

Homogeneous and heterogeneous alkyl-alkoxo-lanthanide type catalysts for polymerization and block-copolymerization of ethylene and methyl methacrylate

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Abstract

The combination of the neodymium *tert*-butoxide $\text{Nd}_3(\mu_3\text{-O}^t\text{Bu})_2(\mu_2\text{-O}^t\text{Bu})_3(\text{O}^t\text{Bu})_4(\text{THF})_2$ (**1**), resulting from the metathetic exchange between NdCl_3 and Bu^tONa in THF, with 1 equiv. of a dialkylmagnesium reagent affords a moderately active cyclopentadienyl-free lanthanide catalyst for the pseudo-living polymerization of ethylene. Polymerizations performed under mild conditions (0 °C, 1 atm) in the presence of PhSiH_3 or H_2 as a transfer agent led to low molecular weight linear polyethylenes with activities in the range 5–20 kg PE (mol Nd)⁻¹ atm⁻¹ h⁻¹. In the absence of such a co-reagent, highly linear and crystalline polyethylenes of high molecular weight are produced with ca. halved activity. Under those reaction conditions, a polymer-like precipitate (**2**) forms during the polymerization course. Most interestingly, solid **2** proved to be an equivalent catalyst to the initial in situ system for the slurry polymerization of ethylene. Solid **2**, which is assumed to be the Nd-polyethylenyl intermediate, shows also significant ethylene polymerization activity under solid–gas conditions and enables the efficient preparation of ethylene-methyl methacrylate diblock copolymers. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Although neutral dicyclopentadienyl-lanthanide type alkyl/hydride complexes [$\{\text{Cp}_2\text{LnR}\}_n$] have been much less studied than their group IV metallocene homologues [1–5], they have received much attention since 20 years as ethylene polymerization catalysts

[6–10]. One of the reason for this interest lies in their intrinsic high polymerization activity, while group IV metallocenes require an activator (MAO, $\text{B}(\text{C}_6\text{F}_5)_3$, etc.) to generate active d⁰ cationic species [11]. Also, their propensity to initiate ethylene polymerization in a living fashion as well as that of polar monomers, e.g., methyl methacrylate (MMA), enabling the sequential diblock copolymerization of these monomers, is a unique peculiarity which renders these systems attractive for polymer chemists [12–14]. To overcome problems due to the inherent high sensitivity of alkyl-lanthanide species, we have shown that the in situ alkylation of readily available, stable chlorolanthanocene precursors by dialkylmagnesium reagents

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provides a useful method for the same polymerization reactions [15–17] and also for the formation of long chain dialkylmagnesium derivatives [18].

Post-metallocene catalysts based on isolobal ancillary ligands other than the usual Cp-type ligands are nowadays the subject of thorough investigation [19]. In this respect, hard, electronegative π -donor ligands such as alkoxides/aryloxides are particularly attractive for lanthanides because they offer strong metal–oxygen bonds that are expected to stabilize complexes of these electropositive metals.¹ Also, the large variety of these ligands readily obtained from alcohols allows considerable variation in steric and electronic features (see Footnote 1). However, although the mixed Cp–aryloxide complex $[Y(C_5Me_5)(O-2,6-Bu_2^tC_6H_3)(\eta-H)]_2$ has been successfully used for the polymerization of ethylene and higher α -olefins [21,22], the few structurally well-defined Cp-free lanthanide alkyl-alkoxide (aryloxides) complexes so far reported proved surprisingly inefficient for ethylene polymerization purposes.² In direct line with our previous studies [15–18], we report here an in situ combination between a homoleptic neodymium alkoxide and a dialkylmagnesium reagent that provides a new Cp-free catalyst for ethylene and MMA homo- and diblock-polymerization [24].

2. Experimental

2.1. Materials and instruments

All the operations were performed under dry argon using standard Schlenk techniques or in a dry glovebox under nitrogen. THF and toluene were freshly distilled from sodium benzophenone ketyl under nitrogen and degassed prior to use. NaOBU^t (97%, Aldrich) was dried at 130 °C under 10^{-3} Torr prior to use. Anhydrous NdCl₃ (99.9%, Strem) and di(*n*-hexyl)magnesium (Mg(*n*-hex)₂, 20% (w/w) solution in heptane, Akzo Nobel) were used as received.

¹ For a recent review on alkoxy and aryloxy chemistry of lanthanides, see [20].

