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Review

Group 3 metal catalysts for ethylene and α-olefin polymerization

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Contents

Abstract

This review focuses on the use of group 3 organometallic catalysts for ethylene and α-olefins polymerization, as well as for functionalization of such poly(α-olefin) chains. It describes the evolution from initially designed neutral alkyl (hydrido) bis(cyclopentadienyl) complexes of trivalent lanthanides towards ansa-bridged ligand systems, "constrained-geometry" hemi-metallocenes, divalent lanthanidocenes, and the most recent cyclopentadienyl-free systems.

Keywords: Lanthanides; Polymerization; Metallocenes; Post-metallocenes; Single-site catalysts; Olefins; Diblock copolymerization

1. Introduction

Polyolefin-based materials find a wide range of applications in packaging, automotives, pipes, textiles, ... The overall resin market estimated at 80 million tons in 2002 is expected to increase at an average annual growth rate of 7%, likely reaching 100 million tons by 2007. After a century of development, polymerization of α-olefins is still a subject widely investigated in both academic and industrial research centers, and further evolutions are even so expected.

The appearance of transition-metal polymerization catalysis in the early 1950s with the Phillips and Ziegler–Natta's systems has changed the face of the polyolefins industry. While harsh conditions were required for the synthesis of

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branched low density polyethylene (LDPE) via free radical polymerization, heterogeneous organometallic catalysts enabled the synthesis of high density PE (HDPE), linear low density PE (LLDPE), and high molecular weight, highly stereospecific polypropylene (PP) at low temperature and pressure. Another significant breakthrough in the polyolefins area was the appearance of homogeneous group 4 metallocene catalysts (for reviews and leading references see [1]), followed more recently by “post-metallocene” chemistry (in general, non-cyclopentadienyl complexes) (for reviews and leading references see [2]). These molecular catalysts enabled the establishment of direct correlations between catalyst structure and polymer microstructure, and different kinds of stereoregular polyolefins, many of them new, to be synthesized along with high activities.

Although they have been much less studied than their group 4 homologues, metallocene and post-metallocene complexes of group 3 metals, especially of the lanthanides, have received much attention since 25 years as ethylene/α-olefin polymerization catalysts (for reviews on recent developments in organolanthanide-mediated polymerizations of any type of monomers see [3]). One historic reason for this interest lies in the intrinsic high polymerization activity of neutral alkyl (hydrido) group 3 metal complexes towards ethylene, while group 4 systems require an activator (MAO, $B(C_6F_5)_3$, ...) to generate active d^0 cationic species. Also, their propensity to initiate ethylene/α-olefins polymerization in a “controlled-living” fashion as well as that of polar monomers, e.g. (meth)acrylates and lactones, enabling the sequential diblock copolymerization of these monomers, is a unique functionalizing peculiarity which renders these systems attractive for polymer chemists. Not to mention the remarkable polymerization abilities of lanthanide-based systems towards other monomers, such as dienes and styrenics [3].

This review focuses on the use of such group 3 metal catalysts for ethylene and α-olefins polymerization, as well as for functionalization of such poly(α-olefin) chains. It describes comprehensively the evolution of this field, from initially designed neutral alkyl (hydrido) bis(cyclopentadienyl) complexes of trivalent lanthanides towards ansa-bridged ligand systems, “constrained-geometry” hemi-metallocenes, divalent lanthanidocenes, and Cp-free systems which have very recently retained much attention. Rating of the polymerization effectiveness of catalysts is based on activity data available from literature according to Gibson’s scale [2a], ranging from very low (<1 kg (polym) mol $(Ln)^{-1}$ bar^{-1} h^{-1}), moderate (10–100 kg mol^{-1} bar^{-1} h^{-1}), to very high (>1000 kg mol^{-1} bar^{-1} h^{-1}).

2. Single-component lanthanidocene catalysts

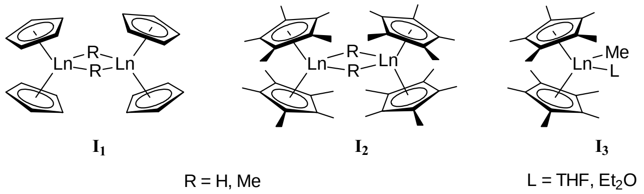


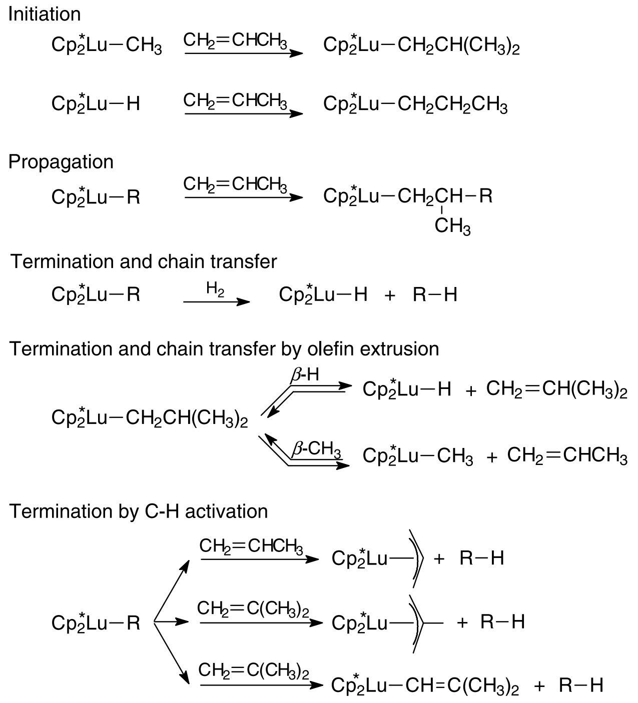
Fig. 1. Usual trivalent lanthanidocene complexes.

Neutral bis(cyclopentadienyl) alkyl/hydrido complexes of trivalent group 3 metals $[(\eta^5\text{-}C_5R_5)_2MR']_n$ (R_5: H_5 (Cp), Me_5 (Cp*); R′: H, Me; $n = 1, 2$) are isoelectronic with cationic group 4 alkyl metallocenes $[(\eta^5\text{-}C_5R_5)_2MR]^+$ (M: Ti, Zr, Hf) (Fig. 1). This analogy has been used in the original design of group 3 olefin polymerization catalysts. Such neutral complexes rapidly revealed a high intrinsic reactivity towards ethylene without preliminary activation. It was thus envisioned that this feature might be a significant economic advantage over the conventional group 4 metallocene catalysis, usual co-catalysts such as MAO or trialkylaluminum becoming useless.

It is probably with this economic aspect in mind that Ballard et al. at ICI developed bis(cyclopentadienyl) alkyl complexes of scandium, yttrium and lanthanides with various Cp-type ligands for ethylene polymerization [4]. The activity observed was moderate (10−100 kg (PE) mol $(Ln)^{-1}$ bar^{-1} h^{-1}) irrespective of the metal. On the other hand, the substituents on the Cp ring had a marked influence on the activity: the higher the steric hindrance, the higher the activity and the lower the molecular weight of the polymers. This was tentatively correlated to the easier dissociation of the starting dimer precursor due to the greater steric influence, leading to a larger amount of active species, and to the shorter lifetime of the active species with bulkier substituents, respectively.

Few years later, a report from Watson et al. at DuPont showed that ethylene polymerization with group 3 metal catalysts was still of interest for industry [5]. They showed that the complexation of $[Cp^*_2LuMe]_2$ with an equimolar amount of ether leads to active species for the synthesis of HDPE. However, the most interesting results arose from the spectroscopic studies aimed at the establishment of propene insertion mechanism, which was at that time one of the clearest experimental model for coordination catalysis of olefin polymerization (Scheme 1) [6].

