

Synthesis and characterization of anionic lanthanide complexes $\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ (Ln = Yb, Sm, Nd) and their catalytic activity for the polymerization of methyl methacrylate

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Abstract

The syntheses and structures of a series of new lanthanide complexes supported by a chelating diamide ligand *N,N'*-bis(trimethylsilyl)-*o*-phenylenediamine are described. Anhydrous LnCl_3 reacts with $\text{Li}_2[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]$, followed by treatment of $\text{NaC}_5\text{H}_4\text{Me}$ in 1:1:2 molar ratio to afford the corresponding anionic complexes: $\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ [Ln = Yb (**1**), Sm (**2**), Nd(**3**)] in high yield. These complexes were characterized by elemental analysis, IR and ^1H NMR. The molecular structures of **1** and **2** were further determined by X-ray diffraction techniques to be an ion-pair complex composed by an anion $[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2$ and a cation $[\text{Li}(\text{DME})_3]$. Complexes **1**–**3** showed high catalytic activity for the polymerization of methyl methacrylate (MMA) at r.t., giving the syndiotactic-rich polymers with relatively narrow molecular weight distributions ($M_w/M_n = 1.64$ – 1.82).

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1. Introduction

The anionic Sm(II) complexes of $[(\text{C}_5\text{Me}_5)(\text{THF})_x\text{Sm}(\text{ER})(\text{C}_5\text{Me}_5)\text{K}(\text{THF})_y]_n$ (ER = OAr, SAR, NR₂, SiH₃, CHR₂) were reported to be active catalysts for the homopolymerization of ethylene, and styrene, as well as their block copolymerization, whereas the corresponding neutral complexes $[(\text{C}_5\text{Me}_5)(\text{THF})_x\text{Sm}(\text{ER})]$ are inactive under the same conditions [1]. The “ate” allyl complexes of lanthanides $\text{K}[\text{Ln}\{\text{C}_3\text{H}_3(\text{SiMe}_3)_2\}_4]$ and $[\text{Ln}\{\text{C}_3\text{H}_3(\text{SiMe}_3)_2\text{SiMe}_2\}_2\{\mu\text{-K}(\text{THF})\}(\text{THF})_x]_\infty$ were found to exhibit much higher activity than the neutral ones $\text{Ln}[\text{C}_3\text{H}_3(\text{SiMe}_3)_2]_3$ for the polymerization of MMA as real single-component catalysts [2]. Recently, we addressed that the anionic lanthanide

phenolates can be used as single-component initiators for the ring-opening polymerization of ϵ -caprolactone, and the reactivity is much higher than that for the corresponding neutral lanthanide phenolates [3]. The anionic complexes as single-component catalysts in the polymerization of polar monomers have still attracted much less attention, even though they show better catalytic activity in comparison with the neutral complexes.

In the other hand, while various neutral lanthanide complexes supported by chelating diamide ligand, an alternative to cyclopentadienyl-based ligand, have been synthesized and studied as precatalysts in homogeneous catalyses [4], a few anionic lanthanide complexes with diamide ligand have been prepared so far [5–8]. Of those only two examples concerning with their catalytic behavior were published; one is $[\text{Li}(\text{THF})_4][\text{Ln}\{(\text{R})\text{-C}_{20}\text{H}_{12}(\text{NR})_2\}_2]$, reported by Schulz and coworkers [7], the other is the anionic (hexa-1,5-diene-1,6-diamide)neodymium complexes, which can

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catalyze the 1,4-cis polymerization of buta-1,3-diene in the presence of MMAO as cocatalyst [8]. In this connection it is of interest to further study on the chemical behavior of anionic lanthanide amide derivatives. Very recently, we have been starting a project on the chemistry of anionic lanthanide complexes and found that the anionic lanthanide complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}\{\text{Li}(\text{DME})_3\}$ [$\text{Cp}' = \text{C}_5\text{H}_5$, $\text{Ln} = \text{Yb}$; Sm ; $\text{Cp}' = \text{MeC}_5\text{H}_4$, $\text{Ln} = \text{Yb}$] could initiate the polymerization of MMA in high activity under mild conditions, while CpLi , $\text{Li}_2[\text{Me}_2\text{Si}(\text{NPh})_2]$ and Cp_3Ln , bisamide lanthanide chloride showed very low activity under the same conditions [9]. In our continual study we have synthesized a series of new anionic lanthanocene complexes supported by *N,N'*-bis(trimethylsilyl)-*o*-phenylenediamine ligand, $\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ [$\text{Ln} = \text{Yb}$ (**1**), Sm (**2**), Nd (**3**)] and examined their catalytic activity for the polymerization of methyl methacrylate (MMA). It was found that these complexes could catalyze the polymerization of MMA as single-component catalysts in high activity at r.t. yielding the syndio-rich polymers. The activity is much higher than those found for $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}\{\text{Li}(\text{DME})_3\}$ published previously. Here we would like to report the results.

