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Lanthanide borohydrido complexes for MMA polymerization: syndio- vs iso- stereocontrol

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This paper presents an extensive study of the polymerization of MMA with borohydrido lanthanide complexes for the first time. Catalytic systems are made from a lanthanide derivative bearing zero one, or two bulky ligands: substituted cyclopentadienyl ($Cp^{*\prime} = C_5Me_4nPr$, $Cp^{4i} = C_5HiPr_4$, $Cp^{Ph3} = H_2C_5Ph_3$-1,2,4), and/or diketiminate ([(*p*-tol)NN] = [(*p*-$CH_3C_6H_4$)N(CH_3)C]$_2$CH), in the presence of variable quantities of alkylating agent. With BuLi in apolar medium, highly isotactic polymer (up to 95.6%) is formed. In THF, syndiotactic-rich PMMA is obtained whatever the nature of the co-catalyst (BuLi or Mg^nBu_2). The presence of an electron-withdrawing ligand such as Cp^{Ph3} allows high syndioregularity, up to 81.8% at 0 °C, together with the highest conversion. There is quite good concordance between calculated and experimental molecular data in THF. Divalent $Cp^{*\prime}{}_2Sm^{II}$(THF) and $(Cp^{Ph3})_2Sm^{II}$(THF) are active as single-component initiators; the former affords PMMA 88% syndiotactic at 0 °C. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: lanthanides; borohydride; MMA polymerization; PMMA; tacticity

INTRODUCTION

During the last two decades the use of organolanthanide complexes for catalysis has developed extensively,[1] especially in favour of polymerization.[2,3] Among these complexes, hydrides and alkyls are the most preferred. However, if the lanthanide hydrides have been proved to be powerful catalysts for many interesting chemical transformations, their access remains a challenging problem, since they are exceedingly reactive.[4] Also, they are obtained by hydrogenolysis of alkyl derivatives, which require rigorous protection against air or moisture.[5] More recently, some new trends have appeared, such as the search for alternatives to the ubiquitous [Ln]-H or [Ln]-R functions, i.e. the *in situ* alkylation of a pre-catalyst,[6] or the use of borane-supported hydrides [Ln]-HBR_3[7] or borohydrides [Ln]-BH_4.[8] In sharp contrast to [Ln]-H compounds, complexes bearing a [Ln]-BH_4 function are easily obtained and very stable. Lanthanide borohydrides have been described as active towards ε-caprolactone polymerization, showing a behaviour very similar to that of a pure lanthanide hydride.[9] On the other hand, towards apolar monomers, such compounds display a typical halide behaviour: the presence of a MgR_2 co-catalyst is necessary to enable isoprene[10] or ethylene[11] polymerization.

The controlled polymerization of methyl methacrylate was thoroughly explored in the 1990s,[12,13] and particularly with lanthanide initiators.[14–18] Among the reasons for this interest is the search for processes affording high-value materials, like syndiotactic PMMA.[19–21] Lanthanide complexes[3,14,16,19,22–24] have been found to be particularly efficient for this purpose, with syndiotacticity exceeding 95%, but obtained at a very low (−95 °C) temperature. The high syndioregularity seems to be correlated to the use of ancillary bulky ligands, diketiminate or peralkylated Cp groups, but earlier studies also showed the importance of the solvent,[25–27] and the presence of a co-catalyst.[28] Anionic polymerization of MMA initiated by cuprate reagent resulted in highly syndiotactic materials when the experiments were conducted in polar solvent,[29] and were predominantly isotactic in toluene.[30]

In the course of our studies concerning the evaluation of lanthanide borohydrides for polymerization,[10,11,31] we investigated the potential of such versatile compounds as

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initiators vs MMA. Experiments were carried out with different borohydrido complexes bearing 1, 2 or 3 BH_4 functions. The results are presented and discussed in the following paper in terms of nature of the metal (Sm or Nd), electron donation ability and bulkiness of the ancillary ligands. The role of the polarity of the solvent and the presence of different alkylating reagents as co-catalysts were also investigated.

EXPERIMENTAL

Materials and methods

All manipulations were carried out under argon atmosphere and using a Jacomex glove box and standard Schlenk techniques. Toluene and THF (Aldrich) were dried and deoxygenated by storage over sodium–benzophenone ketyl before use. BuLi (1.6 M hexane) and $Mg^{n}Bu_2$ (1.0 M heptane; Aldrich) were used as received. $(2,6\text{-}^{t}Bu\text{-}4\text{-}Me\text{-}C_6H_3O)_2AlEt$ was prepared as described.[22,35] MMA (Aldrich) was washed in 10% wt NaOH, then in deionized water until neutral pH. The monomer was distilled and dried twice on CaH_2, stored under argon over molecular sieves and redistilled before use. ^1H NMR spectra were recorded on a Bruker Avance 300 spectrometer at 300 K. Chemicals shifts are expressed in parts per millions downfield from external TMS. Elemental analyses were performed with a Fisons EA 1108 CHON apparatus.

