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Ring-Opening Polymerization of Lactide with Group 3 Metal Complexes Supported by Dianionic Alkoxy-Amino-Bisphenolate Ligands: Combining High Activity, Productivity, and Selectivity

Abderramane Amgoune,[a] Christophe M. Thomas,[a] Thierry Roisnel,[b] and Jean-François Carpentier*[a]

Abstract: A series of new alkoxy-amino-bis(phenols) (H_2L **1**–**6**) has been synthesized by Mannich condensations of substituted phenols, formaldehyde, and amino ethers or diamines. The coordination properties of these dianionic ligands towards yttrium, lanthanum, and neodymium have been studied. The resulting Group 3 metal complexes have been used as initiators for the ring-opening polymerization of *rac*-lactide to provide poly(lactic acid)s (PLAs). The polymerizations are living, as evidenced by the narrow polydispersities of the isolated polymers, together with the linear natures of number average molecular weight versus conversion plots and monomer-to-catalyst ratios. Complex [Y(L**6**)-{$N(SiHMe_2)_2$}(THF)] (**17**) polymerized *rac*-lactide to heterotactic PLA (P_r = 0.90 at 20 °C) and *meso*-lactide to syndiotactic PLA (P_r = 0.75 at 20 °C). The in situ formation of [Y(L**6**)(O*i*Pr)-(THF)] (**18**) from **17** and 2-propanol resulted in narrower molecular weight distributions (PDI = 1.06). With complex **18**, highly heterotactic PLAs with narrow molecular weight distributions were obtained with high activities and productivities at room temperature. The natures of the ligand substituents were shown to have a significant influence on the degree of control of the polymerizations, and in particular on the tacticity of the polymer.

Keywords: biodegradable polymers · lactide · lanthanides · polymerization · tacticity

Introduction

Biodegradable polymers have recently attracted much interest as replacements for conventional oil-based materials.[1] Among the most promising candidates in this class of materials are aliphatic polyesters and, in particular, poly(lactic acid)s (PLAs).[2] These polymers, derived from 100% renewable resources such as corn or sugar beets, have many properties similar and sometimes superior to those of traditional olefin-based polymers, with the added benefit of biodegradability.[3] Although several methods for synthesis of PLAs exist, the most convenient and promising route is the ring-opening polymerization (ROP) of lactide, in which the driving force for polymerization is the relief of ring strain.[4] Stereochemistry plays an important role in PLAs, determining the mechanical properties, biodegradability, and ultimately the end use of the material.[1,3] There has been particular emphasis over the past decade on the synthesis of discrete, well characterized complexes that function as active polymerization initiators.[5] These recent advances in catalyst design have resulted in a variety of PLA architectures being obtained from the enantiomerically pure monomers, the racemic mixture, or *meso*-lactide (Scheme 1).[6] Systematic studies have demonstrated the influence both of the initiating group and of the ligand architecture on polymerization behavior.[7]

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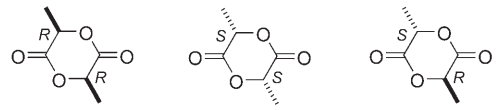
Supporting information (NMR data for complexes **14** and **18** generated in situ; representative homonuclear decoupled ^{1}H NMR and MALDI-TOF spectra, and GPC trace of a poly(lactic acid) (entry 4, Table 3) for this article is available on the WWW under http://www.chemeurj.org/ or from the author.

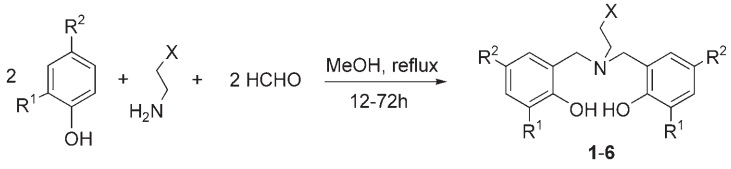


Scheme 1. Stereoisomers of lactide.

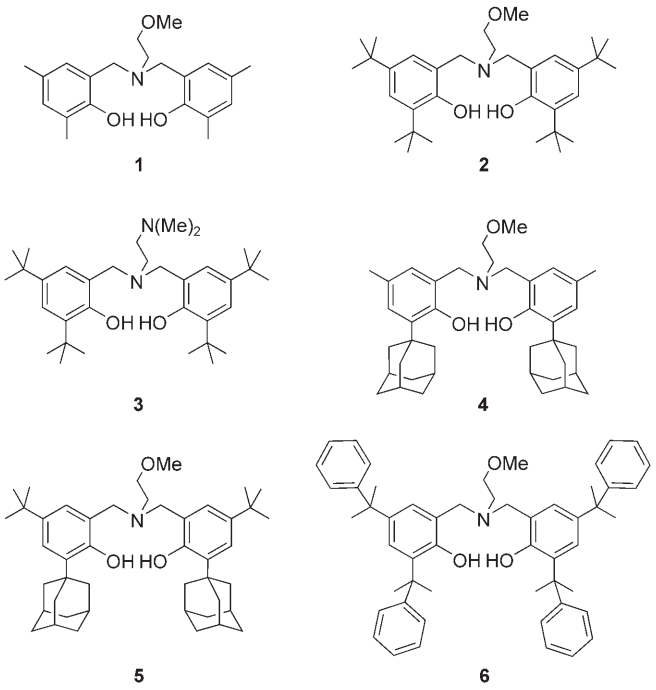
Among the variety of initiators, zinc and magnesium complexes bearing sterically demanding achiral β-diiminato ligands are notable as highly active for the polymerization of *rac*-lactide to heterotactic poly(lactic acid) by a chain-end control mechanism in which the last unit in the growing polymer chain influences which enantiomeric form of the monomer is incorporated next.[6e–i] Coates and co-workers first reported the sensitivity of this polymerization to ligand sterics.[6h] In particular, the authors described the importance of steric bulk in the *N*-aryl substituents of β-diiminate ligands, with subtle ligand modifications resulting in dramatic effects on activity and selectivity.[6h] We also recently reported the synthesis of heterotactic PLA from *rac*-lactide with a single-site Group 3 metal complex that controls stereochemistry by a chain-end control mechanism.[6n] To expand upon this initial work, we were interested in investigating the effect of complex architecture on lactide polymerization behavior (i.e., initiator selectivity and activity). Our approach for determining the structure/reactivity dependence was based on fine-tuning of the ancillary ligand and study of the effect on the catalytic reactivity. For this purpose, we have designed and synthesized new Group 3 metal complexes bearing dianionic alkoxy-amino-bisphenolate ligands. Details of the synthesis, structures, and polymerization performances of these new complexes are reported here.

Results and Discussion

Synthesis of bisphenolate Group 3 metal complexes: Diamino and alkoxy-amino-bisphenol ligands H_2L **1–6** (of which **1** and **4–6** are new) were synthesized by double Mannich condensations of the corresponding substituted phenol, formaldehyde, and the appropriate alkoxy-amine or diamine (Scheme 2).[8] They can be isolated in moderate to high yields as white microcrystalline powders (Scheme 3). Some of these *N*,*N*-substituted compounds were difficult to obtain because of the side-formation of benzoxazines, which takes place through cyclization of the intermediary *N*-substituted



Scheme 2. Synthesis of bisphenolate ligands **1–6**.

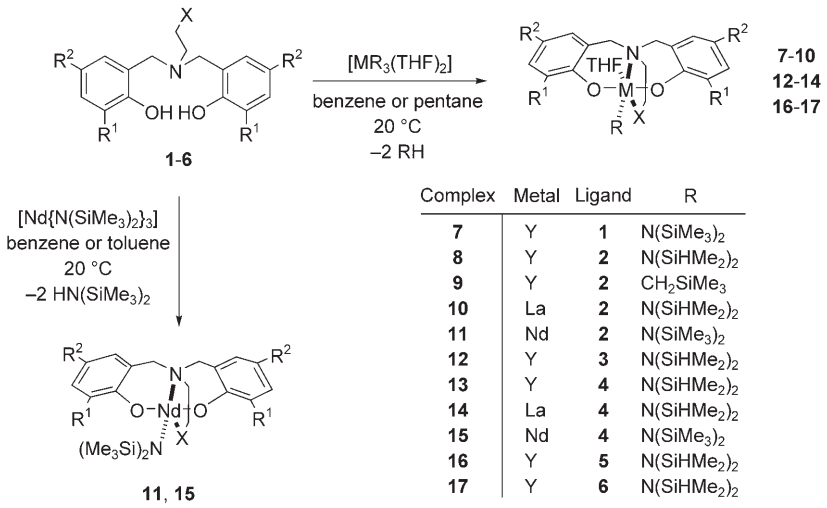


Scheme 3. Bisphenolate ligands screened.

product.[8] The nature of the substituent *ortho* to the phenolic hydroxy group plays an important role in determining the course of the reaction. All spectroscopic data for **1–6** are given in the Experimental Section.

Group 3 precursors $[MR_3(THF)_2]$ (M = Y, La; R = CH_2SiMe_3, $N(SiHMe_2)_2$) and $[Nd\{N(SiMe_3)_2\}_3]$ were each treated with one equivalent of each of the neutral bisphenols H_2L **1–6** to give the corresponding yttrium and lanthanum complexes [(L)M(R)(THF)] **7–10**, **12–14**, **16**, and **17**, and $[(L)Nd\{N(SiMe_3)_2\}]$ **11** and **15** in good yields (Scheme 4). A key event in this reaction is the protonolysis of two of the bulky amido or carbyl ligands in the homoleptic precursor by the relatively acidic bisphenols.[9,10] The products were easily isolated as white solids by evaporation of volatiles and washing of the residues with pentane. The compounds are quite air- and moisture-sensitive, readily soluble in aromatic hydrocarbons (toluene, benzene), and slightly soluble in aliphatic hydrocarbons (pentane, hexanes). These complexes were characterized by elemental analysis and X-ray diffraction studies in some cases, and by NMR spectroscopy for diamagnetic complexes **7–10**, **12–14**, **16**, and **17**.

