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Kinetics and Mechanism of L-Lactide Polymerization by Rare Earth Metal Silylamido Complexes: Effect of Alcohol Addition

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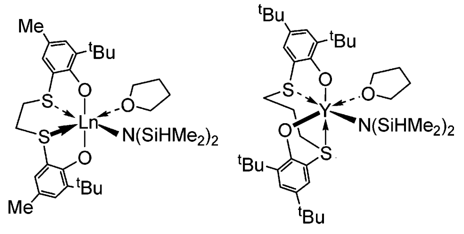
ABSTRACT: The ring-opening polymerization of L-lactide initiated by rare earth metal silylamido complexes [Ln(OSSO){N(SiHMe$_2$)$_2$}(THF)] (**1**−**3**: Ln = Y, Lu; OSSO = 1, ω-dithiaalkanediyl-bridged bisphenolato) was studied. MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy suggested that the polymerization proceeded via a conventional coordination−insertion mechanism involving silylamide ligand as the initiating group and the cleavage of acyl−oxygen bond of the monomer. A two-stage linear relationship between ln([LA]$_0$/[LA]$_t$) and the polymerization time was observed for the yttrium complex [Y(pdtbp){N(SiHMe$_2$)$_2$}(THF)] (pdtbp = 1,5-dithiapentanediyl-bis{4,6-di-*tert*-butylphenolato}, **3**). In both stages, the polymerization showed first-order kinetics for the monomer concentration. The first-order dependency of the initiator concentration was only observed when the monomer conversion to PLA was less than 50−60%. The aggregation of the active growing polymer chain into dimeric structure occurred in the second stage. In contrast, the in situ generated alkoxide initiator [Ln(OSSO){N(SiHMe$_2$)$_2$}(THF)]/^{i}PrOH showed a different behavior. When **3** was reacted with 2-propanol in 1:2 ratio, the in situ generated alkoxides initiated the living polymerization of L-lactide. Neither aggregation nor intramolecular transesterification was observed over the entire conversion range. Polylactides with controlled molecular parameters (M_n, end groups) and low polydispersities were formed as a result of fast alkoxide/alcohol exchange.

Introduction

Metal alkoxides [M(OR)$_m$] are known to be highly efficient initiators for the ring-opening polymerizations of cyclic esters such as lactides and lactones.[1] It is also agreed that they are not structurally simple and mostly aggregated both in solution and in crystalline state via μ-alkoxo bridges.[2] An ideal structure for a well-defined single site initiator [L$_n$M(OR)], suitable for kinetic and mechanistic studies, would possess one active alkoxy group bonded to the metal center M capable of initiation; a sterically bulky, polydentate ligand L$_n$ would occupy most of the coordinating sphere and prevent intermolecular reactions, in particular aggregations. Structurally well-characterized metal alkoxides do usually initiate the controlled polymerization or even the living polymerization via the coordination−insertion mechanism to afford polyesters with narrow molecular weight distributions and defined end groups.[3]

Recently, metal complexes with amide and alkyl groups as initiating groups instead of an alkoxy ligand have been introduced.[4] Especially in rare-earth metal chemistry, a growing number of structurally well-characterized complexes with silylamide or alkyl groups have been synthesized and investigated for lactide and lactone polymerizations.[5,6] What is confusing is that a structurally well-characterized monomeric metal amide of the general formula [L$_n$M(NR^{1}R^2)] can indeed initiate the ring-opening polymerization of cyclic esters but afford polyesters with obvious lack of control, broad molecular weight distributions (PDI: 1.2−2.0), and no identifiable end groups.[4,5] These observations led to ambiguous conclusions about the nature of active species and raised the question whether the nature of the initiating group have a strong influence on the polymerization process.[5] We encountered similar problems in the L-lactide polymerization initiated by rare earth metal silylamido complexes with 1,ω-dithiaalkanediyl-bridged bisphenolato ligands [Ln(OSSO){N(SiHMe$_2$)$_2$}-(THF)] (Ln = Sc, Y, Lu).[6] A recent study in the Ph$_2$SnX$_2$ system (X = NMe$_2$, O^{i}Pr) showed that the initiating group had a remarkable influence on the nature of the polymer formed due to the relative stabilities of SnOCH-MeC(O)X moieties.[4d] We describe here that different kinetics and mechanism are involved in the polymerization of L-lactide by rare earth metal silylamido complexes (Scheme 1) compared with the in-situ generated alkoxide systems.

Scheme 1



1 (Ln = Y); **2** (Ln = Lu) **3**

Experimental Section

Materials. All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Glassware and vials used in the polymerization were dried in an oven at 120 °C overnight and exposed to vacuum−argon cycle three times. Toluene and THF were distilled under argon from sodium/benzophenone ketyl prior to use. Dichloromethane was distilled from calcium hydride. Benzene-d_6, chloroform-d, and other reagents were carefully dried. All of the rare earth complexes were prepared as described previously.[6] L-Lactide (Aldrich) was recrystallized with dry toluene and then sublimed twice under vacuum at

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Table 1. Ring-Opening Polymerization of L-Lactide by Complexes 1–3[a]

initiator	$[LA]_0/[Ln]_0$	solvent	temp (°C)	time (h)	conv (%)	$M_c{}^b$ ($\times 10^4$)	$M_n{}^c$ ($\times 10^4$)	$M_n'{}^d$ ($\times 10^4$)	M_w/M_n
1	300	THF	25	0.1	94	4.06	8.91	5.17	1.59
	300	THF	22	0.17	85	3.65	8.71	5.05	1.59
	300	THF	22	1	92	3.98	9.46	5.49	1.68
	750[e]	THF	22	1	89	9.62	24.5	14.2	1.84
	1500[e]	THF	22	1	77	16.65	36.0	20.9	1.98
	300	CH_2Cl_2	25	1	67	2.90	7.04	4.08	1.97
	300	Tol	25	1	76	3.29	6.67	3.87	1.49
2	300	THF	25	0.1	97	4.19	13.2	7.08	2.15
	300[f]	THF	22	1	88	3.80	15.0	8.70	1.84
	1500[e]	THF	22	1	91	20.75	63.5	36.8	1.81
	300	CH_2Cl_2	25	1	87	3.76	9.19	5.33	2.29
	300	Tol	25	1	99	4.28	9.48	5.50	1.87
3	300	THF	25	24	97	4.19	5.06	2.93	1.28
	300	THF	22	1	35	1.51	3.48	2.02	1.39
	300	THF	22	24	76	3.27	5.06	2.93	1.31
	150[e]	THF	20	13	100	2.16	3.54	2.05	1.47
	150[e]	CH_2Cl_2	20	24	44	0.95	1.64	0.95	1.95[g]
	150[e]	Tol	20	24	18	0.39	0.92	0.53	1.36
	300	Tol	22	24	33	1.43	2.25	1.31	1.45

[a] Polymerization carried out with 0.87 M solution of L-lactide unless otherwise indicated. [b] $M_c = ([LA]_0/[Ln]_0) \times 144.13 \times$ conversion (%). [c] From SEC measurement. [d] Using a correcting factor 0.58 for M_n. [e] $[LA]_0 = 2.17$ M. [f] $[LA]_0 = 0.29$ M. [g] Bimodal.