The syntheses of KCp^{Ph3} ($Cp^{Ph3} = H_2C_5Ph_3$-1,2,4),[43] [(*p*-tol)NN]K ([(*p*-tol)NN] = $[(p\text{-}CH_3C_6H_4)N(CH_3)C]_2CH$[44] and of the lanthanides complexes: $Ln(BH_4)_3(THF)_3$ [Ln = Nd (**1a**), Sm (**1b**)],[45] $Cp^{*\prime}Ln(BH_4)_2(THF)_2$ [Ln = Nd (**2a**), Sm (**2b**)] ($Cp^{*\prime} = C_5Me_4nPr$),[36] $Cp^{4i}_2Sm(BH_4)$ (**4**) ($Cp^{4i} = C_5HiPr_4$),[46] $Cp^{*\prime}Ln\{(p\text{-}tol)NN\}(BH_4)$ [Ln = Nd (**7a**), Sm (**7b**)],[44] $Cp^{4i}_2Sm^{II}$ (**9**)[41] $Cp^{*\prime}{}_2Sm^{II}(THF)$ (**10**),[40] and $(Cp^{Ph3})_2Sm^{II}(THF)$ (**11**)[40] were described in the referenced papers.

Attempted synthesis of $Cp^{Ph3}Sm(BH_4)_2(THF)_2$ (3)

The bulk synthesis was performed as described for **2b**. A flame-dried vessel was charged in the glove box with 452 mg (1.10 mmol) of $Sm(BH_4)_3(THF)_3$ (**1b**) and 365 mg (1.10 mmol) of KCp^{Ph3}. The vessel was connected to the vacuum line, and toluene (40 mL) was added by vacuum distillation. After 16 h stirring at room temperature, the usual work-up afforded 680 mg of a red powder. ^1H NMR analysis showed the formation of two set of signals compatible with the formation of $(Cp^{Ph3})Sm(BH_4)_2(THF)_2$ (**3**) (major product, 85%) and $(Cp^{Ph3})_2Sm(BH_4)(THF)$ (**6**) (minor product, 15%). By addition of the required quantity of KCp^{Ph3}, the signals of **6** decreased significantly. It was observed that the addition of a very large excess of **1b** was necessary to eliminate the signals of **6**. Attempts to purify **3** by selective crystallization failed: according to ^1H NMR, it was always contaminated by 10–15% **6**. ^1H NMR (C_6D_6): 10.0 (s, 2H, HCp), 7.85 (dd, 2H, *o′*-Ph), 7.55 (d, 4H, *o*-Ph), 7.02 (m, 3H, *m′p′*-Ph), 6.95 (t, 2H, *p*-Ph), 6.85 (t, 4H, *m*-Ph), 2.8 (16H, THF), 0.5 (16H, THF), −9.2 (m, 8H, BH_4). A second synthesis was performed by mixing **6**, 200 mg (0.242 mmol) and **1b**, 110 mg (0.27 mmol) in 20 ml of toluene. The solution was refluxed for 16 h, then evaporated and extracted with pentane affording 210 mg of crude material. As before, the isolated product contained nearly 20% of **6** (NMR control). Obviously the mono-substituted complex **3** is in equilibrium with **1b** and **6**, as frequently observed for ligands of poor electron donating ability.[47,48] Crude **3** was thus used just as it is for further polymerization experiments.

Direct synthesis of $(Cp^{Ph3})_2Sm(BH_4)(THF)$ (6)

A flame-dried vessel was charged in the glove box with 151.8 mg (0.36 mmol) of $Sm(BH_4)_3(THF)_3$ and 243.6 mg (0.72 mmol) of KCp^{Ph3}, then 5 mL of toluene were added by vacuum transfer. The resulting solution was stirred for one night under argon atmosphere at room temperature. An orange solution was obtained. The solvent was evaporated and the precipitate was extracted twice with 10 mL of pentane. The solution was dried, giving a red powder ($m = 225$ mg, 75.6%). A sample of analytical purity was isolated as a toluene solvate, after two pentane–toluene extraction allowing the elimination of remaining salts. Anal. calcd for $C_{50}H_{46}OSmB$, 0.5 toluene: C 73.84; H 5.79; found C 74.17; H 5.55. ^1H NMR (C_6D_6) was identical as observed for an NMR synthesis of **6** by adding in C_6D_6 5.2 mg ($1.26\,10^{-5}$ mol) of **1b** to 8.4 mg ($2.53\,10^{-5}$ mol) of KCp^{Ph3}: 12.7 (s, 2H, HCp), 11.0 (s, 2H, HCp), 9.2 (br, 4H, o_1-Ph), 7.2 (br, 6H, m_1, p_1-Ph), 7.0 (d, 4H, *o*-Ph), 6.7 (t, 2H, *p*-Ph), 6.6 (t, 4H, *m*-Ph), 6.4 (t, 2H, p_2-Ph), 6.0 (br, 4H, m_2-Ph), 5.0 (br, 4H, o_2-Ph), −1.6 (d, 8H, THF), −16.3 (m, 4H, BH_4).