The ^1H and ^{13}C NMR data for yttrium and lanthanum complexes **8–10**, **13, 14**, **16**, and **17** in $[D_6]$benzene at room temperature are in each case indicative of the formation of a single, monomeric species with rigid C_s symmetry on the NMR timescale, with the phenoxy groups in the *trans* configuration. This is evidenced by the symmetry-related phenolate rings, as well as the ^1H AB spin systems for the two benzylic methylene units and the single resonance for the silylamido or carbyl group. The ^1H and ^{13}C resonances corresponding to the coordinated THF molecule are clearly shift-



Complex	Metal	Ligand	R
7	Y	**1**	$N(SiMe_3)_2$
8	Y	**2**	$N(SiHMe_2)_2$
9	Y	**2**	CH_2SiMe_3
10	La	**2**	$N(SiHMe_2)_2$
11	Nd	**2**	$N(SiMe_3)_2$
12	Y	**3**	$N(SiHMe_2)_2$
13	Y	**4**	$N(SiHMe_2)_2$
14	La	**4**	$N(SiHMe_2)_2$
15	Nd	**4**	$N(SiMe_3)_2$
16	Y	**5**	$N(SiHMe_2)_2$
17	Y	**6**	$N(SiHMe_2)_2$

Scheme 4. Synthesis of Group 3 metal complexes **7**–**17**.

ed from those observed for the free solvent ($\delta(^1H) = 3.57$ and 1.40 ppm; $\delta(^{13}C) = 67.80$ and 25.72 ppm in [D_6]benzene). Additionally, the ^1H resonances for the side arm OMe groups in complexes **8**–**10**, **13, 14**, **16**, and **17** were found to be shifted by approximately 0.2–0.6 ppm from those in the corresponding free ligands, confirming a six-coordinated geometry. This assignment of solution structures was supported by single-crystal X-ray structure analyses of **8**–**10** and **13**. The solid-state structures of **8**–**10** have been reported in preliminary communications and will not be discussed further here.[6n,9a]

Single crystals of the new adamantyl-substituted complex **13** suitable for X-ray diffraction were obtained by slow evaporation of a saturated toluene solution at room temperature. The ORTEP plot of the complex with its atom numbering scheme is illustrated in Figure 1 and selected bond lengths and angles are listed in Table 1. Overall, the structure of **13** is closely related to that of the parent *tert*-butyl-substituted complex **8**.[6n] Complex **13** adopts a distorted octahedral coordination geometry around the yttrium atom,

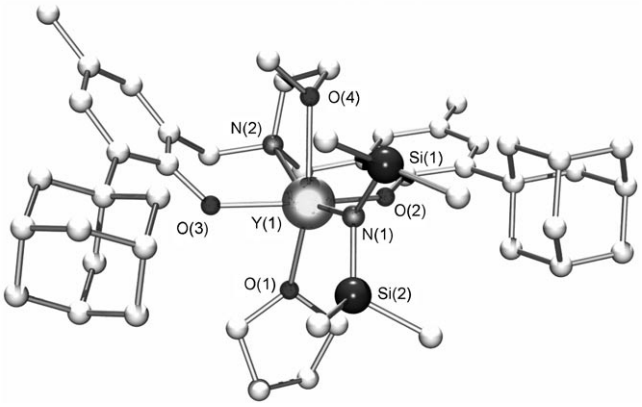


Figure 1. Molecular structure of complex **13**; all hydrogen atoms and solvent molecules are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for complex **13**.

Y(1)–O(2)	2.148(2)	O(2)-Y(1)-O(3)	151.88(9)
Y(1)–O(3)	2.173(2)	O(2)-Y(1)-N(1)	101.29(10)
Y(1)–N(1)	2.296(3)	O(3)-Y(1)-N(1)	106.80(9)
Y(1)–O(1)	2.318(2)	O(2)-Y(1)-O(1)	84.65(8)
Y(1)–O(4)	2.370(2)	O(3)-Y(1)-O(1)	82.23(8)
Y(1)–N(2)	2.597(3)	N(1)-Y(1)-O(1)	115.52(9)
Si(2)–N(1)	1.702(3)	O(2)-Y(1)-O(4)	90.88(9)
Si(1)–N(1)	1.700(3)	O(3)-Y(1)-O(4)	90.87(9)
		N(1)-Y(1)-O(4)	88.96(9)
		O(1)-Y(1)-O(4)	155.52(8)
		O(2)-Y(1)-N(2)	76.02(9)
		O(3)-Y(1)-N(2)	78.85(9)
		N(1)-Y(1)-N(2)	155.81(10)
		O(1)-Y(1)-N(2)	88.37(9)
		O(4)-Y(1)-N(2)	67.22(9)
		Si(1)-N(1)-Si(2)	120.00(17)

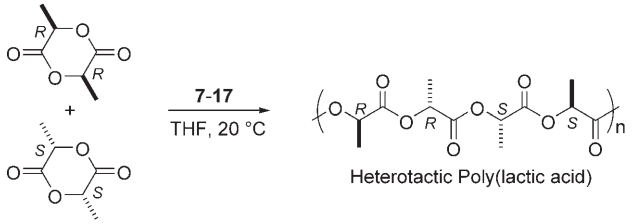
from the THF ligand, leaving a relatively open cleft for the bis(dimethylsilyl)amido group. The $Y–O_{ether}$ bond length of 2.370(2) Å in **13** is particularly short in relation to those observed for other $Y–O_{ether}$ bonds, which are generally in the 2.45–2.50 Å range,[9] and also in the parent *tert*-butyl-substituted complex **8** ($Y–O_{ether} = 2.414(2)$ Å). This short $Y–O_{ether}$ bond reflects a weak *trans* influence of the THF ligand. The silylamido ligand is located *trans* to the nitrogen atom of the bisphenolate ligand, the angle N(1)-Y(1)-N(2) being 155.81(10) Å. The $Y–N_{amido}$ (2.296(3) Å) and $Y–N_{amine}$ (2.597(3) Å) bond lengths are not far from those found in other octahedral yttrium(III) phenolate complexes.[9] Furthermore, there is no evidence of any significant Si–H–Y agostic interaction as frequently observed in similar compounds.[10] Indeed, the Si(1)-N(1)-Si(2) bond angle of 120.0(2)° in **13** falls into the range of values reported for classical Si-N-Si angles (119.93–129.58°).

The preparation of two complexes—**7** and **12**—was found to be more complicated. Firstly, a mixture of species was obtained upon treatment of **1** with one equivalent of [Y-

with all four donors of the bisphenolate ligand bound to the metal center. One THF ligand and one bis(dimethylsilyl)amido group occupy the remaining *cis* positions. The oxygen phenolate atoms of the ligand are arranged *trans* to each other, with Y–O distances of 2.148(2) Å and 2.173(2) Å. Because of the constraints imposed by the ligand, however, the O(2)-Y(1)-O(3) angle—of 151.88(9)°—is significantly smaller than 180°. The aryl rings of the phenolate moieties fold back toward the pendant 2-methoxyethyl arm and are somewhat bent away

$\{N(SiHMe_2)_2\}_3(THF)_2]$, and complete purification could not be achieved. Key ^{1}H NMR resonances included four ArC*HH* AB spin systems and at least two singlets for the Y–$N(Si(CH_3)_3)_2$ hydrogens, of which one series accounted for about 50% of the total. The enhanced steric flexibility within **1**, originating from the presence of less bulky methyl groups, and the corresponding more opened coordination sphere at the metal center might be responsible for the formation of a mixture of monomeric (**7**) and dimeric species.[9d,11] Further complexes derived from ligand **1** were not studied for that reason. Secondly, treatment of [Y-$\{N(SiHMe_2)_2\}_3(THF)_2$] with bisphenol **3**, which has a pendant amine arm, proceeded in toluene with selective elimination of two equivalents of $HN(SiHMe_2)_2$, but the room temperature ^{1}H NMR spectrum showed broad resonances, indicative of fluxional behavior. The ^{1}H NMR spectrum at 60°C displayed two sets of sharp resonances for the aryl and Si*H*Me_2 hydrogens, suggesting that another species is formed in addition to **12**.[12]

Ring-opening polymerization of *rac*-lactide: Amido and carbyl complexes **7–17** are active initiators for the controlled ROP of *rac*-lactide under mild conditions (Scheme 5). Representative polymerization data are summarized in Table 2. Homopolymerization of *rac*-lactide with the prepared group 3 metal complexes proceeds rapidly at 20°C, equally in toluene and THF solvents in terms of activity. In all cases, complete conversions of the monomer into PLA are achieved within 1 h for monomer-to-initiator ratios of up to 500. All the polymers produced have narrow molecular weight distributions and number-average molecular mass (M_n) values close to the theoretical ones (calculated on the assumption that each silylamide or carbyl group initiates the polymerization). These data indicate that the polymerization had proceeded in a living fashion: that is, without any significant side reactions. To illustrate this living character, the diblock copolymerization of *rac*-lactide and caprolactone was achieved, by a two-step sequential procedure, to provide a well defined poly(lactide-*block*-caprolactone) (PLA-*block*-PCL) copolymer (Scheme 6).[13] The first step involved living ROP of *rac*-lactide ([LA]/[**8**] = 100, 20°C, 1 h) to yield a pre-polymer with an amino end group R_2N–PLA–O–[Y]. The reaction proceeded in a stereoselective way (vide infra) to give a macroinitiator with heterotactic PLA sequence (M_n = 18300 g mol^{-1}; M_w/M_n = 1.30, P_r = 0.80). In the second step, polymerization of ε-caprolactone ([CL]/[Y] = 100) with the new macroinitiator R_2N-PLA–O– [Y] occurred under mild conditions (THF, 20°C, 12 h) to give a single diblock PCL-*block*-PLA ($M_{n,exp}$ = 32900 g mol^{-1}; M_w/M_n = 1.25).



