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Chapter 1

End-capped Oligomers of Ethylene, Olefins and Dienes, by means of Coordinative Chain Transfer Polymerization using Rare Earth Catalysts

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Additional information is available at the end of the chapter

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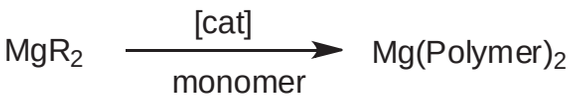
1. Introduction

Polymerization catalysis has seen a huge development with the progress of organometallic chemistry. Metallocenes, post-metallocenes, and constrained geometry complexes (CGC), have been used as single-site catalysts by polymerists, with the aim to elaborate polymeric materials with improved properties that can't be attained by other synthetic strategies [1]. Since the beginning of the 21st century and besides the search for new organometallic structures that could be exploited as potential catalysts, new methods and concepts have been developed, aiming at better controlling polymerization catalysis. Living (up to Immortal) Polymerization [2], Chain Walking [3] Chain Shuttling [4] have emerged. Mastering transfer reactions in polymerization catalysis, as Coordinative Chain Transfer Polymerization (CCTP) [5], has reappeared recently as a tool that would allow a better control of the whole process, and would also open the way to unprecedented macromolecular architectures. On the other hand, mastering of transfer reactions in polymerization catalysis is also of high interest because it allows the preparation of functionalized oligomers.

We will describe in this chapter some representative examples of our recent results that illustrate the possibilities offered by controlling transfer reactions in rare earth mediated oligomerization catalysis. In particular, the association of dialkylmagnesium with rare earth (RE) precatalysts afforded active combinations for the oligomerization of a series of olefins including ethylene, octene, styrene, butadiene, isoprene and β-myrcene. Chain transfer on the magnesium atom afforded long chain di(polyolefin)magnesium derivatives (see scheme 1). Characterizations and applications of these end-capped oligomers will then be largely developed.

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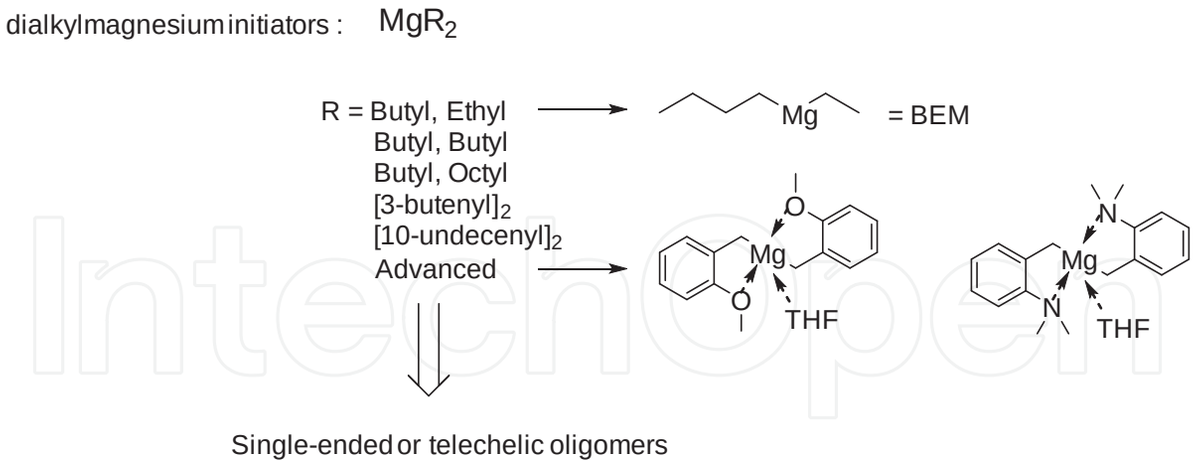
Scheme 1. End-capped oligomers starting from dialkyl magnesium

Particular emphasis will be given to the ease of implementation of the process demonstrating its usefulness as a versatile tool for the elaboration of high-added value macromolecular objects. This facility is illustrated by the possibility that we disclosed, to assess a large set of RE/MgR_2 combinations, including *in situ* synthesized catalysts as depicted on scheme 2. In particular, homoleptic, mono or bis-substituted complexes can straightforwardly be prepared in the catalytic mixture, simply starting with RE salts [6].



Scheme 2. *In situ* synthesis of catalytic species as a convenient process.

These results are rooted in the pioneering breakthrough of Pr Mortreux [7-9] and their impact is well-illustrated by subsequent exploitation by other groups [10-19] and a booming development in chain transfer agents. Moreover, in the case where the alkyl-Mg group contains a functional moiety (ie aromatic ether, amino or alkenyl), this may afford telechelic oligomers [12] (see scheme 3)



Scheme 3. Examples of dialkylmagnesium initiators

The starting compounds of the process are based on dialkyl magnesium compounds MgR_2 (see scheme 3). Solutions in hydrocarbons are commercially available, including at the industrial scale, for example: dibutylmagnesium (Aldrich, 1 M in hexane), butylethylmagnesium (Texas Alkyls, 20% in heptane) or butyloctylmagnesium (Akzo Nobel, 20% in heptane). Alternatively, more sophisticated dialkylmagnesium compounds were synthesized as sake of

functionalized initiators, for example bis(ortho-dimethylaminobenzyl)magnesium(THF), bis(ortho-methoxybenzyl)magnesium(THF) [20], bis(3-butenyl)magnesium(dibutylether)$_2$ and bis(10-undecenyl)magnesium(dibutylether)$_2$ [12]. Shorter compounds i. e. the diethyl or dimethyl and even the dihydrido magnesium compounds were excluded of the field of this study due to their insolubility. Some difficulties were encountered when using the well-known RMgX Grignard reagents for two distinct reasons: first, the halide atoms clearly compete with alkyl groups on the active centers and disturb equilibria resulting to the formation of the active Cat-R species; second, ethers are the usual solvents of Grignard species while they are inhibitors of the polymerization due to high oxophilicity of the catalyst metal. Hence, specially designed initiators were conveniently obtained by conversion (Schlenk equilibrium, see scheme 4) of Grignard reagents into dialkylmagnesium compounds by means of MgX_2(dioxane) precipitation and concentration of the filtrated solution to a minimum level of ethers.