It was shown that propene reacts with $[Cp^*_2LuMe]_2$ to produce only oligomers, indicating that transfer and termination reactions are faster than propagation. Monomer insertion proceeds regiospecifically into the Lu–CH_3 bond to give exclusively the isobutyl complex. Subsequent insertion into the Lu−isobutyl bond is much slower because of the bulkiness of the alkyl group. Transfer and termination reactions were well identified. The isobutyl complex arising from the first monomer insertion undergoes very slow and reversible β-H elimination to form isobutylene and a lutetium hydride. Simultaneously, a predominant β-Me extrusion occurs. Both reactions are thermodynamically unfavorable but proceed detectably because other reactions consume the



Scheme 1. Key-steps in olefin polymerization promoted by group 3 metal complexes [6].

olefinic co-products. The latter reactions are chain transfer with H_2 and terminations by C–H activation. Abstraction of an allylic methyl C–H from propene or isobutylene gives allylic complexes, which do not react further with propene (vide infra).

Bis(cyclopentadienyl) alkyl complexes of yttrium were first reported by Teuben and co-workers, showing comparable results to those obtained with lutetium [7]. Further investigations were recently conducted with $[Cp^*_2YH]_2$ by Casey et al. [8]. The authors explained why only propene could not be polymerized using this complex, comparing ethylene, propene and 1-hexene polymerizations. For ethylene, the insertion into the straight metal−alkyl bond is very rapid because of the high reactivity of the monomer and the resulting unbranched alkyl chain. Also, β-H elimination, the only possible transfer reaction, is very slow relative to propagation. For propene, chain extension is slower due to lower monomer reactivity and because of the branched growing alkyl chains that exhibit propagation step approximately 200 times slower than straight alkyl chains. Chain termination by hydrogen abstraction of an allylic sp^3 C–H from propene to give an η^3-allyl yttrium complex is much faster than β-H elimination and occurs at the same rate as propene insertion. For 1-hexene, chain extension is expected to be about as fast as for propene, but termination is much slower because the monomer has only less reactive allylic methylene hydrogens and no reactive allylic Me groups. The reactivity of $[Cp^*_2YH]_2$ towards C–H bonds decreases in the order of allyl $CH_3 \gg$ vinyl C–H $\gg$ allyl CH_2. Complementary kinetics results reported the existence of three distinct olefin insertion mechanisms with $[Cp^*_2YH]_2$, depending on alkene substitution [8].

Quantum chemical investigation of the initial steps of yttrium-mediated polymerization of ethylene and propene confirmed experimental information and provided additional clues [9]. The catalyst chosen for this study was $[Cp_2YH]_2$. It was shown that the reaction sequence starts with the formation of an electrostatically bound encounter complex between the catalyst and olefin, followed by the insertion of the monomer into the Y–H bond, and eventually formation of a $Cp_2Y–C_2H_5$ or $Cp_2Y–C_3H_7$ species. For both monomers, several energetic pathways leading to the catalyst-monomer complexes were identified. The overall reaction is exothermic by 22.2 and 19.5 kcal mol^{-1} for ethylene and propene, respectively. The formation of a “Y” shape monomer-catalyst complex, which prevents the subsequent insertion of the next incoming monomer unit due to severe steric problems, is the hypothesis proposed for explaining the impossibility to polymerize propene with this kind of catalyst.

A similar reactivity towards propene was observed with scandium complexes by Bercaw and Thompson [10]. Because of the lower reactivity of scandium derivatives, the elementary steps of polymerization were clearly identified. With excess propene, $Cp^*_2ScH(THF)$ leads to a stepwise reaction. A rapid insertion into the Sc–H bond is first observed, followed by a slower elimination of propane and generation of a *trans*-propenyl derivative, which is not reactive towards propene. Later, insertion and β-H elimination in ethylene polymerization was investigated using a series of permethylscandocene alkyls [11]. Second-order rate constants for ethylene insertion into Sc–C bonds at −80 °C were measured by ^{13}C NMR spectroscopy. It was shown that the nature of the M–C(H) bond affects the ethylene insertion rate (Sc–H $\gg$ $Sc–CH_2(CH_2)_nCH_3$ > Sc–*n*Pr > Sc–Et > Sc–Ph). A stronger bond results in a lower insertion rate and stabilizing β-agostic interaction also serves to retard ethylene insertion. The β-H elimination rate was measured by rapid trapping of $[Cp^*_2ScH]$ with 2-butyne. The relative order of reactivity is R: $p-NMe_2Ph > CH_3 > CH_2CH_3 > Ph > H > p-CF_3Ph$ (Table 1).

The results reported by Marks and co-workers enabled a nice comparison between late and early lanthanide polymerization chemistry [12]. They studied the synthesis and

Table 1
Rate constants for β-H elimination of $[Cp^*_2ScR]$ complexes [11]

R	*T* (K)	*k* (s^{-1})
CH_2CH_3	290	3.98×10^{-4}
$CH_2CH_2CH_3$	275	3.01×10^{-4}
$CH_2CH_2CH_2CH_3$	285	7.63×10^{-4}
$CH_2CH_3SiMe_3$	298	5.38×10^{-6}
CH_2CH_2Ph	290	5.23×10^{-4}
$CH_2CH_2(p-CH_3Ph)$	290	1.04×10^{-3}
$CH_2CH_2(p-NMe_2Ph)$	265	3.74×10^{-6}
$CH_2CH_2(p-CF_3Ph)$	295	1.32×10^{-4}

Table 2
Ethylene polymerization by $[Cp^*_2LnH]_2$ compounds: effect of the nature of Ln metal [12]

Ln	Concentration (μM)	Time (s)	Activity ($kg\,mol^{-1}\,bar^{-1}\,h^{-1}$)	M_n ($\times 10^{-3}$)	M_w/M_n	Chains/Ln
La	26	5	1.46×10^5	428	1.97	0.43
Nd	22	5	1.37×10^5	590	1.81	0.32
Lu	25	45	9.72×10^3	250	1.50	0.49

Reactions carried out in cyclohexane at 25 °C.

application of monomeric bis(Cp*) hydrocarbyl and dimeric hydride complexes of La, Nd, Sm and Lu. At room temperature and 1 bar ethylene pressure, $Cp^*_2LnCH(TMS)_2$ complexes (Ln: La, Nd and Lu) failed to react with ethylene over the course of several hours. However, reaction with H_2 under mild conditions gave the corresponding $[Cp^*_2LnH]_2$ complexes that undergo rapid reaction with ethylene (turnover frequency exceeded $1800\,s^{-1}$) and present measurable activity even at −80 °C. However, this high activity may be observed only for short reaction times and the efficiency of initiation remains modest. The approximate order of reactivity follows decreasing ionic radius: La $\geq$ Nd $>$ Lu (Table 2).

However, the kinetics of the polymerization, as well as the molecular weight of the resulting polymers, are limited by mass transport. Insignificant β-H elimination and relatively narrow molecular weight distributions ($M_w/M_n \approx 2$) were noticed and are consistent, respectively, with a living character of the polymerization and a single-site catalyst (Table 3). In each case, low initiation efficiency, i.e. formation of less than one polymer chain per metal center, was observed. In addition, La and Nd complexes react rapidly with propene and 1-hexene at −10 °C to yield equal quantities of the disproportionation products, i.e. alkane and metal η^3-alkenyl species. Interestingly, the analogous neutral silyl complexes $Cp^*_2NdSiH(SiMe_3)_2$ showed comparable reactivity towards ethylene [13].

The sterically very crowded $SmCp^*_3$ was surprisingly reported by Evans et al. to be active for ethylene polymerization [14]. Under mild conditions, an ultrahigh molecular weight polymer was obtained; the latter could not be analyzed with the usual analytical techniques ($M_w > 2 \times 10^6$). The authors suggested that one of the ring slips to form a η^1-C_5Me_5 intermediate, which can then insert ethylene or alternatively eliminate tetramethylfulvene to form a catalytically-active $[Cp^*_2SmH]$ species (Scheme 2).