50 °C. 2-Propanol was dried over calcium hydride prior to distillation.

Instruments and Measurements. NMR spectra were recorded on a Bruker DRX 400 and Varian 200 and 500 spectrometers at 25 °C (^{1}H: 200, 400, 500 MHz; ^{13}C: 100, 125 MHz). Chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane. Molecular weights and polydispersities were determined by size exclusion chromatography (SEC) in THF at 35 °C, at a flow rate of 1 mL/min utilizing an Agilent 1100 Series HPLC, a G1310A isocratic pump, an Agilent 1100 Series refractive index detector, and 8 × 600 mm, 8 × 300 mm, and 8 × 50 mm PSS SDV linear M columns. Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ($10^3 < M_n < 2 \times 10^6$ g/mol). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded using a Bruker Reflex II mass spectrometer (Bremen, Germany) equipped with a N_2 laser (337 nm) operating at a pulse rate of 3 Hz. The ions were accelerated with pulsed ion extraction by a voltage of 20 kV and detected using a microchannel plate detector. The analyzer was operated in reflection mode. Samples were dissolved in THF; 2,5-dihydroxybenzoic acid (DHBA) was used as the matrix material, and potassium trifluoroacetate was added to facilitate ionization.

Kinetic Experiments. In a Braun Labmaster glovebox, initiator solution from a stock solution in THF or toluene was injected sequentially to a series of 6 mL vials loaded with L-lactide and suitable amounts of dry solvent. After specified time intervals, each vial was taken out of the glovebox; an aliquot was withdrawn and quenched quickly with *n*-pentane, and the reaction mixture was quenched at the same time by adding excess amount of *n*-pentane and one drop of water. All the volatiles in the aliquots were removed, and the residue was subjected to monomer conversion determination which was monitored by integration of monomer vs polymer methine or methyl resonances in ^{1}H NMR ($CDCl_3$). The precipitates collected from the bulk mixture were dried in air, dissolved with dichloromethane, and sequentially precipitated into methanol. The obtained polymer was further dried in a vacuum oven at 60 °C for 16 h for SEC analysis. Each reaction was used as one data point. In the cases where 2-propanol was used, the catalyst solution in toluene was treated first with the solution of 2-propanol in toluene for 10 min and then injected to the solution of L-lactide. Otherwise, the procedures were the same.

NMR Reactions. In a typical experiment, complex **3** (10 mg, 0.012 mmol) was weighed in a screw-cap NMR tube, 0.5 mL of benzene-d_6 was added to dissolve the solid, 2-propanol (0.75 mg, 0.012 mmol) in 0.1 mL of benzene-d_6 was then added, and the solution was quickly shaken. The ^{1}H NMR spectra were recorded after 10 min. L-Lactide (35.7 mg, 0.25 mmol) was added to the NMR tube and quickly shaken. The ^{1}H NMR spectra were recorded in intervals until full conversion was reached.

Oligomers for MALDI-TOF Measurements. *Method A*: To the stirred solution of L-lactide (0.125 g, 0.87 mmol) in THF (1.5 mL), the fresh prepared solution of complex **3** (35 mg, 0.043 mmol) in THF (0.5 mL) was injected at 22 °C ($[LA]_0/[Y]_0 = 20$). The polymerization mixture was stirred for 24 h and then quenched with *n*-pentane and one drop of water; the precipitated oligomers were collected and dried in air and used for MALDI-TOF measurement. *Method B*: The solution of complex **3** (17.5 mg, 0.022 mmol) in toluene (0.4 mL) was treated with the solution of 2-propanol in toluene (2.6 mg of 2-propanol in 0.1 mL of toluene) for 10 min and then injected to the stirred solution of L-lactide (0.125 g, 0.87 mmol) in toluene (2.5 mL) at 22 °C and stirred for 5 min ($[LA]_0:[^iPrOH]_0:[Y]_0 = 40:1:2$). The workup procedures were the same as method A.

Results and Discussion

Polymerization with [Ln(OSSO){N(SiHMe$_2$)$_2$}(THF)]. Previously, we showed that rare earth metal silylamido complexes [Ln(OSSO){N(SiHMe$_2$)$_2$}(THF)] (Ln = Sc, Y, Lu) were active initiators for the ring-opening polymerization of L-lactide under mild conditions.[6] The initiator performance was strongly influenced by the ligand environment and the central metal. The lutetium complex **2** with the 1,4-dithiabutanediyl-bridged bisphenolate ligand afforded the highest activity in THF. In this work, the polymerizations initiated by the yttrium complexes **1** and **3** and the lutetium complex **2** have been further investigated in detail.

Complexes **1** and **2** with the sterically less demanding ligand are generally more active than complex **3**. All three complexes show higher activity in THF than in CH_2Cl_2 or toluene; the polymerization rates in CH_2Cl_2 and toluene are comparable (Table 1). However, different from our previous results,[6] the number-average molecular weights (M_n, SEC) of the PLAs significantly deviate from the theoretical values (calculated on the assumption that each silylamide ligand initiates the polymerization) and the molecular weight distributions (M_w/M_n) are rather broad.[7] Duda et al. suggested that in order to obtain the correct M_n value of PLAs, the