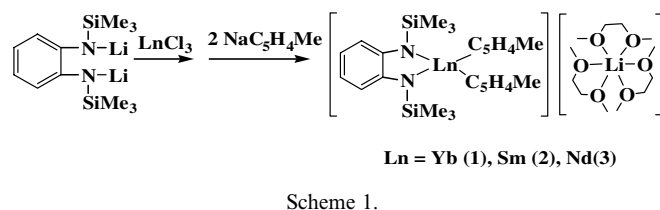
2. Results and discussion

2.1. Synthesis and characterization of anionic complexes

The metathesis reaction of anhydrous lanthanide trichloride (LnCl_3) with a less bulky amide metal salt yields an anionic lanthanide amide complex quite commonly, as the demand of coordination saturation of lanthanide metal [10]. We have reported that the metathesis reaction of LnCl_3 with a less bulky bisamide lithium $\text{Li}_2[\text{Me}_2\text{Si}(\text{NPh})_2]$, followed by the treatment of NaCp' afforded the anionic complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}\{\text{Li}(\text{DME})_3\}$ [$\text{Cp}' = \text{C}_5\text{H}_5$, $\text{Ln} = \text{Yb}$; Sm ; $\text{Cp}' = \text{MeC}_5\text{H}_4$, $\text{Ln} = \text{Yb}$] in high yield [9]. In order to see the influence of amide on the chemistry behavior of this kind of complexes, the bridged diamide ligand, *N,N'*-bis(trimethylsilyl)-*o*-phenylenediamine ($\text{H}_2\text{-}o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4$), was chosen here. The bridged diamine was synthesized according to the literature procedure [11] and the corresponding lithium salt was prepared by its reaction with *n*-BuLi in hexane. Anhydrous LnCl_3 reacts with $\text{Li}_2[o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4]$, followed by the treatment with $\text{NaC}_5\text{H}_4\text{Me}$ in 1:1:2 molar ratio to afford the corresponding anionic complexes: $\{[o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ [$\text{Ln} = \text{Yb}$ (**1**), Sm (**2**), Nd (**3**)] in high yield (Scheme 1). The cation in each complex is $\text{Li}(\text{DME})_3$, not $\text{Na}(\text{DME})_3$.

These complexes are air- and moisture-sensitive. They are soluble in tetrahydrofuran (THF), dimethylethylether (DME) and toluene, but sparingly in hexane.

Complexes 1–3 were characterized by elemental analysis, IR and ^1H NMR, and further by X-ray diffraction in the cases of complexes 1 and 2. Crystals of complexes 1 and 2 suitable for X-ray diffraction were grown from



DME. The molecular structure diagram of complexes **1** and **2** are shown in Figs. 1 and 2, respectively. Selected bond lengths and angles are given in Table 1, and the details of the crystallographic data are listed in Table 2.

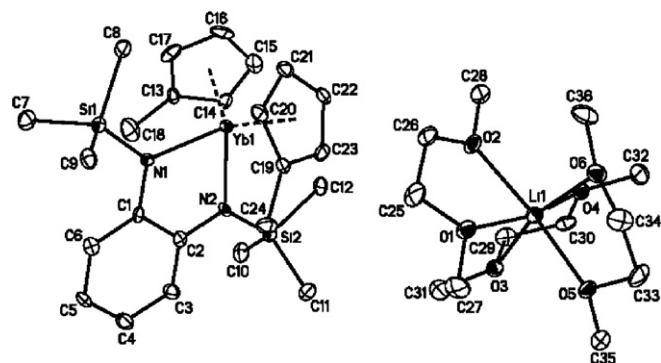


Fig. 1. The molecular structure of complex **1**. Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