Synthesis of $(Cp^{Ph3})Sm\{(p\text{-}tol)NN\}(BH_4)$ (8)

A flame-dried vessel was charged in the glove box with 410 mg (0.1 mmol) of $Sm(BH_4)_3(THF)_3$ (**1b**), 332 mg (0.1 mmol) of KCp^{Ph3} and 330 mg (0.1 mmol) of (*p*-tol)NNK then 50 mL of toluene were added by vacuum transfer. A red solution was obtained after 22 h stirring. The solution was dried and the solid was extracted with pentane. After slow evaporation, an orange powder was obtained ($m = 420$ mg, 57.5%). Anal. calcd for $C_{46}H_{50}OSmBN_2$: C 68.53; H 5.57; N 3.80; found C 67.45; H 6.15; N 4.12. ^1H NMR (C_6D_6): 10.12 (s, 1H, H diimine), 9.28 (d, 2H, *o′*-Ph), 8.89 (d, 4H, *o*-Ph), 7.86 (t, 2H, *m′*-Ph), 7.72 (t, 1H, *p′*-Ph), 7.25 (2t, 6H, *m*,*p*-Ph), 5.29 (s, 2H, HCp), 3.28 (d, 4H, *p*-tol), 3.15 [s, 3H, Me(*p*-tol)], 0.099 (s, 6H, N-Me), −1.45 [m, 4H, Me(*p*-tol)], −6.2 (m, 4H, BH_4).

In situ preparations of 4′, 5′, 6′

The procedure was different for these compounds; they were not isolated but prepared *in situ* by mixing the reactants, and the resulting solution was used as it was for subsequent polymerization experiments: starting materials (**1b**, 10.3 mg, 25×10^{-3} mmol + KCp^{4i}, 13.4 mg, 50×10^{-3} mmol; **2a**, 10.5 mg, 22×10^{-3} mmol + $KCp^{*\prime}$, 5.3 mg, 26×10^{-3} mmol; **3**, 13.7 mg, 22×10^{-3} mmol + KCp^{Ph3}, 8.4 mg, 25×10^{-3} mmol, respectively) were charged in a vessel containing the required solvent (THF or toluene, 5 mL). The mixture was stirred at room temperature for several hours. A 5 mL aliquot of solvent were added just before polymerization. Considering that the expected compound was quantitatively formed in the case of **4′** and **6′** (^{1}H NMR check, by comparison with spectral data of the known products **4** and **6**), the method, which had also proved efficient for the synthesis of $Cp^{*\prime}{}_2Sm(BH_4)(THF)$ (anal. calcd for $C_{46}H_{50}OSmBN_2$: C 68.53; H 5.57; N 3.80; found C 67.45; H 6.15; N 4.12, to be published), was adopted for **5′** as well.

Polymerization of MMA

In a glove box, to a solution containing the pre-catalyst (2.5×10^{-5} mol) dissolved in 10 mL of solvent or the *in situ* freshly prepared pre-catalyst (see above), was added the required amount of co-catalyst at room temperature. The vessel was sealed with a glass stopper and a rubber septum. After stirring for 5 min, the vessel was transferred on a Schlenk line at the desired temperature. The polymerization was started by direct addition of monomer to the catalyst solution by means of a syringe. The mixture was then allowed to stir for a given time or until the viscosity of the medium had stopped the magnetic barrel. The experiment was ended up by opening the vessel in air and the successive addition of standard water-containing solvent. The solution was poured in ethanol with vigorous stirring, leading to the precipitation of the polymer, which was filtrated and dried 24 h under vacuum at room temperature.

Characterization of PMMA

^{1}H NMR was recorded on Bruker AC 300 using $CDCl_3$ as solvent at 300 K. Chemical shifts were referenced to residual $CHCl_3$ in the solvent ($\delta = 7.26$ ppm). Molecular weights were determined by size exclusion chromatography on a Gynkotek P580A apparatus equipped with two Jordi Gel DVB mixed B columns and an IOTA 2 refractive index detector. Polymer samples were dissolved in THF (10 mg mL^{-1}) and elution was performed at 1 mL min^{-1} in THF at 20 °C. Number-average molecular weights ($\overline{M}_n$) and polydispersity indices ($\overline{M}_w/\overline{M}_n$) of PMMA are given with respect to polystyrene standards. Differential scanning calorimetry (DSC) measurements were performed on a TA Instruments 2920 DSC. Samples of ca. 10 mg were scanned under nitrogen flow (60 mL min^{-1}; ramp rate 10 °C min^{-1}). Glass transition temperatures were determined on the second scan to ensure identical thermal histories.