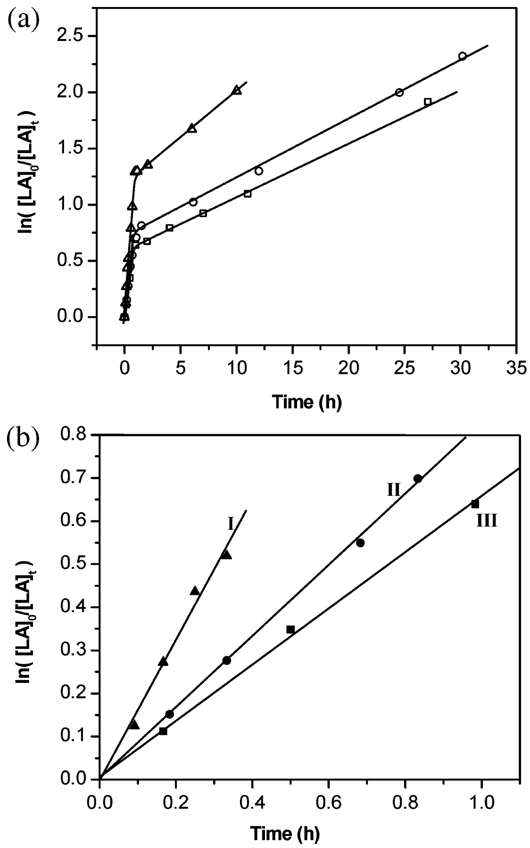


Figure 1. Semilogarithmic plots of LA conversion with time in THF at 22 °C using **3** as initiator, $[LA]_0 = 0.87$ M: (a) entire range; (b) enlargement of the first linear parts. $[LA]_0/[Y]_0 = 100$ (△, ▲), 200 (○, ●), and 250 (□, ■). For plot I, $k_{app} = 4.54 \times 10^{-4}$ s^{-1} (linear fit, $R = 0.995$); plot II, $k_{app} = 2.31 \times 10^{-4}$ s^{-1} (linear fit, $R = 0.999$); and plot III, $k_{app} = 1.81 \times 10^{-4}$ s^{-1} (linear fit, $R = 0.999$).

experimental value obtained from the SEC traces using polystyrene standards has to be multiplied by a factor of 0.58 ($M_n \leq 2 \times 10^4$).[2c,8] In Table 1, the number-average molecular weighs (M_n, SEC) after correction do give reasonable values (M_n') which are considered to indicate the real molecular weights of the polymers.

From the results in Table 1, we found that the polymerization initiated by rare earth metal silylamido complex **3** is better controlled than those by **1** and **2**. For a given complex, the polymerization performed in CH_2Cl_2 is less controlled, giving PLAs with rather broad or bimodal molecular weight distributions due to transesterifications.

Kinetics. Conversions of L-lactide at various concentrations of **3** in THF at 22 °C were monitored by ^{1}H NMR spectroscopy for individual runs at different intervals ($[LA]_0 = 0.87$ M; $[Y]_0 = 3.46-8.67$ mM, $[LA]_0/[Y]_0 = 100-250$). The semilogarithmic plots are shown in Figure 1.

To our surprise, curved lines consisting of two linear stages were obtained in each case. As shown in Figure 1b, in the first stage, the polymerizations are first-order in monomer concentration. Thus, the polymerization of L-lactide by **3** should proceed according to eq 1, where $k_{app} = k_p[Y]^x$. k_{app} and k_p are the apparent propagation and propagation rate constants, respectively. When ln k_{app} vs ln $[Y]_0$ was plotted, a straight line with a slope of 1.00 ± 0.02 resulted. The polymerization of L-lactide by **3** follows an overall kinetic law given by eq 2 with $k_p = 0.052$ L mol^{-1} s^{-1}. It indicates that in the first stage of the polymerization by **3** the active species is single-site, whose concentration is equal to the concentration of complex **3**.

$$-d[LA]/dt = k_{app}[LA] \qquad (1)$$

$$-d[LA]/dt = k_p[Y][LA] \qquad (2)$$

After the first stage and a very short transition period, we find that the linear relationship between $\ln([LA]_0/[LA]_t)$ vs time with different slope is valid until monomer conversion up to 90%. Therefore, the polymerization is still first-order for the monomer concentration in each case, but with a reduced apparent polymerization constant k_{app}*. To determine the order for $[Y]_0$ in the second stage, we plotted ln k_{app}* against ln $[Y]_0$. From the plot, a linear line with a slope of 0.56 ± 0.05 was obtained. Concerning the second stage, the kinetics of L-lactide polymerization by complex **3** could be described by eq 3.

$$-d[LA]/dt = k_p{}^*[Y]^{0.5}[LA] \qquad (3)$$

To fit this equation, a k_p* value of 2.31×10^{-4} L mol^{-1} s^{-1} was obtained. Fractional dependency upon initiator concentration has been observed for aluminum, yttrium alkoxides, and other systems.[4g,5c,9] Normally an aggregation process is believed to be involved. According to the literature,[10] when one assumes that an aggregate equilibrates with monomeric active polymer chain and the propagation occurs only from the latter, an expression given as eq 4 could be deduced. Here P_n is a metal-capped active polymer chain with a polymerization degree of n, $(P_n)_m$ is the aggregate of metal-capped polymer chains, and m is the aggregation number.

$$(P_n)_m \xrightleftharpoons{K_{da}} mP_n$$

$$P_n + LA \xrightleftharpoons{k_p{}^*} P_{n+1}$$

$$k_{app} = \{(k_p{}^*K_{da}{}^{1/m})(m^{1/m})\}[Y]_0{}^{1/m} \qquad (4)$$

Thus, the slope of the experimental plot of ln k_{app}* vs ln $[Y]_0$ gives the inverse of the aggregation number m. With the limitation of m being restricted to an integer value, the aggregation number of 2 is obtained for the second stage. For other reported initiator systems, the aggregation usually occurs over the entire polymerization process, and no such clear two-stage kinetics has been observed.[4g,5c,9,10] The monomeric active species with the growing polymer chain are apparently stabilized by excess amount of monomer. With the increase of monomer consumption (monomer conversion > 50−60%), the aggregation to dimeric structure occurs extensively, which equilibrates with the monomeric active polymer chain. This process results in a slower apparent propagation rate at high monomer conversions.

From the SEC analysis, the polymers obtained over the entire conversion range are monomodal. There is a linear increase of M_n' (SEC, corrected) with the monomer conversion (Figure 2) although the plot somewhat deviates from the theoretical dependence. The polymer chains formed in the first stage apparently continue to propagate in the second linear stage.

However, there is no further linear increase of M_n' with the conversion when $[LA]_0/[Y]_0 = 100$ (Figure 3). The molecular weights of the polymers reached at 24%

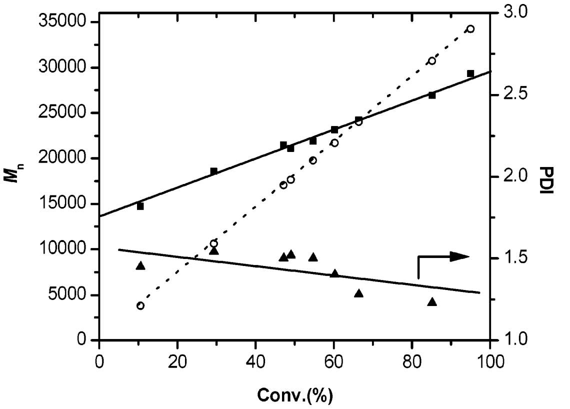


Figure 2. Plots of M_n vs monomer conversion for L-lactide polymerization using **3** as initiator: (■) M_n' (SEC, polystyrene standards, multiplied by 0.58); (○) M_n (theory); (▲) PDI (M_w/M_n, from SEC). Conditions: $[LA]_0/[Y]_0 = 250$, $[LA]_0 = 0.87$ M, THF, 22 °C.