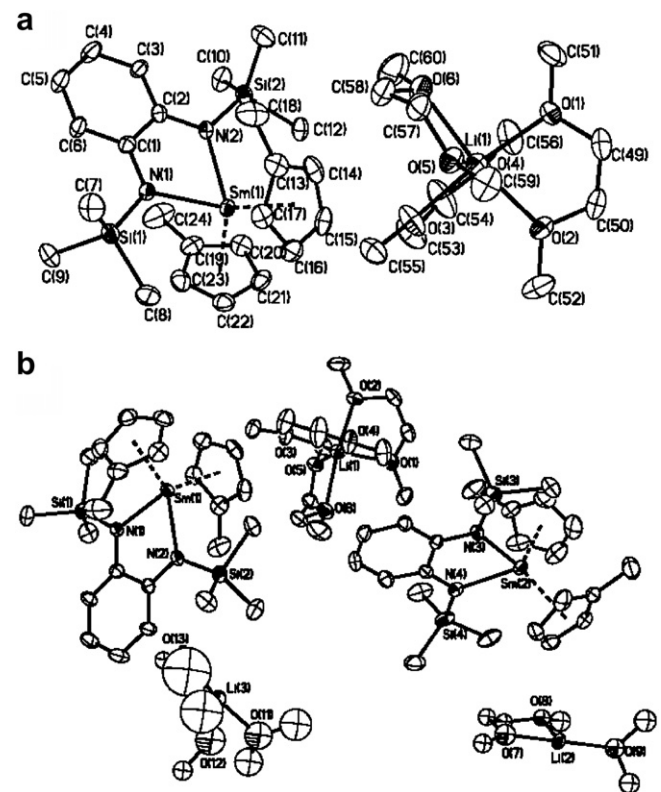


Fig. 2. (a) The molecular structure of complex **2**. Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity. (b) The unit cell for complex **2**. Thermal ellipsoids are drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for **1** and **2**

	1	2		1	2
<i>Bond distance</i>					
Ln(1)–N(1)	2.239(6)	2.322(5)	Ln(1)–C(23)	2.656(8)	2.748(7)
Ln(1)–N(2)	2.235(7)	2.334(5)	Si(1)–N(1)	1.720(7)	1.715(5)
Ln(1)–C(13)	2.669(8)	2.786(7)	Si(2)–N(2)	1.714(7)	1.714(5)
Ln(1)–C(14)	2.648(9)	2.777(7)	O(1)–Li(1)	2.096(16)	2.081(12)
Ln(1)–C(15)	2.637(9)	2.755(7)	O(2)–Li(1)	2.168(15)	2.137(12)
Ln(1)–C(16)	2.639(9)	2.723(7)	O(3)–Li(1)	2.237(16)	2.078(12)
Ln(1)–C(17)	2.650(9)	2.754(7)	O(4)–Li(1)	2.092(16)	2.115(12)
Ln(1)–C(19)	2.669(8)	2.769(7)	O(5)–Li(1)	2.104(15)	2.158(12)
Ln(1)–C(20)	2.654(8)	2.762(7)	O(6)–Li(1)	2.125(16)	2.187(12)
Ln(1)–C(21)	2.656(9)	2.753(7)	Ln(2)–N(3)	2.234(6)	2.333(5)
Ln(1)–C(22)	2.649(8)	2.749(7)	Ln(2)–N(4)	2.233(6)	2.342(5)
<i>Angle (°)</i>					
N(2)–Ln(1)–N(1)	76.8(2)	73.45(17)	N(2)–Ln(1)–C(17)	119.0(3)	116.3(2)
C(1)–N(1)–Si(1)	121.2(5)	120.9(4)	N(1)–Ln(1)–C(13)	88.5(2)	92.1(2)
C(1)–N(1)–Ln(1)	112.9(5)	114.8(4)	N(1)–Ln(1)–C(14)	116.3(3)	119.9(2)
Si(1)–N(1)–Ln(1)	125.8(3)	124.3(3)	N(1)–Ln(1)–C(15)	137.5(3)	135.6(2)
C(2)–N(2)–Ln(1)	113.0(5)	114.4(4)	N(1)–Ln(1)–C(16)	117.1(3)	112.1(2)
C(2)–N(2)–Si(2)	121.4(6)	121.8(4)	N(1)–Ln(1)–C(17)	89.2(3)	87.4(2)
Si(2)–N(2)–Ln(1)	125.6(3)	123.7(3)	O(1)–Li(1)–O(2)	75.5(5)	78.7(4)
N(2)–Ln(1)–C(13)	89.8(3)	90.0(2)	O(4)–Li(1)–O(3)	77.8(5)	77.5(4)
N(2)–Ln(1)–C(14)	84.5(3)	90.7(2)	O(5)–Li(1)–O(6)	77.8(5)	76.4(4)
N(2)–Ln(1)–C(15)	109.6(3)	117.6(2)	N(4)–Ln(2)–N(3)	77.1(2)	71.90(17)
N(2)–Ln(1)–C(16)	134.5(3)	137.3(2)			