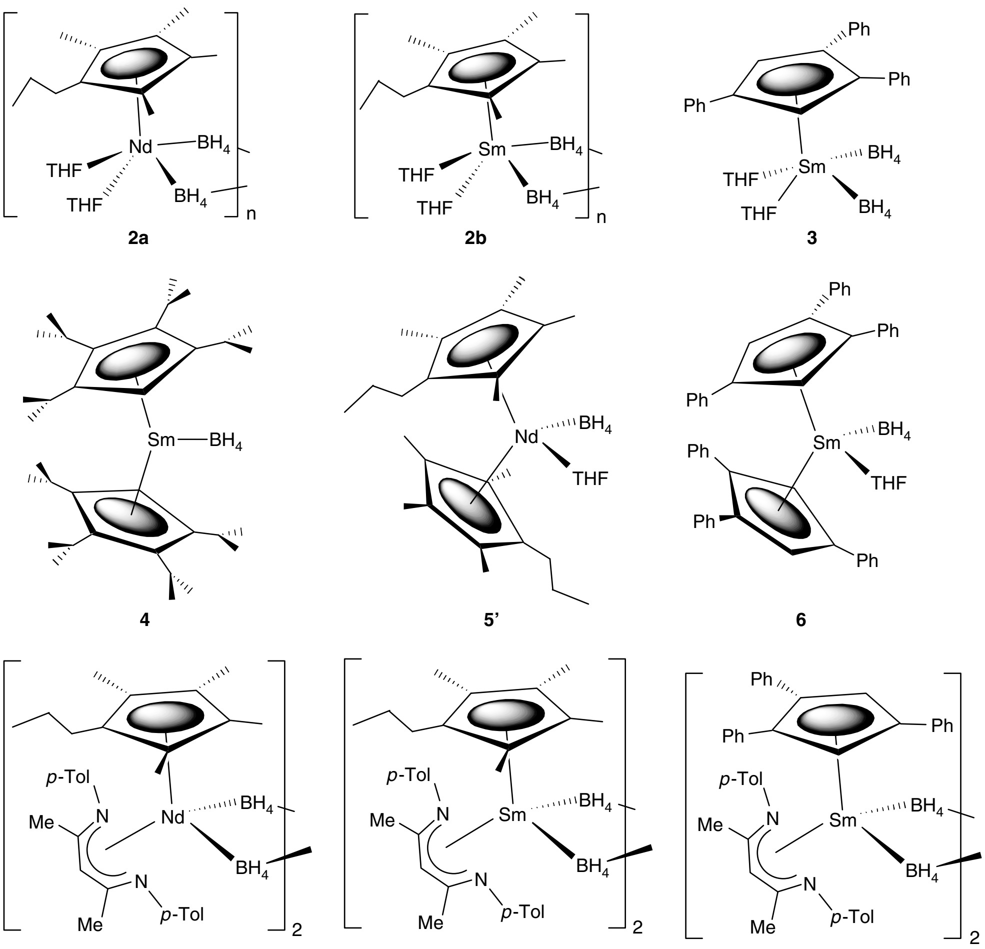
RESULTS AND DISCUSSION

Preliminary experiments were conducted by using $Cp_2^{4i}Sm(BH_4)$ (**4**), in the absence of co-catalyst. With a MMA : **4** ratio of 50, quantitative consumption of the monomer was obtained within 4 h at room temperature. The polydispersity was acceptable, 1.45, but the $\overline{M}_n$ value was found to be much higher than expected (ca. 100 times higher), denoting that only a small percentage of the catalyst had initiated the reaction. However, these preliminary results were considered motivating since significant control of the tacticity (rr 76%) was observed, in sharp contrast to the conventional, aspecific, radical polymerization of MMA.

The formation of such a high molecular weight polymer was tentatively attributed to the mechanism of the initiation reaction. Indeed, a borohydride group can react with a conjugated carbonyl function, following 1,2- or 1,4-addition. As shown by Yasuda *et al.*, only the latter pathway leads to an enolate, active in MMA polymerization,[14] whereas, upon 1,2- addition, the resulting alkoxy group is inactive towards the monomer. It is well known that hard hydrides or Grignard reagents lead preferentially to 1,2-addition, whereas soft reagents such as cuprates give rise to a major ratio of 1,4-addition.[32] Whereas a reagent made from a group III metal remains essentially hard in nature, the controlled polymerization of MMA could, however, be obtained from lanthanide alkyl organometallic derivatives.[33] In order to induce a softer character, we attempted to change the hard (boro)hydride ligand for a softer carbon derivative. A series of neodymium and samarium borohydrides complexes were used in this frame. Borohydrides groups were substituted by zero (S0), one (S1) or two (S2) sterically demanding groups (Fig. 1), and we studied the activity of such complexes, as pre-catalysts, in the presence of variable quantities of alkylating reagent.