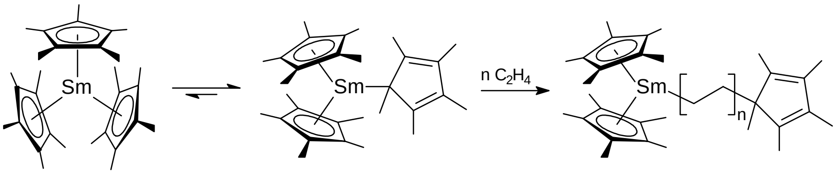
3. Binary lanthanidocene catalyst systems

The above complexes, especially hydride complexes $[Cp_2LnH]_2$, are very sensitive, and their multistep synthesis as their handling remain arduous. An alternative to circumvent this difficulty is the in situ formation of alkyl-lanthanide species from readily available precursors, e.g. a chlorolanthanidocene such as $Cp^*_2NdCl_2Li(OEt)_2$. Combination of the latter with a dialkylmagnesium compound generates an active, stable ethylene polymerization catalytic system in which, under gentle conditions (≤80 °C, 1 bar), a living ethylene growth chain transfer reaction between the MgR_2 species and the catalytically active lanthanidocene complexes takes place, yielding eventually long chain dialkylmagnesium compounds $Mg(C_nH_{2n+1})_2$ (n up to 100) with a narrow distribution (Scheme 3) [15,16]. The activities are lower than those observed with the corresponding single-component hydrido complexes ($8000\,kg\,(PE)\,mol\,(Nd)^{-1}\,bar^{-1}\,h^{-1}$ at 50 °C in

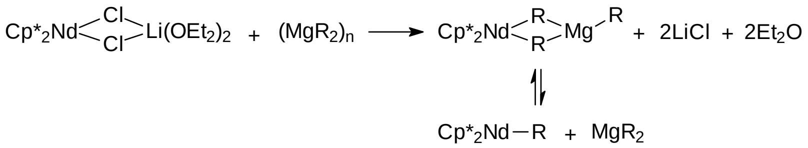
Table 3
Effect of catalyst concentration and reaction time with $[Cp^*_2NdH]_2$ [12]

Concentration (μM)	Time (s)	Activity ($kg\,mol^{-1}\,bar^{-1}\,h^{-1}$)	M_n ($\times 10^{-3}$)	M_w/M_n	Chains/Nd
11	10	1.13×10^5	–	–	–
22	5	1.37×10^5	590	1.81	0.32
60	10	3.84×10^4	233	4.46	0.46
60	60	2.32×10^4	–	–	–
60	180	8.23×10^3	–	–	–
22[a]	600	5.22×10^2	648	1.95	0.13

[a] Reactions carried out in cyclohexane at 25 °C except at −78 °C.



Scheme 2. Proposed mechanism for ethylene polymerization with $SmCp^*_3$ [14].

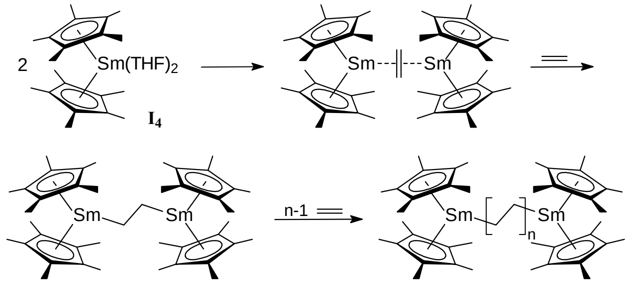


Scheme 3. Chain transfer reaction with chloroneodymocene/MgR_2 catalyst systems [15].

cyclohexane) [16]. However, the much more stable active species in the case of the in situ system enabled higher productivities. The kinetics and molecular weights depend on the Mg/Nd ratio and polymerization temperature. Initial activity decreases with an increase of this ratio. Under supercritical conditions (200 °C, 1200 bar), in a pilot plant devoted to classical Ziegler–Natta catalysts, and using a BuMgEt/Nd ratio of 3, the productivity into highly linear polyethylene could reach up to 20,000 kg (PE) mol (Nd)$^{-1}$, leading to a polymer in which the (Ln + Mg) content is lower than 10 ppm; the corresponding activity was calculated as 2×10^4 insertions per second (ca. 1500 kg (PE) mol (Nd)$^{-1}$ h^{-1} bar^{-1}) [15]. It is worth mentioning that during this work, using $[Cp_2YCl]_2$ as the catalyst precursor, similar results (14,000 kg(PE).mol(Y)$^{-1}$) were obtained upon addition of 1 eq. of an ylide before the alkylation process. Also, under the same conditions, MAO-activated Cp_2ZrCl_2 (MAO/Zr = 100) compares well with the above lanthanidocene catalysts, giving rise to a somewhat lower productivity (8000 kg (PE) mol (Zr)$^{-1}$), but where a copolymerization with 1-butene was observed, in contrast with the neodymium and yttrium catalysts [15]. It should be noticed that for the alkylation process of the above chlorolanthanidocenes, only MgR_2 and *n*-BuLi are suitable, as neither $AlEt_3$, $AlEt_2Cl$ and $ZnEt_2$ enabled ethylene polymerization to take place. The authors initially presumed that the lower electropositivity of aluminum was insufficient to generate an alkyl-lanthanide species. The possible formation of unreactive $[Cp^*_2Ln][AlR_4]$ species was also mentioned [15]. Other alkylating agents such as $AlEt_3$, MAO, DIBAL-H/*n*-BuLi (1:1) and $NaAlEt_4$ were successfully applied with the monosubstituted neodymocene $(\eta^5\text{-}t\text{BuC}_5H_4)_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$ for ethylene (co)polymerization [17]. $(\eta^5\text{-}t\text{BuC}_5H_4)_2Nd(\mu\text{-}Cl)_2Li(OEt_2)_2$/aluminate systems behave roughly like $Cp^*_2NdCl_2Li(OEt)_2/MgR_2$ since stable activities were observed along with chain transfer between neodymium and aluminum.

4. Divalent lanthanidocene catalysts

The use of cyclopentadienyl-type ligands was not simply restricted to trivalent lanthanides. In the early 1980s, Evans et al. reported the synthesis of divalent complexes $(\eta^5\text{-}C_5H_5)_2ML_n$ (L: Et_2O, THF; $n = 0, 1, 2$; M: Sm, Eu, Yb) [18]. Among these, samarium complexes exhibited activity in ethylene polymerization. At this time, the mechanism was unclear. Watson et al., who worked also on these catalysts, found that only ether-coordinated complexes could polymerize ethylene [5,6]. Only 15 years later, a polymerization mechanism with divalent lanthanidocenes was reported [19]. The complexation of one ethylene molecule by two samarium complexes generates, after an electron transfer reaction, two trivalent alkyl-lanthanidocene species linked by an ethylene bridge, this difunctional initiator acting as two single trivalent species (Scheme 4).



Scheme 4. Ethylene polymerization with divalent lanthanidocene catalysts [19].

5. Ansa-lanthanidocene catalysts

The main limitation of conventional lanthanidocene polymerization catalysts is their inefficiency in α-olefin polymerization, particularly that of propene, most likely due to the fast and irreversible allylic C–H activation (vide supra). In order to suppress this side reaction, new sterically demanding ligands were designed. The latter are based on bridged-Cp ligands possessing narrow Cp–Ln–Cp bite angles (115–117°) in comparison with their analogous non-bridged complexes (135–140°), creating additional available space around the metal center, i.e., favoring monomer approach. In addition, the incorporation of bridged ligands affects the electronics configuration due to changes in orbitals overlapping. However, allylic C–H activation remains possible.

Marks and co-workers reported the first ansa-lanthanidocene complexes in 1985 [12,20]. $[Me_2Si(\eta^5\text{-}C_5Me_4)_2LnH]_2$ (Ln: Nd, Sm, Lu) complexes were found to be active for propene oligomerization and ethylene/1-hexene copolymerization, while 1-hexene led to the formation of dimers under D_2 atmosphere. Effective α-olefin polymerization was observed with the more sterically crowded ligand $Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{BuC}_5H_2)_2$ [21]. The resulting yttrium C_2-symmetric complex enabled highly isotactic α-olefin polymerization (*mmmm* > 97%). However, rather low molecular weight polymers were obtained. High molecular

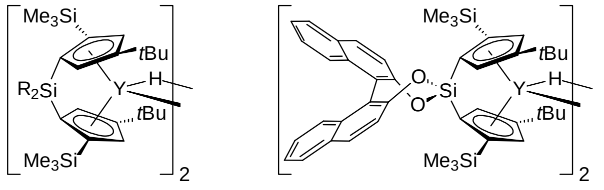


Fig. 2. Examples of ansa-lanthanidocene catalysts for α-olefin polymerization [21,22].

