the system. The authors claimed that this finding is applicable to other coordinative initiator systems. This prediction is in agreement with our observations, owing to the high heteroselectivity displayed by amino-bis(phenolate) yttrium initiators **23–25**, **29**, **32**, and **33** in THF, whereas in toluene propagating species generate nearly atactic materials.

Role of the ligand and the metal center on stereoselectivity

To examine the influence of the amino-bis(phenolate) ligand substituents on the microstructures of the produced PLAs, we studied in detail the *rac*-LA polymerization ability of complexes **23–33** having a series of substituents at the R^1 and R^2 positions. The factors investigated include steric and possible electronic effects derived from the substituents on the aromatic rings, as well as on the pendant side arm (Fig. 9). We chose bulky group as the *ortho*-phenolate substituent R^1 in order to favor mononuclear complex formation and limit chain aggregation during polymerization reactions [33]. Inspired by the work of Busico [34] and Fujita [35], who demonstrated the strong influence of ligand substituent on the olefin polymerization activity and stereoselectivity governed by chain-end control mechanism, we prepared complexes with *ortho*-adamantyl **29**, **30**, **32**, and *ortho*-cumyl groups **33**. Complex **23**, which bears *ortho*-methyl groups at the phenolate rings (Fig. 9), gave low selectivity for heterotactic PLA, probably due to the higher tendency to form aggregated species (Table 2, entry 1) [25b]. This lack of tacticity is also consistent with previous observations that bulky ligands are required for stereochemical control in the polymerization of *rac*-LA via a chain-end control mechanism [31,36]. In such a reaction, the presence of bulky ligands increase the influence of the stereogenic center of the last inserted monomer, which controls the stereochemistry of propagation [31,32]. Influence of the side arm is illustrated with complex **28** (X = NMe_2) which was found to be as reactive as complex **24** (X = OMe) in the polymerization of LA, but significantly less stereoselective (P_r = 0.80 for **24**, entry 2; P_r = 0.60 for **28**, entry 8). Because of the uncertainty in the definition of **28**, we cannot conclude if this decrease in stereoselectivity reflects a direct influence of the pending X functionality, or competition between different initiating species. However, we recently evidenced the side arm influence by substituting the $CH_3OCH_2CH_2N$ group in complex **24** with a CH_3N group (**24bis**). Complex **24bis** was successfully isolated and characterized prior to polymerization tests. Such a modification results in a decrease of the polymerization control (PDI = 1.60) and stereoselectivity (P_r = 0.71) (Scheme 4). This influence may be due to the vacant coordination site, which could lead to additional solvent ligation and consequently affect the catalyst stability and the polymer tacticity.



23

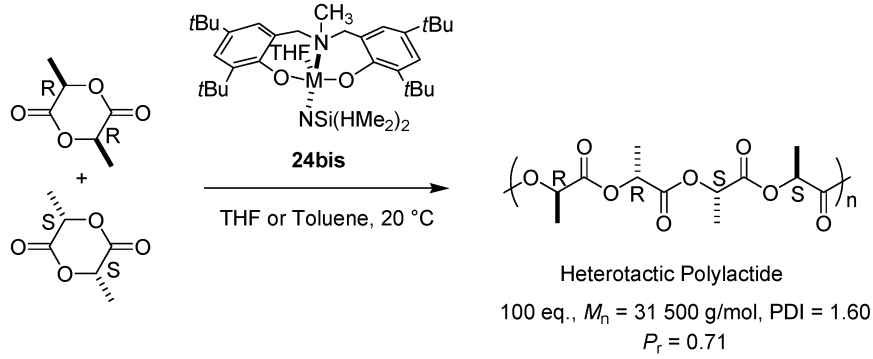
28

29: M = Y, R = N(SiHMe$_2$)$_2$; R^2 = Me
30: M = La, R = N(SiHMe$_2$)$_2$; R^2 = Me
32: M = Y, R = N(SiHMe$_2$)$_2$; R^2 = *t*Bu

27: R^1 = adamantyl; R^2 = *t*Bu
31: R^1 = R^2 = *t*Bu

33

Fig. 9 Active complexes for the ROP of *rac*-LA.



Scheme 4 Influence of the side arm ligand on the polymerization of *rac*-LA.