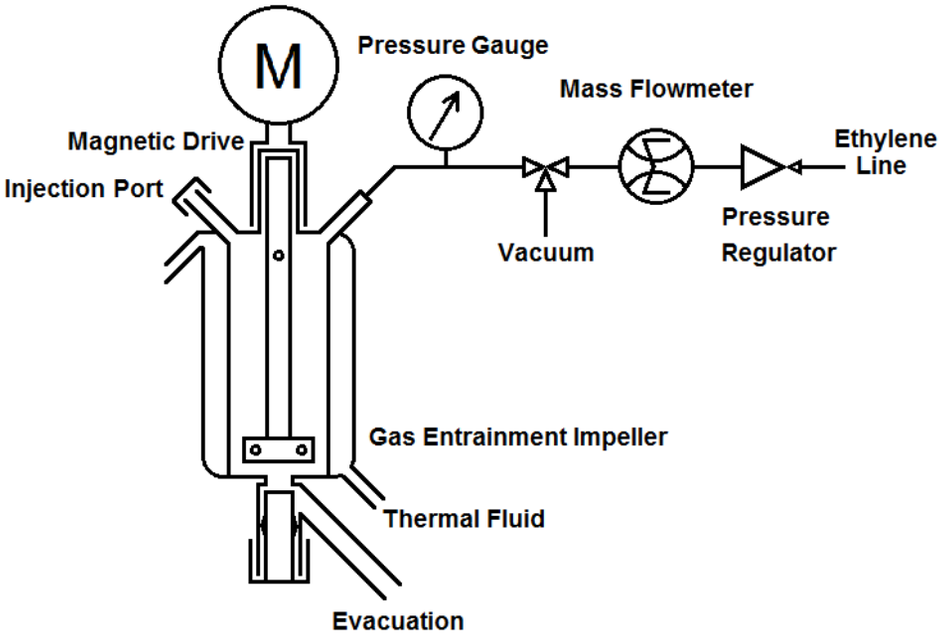
Scheme 4. Schlenk equilibrium

2. Oligomers of Ethylene

2.1. Ease of implementation

Unlike for liquid monomers, which can be handled with classical Schlenk techniques, gaseous ethylene (at standard conditions) requires particular equipment as, for example, with solution process. The convenient solvents tested were hydrocarbons, and among them linear or cyclic alkanes, aromatics, possibly halogenated. Rigorous exclusion of air, moisture and protic impurities was reached by working with a sealed reactor equipped with a vacuum line (see scheme 5). After a purge with clean gas, a simple wash with a sacrificial batch of dialkylmagnesium solution enabled the required purity level. Since ethylene polymerization is highly exothermic, the reactor was correctly thermostated. In the same way, kinetic limitations due to dissolution rates of ethylene were overtaken by powerful stirring. Ethylene inlet was regulated at a constant pressure, at atmospheric or higher pressure. A mass flowmeter and a data acquisition system recorded the exact amount of ethylene consumed all along the reaction, hence allowing deducing the average molar mass of the chains at any time.

The catalytic species for ethylene insertions in alkyl chains were obtained *in situ* by adding to the dialkylmagnesium reagent a solution of a rare earth salt containing also the necessary amount of ligand under its protio form, to obtain the pre-catalyst in solution (see next paragraph). As a typical example, two equiv of pentamethylcyclopentadiene ligand will afford the *in situ* formation of a decamethylmetallocene. Several metals were tested, for example yttrium, lanthanum, neodymium, samarium and lutetium [21-22]. Although the catalytic