Table 2
Details of the crystallographic data of complex **1** and **2**

	1	2
Empirical formula	C ₃₆ H ₆₆ N ₂ LiO ₆ Si ₂ Yb	C ₇₂ H ₁₃₂ Li ₂ N ₄ O ₁₂ Si ₄ Sm ₂
Formula weight	859.07	1672.76
Crystal colour	Blue-green	Brown-yellow
Temperature (K)	153.2	193.2
Wavelength (Å)	0.7107	0.7107
Size (mm)	0.32 × 0.25 × 0.10	0.70 × 0.40 × 0.26
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	16.4808(13)	42.550(4)
<i>b</i> (Å)	15.3193(13)	22.0431(18)
<i>c</i> (Å)	33.921(3)	20.109(2)
α (°)	90	90
β (°)	94.971(2)	111.646(2)
γ (°)	90	90
<i>V</i> (Å ³)	8532.0(12)	17531(3)
<i>Z</i>	8	8
<i>D</i> _{calc} (g cm ⁻³)	1.338	1.268
Absorption coefficient (mm ⁻¹)	2.289	1.434
<i>F</i> (000)	3560	6992
θ (°)	3.02–25.35	3.02–25.35
Reflection collected	75901	85067
Independent reflections	15549	16009
Variables	894	839
<i>R</i> [<i>I</i> > 2 σ (<i>I</i>)]	0.0765	0.0672
<i>R</i> _w	0.1194	0.1370
Goodness-of-fit on <i>F</i> ²	1.191	1.150

Complexes **1** and **2** are crystallized in the same monoclinic spaces and have the analogous solid structure as shown in Figs. 1 and 2a. Both complexes contain crystallo-

graphically independent an anion $\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}^-$ and a cation $[\text{Li}(\text{DME})_3]^+$. The lanthanide ion is coordinated to two nitrogen atoms from the chelating diamide ligand and two cyclopentadienyl groups in η^5 -fashion. The coordination geometry around the lanthanide ion is best described as a pseudo-distorted tetrahedron. The lithium atom in the cation coordinated to six oxygen atoms from three DME molecules to adopt a distorted octahedral geometry. The overall structure is similar to those found for $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}[\text{Li}(\text{DME})_3]$ [9]. Some differences between the two complexes were observed: a normal monomeric ion-pair structure for complex **1**, whereas two different moieties coexisted in unit cell for complex **2**; one is normal ion-pair structure and the other is an anion $[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2$ sharing with two halves of cations $[\text{Li}(\text{DME})_3]$ (Fig. 2b). Therefore, the formulae for complex **2** is best described as $\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}[\text{Li}(\text{DME})_3]\{[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}2\{1/2[\text{Li}(\text{DME})_3]\}$.

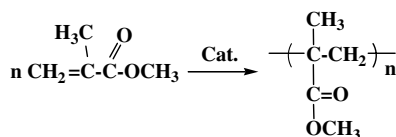
The average lanthanide–carbon (ring) bond length for **1** and **2** are 2.653 and 2.748 Å, respectively, which are comparable when the difference in the ionic radii between Yb and Sm is considered. These values can also be compared with those found in complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}[\text{Li}(\text{DME})_3]$ (2.640 Å) and $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{SmC}_5\text{H}_5\}[\text{Li}(\text{DME})_3]$ (2.727 Å) [9]. The Yb–N bond lengths in complex **1** are 2.233(6) and 2.239(6) Å, which are comparable with those for the complexes $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}[\text{Li}(\text{DME})_3]$ and $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{C}_5\text{H}_5)_2\}[\text{Li}(\text{DME})_3]$ (2.232(7)–2.250(4) Å) [9]. The Sm–N bond lengths in complex **2** range from 2.322 to

2.342 Å, which are similar to 2.340(4) and 2.332(4) Å in complex $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{SmC}_5\text{H}_5\}\{\text{Li}(\text{DME})_3\}$. The N–Ln–N angle 76.8(2)° for complex **1** and 73.45(17)° for complex **2** are larger than those observed in $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ (70.17(17)°), $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{YbC}_5\text{H}_5\}\{\text{Li}(\text{DME})_3\}$ (70.0(2)°), and $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{SmC}_5\text{H}_5\}\{\text{Li}(\text{DME})_3\}$ (67.13(15)°). The more acute N–Ln–N angle for the complexes supported by a silylene-bridged diamide ligand, $\text{PhNSi}(\text{Me})_2\text{NPh}^{2-}$ than by a phenyl bridged diamide is reasonable.