² To our knowledge, only the neutral dialkyl-aryloxide $(2,6-tBu_2C_6H_3O)Y\{CH(SiMe_3)_2\}$ has been reported to exhibit very low ethylene polymerization activity (9×10^{-3} g PE mmol⁻¹ h⁻¹ bar⁻¹ at RT) [23].

Ethylene (Air Liquide, N35) was pre-purified by passage through a moisture filter (Chrompack, No. 7971). MMA (99%, Aldrich) was distilled twice over CaH₂ and stored at –20 °C under argon.

Catalyst precursor **1** was prepared as follows. In a glovebox, NaOBU^t (2.88 g, 30.0 mmol) was dissolved in THF (50 ml) and transferred to a flask containing a suspension of NdCl₃ (2.51 g, 10.0 mmol) in THF (50 ml). The mixture was stirred for 3 days at 20 °C. The solution was decanted, leaving behind a pasty solid that was discarded. Removal of solvents from the solution at 20 °C and drying the residue under 10^{-2} Torr for 6 h offered a pale-blue solid (3.70 g, 85%) that was directly used for polymerization purpose. Analytically pure samples of Nd₃(μ_3 -OBU^t)₂(μ_2 -OBU^t)₃(OBU^t)₄(THF)₂, obtained by recrystallization of the crude solid from toluene at –5 °C, showed comparable catalytic performances. ¹H NMR (400 MHz, toluene-d₈, 5 °C): δ 41.0 (s, 18H), 17.2 (s, 18H), –1.5 (s, ~8–9H), –14.7 (s, ~8–9H), –21.7 (s, 18H), –25.8 (s, 18H), –29.5 (s, ~8–9H).³

Elemental analysis calcd. (%) for C₄₄H₉₇Nd₃O₁₁ (1234.97): C 42.79, H 7.92; found: C 41.32, H 7.74.

Molecular weights of polymers were determined by size exclusion chromatography (SEC) using polystyrene gel columns at 135–155 °C and *o*-dichlorobenzene as the solvent, with either a PL220 (Polymer Laboratories) apparatus or a Waters apparatus equipped with coupled refractometer and viscosity detectors. The number-average molecular weight (M_n) and polydispersity ratio (M_w/M_n) were calculated by universal calibration with reference to polystyrene standards. ¹H and ¹³C NMR spectra of polymers were recorded on a Bruker AM-400 spectrometer at 130 °C in C₂D₂Cl₄. Melting points (T_m), glass transition temperature (T_g), and crystallinity of polymers were determined by DSC (Setaram DSC 141 apparatus, 10 °C min⁻¹, under nitrogen) and X-ray diffraction (XRD, Siemens D5000 spectrometer, Cu K α _{1,2}, $5^\circ < 2\theta < 55^\circ$) analysis.

³ Due to the paramagnetic Nd centers, the ¹H NMR spectra of **1** proved highly temperature sensitive and optimal resolution (minimal resonances overlapping, line shape) was observed at 5 °C. Inorganic and organometallic issues, including comprehensive spectroscopic and crystallographic studies, will be discussed in a forthcoming paper.

2.2. Polymerization procedures

In situ prepared catalyst. In a typical experiment, a solution of complex **1** (0.37 g, 0.33 mmol) in toluene (10 ml) was added to a solution of $\text{Mg}(n\text{-hex})_2$ (0.98 g, 1.0 mmol) in toluene (10 ml) and the reaction mixture was stirred for 1 h at 0 °C. The resulting brown solution (hereafter denominated as the in situ prepared catalyst) was injected via syringe into a 500 ml Schlenk tube containing toluene (80 ml) kept at 0 °C under 1.1 atm of ethylene (previously saturated solution). Magnetic stirring was started (1100 rpm) and the ethylene consumption was monitored by a mass flowmeter (Aalborg, GFM17) connected to a totalizing controller (KEP) which acts as a flow rate integrator. In the case of ethylene–MMA diblock copolymerization, MMA (5.0 ml, 50 mmol) was injected directly into the Schlenk tube via syringe following ethylene polymerization (typically after 1 h). In both the cases, the reactions were quenched by addition of a 5% HCl–methanol solution to the reaction mixture and the polymer was recovered by filtration and dried under vacuum.