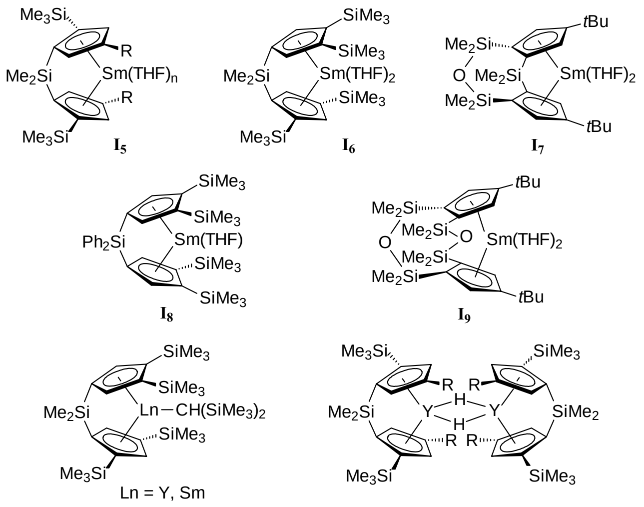


Fig. 3. Ansa-lanthanidocene complexes developed by Yasuda and co-workers [23].

weight isotactic polypentene ($M_n = 119{,}000$, $M_w/M_n = 1.44$, *mmmm* > 95%) could be obtained by replacing the $SiMe_2$ bridge by the corresponding binaphtoxysilyl bridge [22]. These examples of ansa-lanthanidocene catalysts are depicted in Fig. 2.

Yasuda and co-workers did a significant work in this area using mono- and bis(silylated)-bridged ligands and testing the corresponding samarium and yttrium alkyls and hydrides for ethylene and α-olefin polymerization [23]. They showed that the catalytic activity depends on the nature of the metal, the bulkiness of the ligand and the number of THF molecules coordinated (excess of coordinated THF led to polymerization inhibition). Thus, the activity decreases in the order $\mathbf{I}_7 > \mathbf{I}_5 > \mathbf{I}_8 > \mathbf{I}_6 > \mathbf{I}_9$ (Fig. 3).

The use of trivalent ansa-chloroneodymocenes, based on similarly substituted ansa-bridged Cp ligands, was also reported in combination with a dialkylmagnesium co-catalyst (Fig. 4) [24]. These systems enabled ethylene and 1-octene polymerizations yielding di(oligoalkyl)magnesium species, which can be finally hydrolyzed to oligomers. The bulky bridged complexes gave significantly more active catalysts for 1-octene oligomerization ($M_n = 400$–1300, $M_w/M_n = 1.11$–1.65) than systems based on non-bridged complexes; best results were achieved with $\mathbf{I}_{10}$.

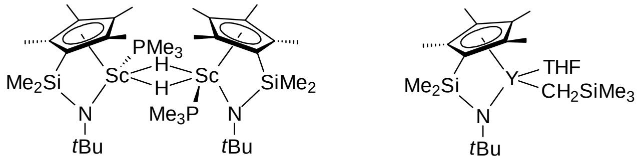


Fig. 5. Examples of "constrained-geometry" catalysts for ethylene polymerization [26,27].

6. Monocyclopentadienyl complexes

6.1. *Constrained-geometry catalysts*

Concomitantly to ansa-lanthanidocenes, half-lanthanidocene complexes were explored [25]. Bercaw and co-workers first reported the use of the "constrained-geometry" amido-monocyclopentadienyl organoscandium precatalyst for α-olefin polymerization (Fig. 5) [26]. The polymerizations were not stereospecific and rather slow, due to the tendency of the 12-electron propagating alkyl to associate free trimethylphosphine, deactivating the reactive complex. Further work from Okuda and co-workers on hydrido and alkyl complexes of yttrium, $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(THF)(\mu\text{-}H)]_2$ and $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)(CH_2SiMe_3)(THF)]$, showed that the latter are promising polymerization initiators for both non-polar and polar monomers (Fig. 5) [27]. Whereas ethylene is slowly polymerized by the hydrido complex at room temperature to give linear PE ($T_m = 136\,^{\circ}C$), none of α-olefins, neither dienes nor styrene, are polymerized. In all these cases, stable mono(insertion) products could be isolated. Note that efficient and controlled polymerization of styrene was developed by the use of the monomeric n-alkyl complex $[Y(\eta^5{:}\eta^1\text{-}C_5Me_4SiMe_2NCMe_3)\{(CH_2CH_2)_nH\}(THF)]$ thus formed.

6.2. *Other monocyclopentadienyl complexes*

Introduction of a Ln–O bond in α-olefin polymerization catalysis was first reported by Schaverien at Shell with a half-metallocene complex (Fig. 6) [28]. This mixed

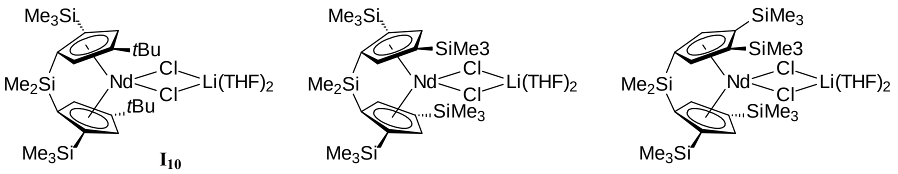
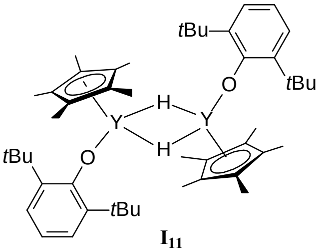


Fig. 4. Ansa-chlorolanthanidocenes used in ethylene and 1-octene oligomerization [24].



I$_{11}$

Fig. 6. Mixed cyclopentadienyl-aryloxide complex for α-olefin polymerization [28].

phenoxy-Cp complex exhibited high activity in ethylene polymerization, while 1-hexene was stereospecifically and smoothly polymerized ($M_n = 9400$; $M_w/M_n = 1.67$ and *mmmm* > 85%).

Unconventional monocyclopentadienyl pyrazinamide derivatives LnCp(MS)$_2$(PzA)$_2$ (Ln: Nd, Sm, Eu, Tb and MS = methanesulfonate) and LnBr$_2$CpPzA (Ln: Nd, Sm) activated with MAO presented catalytic activities of 4–6 kg (PE) mol (Ln)$^{-1}$ bar^{-1} h^{-1} at 70 °C, with Al/Ln ratios of ca. 2000, independently of the lanthanide metal [29]. The formation of cationic species by the reaction of MAO with the organolanthanide compound may be responsible for the catalytic activity (vide infra).

6.3. Divalent monocyclopentadienyl complexes

Divalent half-lanthanidocenes were studied by Wakatsuki and co-workers [30]. The ytterbium complex Me$_2$Si(C$_5$Me$_4$)(NPh)Yb(THF)$_3$ showed no activity for ethylene polymerization in toluene at room temperature under 1 bar, which is in agreement with the results previously reported for other Yb(II) complexes [30a,31]. In contrast, the more reducing Sm(II) complex Me$_2$Si(C$_5$Me$_4$)(NPh)Sm(THF) showed a moderate activity (45 kg (PE) mol (Sm)$^{-1}$ bar^{-1} h^{-1}) under the same conditions, to yield linear PE with high molecular weight ($M_n = 7.26 \times 10^5$) and narrow polydispersity ($M_w/M_n = 1.58$) (Fig. 7). These polymerization data can be compared to those reported for the Cp*/HNAr-, Cp*/HOAr- and Cp*/HPAr-ligated Sm(II) complexes [30a], and the more sterically demanding Me$_2$Si(C$_5$Me$_4$)(PPh)Sm(THF) complex [30c], but contrast with those for the Sm(II) complex [(C$_5$Me$_5$)Sm(SiH$_3$)(THF)(C$_5$Me$_5$)K(THF)]$_n$ ($M_n = 10{,}000$ and $M_w/M_n = 3.51$) [30e].