Complex **32**, which bears ligand **19** with adamantyl group in the *ortho* position of phenolate rings, did not show any appreciable difference in polymerization compared with the parent complex **24** (entries 2–4 and 13, Table 2). This result is consistent with the similarity of the solid-state structures of these two initiators [27b]. Despite the fact that adamantyl phenolate substituents are bulkier than *tert*-butyl groups, both substituents offer the same steric hindrance to the metal center. Therefore, stereoselectivity is not affected. The polymerization data also indicate that the *para*-substituents on the ligand do not significantly affect the ability of the initiator to control monomer enchainment; for instance, changing the ligand *para*-substituents from *tert*-butyl to methyl groups (entries 9 and 13, Table 2) results in no change in heterotacticity (P_r = 0.80). However, it appears that steric (and possibly electronic) modifications of the ligand can lead to a pronounced heterotacticity enhancement of the resulting polymerization. Indeed, by using bulky and conformationally flexible cumyl (α,α-dimethylbenzyl) groups as R^1 and R^2 substituents, we were able to significantly improve heterotacticity (entry 14, Table 2); the PLA produced by **33** at 20 °C is highly heterotactic with a P_r of 0.90 (Fig. 10). However, from the analy-

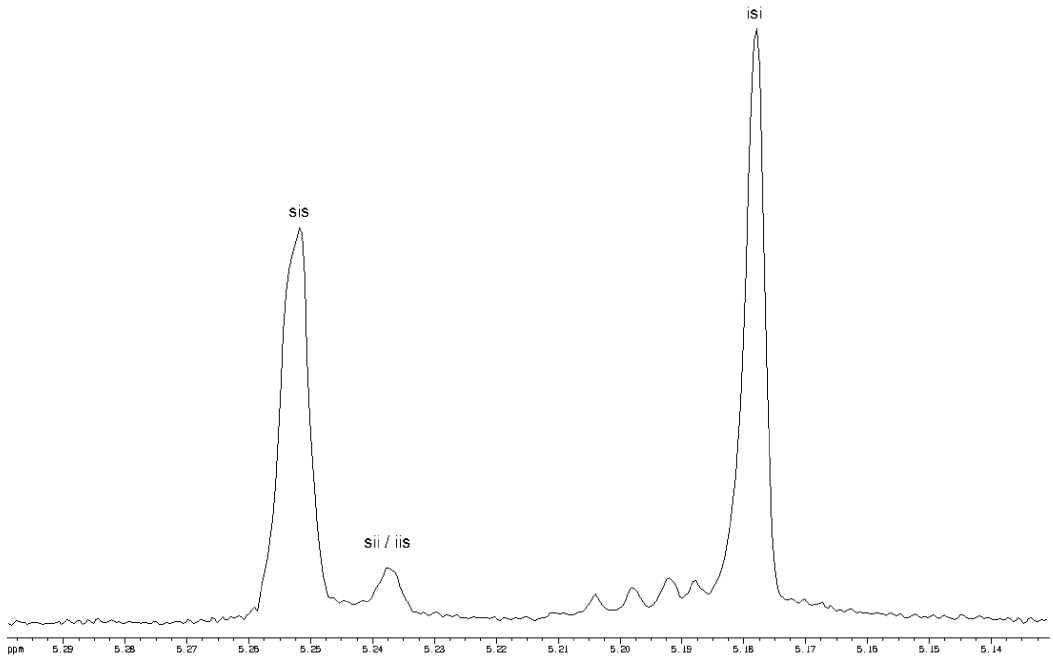
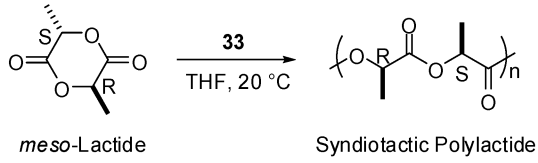


Fig. 10 Methine region of homonuclear CH_3-decoupled ^{1}H NMR spectrum of heterotactic PLA formed with complex **33** (P_r = 0.90) (500 MHz, $CDCl_3$, 20 °C) (*s* and *i* stand for syndiotactic and isotactic dyads, respectively).

ses of the solid-state structure of complexes **24**, **29**, and **33**, we cannot conclude that the cumyl group is more sterically crowding than adamantyl- and *tert*-butyl phenolate substituents [27b].