Isolated catalyst 2. Polymerization reactions involving the isolated solid catalyst **2** were performed after filtration and washing (toluene) at 0 °C, under argon in a sintering glass funnel, of a catalytic reaction mixture obtained from an ethylene polymerization experiment typically conducted as described above over 30 min. Solid **2** was recovered as a beige gummy solid. Gas phase ethylene polymerization was carried out directly in this funnel by contacting the previously isolated solid with ethylene (1.1 atm) at 0 °C.

Diblock ethylene–MMA copolymerization was achieved by reacting a suspension of isolated solid **2** in toluene with MMA at 0 °C. A typical experiment is as follows: upon using a solution of **1** (0.37 g, 0.33 mmol) activated by $\text{Mg}(n\text{-hex})_2$ (0.98 g, 1.0 mmol) in toluene (100 ml) for 1 h at 0 °C allowed to collect, after 10 min of reaction with ethylene at 0 °C, 3.3 g of **2** as a beige precipitate. The latter was filtered-off at 0 °C and washed twice with cold toluene (2–50 ml). To a suspension of **2** in toluene (100 ml) MMA (9.0 ml, 90 mmol) was added and the reaction mixture was stirred for 1 h at 0 °C. After addition of acidified methanol, 4.8 g of crude polymer was obtained. Soxhlet extraction with boiling THF for 72 h led to the solubilization of only 3% of the

crude material. For analytical data of solid **2** and the final copolymer, see text.

3. Results and discussion

The reaction of NdCl_3 with 3.0 equiv. of NaOBU^t in THF at 20 °C for 3 days gives a single primary product **1**, which can be isolated in 80–90% yield as a pale-blue, air sensitive compound. X-ray crystallographic study revealed that **1** is a new trinuclear compound with the formula $\text{Nd}_3(\mu_3\text{-OBU}^t)_2(\mu_2\text{-OBU}^t)_3(\text{OBU}^t)_4(\text{THF})_2$ (Fig. 1) [24] (see Footnote 3).

3.1. Ethylene polymerization reactions

The addition of di(*n*-hexyl)magnesium to a solution of complex **1** in toluene affords a moderately active catalyst for the polymerization of ethylene. Systematic studies revealed that significant polymerization activity is observed for $0.5 < \text{Nd/Mg} < 2.0$ in a temperature range from –50 to 80 °C. Best results in terms of activity are obtained upon using a Nd to Mg ratio of 1.0 at 0 °C. Typical ethylene flow rates observed under such conditions are given in Fig. 2. It appears that the activity reaches its maximum within a few minutes and decreases concomitantly with the appearance of an insoluble polymer-like

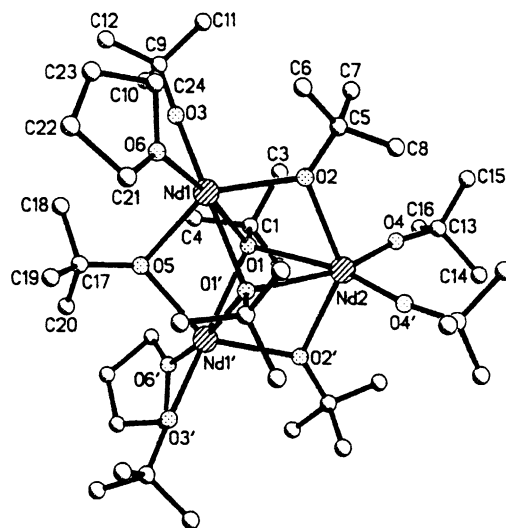


Fig. 1. Solid-state structure of catalyst precursor **1**.

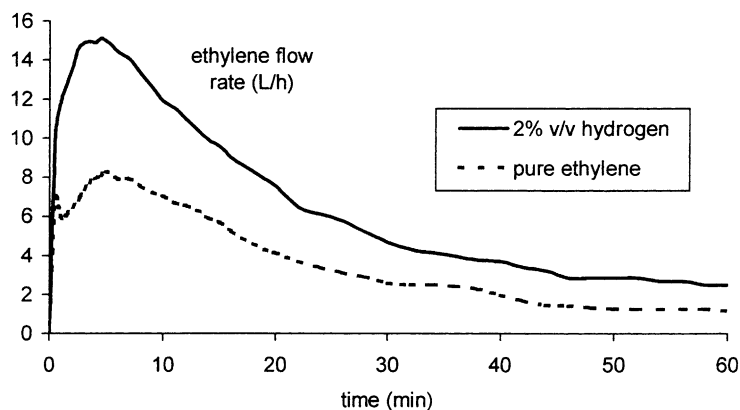


Fig. 2. Typical ethylene flowrates observed with pure C_2H_4 (—) and a 98:2 (v/v) C_2H_4/H_2 mixture (---) (see experimental for reaction conditions).

material. The activity calculated over 1 h at $0^\circ C$ under atmospheric pressure is ca. $5 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$. This can be considered as moderate on Gibson's activity scale [19], but proved ca. two orders of magnitude lower than an equivalent lanthanocene system, e.g., $Cp_2^*SmCl_2Li(OEt)_2/n\text{-BuEtMg}$ (1:1) gave $340 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$ under the same reaction conditions [25].