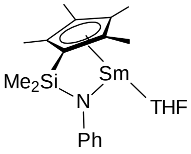


Fig. 7. Divalent half-lanthanidocene catalyst for ethylene polymerization [30].

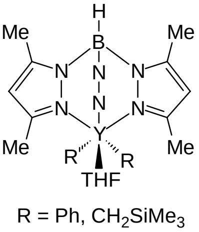


Fig. 8. Tris(pyrazolyl)borates as ancillary ligands for ethylene polymerization [44].

7. Post-lanthanidocene catalysts

Because of the permanent search for new-generation polymerization catalysts, there is considerable interest in developing the organometallic chemistry of group 3 metals involving solubilizing and stabilizing ancillary ligands other than the commonly used cyclopentadienyl-type ligands. Indeed, as already evidenced in group 4 metal chemistry [2], variation of the steric and electronic properties of the ligand may induce improved and/or original polymerization abilities for the related complexes. In fact, many types of alternative ancillary ligand systems have been developed (for recent reviews on fundamental post-metallocene organo group 3 chemistry see [32]), that include alk(aryl)oxides (for a review on lanthanide alkoxides see [33]), cyclooctatetraenides [34], carboranes [35], polypyrazolylborates [36], amides [37], phosphides [38], porphyrins [39], aza- and oxo-crowns [40], benzamidinates [41], β-diketiminates [42], and alkoxyamides [43]. Nonetheless, even if the number of potential alternative ancillary ligands is important, providing a wide unexplored area to the polymer chemist, the reported examples of effective ethylene polymerization using these complexes are not that numerous, and the methodology to obtain post-lanthanidocene active olefin polymerization catalysts remains unclear. This new generation of Cp-free catalysts will be referred as post-lanthanidocenes. These complexes will be divided in two categories, based on the nature of the ancillary ligand: nitrogen- and oxygen-based ligands.

7.1. Nitrogen-based ligands

The use of Trofimenko's tris(pyrazolyl)-based ligands for lanthanide-mediated ethylene polymerization was reported by Bianconi and Long [44]. Tris(3,5-dimethyl-1-pyrazolyl) borohydride (Tp^{Me}) complexes of yttrium of general formula [Tp^{Me}YR$_2$(THF)$_x$] (R: C$_6$H$_5$, CH$_2$SiMe$_3$) and similar ones with variously substituted Tp ligands, as well as analogous lanthanide complexes, were found to be very poorly active in ethylene polymerization, yielding linear PE with extremely high molecular weight (Fig. 8). The different complexes prepared showed variations in polymerization activity. The Tp^{Me}–Y alkyl and hydride complexes yielded linear PE with M$_w$ in some cases exceeding 2×10^6 g mol^{-1},

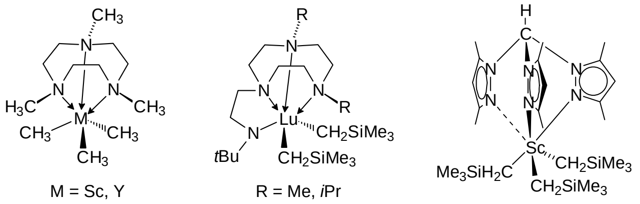


Fig. 9. Neutral triazacyclononane- and tris(pyrazolyl)methane-based complexes [46–48].

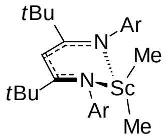


Fig. 10. β-Diketiminato dialkyl scandium complexes for ethylene polymerization [49].

and polydispersities ranging from 2.5 to 4.1. In all cases, including complexes containing large phenyl and trimethylsilylmethyl groups, the polymerization occurred despite the presence of coordinated THF molecules in the initial complexes. The highest (though still very poor) activity was observed with $Tp^{Me}YCl_2(THF)/2t$-BuLi as catalytic system. The use of tris(3-phenyl-1-pyrazolyl) borohydride (Tp^{Ph}) resulted in even smaller quantities of polymer, showing that the steric hindrance at the metal center affects the extent of polymerization. Although these findings were the first results regarding Cp-free lanthanide-based catalyst for ethylene polymerization, this area was not further investigated. The limited stability of Tp ligands towards the Lewis acidic lanthanides might be a likely explanation [45].

The reactivity of yttrium triazacyclononane-based lanthanide complexes towards olefins has been reported by Bercaw et al. Neutral tris(alkyl) complexes (1,4,7-trimethyl-1,4,7-triazacyclononane)$Ln(CH_3)_3$ (Ln: Sc, Y) were found not reactive towards ethylene (Fig. 9) [46]. However, activation of the scandium compound with either $[PhNMe_2H][B(C_6F_5)_4]$ or $B(C_6F_5)_3$ resulted in slow ethylene polymerization and 1-pentene oligomerization (M_n = 4000 and $M_w/M_n = 1.32$), irrespective of the activator. Mountford and co-workers have very recently reported results with similar scandium and yttrium complexes of 1,4,7-trimethyl-1,4,7-triazacyclononane with the bulky CH_2SiMe_3 groups instead of methyl groups on the metal center [47]. Surprisingly, high ethylene polymerization activity was observed upon activation of the scandium derivative with $B(C_6F_5)_3$ (up to 240 kg (PE) mol (Sc)$^{-1}$ bar^{-1} h^{-1} at 30 °C under 5 bar), in sharp contrast with Bercaw and co-worker's results [46]. To account for this difference, it was suggested that the bulkiness of the CH_2SiMe_3 group or the formation of β-Si–C agostic interactions may prevent μ-bridging of cationic metal centers. Also, the authors have extended this strategy to the tris(pyrazolyl)methane $HC(Me_2pz)_3$ ligand (Fig. 9) [47]. Activation of $Sc(CH_2SiMe_3)_3(HC(Me_2pz)_3)$ with $B(C_6F_5)_3$ led to a highly active ethylene polymerization catalyst (290 kg (PE) mol (Sc)$^{-1}$ bar^{-1} h^{-1} at 30 °C under 5 bar), giving PE with a bimodal distribution dominated by a high molecular weight fraction ($M_w = 1.9 \times 10^5$) with a very broad molecular weight distribution (M_w/M_n up to 15). On the other hand, no activity was observed with the parent yttrium derivative. Teuben and co-workers have reported the synthesis of an amido-bis(alkyl) complex [N,N'-R_2-1,4,7-triazacyclononane-N''-$(CH_2CH_2)NtBu]Y(CH_2SiMe_3)_2$ (R: *i*Pr or Me), which leads to cationic active species for ethylene polymerization after reaction with the Brönsted acid activator $[PhNMe_2H][B(C_6F_5)_4]$ (Fig. 9) [48]. The polymerizations were performed under 5 bar ethylene pressure in toluene solution at various temperatures for 10–15 min. Increasing the reaction temperature enhanced the activity (up to 1800 kg (PE) mol (Y)$^{-1}$ bar^{-1} h^{-1}), concomitantly with higher polydispersities. A likely explanation for this observation might be the thermal transformation of the initial cationic alkyl complex into another species that is also active in the polymerization of ethylene.

Another example of cationic catalyst for ethylene polymerization was reported by Piers et al. Preliminary results on β-diketiminato "nacnac" dialkyl scandium complexes showed that one of the dibenzyl derivatives may be activated with $B(C_6F_5)_3$ to form an ion pair [26]. The solid-state structure of this complex showed that the counteranion $[PhCH_2B(C_6F_5)_3]^-$ is strongly η^6-coordinated to the cationic scandium center, a feature that explains the lack of reactivity towards olefins. Given the usual activity observed with such cationic species, the development of bulkier nacnac-type donors with *t*Bu substituents was undertaken to avoid such coordination (Fig. 10) [49]. Activation of the dimethyl and dichloro precursors with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ gave effective catalysts for ethylene polymerization. In slurry batch reactor at 50 °C, PEs with relatively high molecular weights ($M_n \approx 1 \times 10^6$ g mol^{-1}) and polydispersities consistent with a single-site catalyst ($M_w/M_n < 2$) were obtained. Slightly lower activities were measured when the dichloride precursor was used, indicating a slower alkylation of the scandium center. Overall, the activities reported approach those observed for lanthanidocene catalysts, demonstrating once more that scandium cations are highly effective catalysts for ethylene polymerization.