2.2. Catalytic activity of **1–3** for the polymerization of MMA

Pentamethylcyclopentadienyl lanthanide hydride(alkyl) complexes are known to polymerize MMA in a living fashion generating high syndiotactic PMMA [12,13]. In contrast, anionic allyl lanthanide complexes and anionic lanthanide amide complexes catalyzed MMA polymerization giving atactic or syndiotactic-rich PMMA depending on solvent polarity used [9,14,15].

To see the catalytic behavior of complexes **1–3**, their catalytic activity for polymerization of MMA has been tested (Scheme 2). As contrasts, the CpLi, $\text{Li}_2[o-(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]$, Cp_3Yb and bisamide lanthanide chloride were subjected to



Scheme 2.

similar polymerization conditions, trace of PMMA was formed by these complexes. The results are collected in Table 3. In comparison the represented data obtained with $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ (**4**) [9] were also included.

All the complexes were found to be efficient catalysts under mild conditions. The monomer conversion is over 75% for all the polymerizations under the conditions of $[\text{M}]/[\text{Ln}] = 500$, solvent/MMA (v/v) = 2:1, in THF at 30 °C in 3 h (Table 3, entries 1, 5 and 9). Among these complexes the polymerization activity appears to vary with the radius of the lanthanide metals. For example, the conversion reaches to 91% at the ratio $[\text{M}]/[\text{Ln}]$ of 1000(mol/mol) at 30 °C in 3 h using **1**, while 59% and 47% for **2** and **3**, respectively (Table 3, entries 2, 6 and 10). The conversion can still be 50%, even the $[\text{M}]/[\text{Ln}]$ ratio increases to 2000 in the case of **1** (entry 4). The active sequence under the present polymerization conditions is $\text{Nd} < \text{Sm} < \text{Yb}$, which is just opposite to the order of ionic radius, Nd (1.109 Å) > Sm (1.079 Å) > Yb (0.985 Å). The same active order was found for the systems of $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'\}\{\text{Li}(\text{DME})_3\}$ and anionic lanthanide allyl complexes published [14]. But the present active sequence is opposite to that for the system with neutral lanthanide allyl complex [2]. The difference in dependence of activity on ionic radius might be attributed to the different polymerization mechanism, an anionic mechanism proposed for the former cases and a coordination–insertion mechanism for the latter case. The complexes with their larger metal radii and less crowded coordination spheres are generally more active than the related complexes in coordination–insertion polymerization, whereas with a smaller thus more

Table 3
Polymerization of MMA initiated by anionic lanthanide complexes^a

	Init.	Temperature (°C)	[M]/[Ln]	Yield ^b (%)	M_n ($\times 10^4$)	M^w/M^nc	Tacticity ^d (%)		
							mm	rm	rr
1	1	30	500:1	100	2.29	1.73	20.0	26.8	53.2
2	1	30	1000:1	91	3.58	1.65	23.5	23.8	52.7
3	1	30	1500:1	71	3.71	1.79	23.5	24.2	52.3
4	1	30	2000:1	50	4.60	1.91	23.0	24.7	52.3
5	2	30	500:1	100	2.77	1.71	5.3	28.9	65.8
6	2	30	1000:1	59	4.21	1.64	4.5	30.8	64.7
7	2	30	1500:1	44	4.46	1.71	5.6	30.9	63.5
8	2	30	2000:1	32	5.20	1.66	4.7	31.9	63.4
9	3	30	500:1	75	2.81	1.77	4.5	31.0	64.5
10	3	30	1000:1	47	4.03	1.79	4.8	32.6	62.6
11	3	30	1500:1	31	4.76	1.82	5.7	31.8	62.5
12	4	30	500:1	100	3.11	1.58	13.5	30.5	56.0
13	4	30	1000:1	70	3.82	1.70	13.5	32.6	54.0
14	4	30	1500:1	48	4.21	1.77			
15	1^e	30	500:1	82	3.74	1.83	12.8	30.5	56.7
16	1^f	30	500:1	11	2.33	2.02	39.5	34.0	26.5

^a Polymerization condition: solvent/MMA (v/v) = 2:1, THF, 3 h.