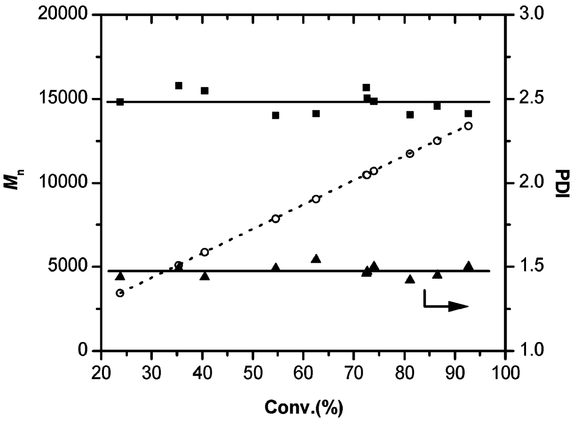


Figure 3. Plots of M_n vs monomer conversion for L-lactide polymerization using **3** as initiator: (■) M_n' (SEC, polystyrene standards, multiplied by 0.58); (○) M_n (theory); (▲) PDI (M_w/M_n, from SEC). Conditions: $[LA]_0/[Y]_0 = 100$, $[LA]_0 = 0.87$ M, THF, 22 °C.

monomer conversion remain nearly constant over the entire conversion range. It is found that the lowest molecular weights (M_n') of the obtained polylactides in the cases of $[LA]_0/[Y]_0 = 200$ and 250 are nearly the same as those in the case of $[LA]_0/[Y]_0 = 100$ (around 15 000), which correspond to about 100 monomer units (L-lactide, MW = 144.13). Therefore, we suggest that an increase of molecular weights vs monomer conversion will be observed when $[LA]_0/[Y]_0 > 100$. Below this ratio, nearly constant molecular weights will be obtained over the entire conversion range. This might be due to the relatively fast propagation rate during the first linear stage as compared to the rate of initiation ($k_p \gg k_i$).

To avoid the aggregation of the active species during the polymerization, dilute conditions were applied. Since complex **3** is not active enough, the polymerization initiated by the lutetium complex **2** were systematically studied in THF under dilute conditions ($[LA]_0 = 0.29$ M, $[Lu]_0 = 0.72-0.96$ mM, $[LA]_0/[Lu]_0 = 300, 400$). The plot of conversions against time shown in Figure 4 indicates the equilibrium polymerization by **2**. The semilogarithmic plots for two different polymerizations were not linear over the entire conversion range. A similar tendency as complex **3** was also not observed. The linear relation was only found when monomer conversion was less than 50−60% (Figure 5). Similarly, when ln k_{app} vs ln $[Lu]_0$ was plotted, a linear line with a slope of 1.12 was obtained. Despite the inaccuracy, the polymerization of L-lactide by **2** follows a kinetic law according to eq 5 when monomer conversion is less than 50%.

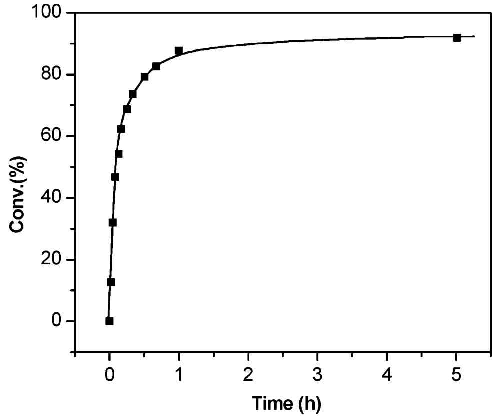


Figure 4. Plot of monomer conversion with time for L-lactide polymerization using **2** as initiator in THF at 22 °C; $[LA]_0 = 0.29$ M, $[LA]_0/[Lu]_0 = 300$.

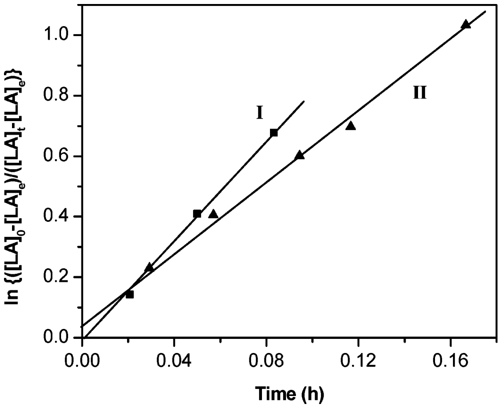


Figure 5. Semilogarithmic plots of LA conversion with time in THF at 22 °C using **2** as initiator, $[LA]_0 = 0.29$ M: (■) $[LA]_0/[Lu]_0 = 300$; (▲) $[LA]_0/[Lu]_0 = 400$. For plot I, $k_{app} = 2.29 \times 10^{-3}$ s^{-1} (linear fit, $R = 0.999$); and plot II, $k_{app} = 1.66 \times 10^{-3}$ s^{-1} (linear fit, $R = 0.997$).

$$-\mathrm{d}[LA]/\mathrm{d}t = k_p[Lu][LA] \tag{5}$$

The nonlinear relationship after this period suggests that the aggregation of active species still exists partially, which could not be completely suppressed by simple dilution. Furthermore, since the lutetium complex **2** is more sensitive than the yttrium complexes, the deactivation of active species during the polymerization is conceivable. The much larger deviation of the molecular weights (M_n') of the PLAs from the theoretical values gives the evidence to the deactivation (Table 1, also see Supporting Information).

Mechanism. From the kinetic studies, rare earth metal complexes **2** and **3** show single-site behavior during the L-lactide polymerization when the monomer conversion is low. To gain some insights into the initiation mechanism, we attempted to observe the 1:1 adduct of lactide with complex **3**. However, no such adduct could be identified from the ^{1}H NMR spectra; polymerization was initiated instead. Because of the fact that no obvious signals for free $HN(SiHMe_2)_2$ were observed, the possibility of the polymerization initiated by the reaction of metal complex with impurities is excluded (the $LnN(SiHMe_2)_2$ moiety is sensitive toward

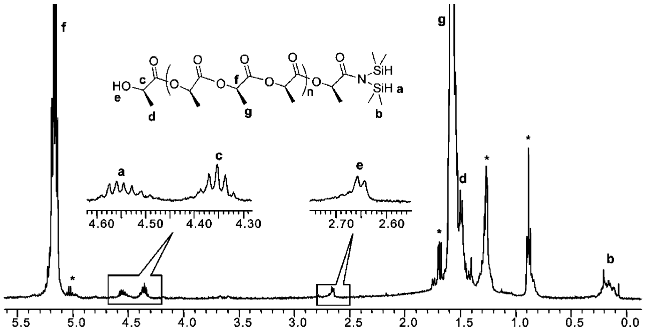


Figure 6. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of the oligomer of L-lactide using **3** as initiator after quenching with wet *n*-hexane (*, hexane and monomer signals). Conditions: $[LA]_0/[Y]_0 = 10$, $CDCl_3$, 22 °C.

