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Synthesis, characterization and L-lactide polymerization behavior of rare-earth metal bis(silylamide) complexes supported by arylamido ligand

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ABSTRACT

Salt metathesis of $LnCl_3$, $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Li$ and $LiN(SiHMe_2)_2$ in 1:1:2 molar ratio in THF produced the mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y (**1**), Lu (**2**), La (**3**)) in good isolated yields. All these complexes were characterized by elemental analysis, NMR spectroscopy and FT-IR spectroscopy. **1** was further structurally authenticated by single crystal X-ray diffraction. These complexes alone could serve as highly active initiators for L-lactide polymerization in toluene at 50 °C. Employing **1** as the initiator, L-lactide polymerization proceeded in a controllable fashion via the coordination-insertion mechanism verified by end group analysis of the oligomer.

1. Introduction

Polylactide (PLA) is a biodegradable and biocompatible macromolecule for its mechanical and physical properties suitable for the applications such as sutures, product packaging, and artificial tissues [1]. One of the most effective methods to prepare PLA is the ring-opening polymerization (ROP) of lactides using metal-based initiators [2]. Among the reported efficient metal-based initiators, some rare-earth metal complexes were found to be highly active for lactide polymerization [3]. However, it is usually assumed that in such polymerization the transformation of rare-earth metal complexes into rare-earth metal alkoxides/aryloxides may dramatically improve polymerization performance [2]. Therefore, in most cases rare-earth metal complexes are employed as pre-initiators and the combination of alcohol is necessary to achieve efficient reactivity in lactide polymerization.

On the other hand, non-Cp ligand scaffolds such as β-diketiminate, amidinate, and phenolate are recently receiving considerable attention in rare-earth metal chemistry [4]. However, most of non-Cp spectator ligands are bounded to central metals through N or O atoms in multi-dentate fashions to stabilize coordination highly unsaturated rare-earth metal ions. In comparison, mono-dentate arylamido frameworks as ancillary ligand in the coordination/organometallic chemistry of rare-earth metals are still far less explored [5].

As our continuous study on lactide polymerization promoted by rare-earth metal complexes [6], we become interested in exploring the reactivity of rare-earth metal complexes supported by arylamido ligand. It was found the mono(arylamido) rare-earth metal bis(silylamide) complexes $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y (**1**), Lu (**2**), La (**3**)) could be prepared in good isolated yields employing salt metathesis strategy. These complexes alone could serve as highly active initiators for L-lactide polymerization. A controllable L-lactide polymerization was observed employing **1** as an initiator. Here we report these results.

2. Results and discussion

2.1. Synthesis and characterization of mono(arylamido) rare-earth metal bis(silylamide) complexes

The mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Ln[N(SiHMe_2)_2]_2(THF)$ (Ln = Y (**1**), Lu (**2**), La (**3**)) were synthesized in 92–97% isolated yields by one-pot salt metathesis reaction from $LnCl_3$, $[2,6\text{-}^iPr_2C_6H_3N(SiMe_3)]Li$ and $LiN(SiHMe_2)_2$ in molar ratio 1:1:2 in THF at room

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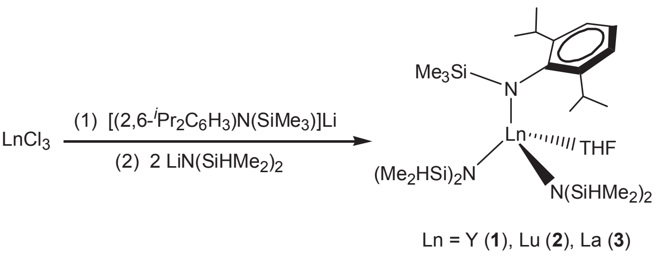
temperature, as shown in Scheme 1. Theses complexes were characterized by elemental analysis, FT-IR spectroscopy and NMR spectroscopy, and they are soluble in THF, toluene and diethyl ether, but sparingly soluble in hexane.

Single crystals of **1** suitable for X-ray diffraction were grown from a mixture solution of toluene and hexane at −30 °C. Single crystal X-ray crystallography shows that **1** is a neutral and mononuclear complex, as shown in Fig. 1. The short bond distance of Y–H(3)(Si3) (2.50(4) Å) indicates there exists agnostic Si–H–Y interaction in the solid state [7]. Therefore, the central metal is five-coordinated to one arylamido ligand through the nitrogen atom in η^1-fashion, two silylamide groups, one agostic H atom, and one THF molecule to form a distorted-trigonal-bipyramidal geometry. The Y–N (arylamido) bond distance in **1** (2.224(3) Å) is consistent with that in the mono-arylamido-ligated yttrium bis(alkyl) complex $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Y}(\text{CH}_2\text{SiMe}_3)_2(\text{THF})$ (2.153(2) Å) [8]. The $\text{Y–N}(\text{SiHMe}_2)_2$ distances in **1** are 2.246(3) and 2.231(3) Å, which are comparable with those in $[\text{PhC}(N\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Sc}[\text{N}(\text{SiHMe}_2)_2]_2$ (2.065(3) Å) [9], and $[\text{TolC}(N\text{-}2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2]\text{Y}[\text{N}(\text{SiHMe}_2)_2]_2(\text{THF})$ (2.250(3) and 2.258(3) Å) [10], if the differences in radii and coordination number are considered [11].