The polyethylene recovered under these conditions, after final hydrolysis, is highly crystalline (ca. 80–90% according to DSC and XRD) with $T_m = 139\text{--}142^\circ C$, $M_n = 2.5\text{--}4 \times 10^5 \text{ Da}$ and $M_w/M_n = 2.3\text{--}2.5$. The analysis of aliquots showed that the molecular weight does not increase significantly with time. The monomodality of GPC profiles is consistent with the formation of only one type of active species. Under these conditions, no low molecular weight chains with vinyl end groups were detected (NMR) in the final polymer, indicating that at $0^\circ C$, $\beta\text{-H}$ elimination and transfer reactions to the monomer are almost absent, if any. Raising the temperature over $20^\circ C$ led, however, to a severe decrease in the polymer yield as well as in the molecular weight (e.g., at $80^\circ C$: $M_n = 1700$, $M_w/M_n = 1.55$, 29% vinylic chain-ends). This is tentatively ascribed to a process involving $\beta\text{-H}$ elimination and subsequent deactivation of the resulting neodymium-hydride species.

The introduction of $PhSiH_3$ (10 equiv. vs. Nd) at the beginning of the reaction did not affect the activity profile and the productivity at $0^\circ C$. The polymer analysis revealed, however, that a transfer reaction

has occurred, as the M_n decreased to ca. 14,300 with $M_w/M_n = 25$. ^{13}C and 1H NMR analysis of the recovered polymer clearly showed the presence of end-capped $PhSiH_2$ -polyethylene, as expected [26]. Dihydrogen proved an even better transfer agent. Using 2% (v/v) of H_2 in ethylene led to almost doubled productivity (ca. $10 \text{ kg mol}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$), compared to the reaction carried out with pure ethylene (Fig. 2). Analysis of aliquots sampled every 10 min over the polymerization course indicated an almost constant M_n value of $17,000 \pm 500$ and a polydispersity M_w/M_n of 5.8, showing that an efficient transfer has also occurred. Effective response of the catalyst system to H_2 was observed in the range 1–10% (v/v).

As already mentioned, in the absence of any transfer agent, the polymerization activity decreases after a few minutes to reach a nearly constant value after 60 min, at ca. 1/10 of the maximal activity (Fig. 2). We observed that the latter could be almost completely and rapidly restored upon adding 1.0 equiv. of $Mg(n\text{-hex})_2$ to the reaction mixture; then, polymerization proceeded as in the initial batch (Fig. 3; dotted line). This suggests that the decrease in the ethylene flow rate during the polymerization course stems from a "drowsiness" of the active species rather than an irreversible deactivation process (vide infra).

In order to determine the distribution of total and active Nd in solution (homogeneous) and in the precipitate (heterogeneous), the latter was isolated by filtration of the reaction mixture and subsequently washed with toluene under rigorous exclusion of oxygen and