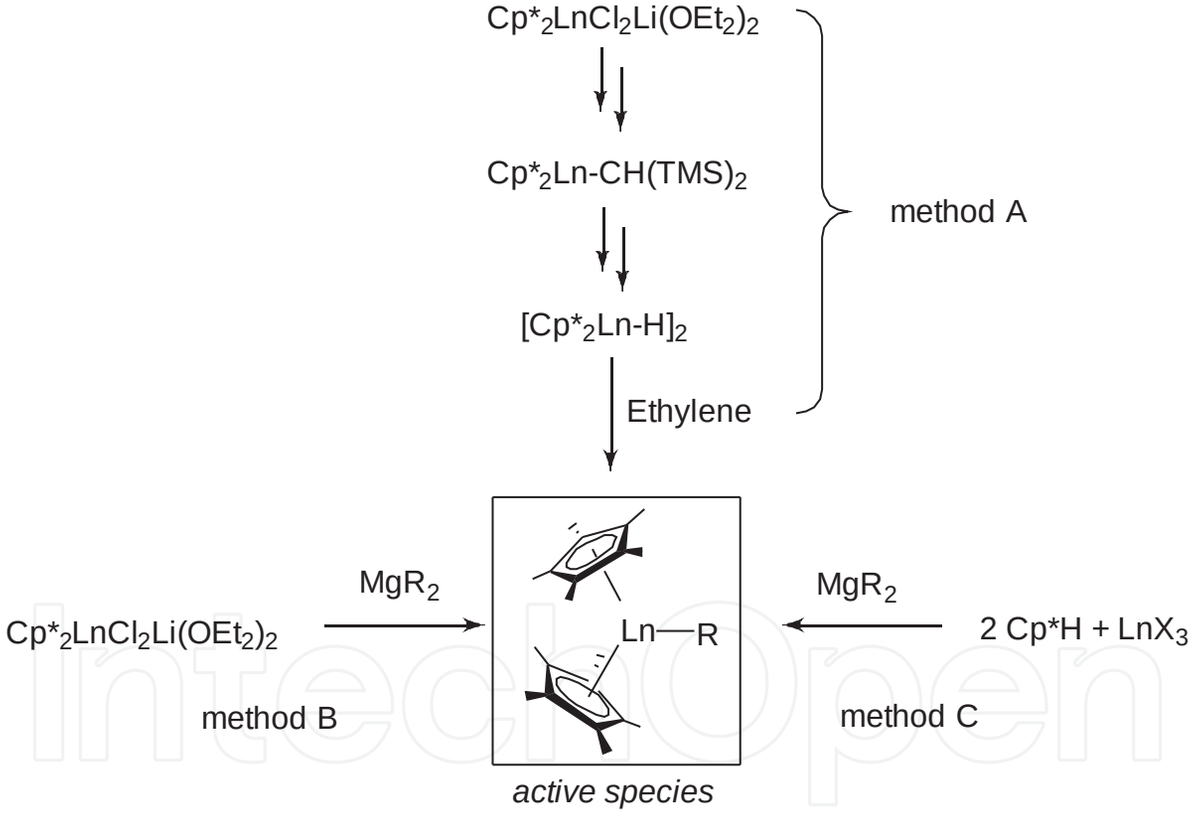


Scheme 5. Reactor equipment

activity and selectivity were clearly different depending on the rare earth nature, these differences were of low importance, as far as ethylene polymerization is concerned [9]. The neodymium species were however much more studied in the literature, probably in relation to their interesting properties for polymerization of other monomers, especially diene monomers. Different anions of the rare earth species were used, for example chloride, borohydride, alkoxides (tertiobutylates, phenates), carboxylates (versatate, 2-ethylhexanoate), phosphates and phosphonates. Once more, differences in reactivity were noticed, but the most important feature concerning the nature of the anionic ligand was the solubility of the corresponding salts. A comparative study between chloride and versatate salts of neodymium gave exactly the same results in terms of oligomers distribution for the same ethylene conversion, but the reaction started immediately with the versatate which was soluble in toluene, while it was sluggish with the insoluble chloride salt. The neodymium versatate has the other advantage to be available at an industrial scale (Solvay-Rhodia Rare Earth Systems), while at a laboratory scale, the neodymium borohydride [23] was preferred for its well-defined structure and its purity, allowing easiest spectroscopic characterizations, hence better control of the generation of catalytic centers.

Well-defined organometallic compounds bearing two pentamethylcyclopentadienyl and an alkyl group in the coordination sphere of the rare earth metal were initially established as best-suited [24]. But these catalytic species, while being very active in polymerization conditions, were found excessively prone to decomposition in the absence of monomer and impossible to store. Hence, several synthetic routes were proposed to generate the catalyst *in situ*, starting from a series of precatalysts (see scheme 6). The earliest route (A) reported in the literature was involving hydride species [21], which can be formed by hydrogenolysis of a crowded alkyl: the bis(trimethylsilyl)methyl (TMS_2CH-). A next route was developed at the turn of the

21st century [25-26] and consisted in the use of a crystalline bis(pentamethylcyclopentadienyl) rare earth chloride (B). The latest route, since a few years [6,27-28], proposed the direct use of a "naked" rare earth salts, as catalyst precursor, which was mixed with two equivalents of ligand precursor (pentamethylcyclopentadiene, C_5Me_5H, noted as Cp*H). When this mixture was added to a solution of dialkylmagnesium in excess, under atmospheric pressure of ethylene, it took only a few seconds to see the activity rising up at the same level as with the use of well-defined catalysts. This was interpreted in terms of alkyl/X ionic metathesis occurring between the rare earth and the magnesium atom affording the formation of rare earth alkyls. In a subsequent step, the Ln-alkyl species was assumed to react with the ligand precursor Cp*H with alkane elimination as irreversible step, to lead to the formation of a $\{Cp^*_2LnR\}$ compound. Clues for this mechanism arose from an NMR study that excluded the other possible pathway: a mixture of dialkyl magnesium and two equivalents of Cp*H gave the expected complex Cp^*_2Mg very slowly compared to the rate of catalyst formation.



Scheme 6. Various strategies leading to the formation of the active species.

Implementation of the reaction was tested at a laboratory scale with the following details given here as an example. In a glove box, the butylethylmagnesium (BEM, 200 μmol) was weighed in a syringe and diluted in 20 mL of toluene (which was degassed by argon bubbling and stored over molecular sieves). The polymerization reactor was purged under vacuum and filled with ethylene. Injection of the BEM solution (200 μmol, 20 mL toluene) in the reactor and stirring at 90°C led to passivation of the inner walls of the reactor. Meanwhile, a new set of BEM

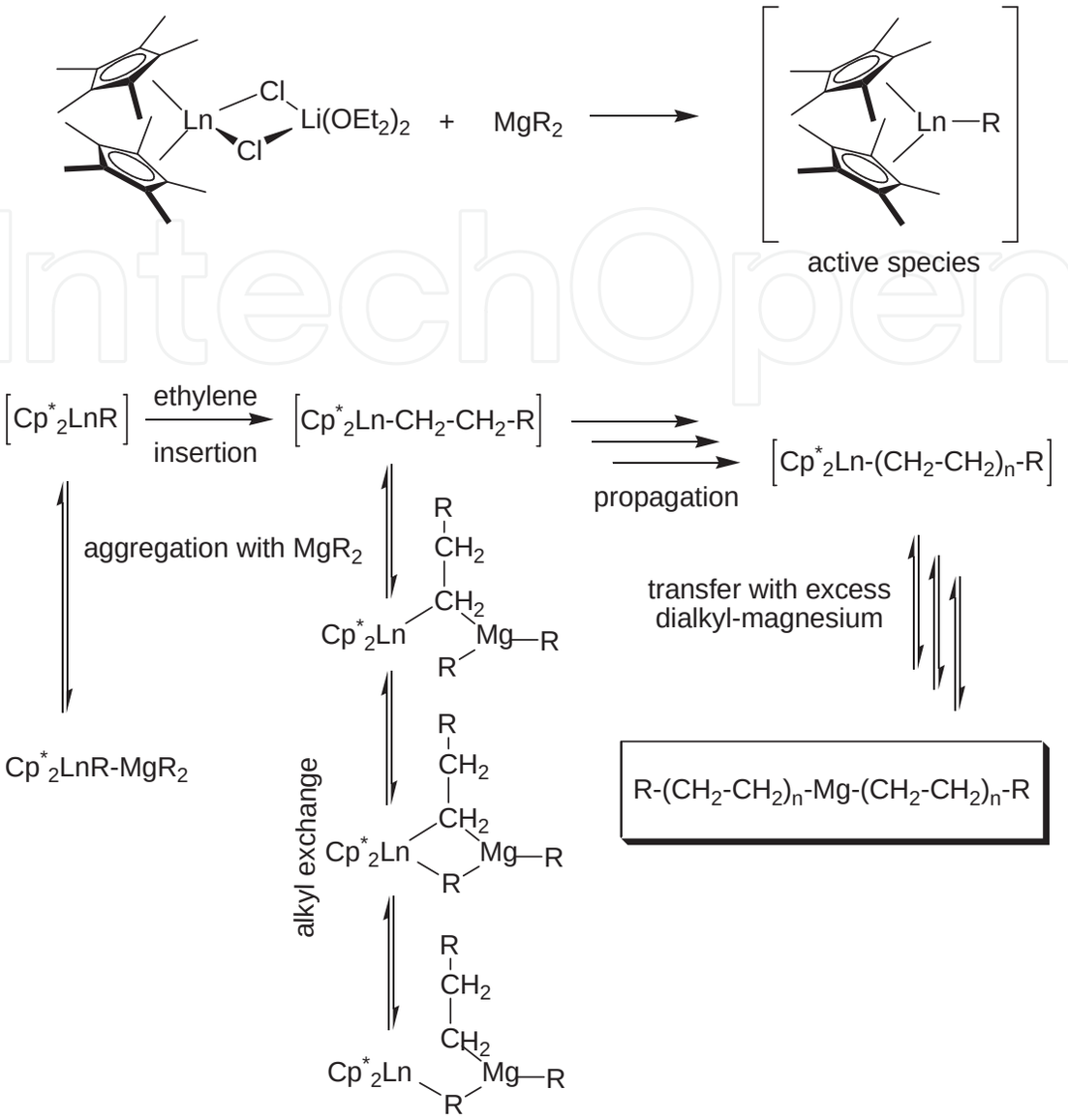
solution was prepared in the glove box. In a 2 mL syringe, neodymium versatate ($NdVs_3$, 13.6 mg, 20.7 μmol) and pentamethylcyclopentadiene (Cp*H, 7.0 mg, 51 μmol) were weighed and diluted with 1 mL of the above BEM solution. After evacuation of the passivation solution, the remaining 19 mL BEM solution was injected in the reactor and stirred until pressure and temperature were stable. Injection of the small syringe solution gave the start of the polymerization. The monitoring of ethylene consumption allowed to measure the amount of ethylene consumed over time, and consequently the theoretical chain length of the polyethylene produced. Reaction can be stopped at a desired degree of polymerization or, if allowed to go free, it will stop spontaneously after a short burst of activity, the average molar mass being around 1000-2000 g/mol. Polymerization quench was possible with any known reactive of Grignard species, typically an electrophile, for example protic compounds produced alkanes, aldehydes or ketones gave secondary or tertiary alcohols, carbon dioxide gave carboxylic acids, iodine gave iodinated alkanes, etc. (see further functionalization section).