Scheme 5. Synthesis of heterotactic PLA.

An important goal of this work was to study the asymmetric incorporation of *rac*-lactide into the polymer backbone. For this purpose, ^{1}H NMR spectroscopy is applicable for determination of the stereochemistry of the poly(lactic acid)s by inspection of the methine region of homonuclear decoupled ^{1}H NMR spectra of the polymers.[14] PLA derived from *rac*-lactide can exhibit up to five tetrad sequences in relative ratios determined by the ability of the initiator to control racemic [*r*-diad] and *meso* [*m*-diad] connectivity of the monomer units.

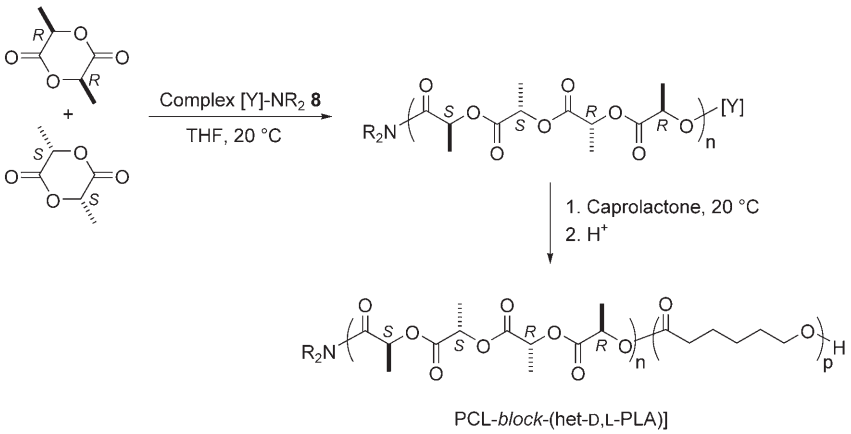
Microstructural analysis of the different PLAs formed from *rac*-LA revealed that at room temperature the Group 3 metal complexes **7–17** exert a significant influence on the tacticity of the polymer formed, as the microstructure is moderately to highly heterotactic (Scheme 5). The peaks were assigned to the appropriate tetrads in accordance with the correlations established in the literature. The major tetrad peaks correspond to those of the *mrm* and *rmr* tetrads, indicative of the heterotactic -*RRSSRRSS*- sequence of the polymer.[14]

One important feature of these systems is that the polymerizations in THF were found to be much more selective than those in toluene.[6n] In a recent paper, Rzepa and co-workers have proposed as a result of computational analysis that the ROP of *rac*-lactide initiated by

Table 2. Promotion of ring-opening polymerization of *rac*-lactide by **7–17** in THF.[a]

Entry	Initiator [I]	[LA]/[I]	Reaction time [min]	$M_{n,calcd}$[b] [g mol^{-1}]	$M_{n,exp}$[c] [g mol^{-1}]	M_w/M_n[c]	P_r[d]
1	**7**	200	10	28800	36000	1.25	0.56
2	**8**	100	5	14400	15500	1.33	0.80
3	**8**	300	10	43200	56200	1.25	0.80
4	**8**	500	20	72100	87000	1.24	0.80
5	**9**	100	5	14400	19000	1.28	0.80
6	**10**	100	5	14400	20400	1.34	0.65
7	**11**	200	10	28800	38500	1.28	0.49
8	**12**	100	5	14400	20900	1.17	0.60
9	**13**	200	10	28800	48000	1.22	0.80
10	**13**	100	5	14400	17300	1.07	0.80
11	**14**	200	10	28800	39400	1.29	0.55
12	**15**	100	5	14400	22000	1.18	0.62
13	**16**	200	10	28800	37800	1.22	0.80
14	**17**	100	20	14400	26300	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. [b] M_n of PLA calculated from $M_{n,calcd}$ = 144.00 × ([LA]/[I]) × conversion LA (conv = 100%). [c] M_n and M_w/M_n of PLA determined by SEC-RI with use of 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.



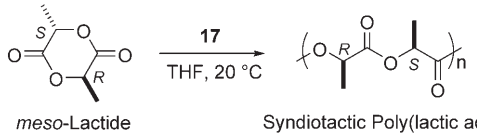
Scheme 6. Synthesis of a polylactide-*block*-polycaprolactone diblock copolymer.

a single-site β-diketiminate magnesium complex [{HC(CMeN-2,6-*i*$Pr_2C_6H_3$)$_2$}Mg(OMe)(THF)] proceeds through two major transition states, with the highest-energy transition state dictating the stereochemistry of monomer insertion to give highly heterotactic PLAs.[15] The results suggested that the solvent plays a key role, serving to balance the system entropically. The authors claimed that this finding should also be applicable to other coordinative initiator systems.[15] This prediction is in agreement with our observations, in view of the high heteroselectivity displayed by the bisphenolate yttrium initiators **7**–**9**, **13**, **16**, and **17** in THF, whereas propagating species in toluene generate nearly atactic materials.

Role of the ligand on the stereoselectivity: To examine the influence of the bisphenolate ligand substituents on the microstructures of the produced PLAs, the lactide polymerization abilities of complexes **7**–**17**—with a series of substituents at the R^1, R^2, and X positions—were examined in detail. The factors investigated include steric and possible electronic effects originating from the substituents on the aromatic rings, as well as those on the pendant amine arm.[16] Bulky groups were chosen as the *ortho*-phenolate substituent R^1 in order to favor mononuclear complex formation and to limit chain aggregation during polymerization reactions.[7b,16] The *para*-phenolate substituent R^2 was varied to provide ligands with differing electron-donating abilities and soluble complexes.

Complex **7**, which bears *ortho*-methyl groups at the phenolate rings (Scheme 3), gave low selectivity for heterotactic poly(lactic acid), probably due to the higher tendency to form aggregated species (Table 2, entry 1).[9d,11] This lack of tacticity is also consistent with previous observations that bulky ligands are required for stereochemical control in the polymerization of *rac*-lactide by a chain-end control mechanism.[6e–i] In such a reaction, the presence of bulky ligands increases the influence of the stereogenic center of the last inserted monomer, which controls the stereochemistry of propagation.[6g,17] Several polymerizations were performed with the yttrium complex **8** with variation of the monomer-to-metal ratio (Table 2, entries 2–4). As shown by the linear relationship between the monomer-to-metal ratio and number-average molecular masses (M_n), good control over polymerization is achieved with this system, even at a catalyst loading of 0.2%, which yielded M_n values as high as 87000 g mol^{-1}. The same P_r value was obtained in all cases. As expected, changing the amido initiator for an alkyl initiator does not affect the selectivity for heterotactic PLA (Table 2, entries 2 and 5). Complex **12** (X = NMe_2) was found to be as reactive as complex **8** (X = OMe) in the polymerization of lactide, but significantly less stereoselective (P_r = 0.80 for **8**, Table 2, entry 2 versus P_r = 0.60 for **12**, Table 2, entry 8). Because of the uncertainty in the definition of **12** (vide supra), we cannot conclude whether this decrease in stereoselectivity reflects a direct influence of the pendant X functionality, or competition between different initiating species. In contrast with the 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 probably reflects the influence of the ionic radius of the metal center. We assume that, since lanthanum and neodymium are larger than yttrium,[18] the environment around the yttrium metal center is more hindered, resulting in better selectivity. Complexes **8** and **16**, which bear ligands **2** and **5** with *tert*-butyl and adamantyl groups, respectively, in the *ortho* positions of the phenolates, did not show any appreciable difference in polymerization (Table 2, entries 2–4 and 13). This is consistent with the previously mentioned similarity of the solid-state structures (i.e., steric crowding) of these two initiators. 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; changing the ligand *para*-substituents from *tert*-butyl to methyl groups (Table 2, entries 9 and 13), for instance, results in no change in heterotacticity (P_r = 0.80). However, it appears that steric and electronic modification of the ligand can give rise to 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,[17a] we were able to improve heterotacticity significantly (Table 2, entry 14); the PLA produced by **17** at 20 °C is substantially heterotactic, with a P_r of 0.90 (90% of the linkages formed are between lactide units of opposite stereochemistry).