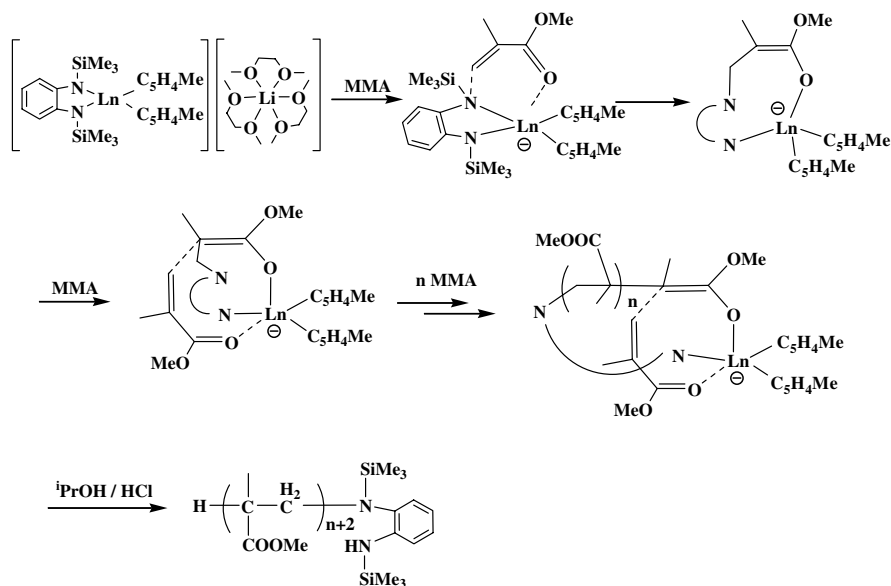
^b Yield = weight of polymer obtained/weight of monomer used.

^c Measured by GPC calibrated with standard polystyrene samples.

^d Carried out using ¹H NMR spectra in CDCl₃ 25 °C.

^e Solvent: THF/toluene = 1/1.

^f Solvent: toluene.



Scheme 3. Postulated polymerization mechanism for the polymerization of MMA.

Lewis acidity metal ion shows more effective monomer-coordination than the larger metal in anionic polymerization.

An anionic mechanism was also supported by the results obtained in different solvents. In the case of complex **1**, the conversion in THF is much higher than that in toluene and the conversion increases with the increasing of THF (Table 3, entries 1, 15 and 16). Recent studies have emphasized the effect of solvent polarity on both activity and microstructure of the resulting PMMA, with more polar solvents THF and dimethoxyethane for the system $[(\text{Me}_3\text{Si})_2\text{N}]_3\text{-Ln}(\mu\text{-Cl})\text{-Li}(\text{THF})_3$ ($\text{Ln} = \text{Nd}, \text{Sm}, \text{and Eu}$) giving increased syndiotacticity [15]. The complex **1** showed a similar behavior, with an rr triad content in THF of up to 53%, while atactic PMMA in toluene (Table 3, entries 1 and 16). The same effect of solvent on the polymer yield and microstructure of PMMA can also be found in other anionic polymerizations of MMA [9,16,18].

The activity is ligand-dependent. For example, the polymer yield reaches to 91% in $[\text{M}]/[\text{Ln}]$ ratio of 1000 at 30 °C in 3 h using **1** as the initiator, while 70% for **4** under the same conditions (Table 3, entries 2 and 13). The active order for the chelating diamide ligand is $[o\text{-(Me}_3\text{SiN)}_2\text{-C}_6\text{H}_4]^{2-} > [\text{Me}_2\text{Si}(\text{NPh})_2]^{2-}$.

It is noteworthy that all the polymers obtained with these anionic complexes showed a unimodal molecular weight distribution, indicating the catalysts really play the role of single-component initiators in the polymerization of MMA. The system produced the polymers with much high molecular weights ($M_n > 10^4$) and relatively narrow molecular weight distributions ($M_w/M_n = 1.64\text{--}1.82$), which is comparable with those of anionic initiators of $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}\{\text{Li}(\text{DME})_3\}$ [9] and better than that with anionic complex $[(3,6\text{-}^t\text{Bu}_2\text{C}_{13}\text{H}_6)\text{Si-Me}_2\text{N}^t\text{Bu}]_2\text{La}][\text{Li}(\text{THF})_4]^+$ [16]. Triad microstructural

analysis of the resulting polymers was carried out using ^1H NMR spectra in CDCl_3 according to the literature [17]. The present polymerization systems all yielded the syndiotactic-rich PMMA and the contents of syndiotacticity range from 52% to 66%.