We also confirmed the influence of the metallic center with Y, La, and Nd complexes. By contrast with Y complexes, the La complexes (Table 2, entries 6 and 11) and the Nd complexes (Table 2, entries 7 and 12) gave poor selectivities. This trend likely reflects the influence of the metal center ionic radius. We assume that, since La and Nd are larger than Y [37], the environment around the Y metal center is more hindered, leading to a better selectivity. We tried to synthesize Sc complexes, to evaluate a smaller metal center, but attempts to isolate and characterize these complexes were unsuccessful. The in situ prepared Sc complex did not lead to a better selectivity than the Y one ($P_r \approx 0.80$).

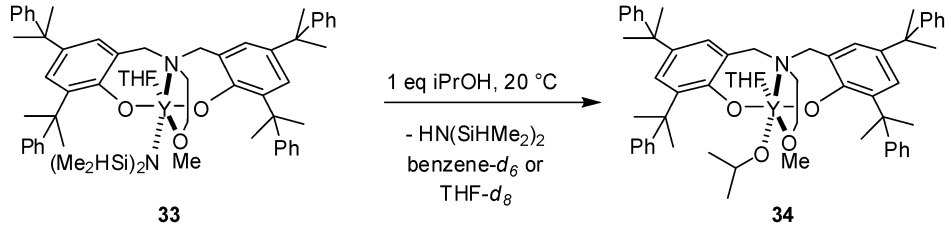
Having identified the most selective catalytic system, complex **33** was then examined for the ROP of *meso*-LA (Scheme 5). After 0.5 h at 20 °C, the reaction proceeded to 97 % conversion ([LA] = 0.44 *M* in THF, [LA]/[**33**] = 100). Analysis of the polymer microstructure using homonuclear CH_3-decoupled ^{1}H NMR revealed that **33** produces syndiotactic-enriched PLA (P_r = 0.75). This is in line with the findings for the β-diiminate zinc complexes developed by Coates and coworkers [31], which also proceed by chain-end control mechanism and give highly heterotactic PLA (P_r = 0.90 at 20 °C) from *rac*-LA and moderately syndiotactic PLA (P_r = 0.76 at 0 °C) from *meso*-LA.



Scheme 5 Synthesis of syndiotactic PLA.

Polymerization of rac-LA in the presence of isopropanol

We decided to investigate the effect of the initiating group by synthesizing group 3 alkoxide initiators for several reasons. First, it is well known that metal alkoxides are very efficient for the controlled ROP of *rac*-LA [3], because of the better nucleophilicity of alkoxide compared to amido or carbyl group [–$N(SiMe_3)_2$, –$N(SiHMe_2)_2$, and –CH_2SiMe_3]. Then, as the isopropoxide initiating group mimics the propagating groups of the presumed active species, it appeared to us interesting to characterize this complex in order to observe possible interactions between the cumyl group and the initiating isopropoxide, which can be related to electronic interactions during the polymerization process [38]. Alkoxide initiators for LA polymerization can be in situ generated by alcoholysis of amido and carbyl complexes using isopropanol. Recently, it was proposed by Okuda that such group 3 metal isopropoxides are aggregated, at least to dimers [20]. To establish the nature of the active initiating species in the polymerization of *rac*-LA, the reactions of Y complexes **24** and **33** with isopropanol were monitored by NMR spectroscopy. These reactions and NMR studies were carried out in two different solvents [27b]. Benzene, a noncoordinating solvent, was used to investigate the influence of the ligand array on the nuclearity of the species; similar studies were performed in THF-d_8, which is the solvent used in polymerization. In the reaction of **33** with 1 equiv of isopropanol in THF-d_8, the room temperature ^1H and ^{13}C NMR spectra established quantitative conversion of the reagents and formation of a single mononuclear product, [Y(**21**)(O*i*Pr)(THF-d_8)] (d_8-**34**) (Scheme 6).



Scheme 6 In situ generation of complex **34**.