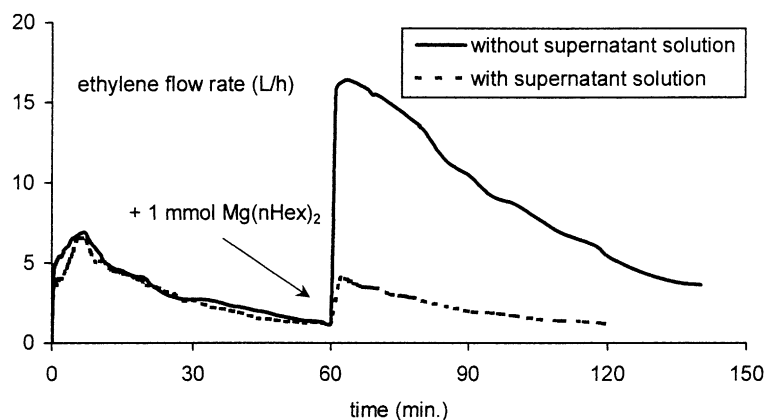


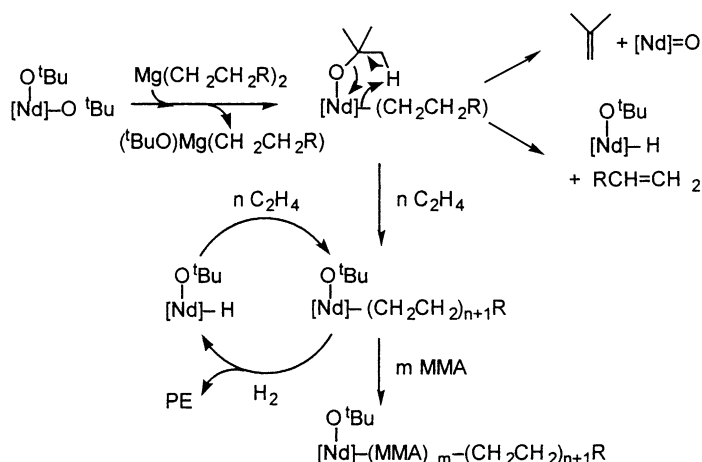
Fig. 3. Reactivation of the in situ $[1+Mg(n\text{-hex})_2]$ and isolated (**2**) catalyst systems by addition of $Mg(n\text{-hex})_2$.

water at 0°C . The beige solid (**2**) recovered was subjected to microanalyses which revealed, over three different samples, that $15\pm 2\%$ of initial Nd (and $20\pm 4\%$ of Mg) is present in the precipitate. Most interestingly, when solid **2** is in contact with ethylene in a toluene slurry (1.1 atm, 0°C), an ethylene consumption takes place at the same extent than in the in situ experiment; in parallel, the clear filtrate that contains ca. 85% of initial Nd proved completely inactive toward ethylene, even upon reactivation with fresh $Mg(n\text{-hex})_2$. This establishes that all of the active species generated from the in situ combination of **1** with $Mg(n\text{-hex})_2$ (1:1) are contained in solid **2**. As a matter of fact, preliminary basic experiments showed that **2** polymerizes ethylene under solid–gas conditions with significant activity (ca. $6\text{ kg mol}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$ over 30 min at 0°C). It is noteworthy, upon addition of 1.0 equiv of $Mg(n\text{-hex})_2$ (vs. initially introduced Nd) to a toluene suspension of **2**, that the activity for ethylene polymerization could be strongly enhanced as compared to the initial polymerization reaction (up to ca. $100\text{ kg mol}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$ vs. $5\text{ kg mol}^{-1}\text{ h}^{-1}\text{ bar}^{-1}$) (Fig. 3). This phenomenon, which is to be related to the aforementioned restoration of the catalytic activity upon addition of $Mg(n\text{-hex})_2$ to the in situ slurry system, is not yet understood. Separate experiments showed that the addition of dialkylmagnesium to a toluene suspension of **2** does not generate soluble neodymium species (i.e., all of the neodymium remains in the precipitate according to analyses of the precipitate and the supernatant solution); this casts doubts on a simple transmetallation

process between insoluble Nd–polyethylenyl species and $Mg(n\text{-hex})_2$.

3.2. Ethylene–MMA diblock copolymerizations

As stated in Section 1, one of the major interests of alkyl–lanthanocenes in polymerization relies on their unique propensity to induce both polymerization of ethylene and polar monomers [12–14]. We investigated therefore the ability of this new Cp-free system to initiate the diblock copolymerization of ethylene and MMA. The efficiency of the synthesis, i.e., the amount of block copolymer vs. homopolymers, was assessed in the case of the in situ catalyst combination $[1+Mg(n\text{-hex})_2]$ and of isolated compound **2**. For this purpose, the final crude (co)polymers were extracted with boiling THF for 3 days in order to separate homo-PMMA from the desired copolymer polyethylene–*block*-PMMA and homopolyethylene. The crude polymer, obtained via initial polymerization of ethylene with the in situ system and subsequent addition of MMA to the reaction mixture, was shown to contain ca. 15–20% of homo-PMMA. This suggests that the in situ combination $[1+Mg(n\text{-hex})_2]$ generates more than one active species for the polymerization of MMA, of which only one is able to initiate the polymerization of ethylene. Indeed, we checked that the solution recovered after filtration of precipitate **2** from the reaction mixture, that contains 80–85% of Nd and Mg initially introduced but proved inactive towards ethylene (vide supra), does initiate the