S0 systems

Table 1 summarizes the results of MMA polymerization obtained with $Nd(BH_4)_3(THF)_3$ (**1a**) and three equivalents of Mg^nBu_2 or four equivalents of BuLi. The choice of this stoichiometry resulted from a previous study devoted to the use of **1a** as an initiator for conjugated diene polymerization.[31] Blank experiments performed with BuLi at 0 °C in toluene and THF afforded isotactic-rich or syndiotactic-rich polymer, respectively, but in very low yields (runs 5, 8). The polymerization of MMA was first performed at −40 °C, in polar (tetrahydrofuran) or non-polar solvent (toluene or hexane). In standard conditions, yields up to 80% (runs 3, 4, 6 and 7) were observed. From Table 1, the nature of the solvent had a decisive influence on the course of the reaction, as also emphasized in a recent study:[34] in THF, whatever the reagent, lithium or magnesium alkyl, a highly syndiotactic material was formed. In contrast, if the reaction was performed in toluene, the choice of the alkylating reagent had a major influence. In the presence of Mg^nBu_2, no stereocontrol was observed (run 2), whereas the use of BuLi led to a highly isotactic PMMA (run 4). Good stereocontrol could be obtained at 0 °C, by adding an aluminium phenoxide (run 3), known to be an activator for MMA polymerization.[22,35] This additive had a major effect in the absence of alkyl co-catalyst, allowing the formation of highly syndiotactic PMMA (run 1). With BuLi as an alkylating agent, activity was also noticeably increased in the presence of the aluminium additive (95% in 3 h for run



2a **2b** **3** **4** **5’** **6** **7a** **7b** **8**

Figure 1. Lanthanide complexes used as pre-catalysts.

Table 1. Results of MMA polymerization using $Nd(BH_4)_3(THF)_3$ **(1a)** as pre-catalyst[a]

Run	Co-catalyst[b]	Solvent	Time (h)	Yield (%)	$10^{-3} \times \overline{M}_n$[c]	PDI[d]	Triad fractions (%) mm	mr	rr
1[e]	—	tol	3	10	35.4	1.8	0.4	18.2	81.4
2[e]	Mg^nBu_2	tol	3	20	7.4	1.8	38.2	19.4	42.4
3[e]	BuLi	tol	3	95	41[g]	1.9	92.7	6.3	1.0
4	BuLi	tol	23	92	34[g]	—	93	6.2	0.8
5[f]	BuLi	Tol	65	27	85	4.7	85.4	10.0	4.6
6	Mg^nBu_2	THF	6	78	45[g]	—	5.7	23.8	70.5
7	BuLi	THF	23	81	110	2.1	2.7	21.8	75.5
8[f]	BuLi	THF	65	6.7	—[h]	—	3.1	22.3	74.6

[a] $T = -40\,°C$, $[Nd] = 2.5 \times 10^{-3}$ M, $[MMA]/[Nd] = 500$.
[b] Mg^nBu_2: three equivalents per Nd; BuLi: four equivalents per Nd.
[c] Determined by SEC against PS standards.
[d] $PDI = \overline{M}_w/\overline{M}_n$.
[e] In the presence of $(2,6\text{-}^tBu\text{-}4\text{-}Me\text{-}C_6H_3O)_2AlEt$ (one equivalent per Nd); $T = 0\,°C$.
[f] In the absence of organometallic pre-catalyst.
[g] In the presence of a shoulder at high molecular weights.
[h] Undetermined.
mm: isotactic triad rate.
mr: atactic triad rate.
rr: syndiotactic triad rate.

3; to be compared with 92% in 23 h for run 4), whereas the tacticity was unchanged.

Most of these results were interesting in terms of stereocontrol, but they were less satisfactory concerning the molecular weights concordance, between measured $\overline{M}_{n(\text{meas.})}$ and calculated $\overline{M}_{n(\text{calc.})}$ obtained according to the following relationship:

$$\overline{M}_{n(\text{calc.})} = \{([\text{monomer}]/[\text{Nd}]) \cdot \text{yield}\}/[\text{co-catalyst}]$$

In most cases, SEC analysis indicated too high molecular weights (110 000 measured for 10 000 expected, run 7, for example). In the presence of an Al activator, the control of macromolecular data was improved, with narrower PDI (ca. 1.8, runs 1–3).