Bis(benzamidinato)yttrium alkyl complexes $[PhC(NSiMe_3)_2]_2YCH_2Ph(THF)$ and $[(PhC(NSiMe_3)_2)Y(\mu\text{-}H)]_2$ were previously reported to be moderately active in ethylene polymerization but inactive towards propene and 1-hexene when employed as neutral catalyst [41d]. Under rather drastic conditions (55 °C, 70 bar ethylene pressure), the hydride complex exhibited low activity (4 kg (PE) mol (Y)$^{-1}$ h^{-1}); the activity noticed with the benzyl derivative was even lower. It seems that either activation of the precatalysts by dissociation or pre-complexation of ethylene is unfavorable in these complexes. This was explained as the consequence

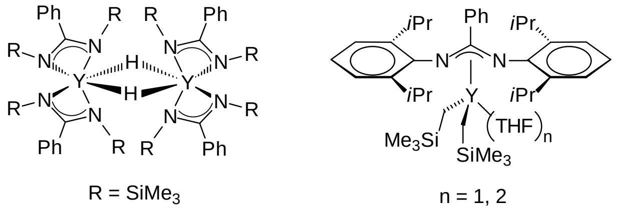


Fig. 11. Benzamidinate complexes in ethylene polymerization [41d,50].

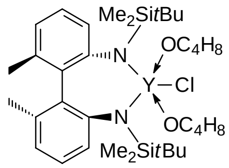


Fig. 13. Low activity bis(silylamido)biphenyl complex in ethylene polymerization [52].

of the high ionic character of these bis(benzamidinato)yttrium compounds, which causes the yttrium orbitals to contract strongly, making them less available to interact with the incoming olefin.

Bambirra et al. reported that the monobenzamidinate dialkyl yttrium complex $[PhC(NAr)_2]Y(CH_2SiMe_3)_2(THF)$ (Ar = 2,6-diisopropylphenyl), when activated with $[PhNMe_2H][B(C_6F_5)_4]$, yields PE with low polydispersity (Fig. 11) [50]. At 50 °C and under 5 bar ethylene pressure, the polymerizations exhibited a “controlled/living” character as evidenced by narrow molecular weight distributions along with the formation of one polymer chain per yttrium. The activities were rather high although they slightly decreased with the reaction time (from 1040 kg (PE) mol $(Y)^{-1}$ bar^{-1} h^{-1} over 5 min to 400 kg (PE) mol $(Y)^{-1}$ bar^{-1} h^{-1} over 30 min). The combination of $[PhC(NAr)_2]Y(CH_2SiMe_3)_2(THF)_2$ with $[PhNMe_2H][B(C_6F_5)_4]$ did not result in effective ethylene polymerization. Likely, the bonding of the second THF molecule to the cationic metal species is sufficiently strong to suppress catalytic activity. However, in the presence of an excess of partially hydrolyzed $Al(iBu)_3$ as scavenger, an effective ethylene polymerization was observed. Lower molecular weights were obtained and the formation of 5 polymer chains per yttrium atom was calculated, irrespective of the reaction time. This observation is in agreement with transfer of the polymer chain from the group 3 metal to the main group metal and vice-versa, and where chain termination by β-H elimination is insignificant.

Also, Fryzuk’s new five-coordinate neutral scandium dialkyl amidodiphosphine complexes $ScEt_2[N(SiMe_2CH_2P\textit{i}Pr_2)_2]$ and $Sc(CH_2SiMe_3)_2[N(SiMe_2CH_2P\textit{i}Pr_2)_2]$ revealed to be active in olefin polymerization (Fig. 12) [51]. The hard amido donor group is necessary to anchor the ligand to this electropositive metal center and this forces the phosphine donors to bind by virtue of their proximity.

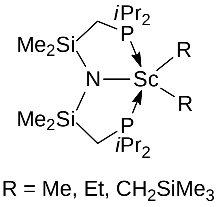


Fig. 12. Scandium dialkyl amidodiphosphine complexes for ethylene polymerization [51].

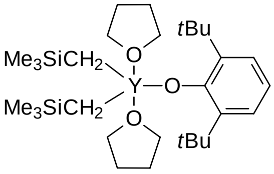
The reaction of ethylene with these neutral bis(hydrocarbyl) complexes resulted in the formation of PE. Unfortunately, the nature of the catalytically active species could not be determined and no report on the activity was mentioned.

Finally, a very low polymerization activity was observed by Tilley and Gountchev with C_2-symmetric bis(silylamido)biphenyl yttrium complexes [52] (Fig. 13), while surprisingly [NON]YR(THF) complexes were found inert towards ethylene ($[NON]^{2-} = [(tBu\text{-}d_6\text{-}N\text{-}o\text{-}C_6H_4)_2O]^{2-}$) [53]. Catalytic activity for the latter complexes was expected since they are isoelectronic to analogous group 4 metal catalysts efficient for the living polymerization of 1-hexene [54]. Exposure of the chloro complex to ethylene (5.5 bar) in the presence of MAO (500 eq.) in toluene produced 0.060 g of PE. Use of the corresponding alkyl complex did not allow higher activity. As postulated previously, steric hindrance, coordinated THF and high ionicity in the bonding might be the causes for such low reactivity towards olefins.

7.2. Oxygen-based ligands

Beside post-lanthanidocene catalysts with nitrogen-based ligands, alk(aryl)oxide ligands are also attractive because they offer strong metal oxygen bonds which can stabilize complexes of these electropositive metals. Also, the great variety of these ligands conveniently obtained from alcohols allows considerable variation in steric and electronic features [33]. However, relatively few examples of oxygen-based post-lanthanidocenes have been reported to be effective catalysts for ethylene polymerization. Among the dozen of structurally well-defined cyclopentadienyl-free lanthanide alkyl-aryloxide complexes that have been described to date [55], only Evans’s neutral dialkyl-aryloxide complex $[Y\{CH(SiMe_3)_2\}_2(O\text{-}2,6\text{-}tBu_2C_6H_3)(THF)_2]$ ($\mathbf{I}_{12}$) has shown very low ethylene polymerization activity (9×10^{-3} kg (PE) mol $(Y)^{-1}$ bar^{-1} h^{-1} at 20 °C under 5 bar ethylene in toluene) (Fig. 14) [56]. No polymer characteristics were available. This poor ability for ethylene polymerization is rather surprising since alkoxy ligands are expected to render the metal center more electron-deficient and more Lewis acidic.

As it was observed with nitrogen-based complexes, cationic complexes exhibit higher activities than neutral precursors. Okuda et al. have reported lutetium alkyl cations bearing crown ethers as oxygenated ligands, $[Lu(CH_2SiMe_3)_2(CE)(THF)_n][B(CH_2SiMe_3)(C_6H_5)_3]$ (CE



I_{12}

Fig. 14. Sole well-defined mixed alkyl-aryloxy complex active in ethylene polymerization [56].

= [12]-crown-4, $n = 1$; CE = [15]-crown-5 and [18]-crown-6, $n = 0$) (Fig. 15) that are very active for ethylene polymerization [57]. The anions were shown to be non-coordinating and the cation formation from alkyl abstraction was possible under mild conditions with BPh_3, the use of the more electrophilic $B(C_6F_5)_3$ being not required. This indicates a high reactivity of the complex, high reactivity observed towards olefins since a significant ethylene polymerization was noticed. Unfortunately, no data are still available concerning either the polymerization conditions or the polymer characteristics.