In order to understand further the possible polymerization mechanism, an oligomer of MMA was prepared from the oligomerization of MMA by using **1** as the initiator with a $[\text{MMA}]/[\text{Ln}]$ (molar ratio) of 10 and terminated by isopropyl alcohol. The end-group analysis of ^1H NMR spectroscopy (CDCl_3 , without TMS) revealed that the polymer contained an amide end-group appeared at 0.05 ppm as a single peak and around 6.10 ppm as multiplets. The results of end-group analysis are consistent with that published previously for the system with $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{LnCp}'_2\}\{\text{Li}(\text{DME})_3\}$ [15]. The postulated anionic polymerization mechanism might be suggested according to the value of molecular weights of the resulting polymers and the end-groups analysis. As shown in Scheme 3, the N of the amide attacks the CH_2 group of MMA to generate a transient species, and the incoming MMA molecule may participate in a 1,4-addition to afford an eight-membered ring intermediate. Then, another MMA molecule may attack the growing end, liberating the coordinated ester group. The polymerization should proceed by repeating these pathways.

3. Conclusion

In summary, a series of anionic lanthanocene complexes $\{[o\text{-(Me}_3\text{SiN)}_2\text{C}_6\text{H}_4]\text{Ln}(\text{MeC}_5\text{H}_4)_2\}\{\text{Li}(\text{DME})_3\}$ [$\text{Ln} = \text{Yb}$ (**1**), Sm (**2**), Nd (**3**)] have been successfully synthesized for the first time. Their structural features of **1** and **2** have been determined by X-ray diffraction study. These anionic complexes were found to be efficient single-component initiators

for the polymerization of MMA under mild conditions, giving syndiotactic-rich polymers.

4. Experimental

All manipulations were performed under pure Ar with rigorous exclusion of air and moisture using standard Schlenk techniques. Solvents were distilled from Na/benzophenone ketyl prior to use. The chelating diamide ligand $H_2\text{-}o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ [11], anhydrous LnCl_3 [19] and the anionic complex $\{[\text{Me}_2\text{Si}(\text{NPh})_2]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}\text{-}\{\text{Li}(\text{DME})_3\}$ **4** [9] were prepared according to the literature procedures. MMA (99%) was distilled over CaH_2 and stored over molecular sieves 4 Å at 0 °C under argon. Molecular weight (M_n) and molecular weight distributions (M_w/M_n) were determined against polystyrene standard by gel permeation chromatography (GPC) on a waters 1515 apparatus with three HR columns (HR-1, HR-2, and HR-4 columns, effective molecular weight range, 100–5000, 500–20000, and 5000–5000000, respectively). THF was used as an eluent at a flow rate of 1.0 mL/min at 30 °C. The melting point was determined in sealed Ar-filled capillary tubes. Carbon, hydrogen and nitrogen analyses were performed by direct combustion on a Carlo—Erba EA 1110 instrument. Analysis of Ln was carried out by complexometric titration of EDTA. The IR spectra were recorded on a Magna-IR 550 spectrometer. ^1H NMR spectra were measured on a Unity Inova-400 spectrometer in C_6D_6 or CDCl_3 .

4.1. Synthesis of $\{[o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Yb}(\text{MeC}_5\text{H}_4)_2\}\text{-}\{\text{Li}(\text{DME})_3\}$ (**1**)

A Schlenk flask was charged with $H_2\text{-}o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ (0.99 g, 3.91 mmol, 10 mL hexane) and a stir bar. The solution was cooled to 0 °C, and $n\text{-BuLi}$ (5.55 mL, 7.82 mmol, 1.41 M in hexane) was added. The solution was slowly warmed to room temperature and stirred for 1 h. Then this solution was added slowly to a pale-gray slurry of YbCl_3 (1.09 g, 3.90 mmol) in 15 mL of THF. The mixture was stirred for 5 h at room temperature, and then $\text{MeC}_5\text{H}_4\text{Na}$ (11.64 mL, 7.80 mmol, 0.67 M in THF) was added. The resulting solution was then stirred for another 48 h and the solvent was removed under vacuo. The residue was extracted with DME and LiCl was removed by centrifugation. Concentration of the extracts and crystallization at 0 °C for few days gave **1** as blue-green crystals (2.62 g, 78%). Mp: 109–110 °C (dec). The ^1H NMR spectrum of this compound displayed very broad resonances and proved uninformative because of the paramagnetism of ytterbium metal. Anal. Calc. for $\text{C}_{36}\text{H}_{66}\text{N}_2\text{LiO}_6\text{Si}_2\text{Yb}$: C, 50.33; H, 7.74; N, 3.26; Yb, 20.14. Found: C, 50.02; H, 7.65; N, 3.52; Yb, 20.33%. IR (KBr pellet, cm^{-1}): 2957 (w), 1626 (m), 1596 (m), 1504 (s), 1441 (m), 1381 (w), 1298 (w), 1249 (s), 1157 (s), 1043 (w), 920 (w), 893 (w), 843 (m), 748 (m), 625 (m), 554 (w), 504 (m), 457 (w).