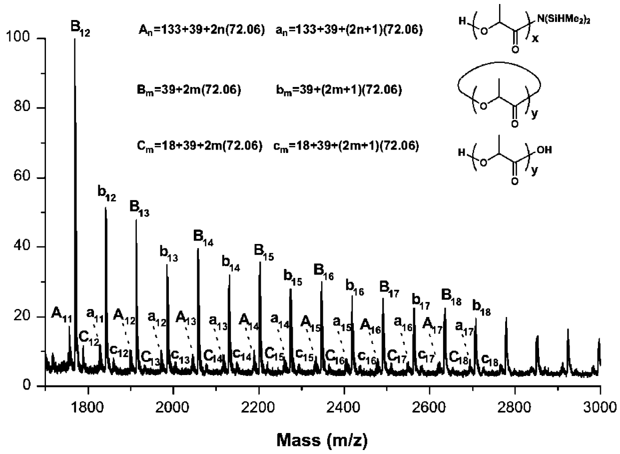


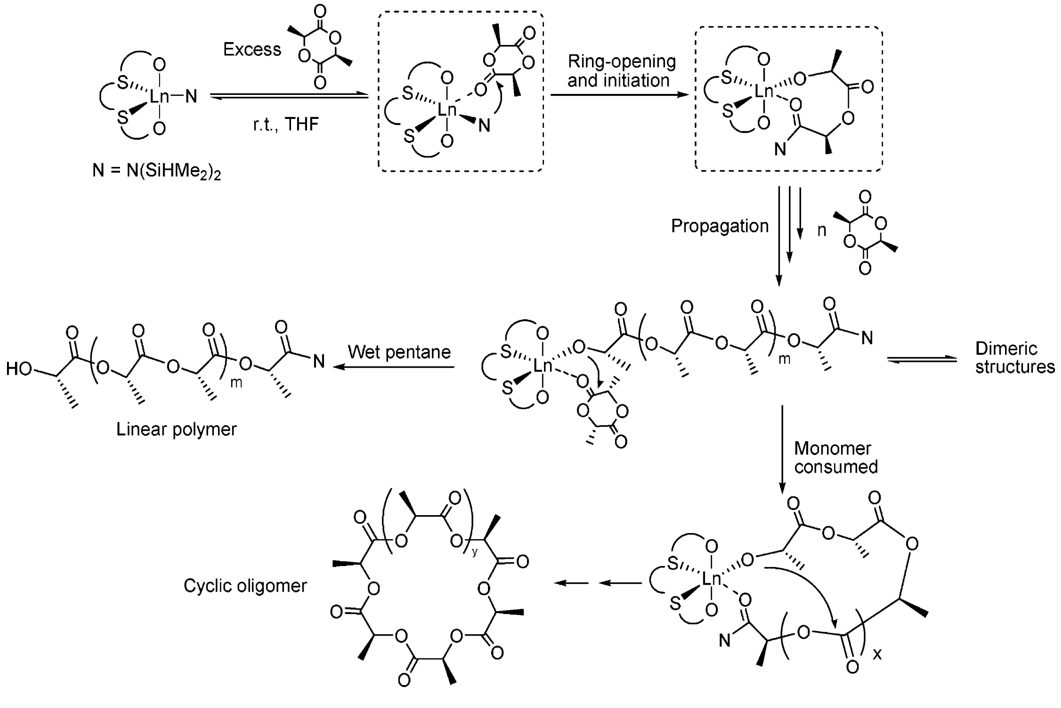
Figure 7. MALDI-TOF mass spectrum of the oligomer of L-lactide using **3** as initiator (doped with K^+). Conditions: $[LA]_0 = 0.4$ M, $[LA]_0/[Y]_0 = 20$, in THF, 24 h at 22 °C.

proton sources producing $HN(SiHMe_2)_2$). Moreover, no aromatic proton signals could be detected in the ^{1}H NMR spectra of the PLAs, suggesting that the bis(phenolate) group was not involved in the polymerization process. Analysis of the oligomers formed by complex **3** at $[LA]_0/[Y]_0 = 10$ (Figure 6) revealed that, besides the signals at 4.33, 2.64, and 1.48 ppm for the end group $HOCH(CH_3)CO-$,[8c] a set of signals in the region of 0.4−0 ppm as well as a multiplet at 4.53 ppm could be distinguished. They are absent in the ^{1}H NMR spectra of PLAs prepared in the presence of 2-propanol. Most likely these signals could be assigned to the $N(SiHMe_2)_2$ group, although no clear coupling pattern was recorded for the methyl group of $N(SiHMe_2)_2$. In the MALDI-TOF mass spectrum (Figure 7), oligomers with $N(SiHMe_2)_2$ end cap can be detected. Therefore, the results from both methods indicate that the silylamido ligand acts as the initiating group in the polymerization of L-lactide by these rare earth silylamido complexes.

In the MALDI-TOF mass spectrum, peaks accounting for oligomers with $N(SiHMe_2)_2$ end caps are not the most intensive ones. Cyclic oligomers dominate, indicating that the intramolecular transesterification occurred extensively. The very small amount of oligomer chains with carboxylic acid end presumably arose from the hydrolysis[4d,11] of $H-[OCH(CH_3)C(O)]_{2n}-N(SiHMe_2)_2$. The spectrum also revealed all three kinds of oligomers with nonintegral LA repeat units due to intermolecular transesterification processes.