Having identified the most selective catalytic system, we then examined complex **17** for the ROP of *meso*-lactide (Scheme 7). After 0.5 h at 20 °C, the reaction had proceeded



Scheme 7. Synthesis of syndiotactic PLA.

to 97% conversion ([LA] = 0.44 M in THF, [LA]/[**17**] = 100). Analysis of the polymer microstructure by homonuclear decoupled ^{1}H NMR revealed that **17** forms syndiotactic enriched PLA (P_r = 0.75). This is in line with the findings for the β-diiminate zinc complexes developed by Coates and co-workers, which also proceed by a chain-end control mechanism and give highly heterotactic PLA (P_r = 0.90 at 20 °C) from *rac*-lactide and moderately syndiotactic PLA (P_r = 0.76 at 0 °C) from *meso*-lactide.[6h]

Polymerization of *rac*-lactide in the presence of 2-propanol: Metal alkoxides have been reported to be effective initiators for lactide ROP, giving polymers both in high yield and with high molecular weight.[6a,c–e,g,h,j,l,7b,19–23] The isopropoxide initiating group mimics the propagating groups of the presumed active species, and complexes with these moieties produce PLAs of predictable molecular weight and with narrow molecular weight distributions.[6g] In contrast, amido and alkyl initiators such as $-N(SiMe_3)_2$, $-N(SiHMe_2)_2$, and $-CH_2SiMe_3$ are usually inferior initiating groups for the ROP of *rac*-lactide at room temperature.[7b] To circumvent this limitation, alkoxide initiators for lactide polymerization can be generated in situ by alcoholysis of amido and carbyl complexes with 2-propanol. Recently it was proposed by Okuda et al. that such Group 3 metal isopropoxides are aggregated, at least to dimers.[7b]

In an attempt to facilitate initiation and to improve further on polymerization performances, we sought to evaluate different alkoxide complexes generated in situ (Table 3). In accordance with Okuda's observations,[7b] addition of 2-propanol to the polymerization reaction affected the activities of complexes **8** and **17** and resulted in narrower molecular weight distributions (PDI = 1.06–1.24). In line with previous observations, changing the initiating group from amido (Table 2, entries 2 and 14) to isopropoxide (Table 3, entries 1 and 4) results in no change in heterotacticity (P_r = 0.80 for **8** and **8**/*i*PrOH; P_r = 0.90 for **17** and **17**/*i*PrOH). Notably, the yttrium alkoxide generated by treatment of **8** with 2-propanol in 1:1 ratio can polymerize 1000 equiv. within 40 min at 20 °C (TOF = 1500 h^{-1}; Table 3, entry 2). In contrast, the system **17**/*i*PrOH is less active than **8**/*i*PrOH; with use of this system, the conversion of 1000 equivalents of monomer is quantitative within 6 h (Table 3, entry 5). We assume that this decrease in activity is due to the presence of a more sterically demanding ligand, which is also believed to be responsible for the better selectivity observed during the polymerization (P_r = 0.90). This result is consistent with the usual trade-off between activity and selectivity. Moreover, the **17**/*i*PrOH system gives significantly higher M_n values than **8**/*i*PrOH, with experimentally determined M_n data in close agreement with the calculated values. To the best of our knowledge, this is the first example of a fast, room-temperature living lactide polymerization that produces high molecular weight heterotactic PLAs (M_n = 160000 g mol^{-1}) with a narrow polydispersity (M_w/M_n = 1.13). Increasing the amount of 2-propanol does not significantly affect the polymerization rate. However, polymerization experiments with complexes **8** and **17** in the presence of two or four equivalents of 2-propanol revealed that an alkoxide/2-propanol exchange occurs during the chain propagation process. Most interestingly, excess free alcohol acts as an efficient chain transfer agent, eventually yielding polymer chains with reduced molecular weights and narrow polydispersities (Table 3, entries 6 and 7).[7b,24] End-group analysis of PLAs prepared in the presence of one or more equivalents of *i*PrOH by MALDI-TOF mass spectrometry showed that the polymer chains were systematically end-capped with an isopropyl ester and a hydroxy group; no cyclic oligomer was detectable (see Supporting Information).

To establish the nature of the active initiating species in the polymerization of *rac*-lactide, the reactions of yttrium complexes **8** and **17** with 2-propanol were examined by NMR spectroscopy. These reactions and NMR studies were carried out in two different solvents: benzene, a noncoordinating solvent, was used to investigate the influence of the ligand array on the nuclearity of the species, whilst similar studies were also performed in [D$_8$]THF, which is the solvent used in polymerization.

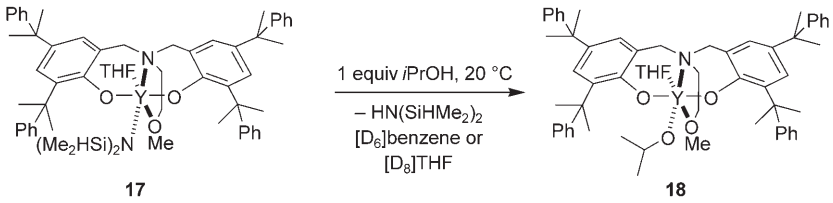
In the reaction between **17** and 1 equiv. of 2-propanol in [D$_8$]THF, the room temperature ^{1}H and ^{13}C NMR spectra established quantitative conversion of the reagents and formation of a single mononuclear prod-

Table 3. Ring-opening polymerization of *rac*-lactide in THF in the presence of 2-propanol.[a]

Entry	Initiator [I]	[LA]/[I]	[*i*PrOH]/[I]	Reaction time [min]	$M_{n,calcd}$[b] [g mol^{-1}]	$M_{n,exp}$[c] [g mol^{-1}]	M_w/M_n[c]	P_r[d]
1	**8**	100	1	5	14400	17000	1.06	0.80
2	**8**	1000	1	40	144000	99000	1.24	0.80
3	**8**	1000	4	40	144000	37900	1.13	0.80
4	**17**	100	1	20	14400	9900	1.06	0.90
5	**17**	1000	1	360	144000	160000	1.13	0.90
6	**17**	1000	2	360	144000	71000	1.13	0.90
7	**17**	1000	4	360	144000	35000	1.08	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. [b] M_n of PLA calculated from $M_{n,calcd}$ = 144.00 × ([LA]/[I]) × conversion LA (conv = 100%), not taking into account chain transfer with excess *i*PrOH. [c] M_n and M_w/M_n of polymer determined by SEC-RI with use of 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.

uct: [Y(L**6**)(O*i*Pr)([D_8]THF)] ([D_8]-**18**) (Scheme 8).[25] The ^{1}H NMR spectrum of **18** in [D_8]THF remains unchanged after several days at room temperature and shows C_s-symmetry features down to −20 °C. Key ^{1}H NMR data for **18** 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. Additionally, the ^{13}C{^{1}H} NMR spectrum of **18** in [D_8]THF contains one signal for two equivalent N*C*H$_2$Ar groups, and two signals for the O*C*H(*C*H$_3$)$_2$ ligand. Essentially the same ^{1}H NMR characteristics were observed for the reaction product of **17** with one equivalent of 2-propanol in [D_6]benzene, indicative of the formation of the same complex **18**.[26] The ^{1}H resonances for the coordinated THF molecule (δ = 3.44 and 1.44 ppm) of **18** in [D_6]benzene are clearly shifted from those observed for the free solvent (δ = 3.57 and 1.40 ppm in [D_6]benzene).[26] The methine hydrogen of the isopropoxide group appears as a multiplet at δ = 4.66 ppm, which is shifted downfield with respect to the signal of free 2-propanol (δ = 3.67 ppm). This signal is broadened and further shifted to δ = 4.22 and 4.05 ppm upon addition of two and three equivalents of 2-propanol, respectively, to **17**, indicative of an exchange process between the isopropoxide ligand in **18** and free 2-propanol.[7b]



17 **18**

Scheme 8. Synthesis of complex **18**.

The ^{1}H NMR spectrum of the reaction product of **8** with one equivalent of 2-propanol in [D_8]THF also contains only one set of resonances, consistently with the presence of a single symmetrical isopropoxide species, as observed in the case of **17**. In contrast, carrying out the reaction in [D_6]benzene resulted in complicated ^{1}H NMR spectra, indicative of the formation of mixtures of species that could not be identified.

These NMR data show that both isopropoxide complexes generated in situ from the reactions between 2-propanol and **8** or **17** are essentially single, monomeric species in THF, which is the solvent used for ROP of lactide. It therefore seems that the difference in catalytic behavior of the systems **8**/*i*PrOH and **17**/*i*PrOH (**18**) does not originate from differences 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.

Conclusion

In summary, bisphenolate Group 3 metal complexes are efficient initiators in the ROP of *rac*-lactide to form poly(lactic acid) polymers with predominantly heterotactic placement of repeat units. Despite recent significant advances in ROP of lactide, the number of selective and productive initiators remains modest. The most notable feature of the isopropoxide initiators described in this study, and in particular of the yttrium complex **18**, is high polymerization activity and productivity in conjunction 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*-lactide. It can be anticipated that this class of Group 3 metal complexes should continue to provide new and interesting results. Future work will explore the mechanism and modification of this system to develop new initiators that exhibit higher stereochemical control during the polymerization reaction.

Experimental Section

General conditions: All manipulations requiring dry atmosphere were performed under purified argon by use of standard Schlenk techniques or in a glovebox. Solvents (toluene, pentane, THF) were freshly distilled from Na/K alloy under nitrogen and were degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Deuterated solvents ([D_6]benzene, [D_8]toluene, [D_8]THF/99.5 % D, Eurisotop) were freshly distilled from sodium/potassium amalgam under argon and were degassed prior to use. Starting materials for the synthesis of ligand precursors **1**–**7** were purchased from Aldrich and were used without further purification. 2-Adamantyl-4-*tert*-butylphenol[27] and ligands **2** and **3**[28] were prepared by reported methods. Ligands **1** and **4**–**7** were synthesized by modifications of the methods reported in the literature.[8] Lanthanide precursors were prepared by literature procedures.[29] *rac*-Lactide (Aldrich) was recrystallized twice from dry toluene and was then sublimed under vacuum at 50 °C. *meso*-Lactide (Purac) was recrystallized twice from dry propan-2-ol.