4.2. Synthesis of $\{[o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Sm}(\text{MeC}_5\text{H}_4)_2\}\text{-}\{\text{Li}(\text{DME})_3\}$ (**2**)

Following the procedure similar to the synthesis of **1**, the reaction of $\text{Li}_2\text{-}o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ (3.54 mmol, 15 mL hexane), SmCl_3 (0.91 g, 3.54 mmol) and $\text{MeC}_5\text{H}_4\text{Na}$ (10.57 mL, 7.80 mmol, 0.67 M in THF) in 40 mL THF afford **2** as orange-yellow crystals (2.13 g, 72%). Mp: 199–200 °C. ^1H NMR (400 MHz, C_6D_6 , 25 °C): δ = 6.54–6.99 (m, 12H, *H*-Ph, *H*-Cp); 3.38 (m, 12H, OCH₂); 3.17 (m, 18H, OCH₃); 1.91 (s, 6H, CpCH₃); 0.27 (s, 18H, SiCH₃). Anal. Calc. for $\text{C}_{36}\text{H}_{66}\text{N}_2\text{LiO}_6\text{Si}_2\text{Sm}$: C, 51.70; H, 7.95; N, 3.35; Sm, 17.98. Found: C, 51.42; H, 7.75; N, 3.54; Sm, 18.36%. IR (KBr pellet, cm^{-1}): 2964 (m), 1621 (m), 1505 (m), 1397 (m), 1227 (s), 1158 (s), 1058 (w), 965 (w), 911 (w), 841 (w), 749 (w), 633 (m), 548 (w), 502 (m).

4.3. Synthesis of $\{[o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4]\text{Nd}(\text{MeC}_5\text{H}_4)_2\}\text{-}\{\text{Li}(\text{DME})_3\}$ (**3**)

Following the procedure similar to the synthesis of **1**, the reaction of $\text{Li}_2\text{-}o\text{-}(\text{Me}_3\text{SiN})_2\text{C}_6\text{H}_4$ (3.91 mmol, 18 mL hexane), NdCl_3 (0.98 g, 3.91 mmol) and $\text{MeC}_5\text{H}_4\text{Na}$ (11.67 mL, 7.82 mmol, 0.67 M in THF) in 40 mL THF at 40 °C afford **3** as blue-green crystals (2.27 g, 70%). Mp: 127–128 °C. The ^1H NMR spectrum of this compound displayed very broad resonances and proved uninformative. Anal. Calc. for $\text{C}_{36}\text{H}_{66}\text{N}_2\text{LiO}_6\text{Si}_2\text{Nd}$ (830.27): C, 52.08; H, 8.01; N, 3.37; Nd, 17.37. Found: C, 52.01; H, 7.85; N, 3.52; Nd, 17.65%. IR (KBr pellet, cm^{-1}): 2956 (m), 1729 (w), 1605 (m), 1505 (s), 1405 (s), 1297 (w), 1250 (s), 1158 (w), 1034 (w), 965 (m), 918 (m), 841 (m), 749 (m), 679(w), 625 (w), 556 (m), 509 (m).

4.4. X-ray structural determination of **1** and **2**

Owing to air and moisture-sensitivity, the suitable single crystals of complexes **1–2** were each sealed in thin-walled glass capillaries for singlecrystal structure determination. Intensity data were collected on a Rigaku Mercury CCD equipped with graphite monochromatized Mo K α (λ = 0.71070 Å) radiation. The crystal structure was solved by a direct method and expanded by Fourier techniques. Atomic coordinates and thermal parameters were refined by full-matrix least-squares analysis on F^2 . All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were all generated geometrically with assigned appropriate isotropic thermal parameters. The structures were solved and refined using SHELXS-97 and SHELXL-97 programs.

4.5. A typical procedure for polymerization reactions

All polymerizations were carried out in 50 mL Schlenk flask under dry Ar atmosphere with a similar procedure. A typical polymerization reaction was given below (Table 3, entry 1). A 50 mL Schlenk flask equipped with a

magnetic stir bar was charged with a solution of 1 mL MMA in THF (0.14 mL). To this solution was added 1.86 mL solution of complex **1** in THF (1.0×10^{-2} M, 1.86×10^{-3} mmol) using rubber septum and syringe. The contents of the flask were then vigorously stirred for 3 h at 30 °C. The polymerization was quenched by ethanol with 5% HCl, precipitated from ethanol, dried under vacuum and weighed.

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Appendix A. Supplementary material

CCDC 634135 and 634136 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.03.016](https://doi.org/10.1016/j.jorganchem.2007.03.016).

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