The ^1H NMR spectrum of **34** in THF-d_8 remains unchanged after several days at room temperature and shows C_s-symmetry features (on the NMR time scale) down to −20 °C. Key ^1H NMR data for **34** include one set of resonances for two equivalent phenolate rings bound to the metal center in a *trans* configuration and a single O*i*Pr ligand, the methine hydrogen of the isopropoxide group appears as a multiplet at δ 4.22, which is shifted downfield with respect to the signal of free isopropanol (δ 3.67) (Fig. 11).

Moreover, the $^{13}C\{^1H\}$ NMR spectrum of **34** in THF-d_8 contains one signal for two equivalent NCH_2Ar groups, and two signals for the $OCH(CH_3)_2$ ligand. Essentially, the same ^1H NMR characteristics were observed for the reaction product of **33** with 1 equiv of isopropanol in benzene-d_6, indicative of the formation of the same complex **34**. Only trace amounts (<5 %) of a second species were observed in this reaction; the unsymmetrical pattern of ^1H NMR resonances suggests it is a dimeric or an aggregated species. The ^1H resonances for the coordinated THF molecule (δ 3.44 and 1.44) of **34** in benzene-d_6 are clearly shifted from those observed for the free solvent (δ 3.57 and 1.40 in benzene-d_6). Complex **34** loses its THF ligand upon drying in vacuum to give also an unsymmetrical complex, as indicated by ^1H NMR spectroscopy in benzene-d_6 [8]. The methine hydrogen of the isopropoxide group appears as a multiplet at δ 4.66, which is shifted downfield with respect to the signal of free isopropanol (δ 3.67). This signal is broadened and further shifted to δ 4.22 and 4.05 upon addition of 2 and 3 equiv of isopropanol to **33**, respectively, indicative of an exchange process between the isopropoxide ligand in **34** and free isopropanol [20]. The ^1H NMR spectrum of the reaction product of **24** with 1 equiv of isopropanol in THF-d_8 contains also only one set of resonances, consistent with the presence of a sin-

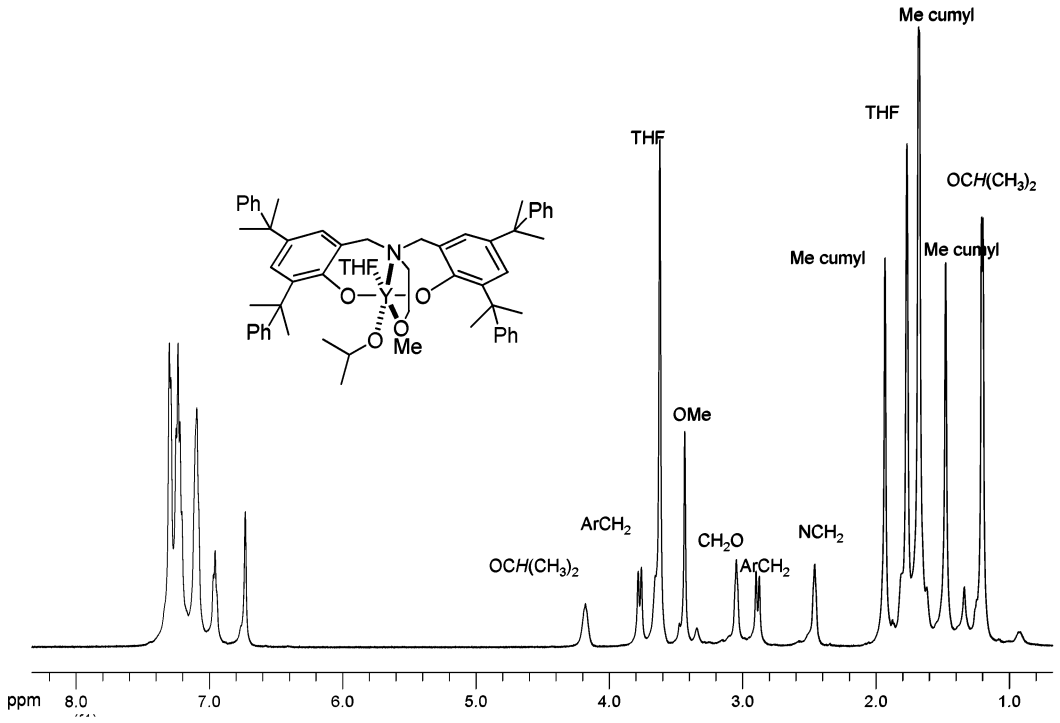


Fig. 11 ^{1}H NMR spectrum of the isopropoxide complex **34** (THF-d_8, 20 °C, 500 MHz).