2.2. L-lactide polymerization

In order to assess the polymerization behavior of complexes **1**–**3**, they were employed as initiators for the ring-opening polymerization of L-lactide. As illustrated in Table 1, all these complexes alone can serve as single-component initiators for L-lactide polymerization in toluene at 50 °C, with an activity trend of **1** ≈ **3** > **2** (runs 1–3, Table 1). Notably, these complexes exhibit high activity in the absence of any alcohol. For instance, using **1** as the initiator, the conversion reaches up to 100% in 5 min even the molar ratio of [LA]/[Y] is increased upon to 2000 (run 7, Table 1). Remarkably, using **1** as the initiator, the molecular weights of the resulting polymers increase linearly with the increase of the molar ratio of monomer-to-initiator [LA]/[Y] from 100 to 2000, while the molecular weight distributions keep nearly constant ($M_w/M_n = 1.53–1.59$) (runs 1, 4–7, Table 1, and Fig. 2). This finding shows that the polymerization proceeds in a controllable fashion under the present conditions.

Because there are three Ln-N σ-bonds in these arylamido-ligated rare-earth metal bis(silylamide) complexes, it raises the intriguing question of which Ln-N bonds actually participates in the reaction when they are employed as the initiators for L-lactide polymerization. To reveal the true active site and gain some insights into the polymerization mechanism, oligomerization of L-lactide by **1** at [LA]/[Y] = 10 molar ratio in toluene was carried out. In the ^{1}H NMR spectrum of the resulting oligomer, no signal for the arylamido ligand is observed, indicating that the ancillary ligand was not engaged in the initiating stage (Fig. 3). Further analysis of oligomer reveals that, besides the resonances around 4.34, 2.67 and 1.48 ppm for the end group of $\text{HOCH}(\text{CH}_3)\text{CO–}$, a set of signals at 0.14 ppm and a multiplet signal at 4.55 ppm can be obviously assigned to the $\text{N}(\text{SiHMe}_2)_2$ group. This result shows that only the silylamido groups acted as the initiating group in the ring-opening polymerization of L-lactide, and the polymerization proceeded in a coordination-insertion mechanism as illustrated in Scheme 2. Besides, although there are two silylamide groups are bonded to each rare-earth metal in these complexes, GPC curves of the resulting polymers are all unimodal, suggestive of an equivalent polymerization behavior of the two silyamide groups.



Scheme 1. Synthesis of complexes **1**–**3**.

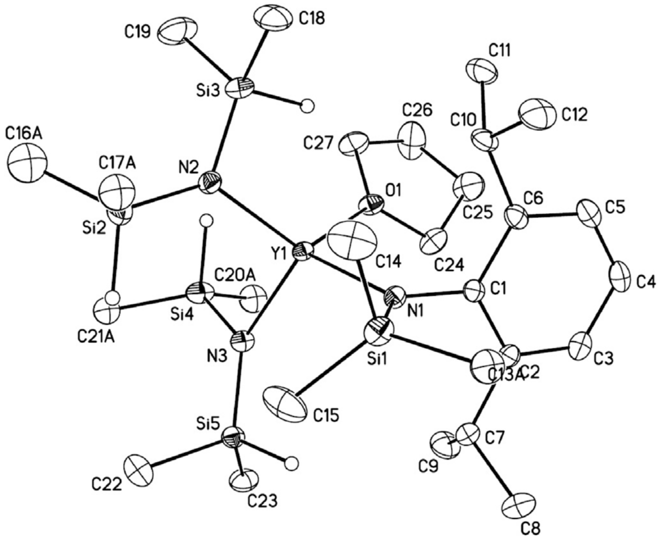


Fig. 1. Molecular structure of **1** with thermal ellipsoids at 20% probability. Hydrogen atoms (except for Si–H) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Y1–N1 = 2.224(3), Y1–N2 = 2.246(3), Y1–N3 = 2.231(3), Y1–H3 = 2.50(4), Y1–O1 = 2.371(2), N1–Y1–N2 = 107.39(11), N1–Y1–N3 = 114.06(11), N1–Y1–O2 = 105.50(9), N2–Y1–N3 = 107.02(10).

3. Conclusions

In summary, the mono-arylamido-ligated rare-earth metal bis(silylamide) complexes $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Ln}[\text{N}(\text{SiHMe}_2)_2]_2(\text{THF})$ (Ln = Y (**1**), Lu (**2**), La (**3**)) could be easily prepared by salt metathesis of LnCl_3, $[2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{N}(\text{SiMe}_3)]\text{Li}$ and $\text{LiN}(\text{SiHMe}_2)_2$ in 1:1:2 molar ratio in THF. These complexes alone were highly active for the ring-opening polymerization of L-lactide in toluene at 50 °C. Employing **1** as the initiator, a controllable polymerization fashion was observed in L-lactide polymerization. End group analysis of the oligomer revealed that the polymerization proceeded via the coordination-insertion mechanism and the active initiation groups were the silylamide groups.

4. Experimental section

4.1. Materials and procedures

All manipulations were performed under pure argon with rigorous exclusion of air and moisture using standard Schlenk techniques and argon-filled glovebox. Solvents (toluene, hexane, and THF) were distilled from sodium/benzophenone ketyl, degassed by the freeze-pump-thaw method, and dried over fresh Na chips in the glovebox. Anhydrous LnCl_3 were purchased from STREM. n-BuLi (1.0 M in hexane solution), $\text{HN}(\text{SiHMe}_2)_2$, SiMe_3Cl and $2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3\text{NH}_2$ were purchased from Acros, and used as received. L-lactide was obtained from Shenzhen Brightchina Industrial Co., Ltd., and was recrystallized twice from hot toluene.