2.2. Mechanism of control

Preferred paradigm for understanding the present reaction came from the concept of "Aufbaureaktion" early developed by Karl Ziegler in the fifties [29]. The process under study at this time aimed at growing the linear chains of alkyl aluminum by insertion of ethylene. When implementing potential catalysts, the investigations were particular fruitful using titanium chloride and were oriented in a new field nowadays known as "Ziegler-Natta polymerization". While being originally restricted to alkyl aluminum compounds, the concept of Aufbaureaktion can be transposed to alkyl magnesium compounds at the condition that a suitable catalyst would be found. Fortunately, in our laboratory, the studies of rare earth complexes as model compounds of Ziegler-Natta catalysts revealed that dialkylmagnesium compounds behaved as efficient transfer agents during the ethylene polymerization with these rare earth complexes. The striking fact was that the transfer process was fast and reversible between magnesium and rare earth. That means that, in the presence of a large Mg/RE ratio, the alkyl chains were essentially observed on magnesium, nevertheless insertion of ethylene seemed to happen homogeneously on all these chains with the activity and selectivity of the rare earth catalyst. Each chain can be considered as continuously transferred from one to another metallic atom, with insertion of ethylene only when it was found on a lanthanide unit. Alkyl chains were observed inactive for ethylene insertion when located on magnesium, so they were named "dormant species" in this case, since they were only waiting for a transfer to lanthanide (see scheme 7).

The mechanism proposed for the observed chain growth on dialkyl magnesium fundamentally contrasts with an anionic mechanism, for example in the chain growth of alkyl lithium as observed in the relevant work of Bergbreiter [30]. In these studies, the alkyl lithium species were modified by the use of tetramethyl ethylene diamine (TMEDA) as a ligand of the lithium atom, rendering the alkyl anion sufficiently reactive to attack the ethylene monomer. Regardless the cost problem arising from the need of up to three equivalent of TMEDA ligand per produced oligomer, the high reactivity of the species and the resulting secondary reactions required to work at very low temperature for further uses.

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Scheme 7. Postulated mechanism for chain growth on dialkylmagnesium.

The mechanism described here clearly belongs to the "catalyzed chain transfer polymerization" concept (CCTP otherwise named coordinative chain transfer polymerization) as recently reviewed by our group [31]. CCTP is part of the new concepts developed in coordination polymerization catalysis in the recent years, also including Living Degenerative Group-Transfer Coordination Polymerization [32], Chain Walking Polymerization (CWP) [33] and Chain Shuttling Polymerization (CSP) [4]. In the area of radical polymerization, a parallel can be seen between Controlled Radical Polymerization mechanisms (Atom Transfer Radical Polymerization, ATRP, Nitroxide Mediated Polymerization, NMP or Radical Addition Fragmentation Transfer RAFT, for example [34]) and the CCTP concept, which is restricted to mechanisms by coordination polymerization. By streamlining, CCTP can be considered as a generalized concept of the original Aufbaureaktion, describing the fast and reversible transfer of chains between a large amount of inexpensive species and a suitable catalyst. Other couples

of such combinations with different metals have been employed, beside the herein described dialkyl magnesium / rare earth metallocene association. For example with diethyl zinc, chain growth was observed using iron complexes with pyridinediimine ligand [5] and with zirconium complexes with salicylaldimine ligand [35]. With trialkyl aluminum compounds, yttrium complexes with pyridinamine ligand [36] and chromium complexes with Cp* ligand were also found successful [37-38]. However, the resulting oligomers in these cases were end caped with zinc and aluminum, respectively, consequently having a different reactivity than the magnesium end capped oligomers.

2.3. Chain length distribution and other characterizations

At the end of the ethylene uptake, a simple way to characterize the oligomers produced was to hydrolyze the C-Mg chains end by any protic reagent; for example by pouring the homogeneous solution of the reactor at 90°C in cold methanol. The slurry had to be well stirred to obtain a fine precipitate, while bubbling argon was necessary in order to avoid oxygen side reactions. Meanwhile, the presence of trace amounts of hydrochloric acid favored the dissolution of all metallic residues. When oligomers with a carbon number under 20 could be neglected, the precipitate was straightforwardly filtered and dried, otherwise a low amount of methanol was used in order to recover the entire mixture for further analyses.

NMR ^{1}H and ^{13}C, as well as IR analyses established the linearity of the chains; absolutely no branching was observed. The chain ends consisted of normal alkyl $–(CH_2)_n–CH_3$ with only trace amounts of vinyl ends $–CH=CH_2$. Some olefins could indeed be produced by a secondary reaction with mechanisms named either β-H elimination, or transfer to ethylene monomer. Low temperature and high magnesium concentration favored the very low amount of such defects. Typically, a temperature of 90°C and toluene solutions between 10^{-1} and 10^{-2} M represented a good compromise.