gle symmetrical isopropoxide species, as observed in the case of **33**. In contrast, carrying out the reaction in benzene-d_6 resulted in complicated ^{1}H NMR spectra, indicative of the formation of mixtures of species that could not be identified. Nuclear Overhauser enhancement spectroscopy (NOESY) experiments demonstrate the spatial proximity between hydrogens of the cumyl ring and the CH of the isopropoxide group. These observations are of great importance when considering C–H•••π interactions, which can occur only when the π-system is close enough to the C–H unit ($d < 4$ Å) [32,39]. Further investigations are in progress to clearly demonstrate the existence of this type of stabilizing interactions. These NMR data show that both isopropoxide complexes in situ generated from the reaction of isopropanol with **24** and **33** are essentially single, monomeric species in THF, which is the solvent used for ROP of LA. It seems, therefore, that the different catalytic behavior of the systems **24**/*i*PrOH and **33**/*i*PrOH (complex **34**) do not originate from difference in the nuclearity of the active species. These results further confirm that subtle steric and possibly electronic features induced by substituents in the phenolate ligands significantly affect the activity and degree of stereocontrol of the polymerization.

In an attempt to facilitate initiation and further improve on polymerization performances, we sought to evaluate these in situ generated alkoxide complexes (Table 3). In agreement with Okuda's observations, addition of isopropanol to the polymerization reaction affected the activity of complexes **24** and **33** and resulted in narrower molecular weight distributions (PDI = 1.06–1.24). In line with previous comments, changing the initiating group from amido (entries 2 and 14, Table 3) to isopropoxide (entries 1 and 4, Table 3) results in no change in heterotacticity (P_r = 0.80 for **24** and **24**/*i*PrOH; P_r = 0.90 for **33** and **33**/*i*PrOH). The yttrium alkoxide generated by reacting **24** with isopropanol in 1:1 ratio can polymerize 1000 equiv within 40 min at 20 °C (TOF = 1500 h^{-1}; entry 2, Table 3). In contrast, the system **33**/*i*PrOH is less active as compared to **24**/*i*PrOH; by using this system, the conversion of 1000 equiv of monomer is quantitative within 6 h (entry 5, Table 3). We assume that this decrease in activity is due to the presence of a more sterically demanding ligand, which is also believed to account

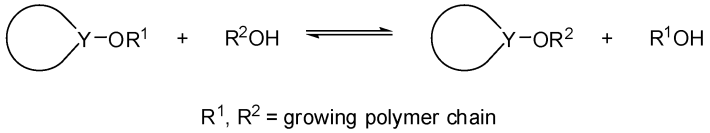
for the better selectivity observed during the polymerization (P_r = 0.90). Moreover, the system **33**/*i*PrOH leads to significantly higher M_n values than **24**/*i*PrOH, with experimental M_n data in close agreement with the calculated ones. To the best of our knowledge, this is the first example of a fast, room-temperature living LA polymerization that produces high-molecular-weight heterotactic PLA (M_n = 160 000 g/mol) with narrow PDI (M_w/M_n = 1.13).

Table 3 ROP of *rac*-LA in THF in the presence of isopropanol.[a]

Entry	[I]	[LA]/[I]	[*i*PrOH]/[I]	$M_{n,calc}$[b] (g mol^{-1})	M_n[c] (g mol^{-1})	M_w/M_n[c]	P_r[d]
1	**24**	100	1	14 400	17 000	1.06	0.80
2	**24**	1000	1	144 000	99 000	1.24	0.80
3	**24**	1000	4	144 000	37 900	1.13	0.80
4	**33**	100	1	14 400	9 900	1.06	0.90
5	**33**	1000	1	144 000	160 000	1.13	0.90
6	**33**	1000	2	144 000	71 000	1.13	0.90
7	**33**	1000	4	144 000	35 000	1.08	0.90
8	**33**	1000	10	14 400	20 100	1.07	0.90
9	**33**	2000	6	48 000	63 000	1.40	0.90

[a]All reactions performed with [*rac*-LA] = 0.44 *M* at 20 °C in THF until completion as determined *by* integration of the methyl resonances of LA and PLA (reaction time: 10–60 min.).
[b]M_n of PLA calculated from the conversion of LA: $M_{n,calc}$ = 144.00 × ([LA]/[I]) × conversion LA.
[c]M_n and M_w/M_n of polymer determined by SEC-RI using polystyrene standards.
[d]P_r is the probability of racemic linkages between monomer units and is determined from the methine region of the homonuclear CH_3-decoupled ^{1}H NMR spectrum.