Binary catalytic systems composed of a lanthanide calix[n]arene (n = 4, 6, 8; Ln: La, Nd, Sm, Dy, Y) complexes and $Al(iBu)_3$ were found to be effective homogeneous catalysts for ethylene polymerization [58]. Linear high molecular weight polymers ($M_\eta > 5 \times 10^5$) with T_m in the range 128–136 °C were obtained along with moderate activities (up to 56 kg (PE) mol (Nd)$^{-1}$ h^{-1}). Neodymium calix[n]arenes activities decreased in the order: $C_6Nd > C_4Nd > C_8Nd$. Although lanthanides are very similar in chemical properties, their catalytic activities in ethylene polymerization are quite different depending on the ligand. A maximum of activity was noticed at 80 and 120 °C for, respectively, C_4Nd and C_6Nd. However, the molecular weight of the polymer decreased with the reaction temperature due to enhanced β-H transfer reaction at higher temperatures. $AlEt_3$ and $Al(iBu)_2H$ proved to be efficient co-catalysts with C_6Nd, while no polymer was produced with $Al(iBu)_2Cl$ as the co-catalyst.

Recently, we have shown that binary systems based on lanthanide alkoxides/phenoxides are also efficient for ethylene polymerization when those inorganic precursors are combined to a dialkylmagnesium derivative [59], the utilization of other alkylating agents giving inefficient catalyst systems [60]. Among the variety of systems studied, the association of the well-defined trinuclear neodymium tert-butoxide $Nd_3(OtBu)_9(THF)_2$ with $Mg(n\text{-}Hex)_2$ under mild conditions (0 °C, 1 bar C_2H_4) allowed for producing highly linear and crystalline (cryst. > 80%) PE with low, though long-lasting activity (5 kg (PE) mol (Nd)$^{-1}$ bar^{-1} h^{-1}). The maximum productivity was obtained for $Nd/Mg = 1.0$; in fact, excess or defect of MgR_2 in these systems resulted in a loss of productivity contrary to chlorolanthanidocene systems that could accommodate Mg/Nd ratios up to 1000 without productivity penalty.[15] Interestingly, the productivity could be enhanced up to 100 kg (PE) mol (Nd)$^{-1}$ bar^{-1} h^{-1} by sequential or continuous MgR_2 addition after the polymerization initiation. The PEs recovered present a molecular weight distribution pretty narrow for a Ziegler–Natta type catalyst ($M_w/M_n = 2.0$–3.0) indicative of a single-site catalyst. The high molecular weights ($M_n = (2\text{–}10) \times 10^5$) are consistent with a low initiation efficiency and the absence of transfer reactions. This confers a "controlled-pseudo-living" character to the polymerization, with the eventual formation of a Nd-polyethylenyl species that precipitates over the polymerization course. These species were quantitatively isolated and authorized effective gas phase polymerization with similar activities as those observed under slurry conditions. The molecular weights could be significantly reduced upon using typical transfer agents such as hydrogen or phenylsilane (vide infra). Thus, M_n as low as 20,000 g mol^{-1} could be obtained, though along with a significant broadening of the molecular weight distribution. Recently, we have succeeded in isolating discrete intermediates from stoechiometric reactions of lanthanide alk(aryl)oxides and dialkylmagnesium [61]. In particular, the reaction of $Nd(OAr)_3$ (THF) (Ar: 2,6-tBu-4-MeC_6H_2) with $Mg(CH_2SiMe_3)_2(Et_2O)$, an alkylating agent that cannot undergo β-H elimination side-reactions, was found to afford in high yield the mixed, post-lanthanidocene species $Nd(OAr)_2(CH_2SiMe_3)(THF)_2$, which was characterized by X-ray analysis.

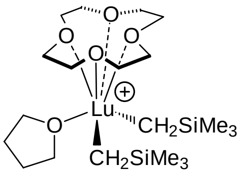


Fig. 15. Crown ether as ancillary ligand for cationic dialkyl lutetium complexes [57].

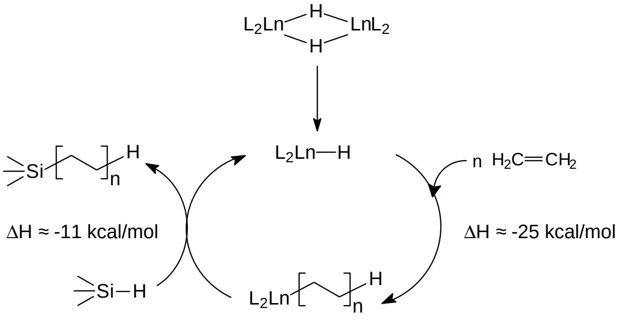
The oligomerization of 1-octene with lanthanide carboxylates or phosphonates associated to AlR_3 in CCl_4 as solvent was reported in the early 1990s [62]. The best results were obtained with a catalytic system based on neodymium-naphtenate associated with $AlEt_3$ in CCl_4. The use of other chlorinated solvents did not bring dramatic changes in the polymerization characteristics and the catalytic activity of early lanthanides seemed to be slightly higher than that of late ones (activity with $Nd(naph)_3$ = 2.5 kg (PO) mol (Y)$^{-1}$ h^{-1} at 50 °C). The catalyst aged for the same time at room temperature gave better results that the one aged at 60 °C. Maximum conversions and highest molecular weights were obtained at Al/Nd molar ratios in the range 6–8. In addition, chain-transfer reactions were evidenced in the polymerization of 1-octene with the $Nd(naph)_3/AlEt_3$ catalyst system. The observed pseudo-first-order kinetics with respect to monomer concentration and the presence of unsaturated bonds in the polymer agreed with the latter.

8. Functionalization of polyolefins

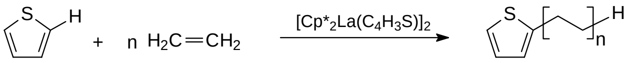
Introduction of polar and/or reactive backbone or terminal functional groups into polyolefins via Ziegler–Natta/coordination processes currently represents a major scientific and technological challenge. The reversible chain transfer reaction between lanthanidocenes-alkyl growing chains and magnesium dialkyls already described (vide supra) is a convenient way to produce higher di(polyethylenyl)magnesium compounds of narrow molecular weight distribution, which have been used as usual Grignard reagents for further functionalization [15e]. Apart from this one-pot, two-step reaction, two main techniques have been reported so far for the terminal mono-functionalization of polyolefins in lanthanide catalysis: chain transfer reactions and sequential diblock copolymerizations.

8.1. Silanes as chain transfer agents

In addition to the desire of introducing functionalities into the polymer, new efficient and selective chain transfer agents were also sought since only limited and frequently non-selective in situ chain transfer means were available for such polymerizations (H_2, β-H/akyl elimination, monomer, main group alkyls). The mechanistic study of organolanthanide-catalyzed olefin hydrosilylation led Marks et al. to utilize $PhSiH_3$ as a transfer agent in lanthanidocene-catalyzed α-olefin (co)polymerizations [63]. It was shown that a Si–H/Ln–C σ-bond metathesis enables the formation of silyl-terminated polymer chains (Scheme 5). Qualitatively, the polymer molecular weights decrease as the silane concentration increases. This behavior is observed for ethylene homopolymerization but also ethylene/1-hexene and ethylene/styrene copolymerizations. Effective transfer reaction was confirmed by the characteristic $PhSiH_2$ resonances in the ^1H and ^{13}C NMR spectra, except for Lu catalysts for which β-H elimination is the predominant chain transfer reaction. Similarly efficient use of $PhSiH_3$ to produce $PhSiH_2$ end-capped polyethylenes was also reported for the binary $Nd_3(OtBu)_9(THF)_2/MgR_2$ systems [60].



Scheme 5. Chain transfer reaction in the presence of a hydrosilane with lanthanidocene catalysts [63].



Scheme 6. Chain transfer reaction in the presence of thiophene with lanthanidocene catalysts [66].