Several analytical methods were used to characterize the distribution of the chain sizes. For mixtures having rather high molar mass, the size exclusion chromatography (SEC or gel permeation chromatography, GPC) at 135°C in trichlorobenzene were found to be the best choice, an example is given in figure 1.

Gas chromatography (GC) was found best suited for oligomers having less than 100 carbons, if the apparatus was equipped with a Simdist metal column, or 60 carbons when using a usual fused silica column. Advantages of this analytical method lie in the identification and quantification of each kind of molecule with a high precision, including the separation of impurities like olefins up to 22 carbons. Use of alkane standards, commercially available for 36, 50 and even 60 carbons, ensured reliable calibration of the flame ionization detector, bypassing an obvious segregation during the evaporation step in the injection port. An example is given in figure 2 [39].

Ultimate characterization of oligomers was reached with mass spectrometry using a time of flight detector and a matrix assisted laser desorption ionization process (MALDI-TOF). However, considering that alkanes represent ones of the most difficult molecules to be ionized,

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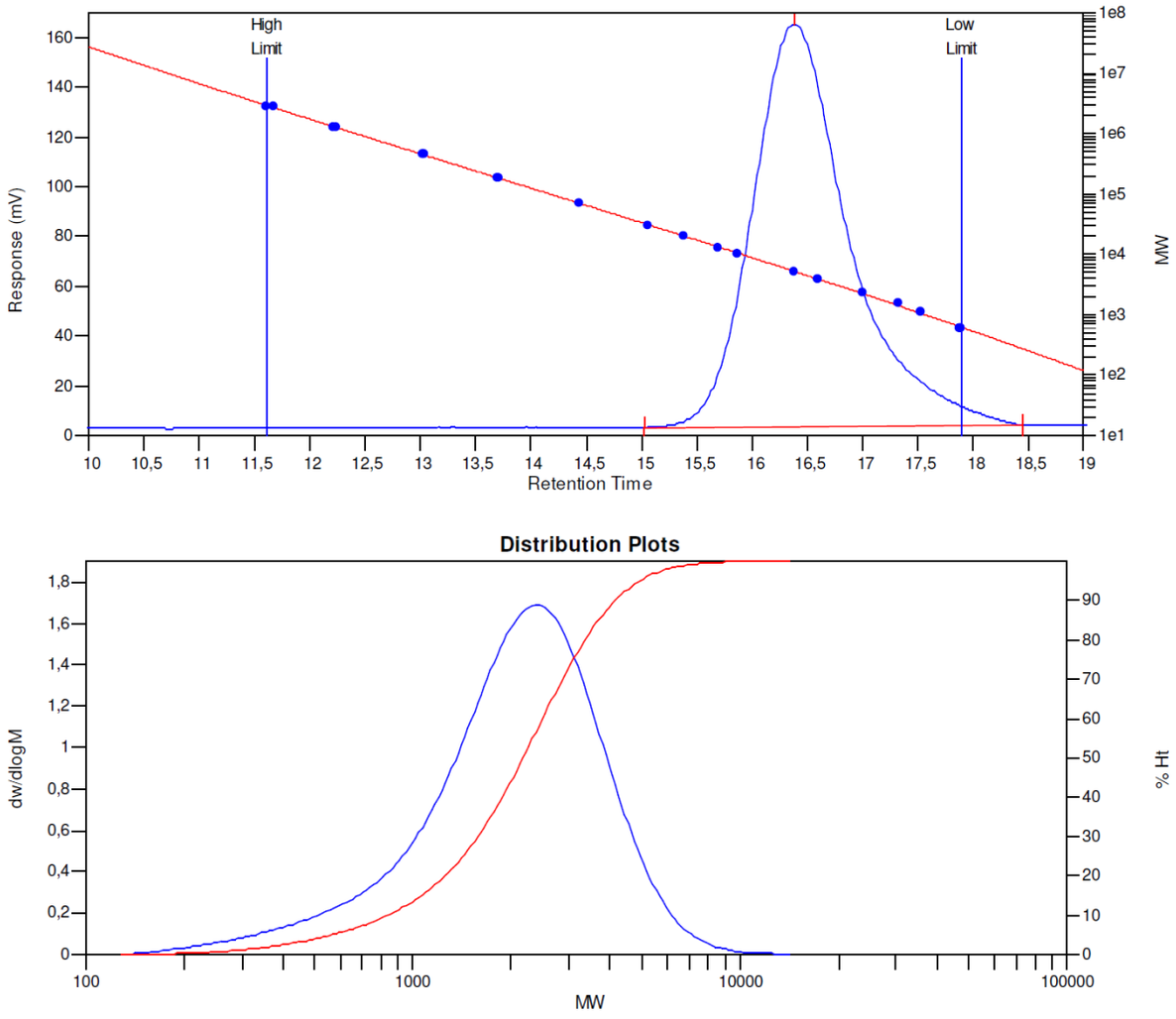


Figure 1. SEC analysis of an oligomer sample with $\bar{M}_n$=1530 g/mol and dispersity Đ=1.55

it is not surprising that we failed to analyze the sample after hydrolysis. Hence we tried to functionalize the crude oligomer mixture, when it was still constituted of alkyl chains end capped with magnesium, with a tag that was easily ionisable [40]. As tag precursor, we looked for a carbonyl compound with fused aromatic cycles and electrodonor substituents. Carbonyl compounds are known to undergo addition of organomagnesium compounds, while fused aromatic cycles with electrodonor substituents would give stable adducts with H^+. With these criteria, the cheap and nicely colored Rhodamine B base was selected. Advantage of the MALDI-TOF analytical method once again is the recognition of individual molecules, complementary to the GC method. However, quantification was distorted by segregation at the evaporation step and we are aware that only the living fraction of the oligomers mixture, once functionalized, can be detected (dead chains, for example olefins, can't be observed by this technique). The spectrum is given in figure 3, with an enlargement showing the good fit between data and a simulated distribution based on Poisson statistics and ^{13}C isotopic abundance.