Remarkably, with an excess of isopropanol, both compounds **24** and **33** behave in "immortal character" leading to polymers with narrow molecular weight distributions, and with a M_n proportional to the number of added isopropanol [27b,40]. In fact, the alkoxide group in the L_nMOR complex is labile to alcohol exchange. Therefore, a rapid exchange occurs between the metal alkoxide and isopropanol, and because the growing species of LA polymerization is an alkoxide, alcohol behaves as a reversible chain transfer agent (Scheme 7). The reaction is initiated by complex **34**, and upon the formation of the alkoxide growing species, a reversible exchange with alcohol takes place. This reversible reaction is rapid enough compared to the polymer growth, and all alcohol molecules present in the system can act as growing species. This behavior was first reported by Inoue for the epoxide polymerization catalyzed by porphyrin aluminum alkoxide initiators [41]. The authors observed, with an excess of methanol, the formation of a polymer with a number of polymer molecules coinciding with the sum of the number of the molecules of the initiator and that of methanol.



Scheme 7 Reversible alcohol exchange reaction.

In our case, increasing the isopropanol amount significantly affects neither the polymerization rate nor the selectivity. The excess of free alcohol yields polymer chains with reduced molecular weights and narrow PDIs (Table 3, entries 6–9) [20]. Preliminary results have shown that as much as 9-fold excess of isopropanol can be added, resulting in a low mean weight diameter (MWD) PLA with a M_n of only 1/10 of that with 1 equiv of isopropanol (Table 3, entry 9) [40]. Even if this type of ex-

change reaction was previously reported for the polymerization of ε-caprolactone [42], there is no reported example of immortal ROP of high ratios of *rac*-LA with a small amount of initiator, leading to the formation of highly heterotactic PLA. Finally, end-group analysis of PLA oligomers by ^{1}H NMR and by MALDI/TOF/MS prepared in the presence of 1 or more equiv of *i*PrOH showed that the polymer chains were systematically end-capped with an isopropyl ester and a hydroxy group; no cyclic oligomer was detectable.

CONCLUSION

Amino-alkoxy-bis(phenolate) group 3 metal complexes are efficient initiators in the ROP of *rac*-LA to form PLAs with a predominantly heterotactic placement of repeat units. The polymerization of *rac*-LA with these achiral complexes occurs via a chain-end control mechanism. Despite recent significant advances in ROP of LA, the number of selective and productive initiators remains modest. The most notable feature of the initiators described in this study is to exhibit high polymerization activity and productivity combined in some cases with high selectivity for heterotactic polymer formation. The steric bulk of the substituents on the aromatic rings, and particularly the *ortho*-phenolate substituents, plays a crucial role in achieving high heteroselectivity for the chain-end controlled polymerization of *rac*-LA. Future work will explore the mechanism and modification of the current system to develop new initiators that exhibit higher stereochemical control during the polymerization reaction. Efforts are also paid to expand on the range of monomers for the preparation of microstructurally controlled materials, as we recently achieved in the polymerization of β-butyrolactone into highly syndiotactic poly(3-hydroxybutyrate) [43] and of 2,5-morpholinediones to generate polydepsipeptides [44].