Chisholm et al. have reported that the ROP of L-lactide by $Ph_2Sn(NMe_2)_2$ produced both rings and chains with bimodal molecular weight distributions, even when conversion was less than 50%.[4d] Under the polymerization conditions with high ratios of $[LA]_0/[Ln]_0 = 100-300$ in the present work, monomodal PLAs were obtained over the entire conversion range. The molecular weight distributions of the polymers became narrower with increasing conversion (Figure 2). From the SEC analysis of the methanol soluble fractions obtained after the precipitation of the PLAs, the existence of low molecular weight cyclic oligomers is excluded. Furthermore, in the ^{1}H NMR spectra of high molecular weight PLAs, the signals of $HOCH(CH_3)C(O)-$ end group could usually be observed. All these observations suggest that cyclic oligomers are not dominant during the polymer-

Scheme 2



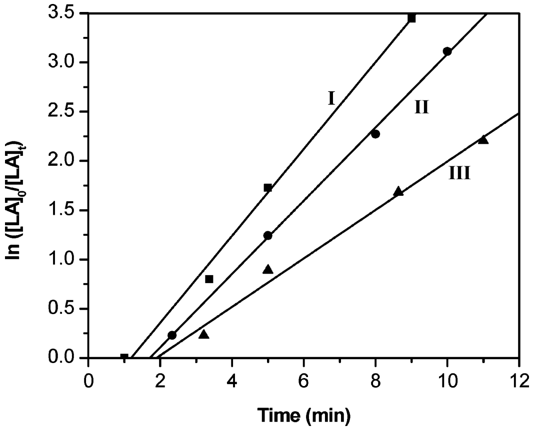


Figure 8. Semilogarithmic plots of L-lactide conversion with time in toluene at 22 °C using **3**/^{i}PrOH as initiators, $[\mathrm{LA}]_0$ = 0.29 M. $[\mathrm{LA}]_0$:$[^i\mathrm{PrOH}]_0$:$[\mathrm{Y}]_0$ = 200:2:1 (■), 250:2:1 (●), and 350:2:1 (▲). For plot I, $k_{\mathrm{app}} = 7.30 \times 10^{-3}$ s^{-1} (linear fit, $R = 0.998$); plot II, $k_{\mathrm{app}} = 6.18 \times 10^{-3}$ s^{-1} (linear fit, $R = 0.999$); and plot III, $k_{\mathrm{app}} = 4.10 \times 10^{-3}$ s^{-1} (linear fit, $R = 0.994$).

ization process. The formation of the cyclic oligomers shown in Figure 7 may have been caused by the extensive intramolecular transesterification after a long postpolymerization period, adopted to ensure the completion of the polymerization.[13b] Similar phenomena were also observed in the ring-opening polymerization of cyclic esters by other initiator types.[8b,12,14]

Polymerization of L-lactide using **1**−**3** yielded stereochemically pure poly(L-lactide) (by ^{1}H and ^{13}C NMR spectroscopy), indicating that the epimerization of the monomer or polymer, usually observed by using ionic initiators,[15] was absent under the polymerization conditions. Therefore, the coordination−insertion nature of the polymerizations by **1**−**3** is operative. The polymerizations in THF were generally faster than those in dichloromethane or toluene. On one hand, the excess THF accelerated the reversible dissociation of the six-coordinate complex to a pseudo-five-coordinated metal species,[6] facilitating the monomer coordination. On the other hand, the coordination of THF to the metal center of the growing sites might increase the nucleophilicity of the active alkoxide moiety, leading to a significant enhancement of the polymerization rate.[1e] From these results, we propose the mechanism for the polymerizations in Scheme 2.[12] The dissociation of the coordinated THF affords a vacant site where the first L-lactide is coordinated cis to the silylamide ligand. This step is followed by a sequential nucleophilic attack on the carbonyl carbon of the coordinated lactide by the silylamide group, cleaving the acyl−oxygen bond to form a metal−alkoxo active end group. This initiation step is followed by continued monomer insertion into the active metal−alkoxo bond. The monomeric structure of active species with growing polymer chain is stabilized by the excess amount of monomer. After the consumption of monomer to a certain degree, aggregation into dimer occurs. In the case of added 2-propanol the longer polymerization time simply led to the intermolecular transesterification (Figure 11). When the monomer is consumed, for the case of silylamide as initiating group, the carbonyl group attached to a silylamide group tends to coordinate to the vacant site. The backbiting of the metal−alkoxo active group to the carbonyl carbons of the polymer chain leads to the formation of cyclic structures. This backbiting becomes significant for low molecular weight PLAs (i.e., low $[\mathrm{LA}]_0/[\mathrm{Ln}]_0$).

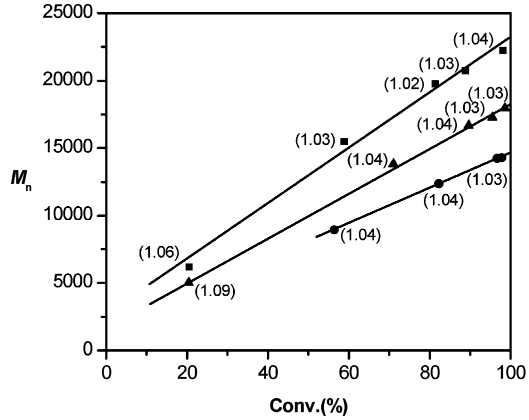


Figure 9. Plots of M_n' (SEC, polystyrene standards, multiplied by 0.58, PDI indicated in parentheses) vs monomer conversion using **3**/^{i}PrOH for L-lactide polymerization, $[\mathrm{LA}]_0$ = 0.29 M, in toluene at 22 °C. $[\mathrm{LA}]_0$:$[^i\mathrm{PrOH}]_0$:$[\mathrm{Y}]_0$ = 350:2:1 (■), 250:2:1 (▲), and 200:2:1 (●).

The influence of the silylamide group is restricted to the initiation step. The initiation by the amide group is slower than the alkoxy group due to the lower nucleophilicity of the silylamide group. Slower initiation combined with fast propagation leads to the broadening of the molecular weight distribution. This also explains that the polymerizations by **3** are more controlled than those by **1** and **2**, since the Lewis acidic metal centers in **1** and **2** in a less sterically bulky ligand environment are more susceptible to nucleophilic attack as compared to **3**. The difference between k_i and k_p for **3** is relatively small as compared to that for **1** and **2**, resulting in a more controlled polymerization by **3**.

Polymerization in the Presence of 2-Propanol. To understand the difference between the initiation by the amide and the alkoxide systems, L-lactide was polymerized with complexes **1**−**3** in the presence of added 2-propanol. Similar to the polymerization of cyclic esters by the in situ generated metal alkoxides in the literature,[16] the polymerizations by **1**−**3**/2-propanol are well-controlled. From the results listed in Table 2, the ratio of 2-propanol to the metal complexes **1**−**3** has a crucial influence on the polymerization rate, especially when complex **3** was used for polymerization. In the presence of excess 2-propanol ($[^i\mathrm{PrOH}]_0/[\mathbf{3}]_0$ = 2−3:1), complete conversions could be reached within several minutes, whereas hours are required when an equivalent amount of 2-propanol was added. Furthermore, higher amounts of 2-propanol led to narrower molecular weight distributions. The yttrium complex **3** in the presence of 2-propanol was found to be significantly more active than **1** and **2**.