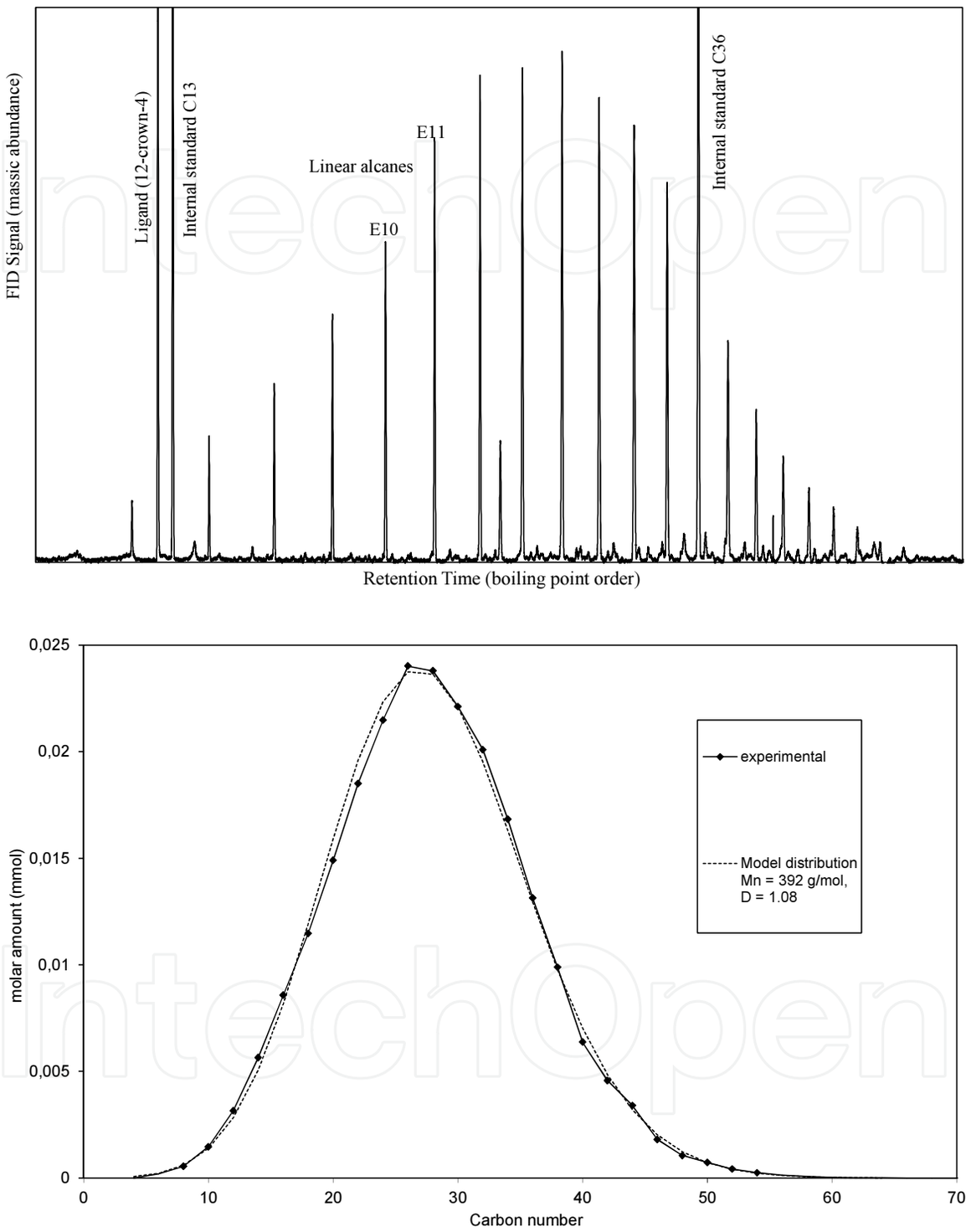


Figure 2. GC analysis of an oligomer sample with $\bar{M}$n=392 g/mol and dispersity Đ=1.08

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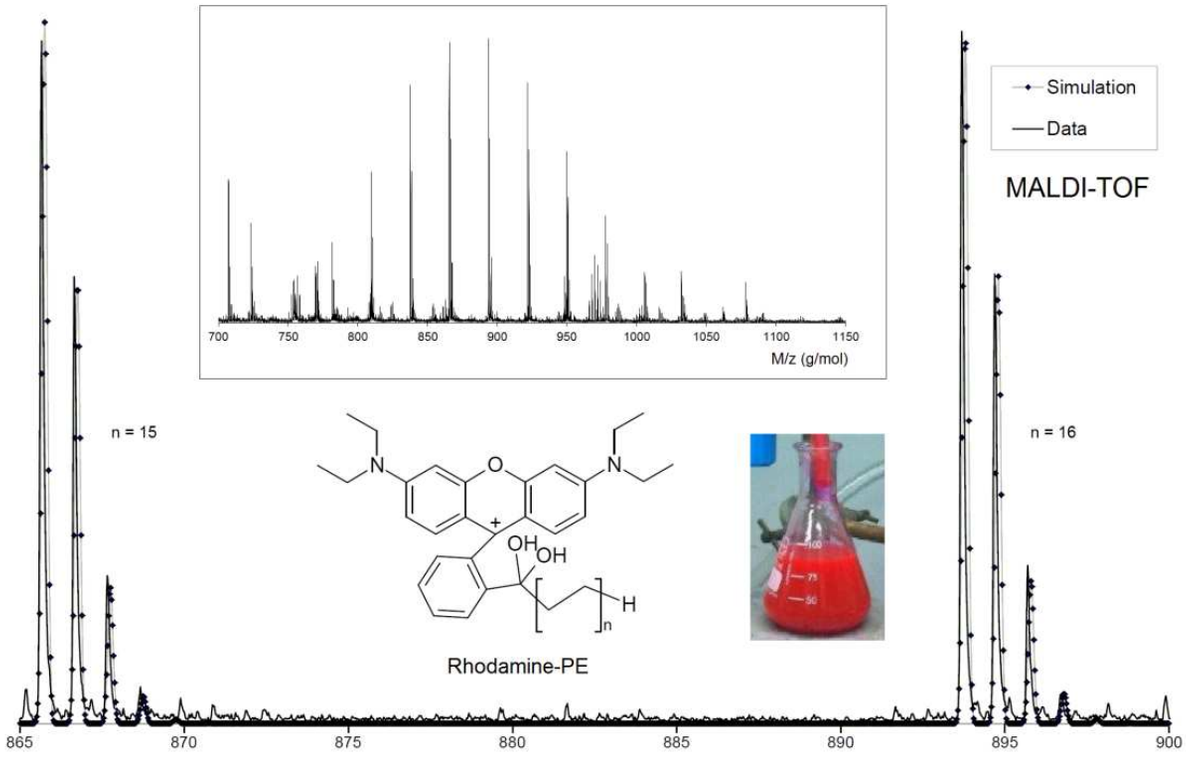


Figure 3. Mass spectrum by MALDI-TOF of an oligomer sample functionalized by Rhodamine B base.