Instruments and measurements: NMR spectra were recorded on Bruker AC 200, AC 300, and AC 500 spectrometers in Teflon valve NMR tubes. ^{1}H and ^{13}C chemical shifts are reported in ppm versus SiMe$_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was carried out through multinuclear 1D (^{1}H, ^{13}C{^{1}H}) and 2D (COSY, HMQC, HMBC, NOESY) NMR experiments. Coupling constants are given in Hertz. Size exclusion chromatography (SEC) of PLAs was performed in THF at 20 °C with a Waters SIS HPLC pump, a Waters 410 refractometer, a DAD-UV detector, and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100 A columns. The number average molecular masses (M_n) and polydispersity indexes (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration. Microstructures of PLAs were measured by homodecoupling ^{1}H NMR spectroscopy at 20 °C in $CDCl_3$ on a Bruker AC 500.

Compound 1: A solution of 2,4-dimethylphenol (1.95 g, 16.0 mmol), 2-methoxyethylamine (0.52 mL, 6.00 mmol), and aqueous formaldehyde (36 %, 1.2 mL, 16 mmol) in methanol (4 mL) was stirred and heated at reflux for 24 h. The mixture was cooled and filtered, and the residue was dissolved in methanol and heated at reflux for 2 h. The mixture was cooled and the white precipitate was filtered off. Recrystallization from

methanol gave white crystals of **1** (1.10 g, 52%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 8.35 (s, 2H; ArOH), 6.85 (s, 2H; ArH), 6.67 (s, 2H; ArH), 3.72 (s, 4H; $ArCH_2$), 3.58 (t, ^3J(H,H) = 5.1 Hz, 2H; NCH_2CH_2O), 3.47 (s, 3H; OCH_3), 2.70 (t, ^3J(H,H) = 4.9 Hz, 2H; NCH_2CH_2O), 2.20 (s, 12H; CH_3) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 152.84, 131.37, 121.24 (Ar-C*q*), 127.68, 127.36, 125.15 (Ar-CH), 70.89 (NCH_2CH_2O), 58.17 (OCH_3), 57.04 (NCH_2CH_2O), 50.77 (CH_2Ar), 20.24, 16.03 (CH_3) ppm; HRMS (70 eV, EI): *m*/*z* calcd for $C_{21}H_{29}N_1O_3$: 343.2147; found 343.2139 [*M*]$^+$.

Compound 4: A solution of 2-adamantyl-4-methylphenol (0.38 g, 1.60 mmol), 2-methoxyethylamine (0.052 mL, 0.60 mmol), and aqueous formaldehyde (36%, 0.12 mL, 1.60 mmol) in methanol (2 mL) was stirred and heated at reflux for 48 h. The mixture was cooled and the supernatant liquid was decanted. The remaining oil was dissolved in methanol and heated at reflux for 2 h. The mixture was cooled and a white precipitate formed. The solid was filtered off to give **4** as white crystals (0.22 g, 62%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 8.37 (s, 2H; ArOH), 6.93 (brs, 2H; ArH), 6.69 (brs, 2H; ArH), 3.67 (s, 4H; $ArCH_2$), 3.48 (brt, ^3J(H,H) = 5.1 Hz, 2H; NCH_2CH_2O), 3.44 (s, 3H; OCH_3), 2.74 (t, ^3J(H,H) = 5.1 Hz, 2H; NCH_2CH_2O), 2.22 (s, 6H; CH_3), 2.15 (s, 12H; CH_2-adamantyl), 2.04 (s, 6H; CH-adamantyl), 1.76 (s, 12H; CH_2-adamantyl) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 153.61, 137.39 (Ar-C*q*), 128.69, 122.71 (Ar-CH), 71.07 (NCH_2CH_2O), 58.13 (OCH_3), 57.44 (CH_2Ar), 51.28 (NCH_2CH_2O), 40.73 (adamantyl), 37.44 (adamantyl), 37.13 (adamantyl), 29.60 (adamantyl), 20.83 (CH_3) ppm; HRMS (4000 V, ESI): *m*/*z* calcd for $C_{39}H_{54}N_1O_3$: 584.4103; found 584.4107 [*M*+H]$^+$.

Compound 5: Pieces of sodium (0.50 g, 0.026 mol) were added to a solution of 4-*tert*-butylphenol (4.00 g, 0.026 mol) in a mixture of *p*-xylene (20 mL) and *N*,*N*-dimethylformamide (10 mL). After complete dissolution of sodium, 1-chloroadamantane (4.55 g, 0.026 mol) was added, and the mixture was heated at 85°C for 24 h. The mixture was cooled, dissolved in ether (100 mL), and extracted with aqueous sodium hydroxide (100 mL of a 10% solution). The aqueous layer was extracted with ether (2×200 mL). Combined organic extracts were washed with water, dried over anhydrous sodium sulfate, and concentrated in vacuum to give an oil. The product was purified by column chromatography (silica gel SI 60 40–63 μm, pentane/ethyl acetate 80:20) to give 2-adamantyl-4-*tert*-butylphenol as a white powder (2.85 g, 40%). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C): δ = 7.25 (s, 1H; ArH), 7.09 (d, ^3J(H,H) = 8.1 Hz, 1H; ArH), 6.59 (d, ^3J(H,H) = 8.1 Hz, 1H; ArH), 4.59 (s, 1H; ArOH), 2.13 (brs, 9H; adamantyl), 1.78 (s, 6H; adamantyl), 1.29 (s, 9H; $C(CH_3)_3$).

A solution of 2-adamantyl-4-*tert*-butylphenol (0.50 g, 1.75 mmol), 2-methoxyethylamine (0.057 mL, 0.65 mmol), and aqueous formaldehyde (36%, 0.17 mL, 1.75 mmol) in methanol (2 mL) was stirred and heated at reflux for 48 h. The mixture was cooled and the supernatant liquid was decanted. The remaining oil was dissolved in methanol (10 mL) and heated at reflux for 2 h. The mixture was cooled and a white precipitate formed. The solid was filtered off to give **5** as a white powder (0.22 g, 52%). ^{1}H NMR (200 MHz, [D$_6$]benzene, 25°C): δ = 8.80 (s, 2H; PhOH), 7.48 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 6.96 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 3.53 (s, 4H; $ArCH_2$), 2.99 (brs, 5H; OCH_3 + NCH_2CH_2O), 2.50 (s, 12H; CH_2 adamantyl), 2.35 (t, ^3J(H,H) = 2.2 Hz, 2H; NCH_2CH_2O), 2.18 (s, 6H; CH adamantyl), 1.92 (brm, 12H; CH_2 adamantyl), 1.37 (s, 18H; $C(CH_3)_3$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 153.39, 140.94, 136.59, 122.07 (Cq Ar), 124.76, 123.36 (Ar), 70.79 (NCH_2CH_2O), 58.12 (OCH_3), 57.63 (CH_2Ar), 50.93 (NCH_2CH_2O), 40.70 (adamantyl), 37.37 (adamantyl), 37.33 (adamantyl), 34.07 (adamantyl), 31.65 ($C(CH_3)_3$), 29.51 ($C(CH_3)_3$) ppm; HRMS (4000 V, ESI): *m*/*z* calcd for $C_{45}H_{66}N_1O_3$: 668.5042; found 668.5037 [*M*+H]$^+$.

Compound 6: A solution of 2,4-dicumylphenol (Aldrich, 5.00 g, 15.1 mmol), 2-methoxyethylamine (0.50 mL, 5.7 mmol), and aqueous formaldehyde (36%, 1.12 mL, 15.1 mmol) in methanol (2 mL) was heated at reflux for 72 h. The mixture was cooled and the supernatant liquid was decanted. The remaining oil was dissolved in methanol and heated at reflux for 24 h. The mixture was cooled and a white precipitate formed. The solid was filtered off to give **6** as a white powder (1.10 g, 30%). ^{1}H NMR (200 MHz, [D$_6$]benzene, 25°C): δ = 8.11 (s, 2H; PhOH), 7.47 (d, ^4J(H,H) = 1.8 Hz, 2H; ArH), 7.33 (t, ^3J(H,H) = 7.7 Hz, 16H; phenyl cumyl), 7.06 (m, 4H; phenyl cumyl) 6.83 (d, ^3J(H,H) = 1.3 Hz, 2H; ArH), 3.28 (s, 4H; $ArCH_2$), 2.68 (brs, 5H; OCH_3 + NCH_2CH_2O), 2.15 (t, ^3J(H,H) = 5.1 Hz, 2H; NCH_2CH_2O), 1.75 (s, 12H; CH_3 cumyl), 1.68 (s, 12H; CH_3 cumyl) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 153.52, 152.16, 151.70, 141.29, 136.51 (C*q* Ar), 128.96, 128.40, 127.63, 126.80, 126.32, 123.57 (Ar), 71.57 (s, NCH_2CH_2O) 58.68 (OCH_3), 57.60 (CH_2Ar), 51.67 (s, NCH_2CH_2O), 43.26 ($C(CH_3)_2$), 42.95 ($C(CH_3)_2$), 31.82 (CH_3), 30.17 (CH_3) ppm; HRMS (4000 V, ESI): *m*/*z* calcd for $C_{53}H_{62}N_1O_3$: 760.4729; found 760.4726 [*M*+H]$^+$.