REFERENCES

1. S. Mecking. *Angew. Chem., Int. Ed.* **43**, 1078 (2004).
2. R. E. Drumright, P. R. Gruber, E. Henton. *Adv. Mater.* **12**, 1841 (2000).
3. O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou. *Chem. Rev.* **104**, 6147 (2004).
4. S. McLain, N. Drysdale. U.S. patent 5 028 667 (1991).
5. S. McLain, T. Ford, N. Drysdale. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **33**, 463 (1992).
6. (a) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra, J. Feijen. *Macromolecules* **29**, 6132 (1996); (b) W. M. Stevels, M. J. K. Ankone, P. J. Dijkstra, J. Feijen. *Macromolecules* **29**, 8296 (1996); (c) V. Simic, V. Girardon, N. Spassky, L. G. Hubert-Pfalzgraf, A. Duda. *Polym. Degrad. Stab.* **59**, 227 (1998); (d) V. Simic, N. Spassky, L. G. Hubert-Pfalzgraf. *Macromolecules* **30**, 7338 (1997); (e) K. Tortosa, T. Hamaide, C. Boisson, R. Spitz. *Macromol. Chem. Phys.* **202**, 1156 (2001); (f) E. Martin, P. Dubois, R. Jerome. *Macromolecules* **33**, 1530 (2000); (g) E. Martin, P. Dubois, R. Jerome. *Macromolecules* **36**, 5934 (2003).
7. O. Poncelet, W. J. Sartain, L. G. Hubert-Pfalzgraf, K. Folting, K. G. Caulton. *Inorg. Chem.* **28**, 263 (1989).
8. H. Ma, T. P. Spaniol, J. Okuda. *Dalton Trans.* 4770 (2003).
9. K. B. Aubrecht, K. Chang, M. A. Hillmyer, W. B. Tolman. *J. Polym. Sci., A: Polym. Chem.* **39**, 284 (2001).
10. S. Arndt, J. Okuda. *Chem. Rev.* **102**, 1953 (2002).
11. W. E. Piers, D. J. H. Emslie. *Coord. Chem. Rev.* **233–234**, 131 (2002).
12. K. Beckerle, K. C. Hultzsch, J. Okuda. *Macromol. Chem. Phys.* **200**, 1702 (1999).
13. B. J. O'Keefe, M. A. Hillmyer, W. B. Tolman. *J. Chem. Soc., Dalton Trans.* 2215 (2001).
14. G. R. Giesbrecht, G. D. Whitener, J. Arnold. *J. Chem. Soc., Dalton Trans.* 923 (2001).
15. L. F. Sanchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann. *Organometallics* **24**, 3792 (2005).