2.4. Functionalizations

The functionalization of ethylene oligomers was demonstrated in the above paragraph by the use of Rhodamine B base. This reaction was an addition of the long chain alkyl magnesium to the carbonyl group of an aromatic lactone. As seen on figure 3, the resulting molecule was an ethylene oligomer covalently bonded to a polar dye. The red color of the dye was retained in the final material, but other physical properties, like solubility for example, were severely modified. As a matter of fact, it was easy to clean by washing with methanol all Rhodamine residues, but it was impossible to decolorize by any way a plastic container (LDPE) in which had been stored the oligomers capped with Rhodamine. A possible explanation would be that the long chains were integrated in the bulk of the container walls. The dye, which is covalently bonded to these long chains, had consequently negligible leaching rates. Applications of this material as permanent ink, non-leaching and readily dispersible in the bulk of non-polar polymers, without any treatment or additives, appeared promising.

Long chain primary alcohols were obtained by a straightforward functionalization of the oligomers with oxygen and then hydrolysis. Indeed, one had simply to follow the next step of the Aufbaureaktion in its application as an industrial process. An analogy can be seen between aluminum and magnesium as far as the reactivity of alkyl metal with oxygen is concerned.

Kinetics of the oxidation of alkyl magnesium were found fast, perhaps faster than hydrolysis, since we detected long chain alcohols as impurities of alkanes if hydrolysis of alkyl magnesium was realized in non-degassed methanol. On the contrary, when long chain alcohols were the desired product, alkane impurities were observed with a peculiar specificity: the distribution of these alkanes was higher in mean molar mass, sometimes up to twice the mean molar mass relative to the parent distribution of alcohols. A possible explanation would be to consider a coupling mechanism of two alkyls resulting either from a reductive elimination or from a Würtz-like reaction. The coupling mechanism would be induced by oxygen on unsolvated dialkyl magnesium compounds. We bypassed this difficulty by using ether additives. Best results (93% functionalization efficiency, see figure 4) were obtained using crown ether of small size (12-crown-4). An advantage of the latter compound was its inertness relative to the rare earth catalyst, allowing its addition at the beginning of the ethylene oligomerization. A this stage, the crown ether had a beneficial effect on the CCTP mechanism by impeding the aggregation of dialkyl magnesium compounds: first, the ethylene insertion kept a high rate irrespective of the magnesium concentration; second, exchange of alkyl groups were found faster, as seen with an improvement of the dispersity. For example figure 2 (Đ=1.08) was obtained with crown ether while figure 1 (Đ=1.55) was obtained without it. Noteworthy, a large range of oxygenated impurities would have more or less the same character (n donor or Lewis base), provided the stoichiometry with respect to magnesium would be between 1 and 2. This explained why it is possible to run the oligomerization process with relatively unclean materials, with good activity and dispersity, but with doubtful and irreproducible results. Figure 4 is the GC trace of a sample of long chain linear alcohols obtained in our best conditions, *i. e.* with 1 equivalent of 12-crown-4. An analysis by ^{13}C NMR spectroscopy is presented in figure 5 for a similar sample but with slightly shorter chains and after precipitation and filtration [6].

Many other functionalizations have been achieved with magnesium end-capped oligomers of ethylene which were synthesized by rare earth/magnesium based CCTP. For example carboxylic acids were obtained in our laboratory by addition of carbon dioxide [9]. Long-chain alkyl tin or alkyl silicium in a star shape were successfully tested [9,41]. An important work has also been realized by Boisson and D'Agosto who focused on the synthesis of thiol and iodine end-capped oligomers by addition of sulphur and iodine on the long-chain dialkyl magnesium, respectively [11]. The iodo compounds were then transformed into the corresponding long chain azides, which were used in click chemistry. Alternatively, the latter azides were hydrogenated into the corresponding amino end-capped oligomers. These examples are not exhaustive and the field of application should be widen since this represents only a part of the larger theme of Catalytic Chain Transfer as recently reviewed by Marks [42].

2.5. Uses as macro-initiators

A special application of magnesium end-capped oligomers was to consider them as macro-initiators and to synthesize block copolymers. A polyethylenyl block can then be grafted to a second block of different nature giving rise to a specialty polymer. Since the linear alkyl group has a lipophilic character, with good crystallization ability, the interest was to associate a