Treatment of [Y{N(SiMe$_3$)$_2$}$_3$] with 1—generation of "7": A solution of **1** (53.4 mg, 0.105 mmol) in toluene (5 mL) was added to a stirred solution of [Y{N(SiMe$_3$)$_2$}$_3$] (60.0 mg, 0.105 mmol) in toluene (5 mL) at room temperature. The mixture was stirred for 12 h at room temperature and for 2 h at 60°C, and volatiles were then removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving a white powder (43.9 mg, 67% based on **7**). ^{1}H NMR (200 MHz, [D$_6$]benzene, 25°C) Key resonances: δ = 5.60 (d, ^2J(H,H) = 11.7 Hz, 0.5H; $ArCH_2$), 5.45 (d, ^2J(H,H) = 11.9 Hz, 0.5H; $ArCH_2$), 5.22 (d, ^2J(H,H) = 12.4 Hz, 0.8H; $ArCH_2$), 5.09 (dd, ^2J(H,H) = 4.0 Hz, ^2J(H,H) = 11.3 Hz, 0.8H; $ArCH_2$), 4.71 (d, ^2J(H,H) = 12.4 Hz, 2H; $ArCH_2$), 4.61 (d, ^2J(H,H) = 12.4 Hz, 2H; $ArCH_2$), 4.03 (d, ^2J(H,H) = 11.9 Hz, 0.6H; $ArCH_2$), 3.58 (d, ^2J(H,H) = 12.4 Hz, 0.6H; $ArCH_2$), 0.37 (brs, 18H; $NSi(CH_3)_3$), 0.31 (s, 16H; $NSi(CH_3)_3$) ppm. Resonances for $HNSi(CH_3)_3$ were also observed [δ = 0.12 (s, 92H)], while those of ArO*H* disappeared. The product was directly engaged in a polymerization experiment.

Compound 8: A solution of **2** (0.153 g, 0.30 mmol) in pentane (5 mL) was added at room temperature to a stirred solution of [Y{N(SiHMe$_2$)$_2$}$_3$(THF)$_2$] (0.189 g, 0.30 mmol) in pentane (5 mL). After the mixture had been stirred for 2 h at room temperature, a white precipitate had formed. To ensure complete reaction, the mixture was stirred for an additional 10 h. The solid was then filtered out, yielding **8** as a white powder (0.163 g, 67%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 7.60 (d, ^4J(H,H) = 2.5 Hz, 2H; ArH), 7.10 (d, ^4J(H,H) = 2.3 Hz, 2H; ArH), 5.14 (m, 2H; SiH), 3.87 (d, ^2J(H,H) = 12.5 Hz, 2H; overlap with THF signal, $ArCH_2$), 3.84 (brm, 4H; α-CH_2 THF), 2.97 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 2.84 (s, 3H; OCH_3), 2.71 (t, ^3J(H,H) = 5.2 Hz, 2H; NCH_2CH_2O), 2.31 (t, ^3J(H,H) = 5.2 Hz, 2H; NCH_2CH_2O), 1.79 (s, 18H; $C(CH_3)_3$), 1.47 (s, 18H; $C(CH_3)_3$), 1.18 (m, 4H; β-CH_2 THF), 0.49 (d, ^4J(H,H) = 3.0 Hz, 12H; $HSi(CH_3)_2$) ppm; ^{1}H NMR (300 MHz, [D$_8$]THF, 25°C): δ = 7.19 (d, ^4J(H,H) = 2.5 Hz, 2H; ArH), 6.91 (brs, 2H; ArH), 4.90 (m, 2H; SiH), 4.00 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 3.58 (m, 4H; α-CH_2 THF, overlap with solvent resonances), 3.26 (m, 7H; $ArCH_2$, OCH_3, NCH_2CH_2O), 2.70 (t, ^3J(H,H) = 5.2 Hz, 2H; NCH_2CH_2O), 1.73 (m, 4H; β-CH_2 THF, overlap with solvent resonances), 1.48 (s, 18H; $C(CH_3)_3$), 1.26 (s, 18H; $C(CH_3)_3$), 0.15 (d, ^4J(H,H) = 3.0 Hz, 12H; $HSi(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 161.38, 136.53, 125.40, 124.11 (Ar), 73.11 (NCH_2CH_2O), 70.96 (α-CH_2 THF), 64.54 (CH_2Ar), 60.43 (OCH_3), 49.57 (NCH_2CH_2O), 35.46 ($C(CH_3)_3$), 34.04 ($C(CH_3)_3$), 32.06 ($C(CH_3)_3$), 30.30 ($C(CH_3)_3$), 24.95 (s; β-CH_2 THF), 4.22 ($HSi(CH_3)_2$) ppm; elemental analysis calcd (%) for $C_{41}H_{73}N_2O_4Si_2Y$: C 61.32, H 9.17, N 3.49; found C 61.74, H 9.36, N 3.36.

Compound 9: A solution of **2** (0.153 g, 0.30 mmol) in pentane (5 mL) was added at 0°C to a stirred solution of [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] (0.148 g, 0.30 mmol) in pentane (5 mL). The mixture was stirred for 2 h at 0°C and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **9** as a colorless powder (0.16 g, 70%). ^{1}H NMR (300 MHz, [D$_6$]benzene, 25°C): δ = 7.59 (d, ^4J(H,H) = 2.5 Hz, 2H; ArH), 7.08 (d, ^4J(H,H) = 2.5 Hz, 2H; ArH), 3.87 (brm, 4H; α-CH_2 THF), 3.76 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 2.92 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 2.88 (s, 3H; OCH_3), 2.44 (t, ^3J(H,H) = 5.3 Hz, 2H; NCH_2CH_2O), 2.21 (t, ^3J(H,H) = 5.3 Hz, 2H; NCH_2CH_2O), 1.80 (s, 18H; $C(CH_3)_3$), 1.46 (s, 18H; $C(CH_3)_3$), 1.27 (brm, 4H; β-CH_2 THF), 0.49 (s, 9H; $Si(CH_3)_3$), 0.40 (d, ^2J(Y,H) = 3.1 Hz, 2H; $CH_2Si(CH_3)_3$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]benzene, 25°C): δ = 161.38, 136.59, 136.40, 125.40, 124.21, 123.90 (Ar), 73.84 (NCH_2CH_2O), 70.66 (α-CH_2 THF), 64.65 (CH_2Ar), 61.09

(OCH_3), 49.09 (NCH_2CH_2O), 35.39 ($C(CH_3)_3$), 34.04 ($C(CH_3)_3$), 32.05 ($C(CH_3)_3$), 30.11 ($C(CH_3)_3$), 24.92 (β-CH_2 THF), 24.70 (d, ^1J(C,Y) = 46.4 Hz; YCH_2), 4.64 ($Si(CH_3)_3$) ppm; elemental analysis calcd (%) for $C_{41}H_{70}NO_4SiY$: C 64.97, H 9.31, N 1.85; found: C 65.11, H 9.65, N 1.74.

Compound 10: A solution of **2** (0.204 g, 0.40 mmol) in pentane (5 mL) was added at room temperature to a stirred solution of [La{$N(SiHMe_2)_2$}$_3$(THF)$_2$] (0.272 g, 0.40 mmol) in pentane (5 mL). The mixture was stirred for 24 h and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **10** as a colorless powder (0.18 g, 92%). ^{1}H NMR (300 MHz, [D_6]benzene, 25°C): δ = 7.57 (d, ^4J(H,H) = 2.3 Hz, 2H; ArH), 7.11 (d, ^4J(H,H) = 2.5 Hz, 2H; ArH), 5.25 (m, 2H; SiH), 3.76 (br m, 4H; α-CH_2 THF), 3.58 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 3.32 (d, ^2J(H,H) = 12.5 Hz, 2H; $ArCH_2$), 3.07 (s, 3H; OCH_3), 2.77 (t, ^3J(H,H) = 5.2 Hz, 2H; NCH_2CH_2O), 2.27 (m, 2H; NCH_2CH_2O), 1.73 (s, 18H; $C(CH_3)_3$), 1.44 (s, 18H; $C(CH_3)_3$), 1.22 (m, 4H; β-CH_2 THF), 0.48 (d, ^4J(H,H) = 3.0 Hz, 12H; $Si(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 25°C): δ = 161.8, 136.6, 135.6, 125.8, 124.3, 123.9 (Ar), 71.9 (NCH_2CH_2O), 69.9 (α-CH_2 THF), 61.6 (CH_2Ar), 60.9 (OCH_3), 50.7 (NCH_2CH_2O), 35.3 ($C(CH_3)_3$), 34.0 ($C(CH_3)_3$), 32.0 ($C(CH_3)_3$), 30.1 ($C(CH_3)_3$), 25.0 (β-CH_2 THF), 3.5 ($Si(CH_3)_2$) ppm; elemental analysis calcd (%) for $C_{41}H_{73}N_2O_4LaSi_2$: C 57.72, H 8.62, N 3.28; found: C 57.91, H 9.03, N 3.18.

Generation of 11: A solution of **2** (18.0 mg, 0.028 mmol) in benzene (1 mL) was added at room temperature to a solution of [Nd{$N(SiMe_3)_2$}$_3$] (14.6 mg, 0.028 mmol) in benzene (1.5 mL). The mixture was stirred for 12 h at room temperature and 2 h at 60°C, and volatiles were then removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **11** as a light blue powder. The product was directly engaged in a polymerization experiment.