S1 systems

Monocyclopentadienyl complexes of the early lanthanides are known to be stable with respect to disproportionation in case of bulky Cp groups only.[36,37] We used as sterically demanding ligands substituted Cp groups: Cp$^{*\prime}$ and Cp$^{\text{Ph3}}$, the latter being very bulky but with fewer donors than a peralkylated one (Fig. 1). Experiments were conducted at 0 °C and results are summarized in Table 2. In THF, the **2a**–BuLi system allowed a syndio control (rr 72.7%, run 9) which is close to that obtained at −40 °C (rr 75.5%, run 7, Table 1). One may observe that, if activities were in general sensibly lower for half-lanthanidocenes in comparison with **1a** (Table 1), the stereocontrol was preserved at 0 °C. In toluene, an excellent iso-control was observed (mm 93.6%, run 10), but yields were lower and molecular weights remained much higher than expected. On that subject, one can remember that the monoCp complex Cp$^{*\prime}$Sm(BH$_4$)$_2$ is not monomeric:[36] it was identified as an associated form, hexanuclear clusters. It is probable that, in toluene, even in the presence of the polar monomer, and after the addition of an alkylating reagent, the precursor remained under an associated form, giving rise to an initiating species that was clearly not a well-defined monomolecular one. On the other hand, in THF, the bridges formed by R or BH$_4$ groups were usually broken and definite monomeric species were formed. No stereospecificity was observed with **2b** and Mg^{n}Bu$_2$ (stoichiometric amount or excess, runs 11, 12) as co-catalyst, whereas the presence of Cp$^{\text{Ph3}}$ ligand seems to induce some syndio-control (run 14).

S2 systems

To be sure that in non-polar solvent the initiators would be under a non-associated form, the use of disubstituted borohydrides seemed opportune: even in non-coordinating solvents, these electron-rich complexes of formula L$_2$Ln(BH$_4$) remain generally monomeric, eventually dimeric, but these dimers are easily cleaved by polar molecules. Ligands were chosen among Cp groups, the same as for the S1 systems, but in order to vary the electronic density around the metal, another bulky ligand, the diketiminate [(p-CH$_3$C$_6$H$_4$)N(CH$_3$)C]$_2$CH, referred to as [(p-tol)NN], was used. This coordinate was in some cases considered as a six-electron ligand like a cyclopentadienyl, but it is essentially dihapto, bonded by the nitrogen atoms and is considered as less of a donor than a Cp group.[38] The difference in the access to the metal governed by the different ligands might induce different stereochemistry for the polymerization reaction. Metallocene **4** and heteroleptic pre-catalysts **7a, 7b** were available in the laboratory, and complexes **6** and **8** were prepared as described (see the Experimental). In some cases, pre-catalysts were prepared directly *in situ*, by addition of the required amount of anionic ligand to a trisborohydride or a bisborohydride precursor, followed by a convenient pre-reaction time. They are noted as **4′** (**1b** + 2KCp^{4i}), **5′** (**2a** + KCp$^{*\prime}$) and **6′**(**3** + KCp$^{\text{Ph3}}$). Selected results are gathered in Table 3.

Table 2. Results of MMA polymerization using monosubstituted organolanthanide pre-catalysts

						Triad fractions (%)				
Run[a]	Pre-catalyst	Co-catalyst[b]	Solvent	Time (h)	Yield (%)	mm	mr	rr	$10^{-3} \times \overline{M}_n$[c]	PDI[d]
9	**2a**	BuLi	THF	19	92	0	27.3	72.7	21.4	2.0
10	**2a**	BuLi	tol	19	48	93.6	5.4	1.0	203/10.6[g]	—
11	**2b**	Mg^{n}Bu$_2$[e]	tol	23	33	48.4	10.5	41.1	—[h]	—
12	**2b**	Mg^{n}Bu$_2$[f]	tol	6	45	40.8	19.6	39.6	—[h]	—
13	**3**	BuLi	tol	16	23	84.1	7.0	8.9	2100/77[g]	n.d.
14	**3**	Mg^{n}Bu$_2$	tol	16	70	16.9	18.1	65.0	1500/210/17[i]	2.0

[a] $T = 0$ °C, [Ln] = 2.5×10^{-3} M, [MMA]/[Ln] = 500.
[b] Mg^{n}Bu$_2$: two equivalents per Ln; BuLi: three equivalents per Ln.
[c] Measured by SEC against PS standards.
[d] PDI = $\overline{M}_w/\overline{M}_n$.
[e] One equivalent per Nd.
[f] Ten equivalents per Nd.
[g] Bimodal.
[h] Undetermined.
[i] Multimodal.