Kinetics in the Presence of 2-Propanol. The ring-opening polymerization of L-lactide by **3**/^{i}PrOH with the ratio of 1:2 was studied systematically. Conversions of L-lactide at various concentrations of **3** in toluene at 22 °C were monitored by ^{1}H NMR spectroscopy for individual runs at different intervals ($[\mathrm{LA}]_0$ = 0.29 M; $[\mathrm{Y}]_0$ = 0.82−1.45 mM, $[^i\mathrm{PrOH}]_0/[\mathrm{Y}]_0$ = 2:1). The semilogarithmic plots for several polymerizations are shown in Figure 8. In each case, first-order kinetics in monomer concentration was observed over the entire conversion range. The polymerization by **3**/^{i}PrOH also follows eq 1. From the plot of ln k_{app} vs ln $[\mathrm{Y}]_0$, a slope of 1.05 ± 0.12 was obtained. Therefore, the polymerization of L-lactide by **3**/^{i}PrOH follows an overall kinetic law according to eq 2, with $k_p = 6.96 \pm 0.04$ L mol^{-1} s^{-1}.

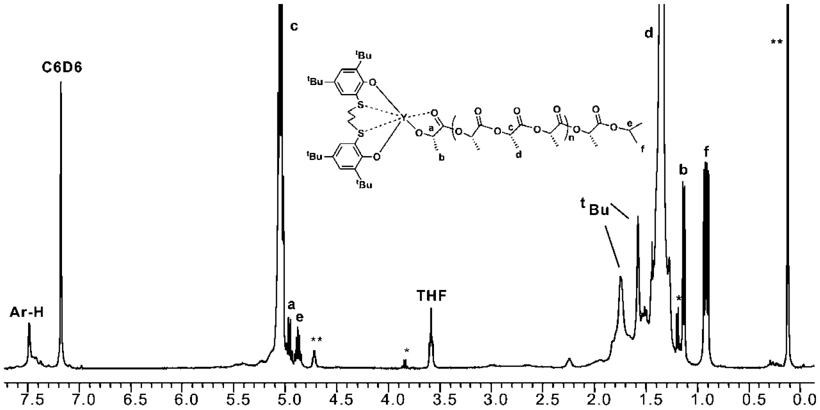


Figure 10. ^{1}H NMR spectrum (400 MHz, C_6D_6) of active L-lactide oligomer by **3**/^{i}PrOH (*, monomer; **, free $HN(SiHMe_2)_2$), $[LA]_0$:$[^iPrOH]_0$:$[Y]_0$ = 20:2:1, at 25 °C.

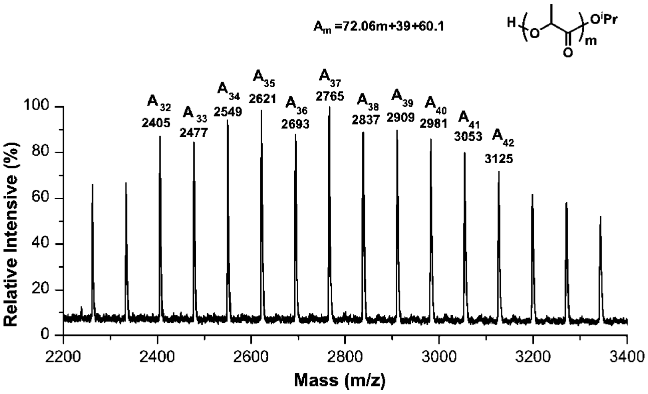


Figure 11. MALDI-TOF mass spectrum of the oligomer of L-lactide obtained by **3**/^{i}PrOH (doped with K^+). Conditions: $[LA]_0$ = 0.87 M, $[LA]_0$:$[^iPrOH]_0$:$[Y]_0$ = 40:2:1, in toluene, 5 min at 22 °C.

This value is significantly larger than k_p = 0.052 L mol^{-1} s^{-1} for the pure silylamido complex **3** and is comparable to k_p = 32.0 L mol^{-1} s^{-1} found for the tris(2,6-di-*tert*-butylphenoxy)yttrium/2-propanol system (1:3 ratio; first order in monomer and initiator concentration, 25 °C; CH_2Cl_2).[16c]

As depicted in Figure 9, the molecular weights (M_n') of the obtained PLAs increased linearly with the conversion in each case, and narrow molecular weight distributions were obtained (PDI 1.02–1.09) for high conversions up to 98%, indicating the living nature of the polymerization. It is noticed that there are induction periods for these systems (Figure 8). When the solution of **3** was added to a mixture of lactide and 2-propanol, polymerization initiated immediately without induction period, although the PDI values of PLA from these experiments slightly increased (PDI 1.05–1.07).

Compared to the complexity met in the initiation by the silylamido complexes, the kinetics of the polymerizations by the in-situ generated alkoxides are simple. Each metal center acts as an active site; no aggregation or deactivation of active polymer chain occurs during the entire polymerization process.

Mechanism in the Presence of 2-Propanol. The formation of alkoxide species was monitored by ^{1}H NMR spectroscopy in C_6D_6. Reactions of **3** with 1, 2, or 3 equiv of 2-propanol afforded the same yttrium alkoxide "[Y(OSSO)(O^{i}Pr)]", except that the isopropoxy signals were broadened and slightly high field shifted with the increasing amount of 2-propanol.[6] Obviously, an exchange process with free 2-propanol is involved. Such an exchange process was absent in the system of $[Y\{N(SiMe_3)\}_3]$ with an excess of 2-propanol ($[^iPrOH]/[Y] > 3$),[16a] where two additional broad peaks characteristic of free 2-propanol molecules could be observed.