Scheme 1. Mechanistic hypotheses for activation and deactivation pathways.

polymerization of MMA to give atactic PMMA in moderate activity.⁴

Conversely, the crude polymer recovered from the reaction of MMA with a slurry of isolated solid **2** in toluene at 0 °C contained only ca. 3% of extractable products; ¹H NMR analysis showed that the latter are low molecular weight MMA-rich block copolymers (MMA/ethylene ~3). The MMA molar fraction in the THF-insoluble material obtained under typical conditions (see Section 2) is 7 ± 2% according to the weight increase, ¹H NMR and SEC analyses (vide infra). The DSC analysis revealed the *T_g* of the PMMA block at 122 °C and the *T_m* of the PE block as a narrow peak at 142 °C. The SEC analyses of the polyethylene obtained from the hydrolysis of an aliquot of **2** (before addition of MMA) and of the final THF-insoluble material showed an enhancement of the molecular weight from *M_n* = 200,000 to *M_n* = 250,000 with a *M_w*/*M_n* of 4.0 (monomodal) in both cases. This confirms the diblock nature of the polymer and in turns that ethylene polymerization using the [1+Mg(*n*-hex)₂] combination proceeds in a living-like fashion to give the Nd-polyethylenyl intermediate **2**. In addition to the monomer efficiency of the process, especially in-

teresting is the possibility to attain block lengths as high as 200,000 for the PE block and ca. 50,000 for the PMMA block. To our knowledge, these values are significantly higher than those so far realized with lanthanocene initiators [12–14], and allow to consider these diblock materials as excellent compatibilizers.

3.3. Initiation and catalytic mechanism

The above results, particularly, the effective transfer reactions using PhSiH₃ and H₂ and the possibility to achieve ethylene–MMA block-copolymerization, are in direct line with reactivity trends observed for lanthanocene initiators [6–10,12–14]. This is consistent with a coordination–insertion mechanism starting from a neodymium-alkyl species produced by alkylation of complex **1** with the dialkylmagnesium co-reagent. NMR investigations of this activation process revealed that 1-hexene is produced from such mixtures at temperatures as low as –30 °C. These observations and the possibility to achieve ethylene polymerization since –50 °C suggests the formation of alkyl-neodymium moieties at low temperature that further react via β -H elimination. In this regard, one may argue that electron-withdrawing *tert*-butoxide ligands, compared to electron-donating Cp-type ligands, facilitate β -H elimination in alkyl-lanthanide species; this is, however, still a controversial issue [28]. On the other hand, the detection of isobutene

⁴ Atactic PMMA with high molecular weight distribution arises from initiation by alkylmagnesium species; the in situ combination [1+Mg(*n*-hex)₂] initiates the pseudo-living polymerization of MMA to give syndiotactic-rich PMMA with very narrow molecular weight distribution [27].

at higher temperature (above RT) indicates that the alkoxy ligand itself may react during this alkylation process, leading to unreactive neodymium oxo species (not formally identified). This may explain, at least in part, that the optimized temperature for the reaction is about 0 °C. Scheme 1 describes both the aforementioned putative mechanism for the production of the [Nd]-{*n*-hex} and [Nd]-H species, and their use as either initiator in the case of ethylene polymerization, followed by MMA copolymerization, or as catalysts (cycle) for the hydride in the case of polymerization using H₂ as a transfer reagent.

4. Conclusion

Ethylene homopolymerization and ethylene–MMA diblock copolymerization have been efficiently performed with a new, simple catalytic system. The latter consists of a readily prepared homoleptic *tert*-butoxy-neodymium trinuclear complex that, upon in situ alkylation with 1 equiv. of a dialkylmagnesium reagent, acts in a similar way as well-defined alkyl-lanthanocene catalysts. The possible isolation of the polyethylenyl growing-chain neodymium intermediate as a solid enables original solid–gas ethylene polymerization and high diblock copolymerization efficiency. The accessibility of the new procatalyst, the possibility to tune steric and electronic features via the alkoxy ligand, and the straightforward synthesis of the active species suggest that further developments in alkoxy-lanthanide and related chemistry will be fruitful in the near future for olefin polymerization; our group is working in this direction.

Acknowledgements

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