NMR-scale reaction between [Y{$N(SiHMe_2)_2$}$_3$(THF)$_2$] and 3—generation of 12: Solid **3** (15.9 mg, 0.030 mmol) was added at room temperature to a solution of [Y{$N(SiHMe_2)_2$}$_3$(THF)$_2$] (17.1 mg, 0.030 mmol) in [D_8]toluene (ca. 0.5 mL) in a Teflon-valved NMR tube. The tube was vigorously shaken and left at room temperature. After 1 h, the reaction was checked by ^{1}H NMR spectroscopy, which indicated complete conversion of the starting yttrium precursor and ligand, with release of two equivalents of free amine $HN(SiHMe_2)_2$. Because of the fluxional behavior of the products formed at room temperature, informative NMR data were obtained at 60°C. Key ^{1}H NMR resonances (500 MHz, [D_8]toluene, 60°C): δ = major species 7.48 (d, ^4J(H,H) = 2.7 Hz, 4H; aryl), 6.88 (br s, 4H; aryl), 5.00 (m, 1H; $SiH(CH_3)_2$) ppm; minor species 7.49 (d, ^4J(H,H) = 3.2 Hz, 4H; aryl), 6.81 (d, ^4J(H,H) = 3.2 Hz, 4H; aryl), 4.90 (m, 1H; $SiH(CH_3)_2$) ppm.

Compound 13: A solution of **4** (0.093 g, 0.159 mmol) in toluene (5 mL) was added at room temperature to a stirred solution of [Y{$N(SiHMe_2)_2$}$_3$(THF)$_2$] (0.100 g, 0.159 mmol) in pentane (10 mL). The mixture was stirred for 12 h at room temperature and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **13** as a colorless powder (0.104 g, 75%). Single crystals of **13** suitable for X-ray diffraction were obtained by slow evaporation of a saturated toluene solution at room temperature. ^{1}H NMR (300 MHz, [D_6]benzene, 25°C): δ = 7.23 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 6.18 (d, ^4J(H,H) = 2.4 Hz, 2H; ArH), 5.21 (m, 2H; $SiH(CH_3)_2$), 3.93 (m, 4H; α-CH_2 THF), 3.74 (d, ^2J(H,H) = 11.9 Hz, 2H; $ArCH_2$), 2.98 (d, ^2J(H,H) = 12.4 Hz, 2H; $ArCH_2$), 2.84 (t, ^3J(H,H) = 4.8 Hz, 4H; NCH_2CH_2O), 2.46 (s, 12H; adamantyl), 2.40 (s, 6H; CH_3), 2.26 (s, 9H; adamantyl + OCH_3), 2.03 (d, ^2J(H,H) = 11.7 Hz, 6H; adamantyl), 1.92 (d, ^2J(H,H) = 11.3 Hz, 6H; adamantyl), 1.23 (m, 4H; β-CH_2 THF), 0.49 (d, ^4J(H,H) = 2.9 Hz, 12H; $SiH(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 25°C): δ = 162.39, 129.78, 128.51 (Ar), 72.41 (NCH_2CH_2O), 69.60 (α-CH_2 THF), 63.38 (CH_2Ar), 58.43 (NCH_2CH_2O), 48.35 (OCH_3), 40.64 (adamantyl), 37.40 (adamantyl), 37.06 (adamantyl), 29.09 (adamantyl), 24.36 (β-CH_2 THF), 20.33 (CH_3), 3.46 ($Si(CH_3)_2$) ppm; elemental analysis calcd (%) for $C_{47}H_{73}N_2O_4Si_2Y$: C 64.50, H 8.41, N 3.20; found: C 64.72, H 8.27, N 3.18.

NMR-scale generation of 14: Solid **4** (10.5 mg, 0.016 mmol) was added at room temperature to a solution of [La{$N(SiHMe_2)_2$}$_3$(THF)$_2$] (10.0 mg, 0.016 mmol) in [D_6]benzene (ca. 0.5 mL) in an NMR tube. The tube was vigorously shaken and left at room temperature. After 12 h, the reaction was checked by ^{1}H NMR spectroscopy, which indicated complete and selective conversion of the ligand and starting lanthanum precursor into **14**. ^{1}H NMR (500 MHz, [D_6]benzene, 25°C): δ = 7.20 (br s, 2H; ArH), 6.80 (br s, 2H; ArH), 5.34 (m, 2H; $SiH(CH_3)_2$), 3.69 (m, 4H; α-CH_2 THF), 3.38 (m, 2H; $ArCH_2$), 3.17 (s, 4H; NCH_2CH_2O), 2.82 (m, 2H; $ArCH_2$), 2.43 (s, 12H; adamantyl), 2.40 (s, 6H; CH_3), 2.19 (s, 9H; adamantyl + OCH_3), 1.99 (d, ^2J(H,H) = 12.8 Hz, 6H; adamantyl), 1.91 (d, ^2J(H,H) = 12.8 Hz, 6H; adamantyl), 1.36 (m, 4H; β-CH_2 THF), 0.49 (d, ^4J(H,H) = 2.9 Hz, 12H; $SiH(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (125 MHz, [D_6]benzene, 25°C): δ = 162.30, 129.70, 128.00 (Ar), 71.29 (CH_2Ar), 69.08 (α-CH_2 THF), 61.48 (NCH_2CH_2O), 48.35 (OCH_3), 40.83 (adamantyl), 37.64 (adamantyl), 37.12 (adamantyl), 29.75 (adamantyl), 25.36 (β-CH_2 THF), 20.98 (CH_3), 3.44 ($Si(CH_3)_2$) ppm.

Generation of 15: A solution of **4** (9.3 mg, 0.016 mmol) in benzene (1 mL) was added at room temperature to a solution of Nd[$N(SiMe_3)_2$]$_3$ (10.0 mg, 0.016 mmol) in benzene (1.5 mL). The solution was stirred for 12 h at room temperature and for 2 h at 60°C, and volatiles were then removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **15** as a light blue powder. The product was directly engaged in a polymerization experiment.

Compound 16: A solution of **4** (0.105 g, 0.16 mmol) in toluene (5 mL) was added at room temperature to a stirred solution of [Y{$N(SiHMe_2)_2$}$_3$(THF)$_2$] (0.100 g, 0.16 mmol) in pentane (10 mL). The mixture was stirred for 12 h at room temperature and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **16** as a colorless powder (0.108 g, 71%). ^{1}H NMR (500 MHz, [D_6]benzene, 25°C): δ = 7.54 (d, ^4J(H,H) = 2.3 Hz, 2H; ArH), 7.08 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 5.20 (m, 2H; $SiHMe_2$), 3.82 (m, 4H; α-CH_2 THF), 3.72 (br s, 2H; $ArCH_2$), 3.11 (d, ^2J(H,H) = 12.4 Hz, 2H; $ArCH_2$), 2.82 (t, ^3J(H,H) = 4.5 Hz, 4H; NCH_2CH_2O), 2.53 (s, 12H; adamantyl), 2.34 (s, 3H; OCH_3), 2.28 (s, 6H; adamantyl), 2.08 (d, ^2J(H,H) = 9.2 Hz, 6H; adamantyl), 1.92 (d, ^2J(H,H) = 10.9 Hz, 6H; adamantyl), 1.47 (s, 18H; $C(CH_3)_3$), 1.23 (m, 4H; THF), 0.49 (d, ^4J(H,H) = 2.9 Hz, 12H; $SiH(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 25°C): δ = 162.39, 125.51, 124.21 (Ar), 72.41 (NCH_2CH_2O), 69.70 (α-CH_2 THF), 63.45 (CH_2Ar), 48.35 (OCH_3), 41.14 (adamantyl), 37.57 (adamantyl), 37.48 (adamantyl), 32.42 ($C(CH_3)_3$), 29.67 (adamantyl), 24.36 (β-CH_2 THF), 4.12 ($Si(CH_3)_2$) ppm; elemental analysis calcd (%) for $C_{53}H_{85}N_2O_4Si_2Y$: C 66.36, H 8.93, N 2.92; found: C 66.24, H 8.73, N 2.57.

Compound 17: A solution of **6** (0.100 g, 0.13 mmol) in toluene (5 mL) was added at room temperature to a stirred solution of Y[$N(SiHMe_2)_2$]$_3$(THF)$_2$ (0.083 g, 0.13 mmol) in pentane (5 mL). The mixture was stirred for 12 h at room temperature and volatiles were removed under vacuum. The residue was washed with a minimal amount of cold pentane and dried under vacuum, giving **17** as a white powder (0.095 g, 68%). ^{1}H NMR (500 MHz, [D_6]benzene, 25°C): δ = 7.53 (br s, 2H; ArH), 7.41 (d, ^3J(H,H) = 7.1 Hz, 8H; cumyl), 7.22 (t, ^3J(H,H) = 7.7 Hz, 4H; cumyl), 7.13 (m, 6H; cumyl), 6.95 (t, ^3J(H,H) = 4.5 Hz, 2H; cumyl), 6.78 (br s, 2H; ArH), 4.80 (br s, 2H; $SiH(CH_3)_2$), 3.35 (br s, 2H; $ArCH_2$), 2.93 (m, 4H; THF), 2.80 (br s, 3H; OCH_3), 2.69 (br s, 2H; $ArCH_2$), 2.48 (br s, 2H; NCH_2CH_2O), 2.16 (br s, 6H; CH_3 cumyl), 2.04 (br s, 2H; NCH_2CH_2O), 1.77 (br s, 12H; CH_3 cumyl), 1.74 (br s, 6H; CH_3 cumyl), 1.10 (m, 4H; THF), 0.48 (br s, 12H; $SiH(CH_3)_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D_6]benzene, 25°C): δ = 161.34 (Cq, Ar), 152.28 (Cq, cumyl), 137.64, 135.79 (cumyl-C), 128.11, 127.17 (Ar), 127.17, 126.21 (cumyl-C), 72.65 (NCH_2CH_2O), 69.70 (α-CH_2 THF), 63.81 (CH_2Ar), 59.87 (OCH_3), 47.14 (NCH_2CH_2O), 42.49 ($C(CH_3)_2$), 31.46 ($C(CH_3)_2$), 27.58 ($C(CH_3)_2$), 24.81 (β-CH_2 THF), 4.40 ($Si(CH_3)_2$) ppm; elemental analysis calcd (%) for $C_{61}H_{81}N_2O_4Si_2Y$: C 69.68, H 7.77, N 2.66; found: C 69.57, H 7.83, N 2.74.