Table 3. Results of MMA polymerization using disubstituted organolanthanide catalysts

						Triad fractions (%)				
Run[a]	Pre-catalyst	Co-catalyst[b]	Solvent	Time (h)	Yield (%)	mm	mr	rr	$10^{-3} \times \overline{M}_n$[c]	PDI[d]
15[e]	**4**	—	tol	4	100	—	—	68.0	540	1.45
16[f]	**4**	BuLi	tol	22	38	92.3	6.3	1.4	337/16[g]	—
17	**4′**	BuLi	tol	20	33	85.2	11.0	3.8	506/15[g]	
18	**4′**	Mg^nBu_2	tol	20	45	40.7	20.3	39.0	12.5[h]	—
19	**5′**	BuLi	THF	21	89	0	27.7	72.3	31	2.1
20	**5′**	Mg^nBu_2	THF	21	33	3.6	18.1	78.3	30.5	3.6
21	**5′**	BuLi	tol	15	57	76.9	11.3	11.8	23[h]	—
22	**5′**	Mg^nBu_2	tol	15	100	23.5	8.5	68.0	Insoluble	
23	**6′**	—	tol	16	90	0	18.2	81.8	418	2.5
24	**6**	BuLi	THF	23	67	2.2	28.4	69.4	31.5	2.1
25	**7a**	BuLi	Tol	16	100	95.6	3.1	1.3	1000	1.5
26	**7b**	BuLi	Tol	16	59	91.8	6.7	1.5	700/24[g]	—
27[f]	**8**	BuLi	THF	24	79	0.5	24.3	75.2	36.4	2.4
28[f]	**8**	BuLi	tol	3	68	93.4	5.0	1.6	700	br.

[a] $T = 0\,°C$, $[Ln] = 2.5 \times 10^{-3}$ M, $[MMA]/[Ln] = 500$.
[b] Mg^nBu_2: one equivalent per Ln; BuLi: two equivalents per Ln.
[c] Measured by SEC against PS standards.
[d] $PDI = \overline{M}_w/\overline{M}_n$.
[e] $T = 25\,°C$, $[MMA]/[Sm] = 50$, $v_{(toluene)} = 1.4$ mL.
[f] $T = -10\,°C$.
[g] Bimodal.
[h] In the presence of a shoulder at high molecular weights.

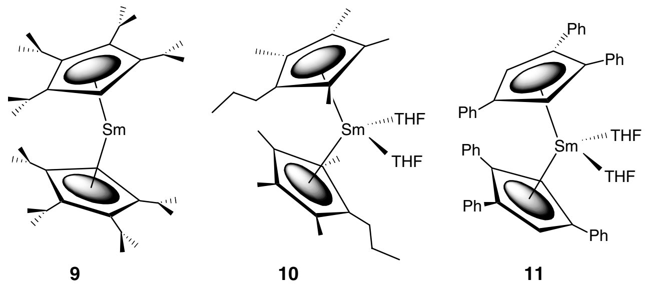
One can first notice that the presence of a co-catalyst is not absolutely necessary: in a preliminary experiment (run 15), complete conversion could be obtained with **4** alone (but for a [monomer]/[catalyst] ratio equal to 50). As shown by runs 16 and 17, performed in similar conditions, **4′** gives rise to results which compare well with those obtained with genuine **4**. In addition, we checked that KBH_4, by-product formed in such *in situ* preparations, was indifferent with respect to MMA polymerization. The use of complexes prepared *in situ* is thus established as legitimate. A high iso-control is obtained with BuLi as alkylating agent (run 16).

With **5′**, SEC data pointed out a more satisfactorily controlled process, in which experimental molecular weights were close to the theoretical ones (runs 19–21). The yield was quantitative when the experiment was performed in toluene and in the presence of Mg^nBu_2 (run 22). The previous tendency was then observed again: highly syndioregular polymer was obtained in THF when using Mg^nBu_2 as a co-catalyst (rr 78%, run 20), whereas isotactic PMMA was formed with BuLi in toluene (mm 77%, run 21). The complex $(Cp^{Ph3})_2SmBH_4$ (**6′**), bearing two bulky cyclopentadienyl ligands, in the absence of alkylating reagent, afforded in apolar medium highly syndiotactic material (rr 81.8%, run 23; a blank test conducted with KCp^{Ph3}–Mg^nBu_2 yielded atactic PMMA). The syndio percentage was lower with additives but the molecular weights could be controlled (run 24).

With complexes bearing a diketiminate ligand, the monomer conversion was only significant in the presence of a co-catalyst. With BuLi, both **7a** and **7b** afforded isotactic polymer (runs 25 and 26), up to 95.6%. The low polydispersity (PDI = 1.5) suggested that one unique active species might have been formed, but only a fraction of the catalyst was probably involved in the process, giving consequently high molecular weight PMMA (run 25). In toluene, **8**–BuLi catalyst afforded isotactic PMMA (run 28), whereas in THF the system allowed preferential and nearly quantitative formation of syndiotactic polymer (run 27).