^{1}H NMR spectroscopic analysis excluded any exchange between the bis(phenolato) ligand and excess amount of 2-propanol. Because of the fact that the 1:1 reaction of complex **3** with 2-propanol only initiated slow polymerization, we suggest that the O^{i}Pr group is bonded to two yttrium centers in the bridging mode. The exchange with excess 2-propanol "activates" the O^{i}Pr group. Several literature reports also indicate that the μ-alkoxy group is less active than the terminal alkoxy group.[13]

When L-lactide was added to the yttrium alkoxide generated by reacting **3** with 2-propanol in 1:2 ratio, the polymerization started instantaneously and the active oligomer could be identified (Figure 10). End-group analysis by ^{1}H NMR spectroscopy of the obtained PLAs showed clearly the existence of $HOCH(CH_3)CO-$ and isopropoxy end groups.[8c,16c] The MALDI-TOF mass spectrum further revealed that only oligomers with these two end groups were formed (Figure 11). No cyclic oligomer was detectable. The presence of free silylamine did not affect the polymerization, indicating that there was no further exchange between alkoxides and free silylamine after the initiation step. Furthermore, no free 2-propanol could be observed in the polymerization, showing that the 2-propanol in excess rapidly exchanged with the growing alkoxides species during the polymerization and acted as an effective chain transfer agent. Since the polydispersities of the obtained PLAs are quite low, this exchange process between alkoxides and free alcohol molecules must be fast with respect to the chain propagation.[16a]

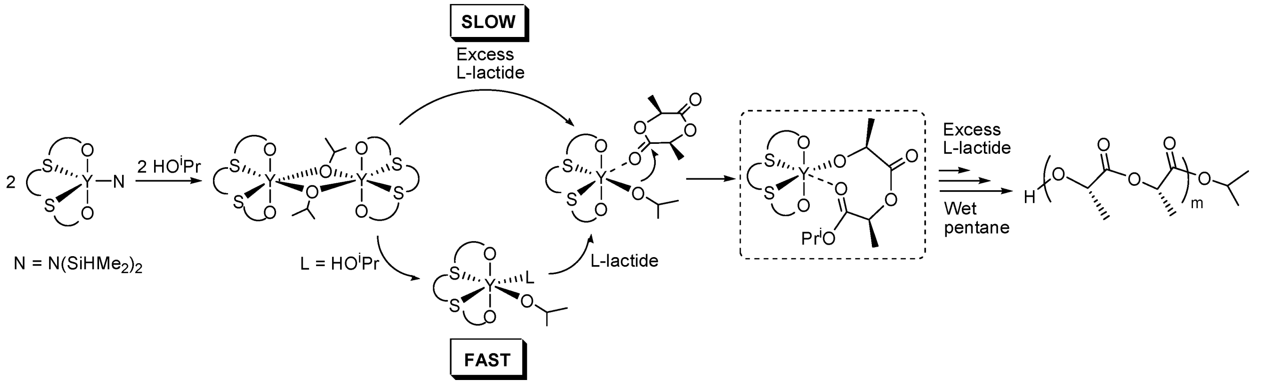
The MALDI-TOF spectrum also revealed the existence of linear oligomers with a nonintegral LA repeat unit, indicating intermolecular transesterification. As depicted in Figure 9, PLAs with narrow molecular weight distributions (PDI 1.02–1.06) were obtained over the entire conversion range, indicating that the transesterifications is absent or negligible during the polymerization process. The intermolecular transesterification observed in Figure 11 should be caused by the long postpolymerization time adopted.[16] It was further evidenced by a separate polymerization run, where the molecular weight distribution of PLAs broadened from 1.05 to 1.14 upon longer reaction time after the full conversion had been reached.

Table 2. Ring-Opening Polymerization of L-Lactide by Complexes 1−3 in the Presence of 2-Propanol[a]

catalyst	$[LA]_0/[Ln]_0/[^iPrOH]_0$	temp (°C)	time (h)	conv[b] (%)	M_c[c] ($\times10^4$)	M_n[d] ($\times10^4$)	M_n'[e] ($\times10^4$)	M_w/M_n
1	300/1/1	22	72	35	1.52	2.40	1.39	1.20
	300/1/2	22	4	27	0.59	1.23	0.71	1.05
	300/1/2	22	24	89	1.93	3.20	1.86	1.17[f]
2	300/1/1	28	25	14	0.61	1.92	1.11	1.13
	300/1/2	28	25	42	0.91	1.29	0.75	1.06
3	300/1/1	22	19	96	4.13	5.75	3.33	1.11
	300/1/2	22	0.08	94	2.03	3.56	2.06	1.02
	300/1/3	22	0.08	95	1.38	2.69	1.56	1.03

[a] Polymerization carried out with 0.87 M solution of L-lactide in toluene unless otherwise indicated. [b] Determined by the integration ratio of the methine protons in monomer and polymer. [c] $M_c = ([LA]_0/[^iPrOH]_0) \times 144.13 \times \text{conversion (\%)} + 60$. [d] Measured by SEC. [e] Using a correcting factor 0.58 for M_n. [f] Bimodal.

Scheme 3



From these observations, we propose the mechanism of L-lactide polymerization initiated by **3**/^{i}PrOH in Scheme 3. The alkoxides generated in situ may exist as a dimer in toluene. Excess 2-propanol cleaves the dimeric structure and promotes an exchange between the 2-propanol and isopropoxy group. When this species is exposed to L-lactide, the monomer is coordinated and sequentially fast insertion occurs, growing into a linear polymer. During the propagation, the alkoxide/alcohol exchange is widely involved,[16a] which reduces the molecular weight of the PLAs by the ratio of the added 2-propanol to the metal complex. Without an excess of 2-propanol, the dimeric structure could also be cleaved by the monomer, but this is a much slower process. In this case, k_i is not fast enough compared to k_p, leading to the broadening of the molecular distribution.

Complexes **1** and **2** show only low polymerization activity in the presence of 2-propanol. This may be due to the less bulky ligand environment of **1** and **2**. The aggregation number of the generated alkoxides is most likely higher than two, and more 2-propanol molecules are required to cleave the aggregate to produce the monomeric species. In fact, we found the polymerization accelerated significantly when the ratio of 2-propanol to **2** of 5:1 was used.

Conclusions

The polymerization of L-lactide by rare earth metal silylamido complexes was compared with that initiated by the in-situ generated alkoxides systems. The silylamide group in these complexes initiated the polymerization. When monomer conversion was not high, this process was first order in monomer concentration as well as in initiator concentration. Aggregation of the active polymer chain occurred subsequently, slowing down the polymerization. Because of the relatively slow initiation by the less nucleophilic silylamide group, the polymerization was not controlled, giving broadly distributed polymers. In the presence of added 2-propanol, metal isopropoxides formed that are aggregated at least to dimers. This in-situ generated alkoxide initiated living polymerization of L-lactide to afford linear PLAs with $HOCH(CH_3)CO-$ and $-O^iPr$ as end groups. The polymerization was first-order in monomer concentration and in initiator concentration over the entire conversion range; no aggregation or deactivation of active polymer chain was observed. Thus, the initiating group has a strong influence on the polymerization process, in particular during the initiation stage.

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Supporting Information Available: ^1H NMR spectra for the reaction of complex **3** with 2-propanol in C_6D_6, ^{13}C NMR spectra of polylactides, plots of ln k_{app} vs ln $[Ln]_0$, and plots of molecular weight vs conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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