8.2. Thiophene as chain transfer agent

Metallocene alkyls and hydrides of group 3 metals are well-known to readily effect hydrocarbon C–H activation, reducing their efficiency in the polymerization of α-olefins such as propene, as inactive η^3-allyl species are formed upon chain termination by allylic C–H activation of the monomer (vide supra) [5,64]. The combination of ethylene polymerization and C–H activation process was hypothesized to be effective for chain transfer reaction and concomitant chain-end functionalization. Teuben and co-workers reported that yttrocene-mediated ethylene polymerization in the presence of pyridine produced 2-ethyl-pyridine due to the high stability of the first insertion product of ethylene into the Ln−pyridyl bond [65]. When the metallation product of thiophene at the 2-position by $[Cp^*_2YH]_2$, i.e. $[Cp^*_2Y(\mu\text{-}C_4H_3S)]_2$, was used, only very sluggish ethylene polymerization took place. However, with the lanthanum analogue complex, the formation of PE with 2-thienyl end-groups was rapidly observed [66]. ^1H NMR analysis indicated that all the polymer chains are capped on one side by a thienyl group, suggesting that C–H activation was the only chain transfer reaction during the polymerization (Scheme 6).

8.3. Diblock copolymerization

8.3.1. Lanthanidocene catalysts

The first example of well-controlled block copolymerizations was allowed by the dual catalytic function of Cp^*_2LnR (Ln: Sm, Yb, Lu; R: H, Me) towards both polar and nonpolar olefins [67]. The copolymerization of ethylene with methyl methacrylate (MMA) was first achieved by Yasuda et al. following a two-step procedure: the homopolymerization of ethylene under mild conditions (1 bar ethylene, 20 °C) is followed by a sequential addition of MMA. Reversed addition of the respective monomers (MMA then ethylene) did not perform the block copolymerisation; only homopolymerization of MMA occurred. The resulting polymers were soluble in 1,2-dichlorobenzene and 1,2,4-trichlorobenzene at 100 °C but insoluble in THF and $CHCl_3$, indicating quantitative conversion into the desired linear diblock copolymer. The extracted copolymers from hot THF displayed molecular weights M_n in the range 13,000–25,000 with M_w/M_n = 1.37–1.90. The molar ratio of PE to PMMA blocks could be controlled voluntarily in the range of 100:1 to 100:103 when M_n of the initial PE was fixed to ca. 10,300. Indeed, increasing M_n of the PE block resulted in a decrease of the relative PMMA-to-PE ratio, especially for $M_n > 12,000$, i.e. when PE precipitates. The encapsulation of the active

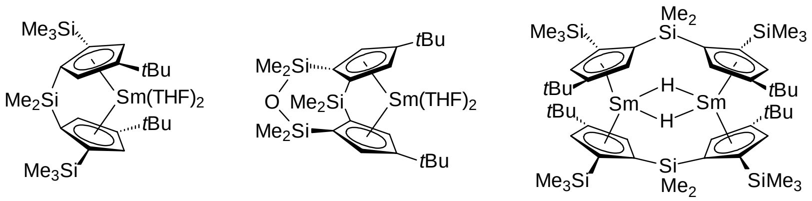


Fig. 16. Effective divalent and trivalent lanthanidocenes in ethylene-MMA ABA triblock and α-olefin-MMA diblock copolymerization [71].

sites by the crystalline PE may inhibit the diffusion of MMA to the active sites and hence causes suppression of further copolymerization. Noteworthy also is the possible ethylene diblock copolymerization with ethyl or methyl acrylate, and δ-valerolactone or ϵ-caprolactone.

The molecular weights of the diblock PE-b-PMMA materials obtained with Cp^*_2LnR species are too low to provide valuable physical properties, in particular miscibility with other polymers and rheological properties (for a recent review on compatibilization of polymer blends see [68]). Thus, higher molecular weight copolymers were prepared using $[Me_2Si(C_5H_3\text{-}3\text{-}SiMe_3)_2SmH]_2$ as catalyst [69]. In this case, M_n up to 70,000 were obtained with $M_w/M_n =$ 1.67–1.69 and a PMMA content that remained relatively high (19 mol%). Even higher molecular weights were obtained with $Cp^*La(CHTMS)_2$ but, as expected, the incorporation of MMA was low (less than 1 mol% for $M_n =$ 136,500) [70].

Block copolymerizations of higher olefins such as 1-pentene and 1-hexene with polar monomers like MMA and ε-caprolactone were achieved using dinuclear trivalent lanthanide complexes (Fig. 16) [71]. The crude products were composed of two kinds of polymers as evidenced by SEC analysis. The extraction products using hot hexane gave rise to the remaining block copolymers, which showed a unimodal pattern. The ratio of olefin to polar monomer unit could be varied from 5:1 to 1:5 by adjustment of the feed ratios of the two monomers. The molecular weights were still quite low (M_n up to 53,000).

Finally, it should be noticed that ABA-type triblock copolymers were also prepared using bridged divalent lanthanide complexes such as meso-$\{Me_2Si(Me_2SiOSiMe_2)(C_5H_2\text{-}3\text{-}t\text{Bu})_2Sm(THF)\}$ and rac-$\{Me_2Si(2\text{-}SiMe_3\text{-}4\text{-}t\text{BuMe}_2SiC_5H_2)Sm(THF)_2\}$ (Fig. 16) [71].

8.3.2. *Post-lanthanidocene systems*

Binary combinations of lanthanide alkoxides, e.g. $Nd_3(O t\text{Bu})_9THF_2$, and $Mg(n\text{-Hex})_2$ were also found to be effective for syndiotactic and pseudo-living MMA polymerization., producing at 0 °C a PMMA with a narrow molecular weight distribution ($M_w/M_n = 1.07$), high molecular weight ($M_n = 60{,}000\text{–}120{,}000$) and high syndiotacticity ($rr = 78\%$) [72]. This lanthanidocene-like polymerization behavior is consistent with the in situ formation of a neodymium alkyl species, in agreement with the results previously described in ethylene polymerization. Thus, it was not surprising to observe the quantitative synthesis of ethylene-MMA diblock copolymers using this original binary catalytic system (yield up to 95%) when ethylene is firstly polymerized [73]. These copolymers present the highest molecular weights ever reported for such material ($M_n > 250{,}000$) along with a significant MMA content (5–15 mol%). DSC and AFM analysis of the copolymers are consistent with the homogeneous dispersion of amorphous domains (PMMA) in a crystalline matrix (PE). The application of this material as compatibilizer for PE-PMMA blends showed interesting preliminary results [61a].

9. Conclusion and perspective

The past 25 years have witnessed a real interest in organogroup 3 species for ethylene and α-olefin polymerization with many reported new catalytic systems. Due to their high intrinsic reactivity, comparable activities to group 4 catalysts were observed for ethylene polymerization with simple bis(substituted cyclopentadienyl) alkyl and hydride complexes $[Cp_2LnR]$. However, the latter are largely limited to the polymerization of sterically unhindered monomers because of the high degree of steric saturation required to stabilize alkyl and hydride complexes of these large and very reactive metals. The appearance of ansa-lanthanidocene complexes allowed better results, but still the activity remains low and the synthesis of the required ligands and corresponding complexes is tedious. The use of binary systems based on chlorolanthanidocene precursors and an appropriate alkylating reagent offers the possibility to avoid such difficult syntheses. Using this strategy gives an attractive opportunity to develop new catalysts which would have probably never been discovered due to the instability of the Ln–alkyl bond responsible for the initiation process. More, this technique allows such catalysts to be tested under industrial conditions in a useful way. The research dedicated to the understanding of the metal-ligand relationships for the stabilization of the active center was extended in recent years to the utilization of non-cyclopentadienyl ligands. Activated organometallic/inorganic lanthanide precursors allowed for satisfactory catalytic activities. Also, particularly noteworthy in this respect are the cationic organolanthanide systems recently developed and which seem to offer quite a high potential. Another advantage of group 3-catalyzed olefin polymerization lies in the easy and multiple options to functionalize in a controlled way the resulting polymers, yielding new materials with improved or novel properties. Consequently, further development of group 3 catalysts should take benefit of this particular feature and thus be focused on the synthesis and characterization of these new polymers. The high polymerization abilities of organolanthanides towards a large range of monomers, some of them were voluntarily not addressed in this review, e.g. dienes and styrenics, will undoubtedly contribute to the elaboration of such original materials.

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