DSC analyses were performed for the most regular PMMAs; T_g were found at 132, 88 and 58 °C, corresponding to runs 23 (81.8% syndio), 18 (atactic), and 16 (92.3% iso), respectively. As expected, the more the syndioregularity, the higher the T_g value.[39]

As a matter of comparison, MMA polymerization experiments were performed with divalent samarocenes **9, 10** and **11** (Fig. 2).[40] No co-catalyst was used, and the experiments were carried out in toluene at 0 °C. The polymerization mechanism was explained in detail by Boffa and Novak. and involved the oxidation of Sm^{II} in Sm^{III} along with the formation of an enolate moiety.[15] The results, summarized in Table 4, clearly show the influence of the ligands surrounding the samarium atom. With samarocene **9**, both low conversion and wide polydispersity may be related to the poor affinity of the complex towards polar molecules,[41] including MMA (run 29). The polymer was found to be 88% syndiotactic with the $Cp^{*\prime}$ ligand (initiator **10**, run 30), one of the best results yet obtained at



9 **10** **11**

Figure 2. The samarocenes used as initiators for MMA polymerization.

Table 4. Results of MMA polymerization using divalent samarocenes catalysts

Run[a]	Initiator	Yield (%)	Triad fractions (%) mm	mr	rr	$10^{-3} \times \overline{M}_n$[b]	PDI[c]
29	**9**	9	14.0	17.6	68.4	24	6.1
30	**10**	37	0	12.0	88.0	146	2.4
31	**11**	99	0.7	21.2	78.1	274	1.5

[a] $T = 0\,°C$, $[Sm] = 2.5\,10^{-3} \times$ M, $[MMA]/[Sm] = 500$, co-catalyst: none, polymerization time: 24 h, solvent: toluene.
[b] Measured by SEC against PS standards.
[c] $PDI = \overline{M}_w/\overline{M}_n$.

0 °C,[24] and 78% with Cp^{Ph3} (initiator **11**, run 31). The behaviour of initiator **11** was very similar to that of **6′** (Table 3, run 23), which argues for the same enolate active species. SEC traces were monomodal with initiators **10** and **11**, indicating that the initiation step occurs readily, leading to one unique active species. The formation of a high $\overline{DP}_n$ polymer with **11** may be related to the more difficult oxidation/initiation step.

CONCLUDING REMARKS

As a summary, borohydride complexes allow MMA polymerization; the BH_4 group thus behaves like a pseudohalide rather than a pure hydride. In the absence of alkylating reagent, higher conversion may be obtained with L_2LnBH_4 complexes rather than with homoleptic $Ln(BH_4)_3$. This is in sharp contrast with the observed sluggishness of $(C_5Me_5)_2SmCl(THF)$.[24]

In THF, there is a clear propensity for syndio-control, whatever the co-catalyst. A more significant syndioregularity is also observed, but in toluene, for two kinds of metallocenes both in the absence of co-catalyst: $(Cp^{Ph3})_2Sm(BH_4)$ and the divalent $Cp^{*\prime}{}_2Sm$. The global unexpectedly high activity for Cp^{Ph3} complexes may be ascribable to the ease of coordination of the monomer to the acidic metal. Consequently, the hypothesis of a pseudo-ionic mechanism in toluene, leading to chain-end control polymerization, can be advanced.

In the presence of an aluminium phenoxide activator, $Nd(BH_4)_3(THF)_3$ affords PMMA more than 80% syndioregular. A very good iso-control (up to 95.6%) is obtained with heteroleptic complexes **7a, 7b** and **8** using BuLi in toluene, as also observed with half-lanthanidocenes and hindered complex **4**.

Regarding the control of macromolecular data, the Ln-BH_4 moiety behaves like an $Ln\text{-}NR_2$[42] or $Ln\text{-}CH(SiMe_3)_2$ one,[16] providing faster propagation than initiation. Among the metallocenes, $Cp^{*\prime}$ trivalent complexes allow a well-controlled polymerization.

CONCLUSION

This paper presents an extensive study of the use of borohydrido complexes of lanthanides for MMA polymerization for the first time. Such complexes allow formation of highly syndiotactic or isotactic material, depending on the nature of ancillary ligands, the polarity of the reaction medium and the presence, or not, of an alkylating agent as co-catalyst.

$Nd(BH_4)_3(THF)_3$ affords highly syndiotactic PMMA, but it is really active only in the presence of an alkylating reagent. Complementary experiments undertaken with divalent samarocenes show that the samarium initiator bearing two bulky $Cp^{*\prime}$ ligands is one of the best catalysts of syndiospecific polymerization of MMA yet described: an 88% syndiotactic PMMA is obtained at 0 °C.

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