16. D. Patel, S. T. Liddle, S. A. Mungur, M. Rodden, A. J. Blake, P. Arnold. *Chem. Commun.* 1124 (2006).
17. B. M. Chamberlain, Y. Sun, J. R. Hagadorn, E. W. Hemmesch, J. Young, G. Victor, M. Pink, M. A. Hillmyer, W. B. Tolman. *Macromolecules* **32**, 2400 (1999).
18. B. M. Chamberlain, B. A. Jazdzewski, M. Pink, M. A. Hillmyer, W. B. Tolman. *Macromolecules* **33**, 3970 (2000).
19. T. M. Ovitt, G. W. Coates. *J. Am. Chem. Soc.* **124**, 1316 (2002).
20. H. Ma, J. Okuda. *Macromolecules* **38**, 2665 (2005).
21. I. Palard, A. Soum, S. M. Guillaume. *Chem. Eur. J.* **10**, 4054 (2004).
22. F. Bonnet, A. R. Cowley, P. Mountford. *Inorg. Chem.* **44**, 9046 (2005).
23. (a) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt. *Inorg. Chem.* **40**, 4263 (2001); (b) E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt. *Organometallics* **20**, 3017 (2001); (c) E. Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, Z. Goldschmidt. *Organometallics* **21**, 662 (2002).
24. A. Kowalski, A. Duda, S. Penczek. *Macromolecules* **33**, 7359 (2000).
25. (a) F. M. Kerton, A. C. Whitwood, C. E. Willans. *Dalton Trans.* 2237 (2004); (b) O. Runte, T. Priermeier, R. Anwander. *Chem. Commun.* 1385 (1996); (c) M. E. G. Skinner, B. R. Tyrell, B. D. Ward, P. Mountford. *J. Organomet. Chem.* **647**, 145 (2002).
26. (a) W. J. Burke, R. P. Smith, C. Weatherbee. *J. Am. Chem. Soc.* **74**, 602 (1952); (b) W. J. Burke, M. J. Kolbezen, C. W. Stephens. *J. Am. Chem. Soc.* **74**, 3601 (1952); (c) W. J. Burke, E. L. M. Glennie, C. Weatherbee. *J. Org. Chem.* **29**, 909 (1964).
27. (a) C.-X. Cai, A. Amgoune, C. W. Lehmann, J.-F. Carpentier. *Chem. Commun.* 330 (2004); (b) A. Amgoune, C. M. Thomas, T. Roisnel, J.-F. Carpentier. *Chem. Eur. J.* **12**, 169 (2006).
28. (a) C.-X. Cai, L. Toupet, C. W. Lehmann, J.-F. Carpentier. *J. Organomet. Chem.* **683**, 131 (2003); (b) P. N. O'Shaughnessy, P. D. Knight, C. Morton, K. M. Gillespie, P. Scott. *Chem. Commun.* 1770 (2003); (c) D. V. Gribkov, K. C. Hultzsch, F. Hampel. *Chem. Eur. J.* **9**, 4796 (2003); (d) W. A. Herrmann, J. Eppinger, M. Spiegler, O. Runte, R. Anwander. *Organometallics* **16**, 1813 (1997).
29. (a) K. A. M. Thakur, R. T. Kean, E. S. Hall, J. J. Kolstad, T. A. Lindgren, M. A. Doscotch, J. I. Siepmann, E. J. Munson. *Macromolecules* 2422 (1997); (b) K. A. M. Thakur, R. T. Kean, M. T. Zell, B. E. Padden, E. J. Munson. *Chem. Commun.* 1913 (1998).
30. The probability of heterotactic enchainment, estimated from the relative intensity of the major tetrad peaks *sis* (δ 5.22 ppm) and *isi* (δ 5.14 ppm) vs. other tetrads (*sii*/*iis*, δ 5.20 and 5.16 ppm; *iii*, δ 5.145 ppm), is $P_r = 0.80$.
31. B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **123**, 3229 (2001).
32. E. L. Marshall, V. C. Gibson, H. S. Rzepa. *J. Am. Chem. Soc.* **127**, 6048 (2005).
33. (a) B. L. B. M. Small. *Macromolecules* **32**, 2120 (1999); (b) L. A. L. Resconi, G. Franciscono. *Macromolecules* **25**, 6814 (1992).
34. V. Busico, R. Cipullo, N. Friederichs, S. Ronca, G. Talarico, M. Togrou, B. Wang. *Macromolecules* **37**, 8201 (2004).
35. M. Mitani, R. Furuyama, J.-I. Mohri, J. Saito, S. Ishii, H. Terao, T. Nakano, H. Tanaka, T. Fujita. *J. Am. Chem. Soc.* **125**, 4293 (2003).
36. (a) M. H. Chisholm, J. C. Gallucci, K. Phomphrai. *Inorg. Chem.* **43**, 6717 (2004); (b) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates. *J. Am. Chem. Soc.* **121**, 11583 (1999).
37. R. Anwander. *Top. Organomet. Chem.* **2**, 1 (1999).
38. Y.-C. Liu, B.-T. Ko, C.-C. Lin. *Macromolecules* **34**, 6196 (2001).
39. Y. Umezawa, S. Tsuboyama, H. Takahashi, J. Uzawa, M. Nishio. *Tetrahedron* **55**, 10047 (1999).
40. A. Amgoune, C. M. Thomas, J.-F. Carpentier. *Macromol. Rapid Commun.* **28**, 693 (2007).

41. (a) T. Aida, Y. Maekawa, S. Asano, S. Inoue. *Macromolecules* **21**, 1195 (1988); (b) T. Aida, S. Inoue. *Acc. Chem. Res.* **29**, 39 (1996); (c) S. Inoue. *J. Polym. Sci., Part A: Polym. Chem.* **38**, 2861 (2000).
42. (a) M.-L. Hsueh, B.-H. Huang, C.-C. Lin. *Macromolecules* **35**, 5763 (2002); (b) T.-C. Liao, Y.-L. Huang, B.-H. Huang, C.-C. Lin. *Macromol. Chem. Phys.* **204**, 885 (2003).
43. A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel, J.-F. Carpentier. *Angew. Chem., Int. Ed.* **45**, 2782 (2006).
44. P. M. Castro, G. Zhao, A. Amgoune, C. M. Thomas, J.-F. Carpentier. *Chem. Commun.* 4509 (2006).