NMR-scale generation of 18 in [D_8]THF: Dry propan-2-ol (0.67 μL, 0.0152 mmol, 1.0 equiv) was added by microsyringe at room temperature to a solution of complex **17** (16.0 mg, 0.0152 mmol) in [D_8]THF. The tube

was vigorously shaken and left at room temperature for 10 min. The reaction was monitored by ^{1}H NMR spectroscopy, which indicated quantitative formation of **18**, along with release of free amine $HN(SiHMe_2)_2$. ^{1}H NMR (500 MHz, [D$_8$]THF, 25 °C): δ = 7.25 (m, 4H; cumyl), 7.20 (m, 8H; cumyl), 7.06 (m, 8H; cumyl), 6.92 (brs, 2H; ArH), 6.69 (brs, 2H; ArH), 4.20 (brm, 1H; C*H*(CH$_3$)$_2$), 3.71 (d, ^2J(H,H) = 12.0 Hz, 2H; ArC*H*$_2$), 3.58 (m, 4H; THF), 3.40 (brs, 3H; OCH$_3$), 3.01 (brs, 2H; NCH$_2$C*H*$_2$O), 2.86 (d, ^2J(H,H) = 12.0 Hz, 2H; ArC*H*$_2$), 2.16 (brs, 2H; NC*H*$_2$CH$_2$O), 2.04 (brs, 6H; CH$_3$ cumyl), 1.77 (m, 4H; THF), 1.60 (brs, 12H; CH$_3$ cumyl), 1.42 (s, 6H; CH$_3$ cumyl), 1.15 (d, ^3J(H,H) = 5.9 Hz, 6H; CH(C*H*$_3$)$_2$) ppm; ^{13}C{^{1}H} NMR (75 MHz, [D$_8$]THF, 25 °C): δ = 162.14 (Cq Ar), 152.07 (Cq cumyl), 134.36 (cumyl-C), 127.38, 126.55 125.70, 125.08, 123.46 (Ar), 72.77 (NCH$_2$*C*H$_2$O), 69.70 (α-CH$_2$ THF), 65.63 (*C*H(CH$_3$)$_2$) 63.72 (*C*H$_2$Ar), 61.15 (O*C*H$_3$), 49.75 (N*C*H$_2$CH$_2$O), 32.37 (*C*(CH$_3$)$_2$), 30.78 (C(*C*H$_3$)$_2$), 28.03 (CH(*C*H$_3$)$_2$), 26.27 (C(*C*H$_3$)$_2$), 24.81 (β-*C*H$_2$ THF).

NMR-scale generation of 18 in [D$_6$]benzene: Dry propan-2-ol (0.67 μL, 0.0152 mmol, 1.0 equiv.) was added by microsyringe at room temperature to a solution of **17** (16.0 mg, 0.0152 mmol) in [D$_6$]benzene. The tube was vigorously shaken and left at room temperature for 10 min. The reaction was monitored by ^{1}H NMR spectroscopy, which indicated quantitative formation of **18**, along with release of free amine $HN(SiHMe_2)_2$. ^{1}H NMR (500 MHz, [D$_6$]benzene, 25 °C): δ = 7.63 (m, 4H; cumyl), 7.51 (m, 8H; cumyl), 7.44 (m, 8H; cumyl), 6.93 (brs, 2H; ArH), 6.79 (brs, 2H; ArH), 4.25 (brs, 1H; C*H*(CH$_3$)$_2$), 3.51 (d, ^2J(H,H) = 11.97 Hz, 2H; ArC*H*$_2$), 3.27 (brs, 8H; THF), 2.94 (brs, 3H; OCH$_3$), 2.41 (brs, 4H; NCH$_2$C*H*$_2$O + ArC*H*$_2$), 2.11 (s, 6H; CH$_3$ cumyl), 1.99 (brs, 2H; NC*H*$_2$CH$_2$O), 1.80 (brs, 12H; CH$_3$ cumyl), 1.72 (s, 6H; CH$_3$ cumyl), 1.32 (brs, 8H; THF), 1.07 (d, ^3J(H,H) = 5.77 Hz, 6H; CH(C*H*$_3$)$_2$) ppm. A minor series of resonances accounting for less than 5% of the total was also observed.

NMR-scale reaction between 8 and 2-propanol in [D$_8$]THF: Dry propan-2-ol (1.00 μL, 0.025 mmol, 1.0 equiv) was added by microsyringe at room temperature to a solution of complex **8** (20.0 mg, 0.025 mmol) in [D$_8$]THF. The tube was vigorously shaken and left at room temperature for 10 min. The reaction was monitored by ^{1}H NMR spectroscopy, which indicated release of free amine $HN(SiHMe_2)_2$ and quantitative transformation of **8** into the corresponding isopropoxide complex. ^{1}H NMR (300 MHz, [D$_8$]THF, 25 °C): δ = 7.18 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 6.91 (d, ^4J(H,H) = 2.2 Hz, 2H; ArH), 4.21 (m, 1H; C*H*(CH$_3$)$_2$), 4.16 (d, ^2J(H,H) = 11.9 Hz, 2H; ArC*H*$_2$), 3.59 (brs, 4H; α-CH$_2$ THF, overlap with solvent resonances), 3.40 (brs, 3H; OCH$_3$), 3.16 (d, ^2J(H,H) = 12.2 Hz, 2H; ArC*H*$_2$), 3.01 (t, ^3J(H,H) = 5.3 Hz, 2H; NCH$_2$C*H*$_2$O), 2.56 (t, ^3J(H,H) = 5.3 Hz, 2H; NC*H*$_2$CH$_2$O), 1.73 (brs, 4H; β-CH$_2$ THF, overlap with solvent resonances), 1.49 (s, 18H; C(CH$_3$)$_3$), 1.26 (s, 18H; C(CH$_3$)$_3$), 1.16 (d, ^3J(H,H) = 5.85 Hz, 6H; CH(CH$_3$)$_2$) ppm.

General polymerization procedure: A Schlenk flask was charged in a glovebox with a solution of the initiator in THF, and a solution of the monomer in the appropriate ratio in THF was added rapidly. The mixture was immediately stirred with a magnetic stir bar at the desired temperature for the desired reaction time. After a small sample of the crude material had been removed with a pipette for characterization by ^{1}H NMR, the reaction was quenched with acidic methanol (0.5 mL of a 1.2 M HCl solution), and the polymer was precipitated with excess methanol. The polymer was then dried under vacuum to constant weight.

General kinetic procedure: The appropriate amount of monomer in THF (1000 equiv., [LA] = 1.0 M) was added to a solution of initiator in THF (5 mL). The mixture was then stirred at 25 °C under N$_2$. At appropriate time intervals, 0.5 mL aliquots were removed and opened to air. The aliquots were then dried to constant weight in vacuo and analyzed by ^{1}H NMR spectroscopy.

Crystal structure determination of 13: A suitable single crystal of **13** was mounted on a glass fiber by the "oil-drop" method. Diffraction data were collected at 150 K by use of an APEX 2 AXS-Bruker diffractometer with graphite monochromatized Mo-K$_\alpha$ radiation (λ = 0.71073 Å). The crystal structure was solved by direct methods, remaining atoms being located from difference Fourier synthesis, followed by full-matrix, least-squares refinement based on F^2 (program SIR-97).[30] Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. One of the methyl groups of one of the $SiMe_2$ fragments is statistically disordered over two distinct positions. This disorder was introduced in the refinement procedure with the aid of the PART instruction in SHELXL, which treated this methyl group as two independent objects (carbon atoms labeled C502 and C512 and the corresponding hydrogen atoms), with a refined occupancy of 62:38. The locations of the largest peaks in the final difference Fourier map calculation and the magnitude of the residual electron densities were of no chemical significance. The unit cell of **13** was found to contain one disordered molecule of toluene. Crystal data: $C_{47}H_{72}N_2O_4Si_2Y_1 \cdot C_7H_8$, M_r = 966.29, triclinic, a = 12.453(5), b = 15.477(5), c = 16.117(5) Å, α = 63.756(5)°, β = 81.559(5)°, γ = 67.151(5)°, V = 2566.3(15) Å^3, T = 150(2) K, space group $P\bar{1}$ (no. 2), Z = 2, ρ_{calcd} = 1.250 g cm^{-3}, crystal size = 0.40 × 0.25 × 0.20 mm^3, μ(Mo$_{K\alpha}$) = 1.228 mm^{-1}, 54735 reflections measured, 11817 unique and 8764 reflections with $I > 2\sigma(I)$, which were used in all calculations. The final $R1$ was 0.0499 (observed data) and $wR2$ was 0.1500 (all data).

CCDC-278313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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