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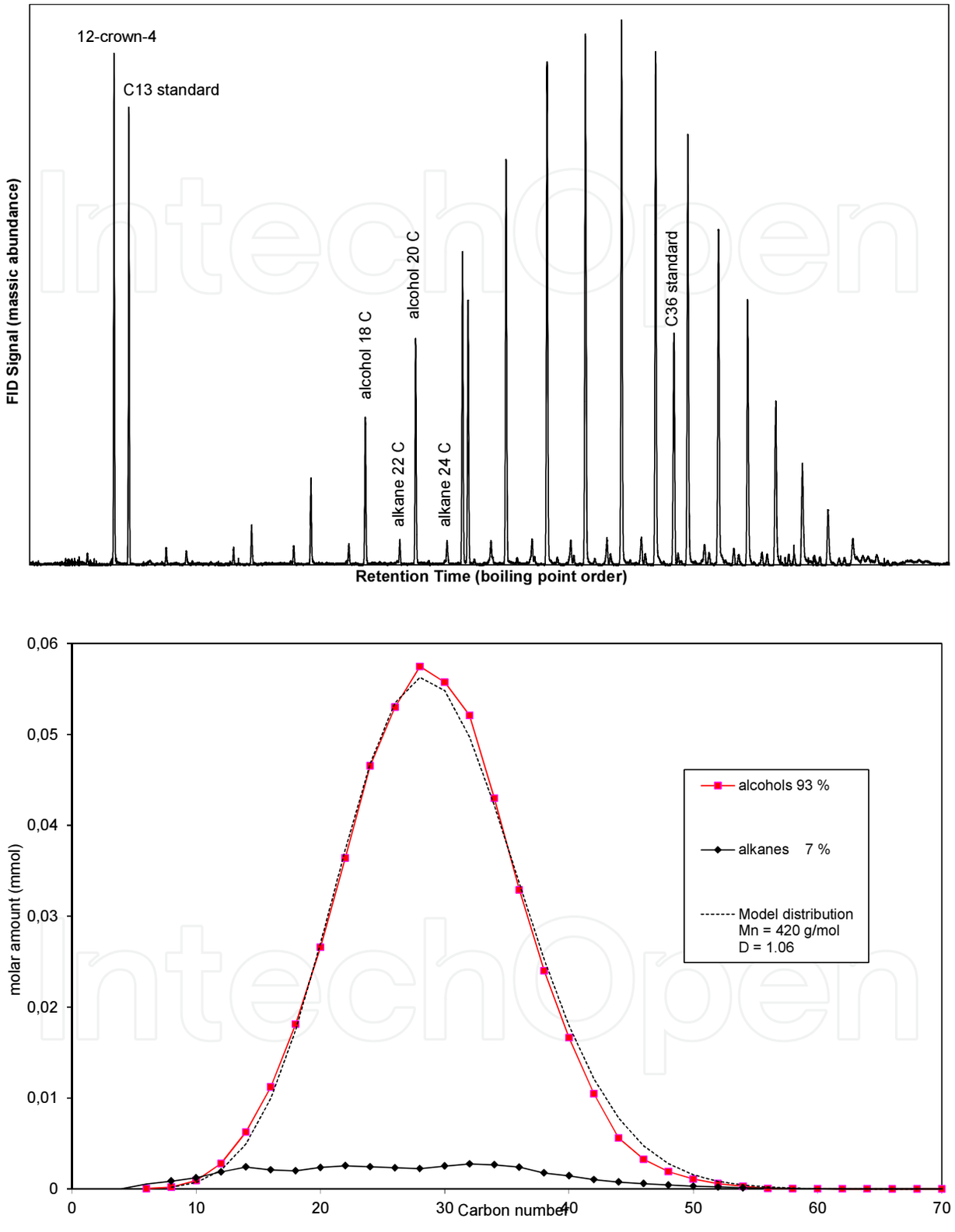


Figure 4. GC analysis of an oligomer sample functionalized to primary alcohols by oxygen.

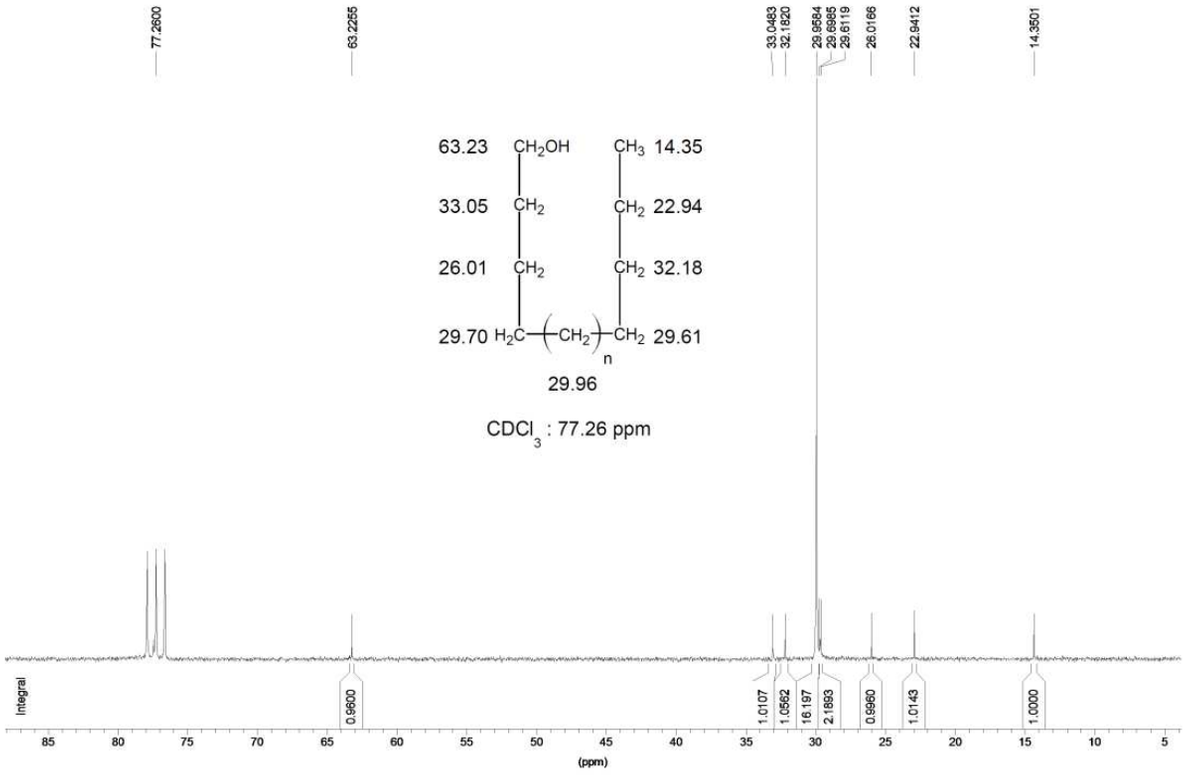
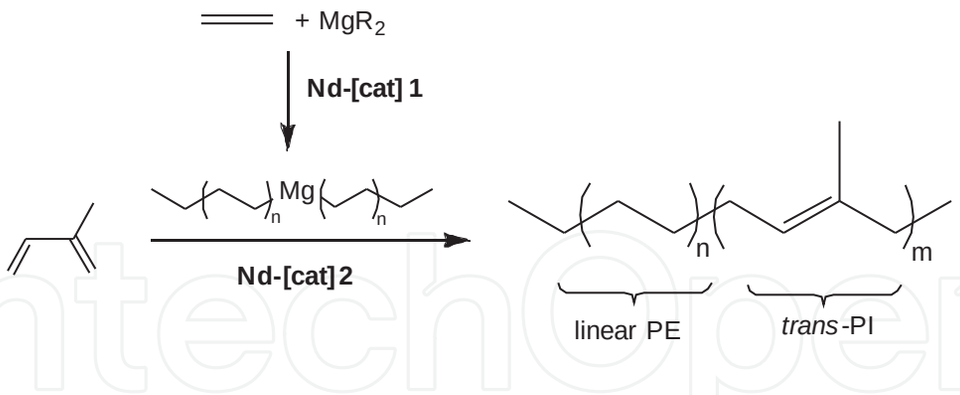


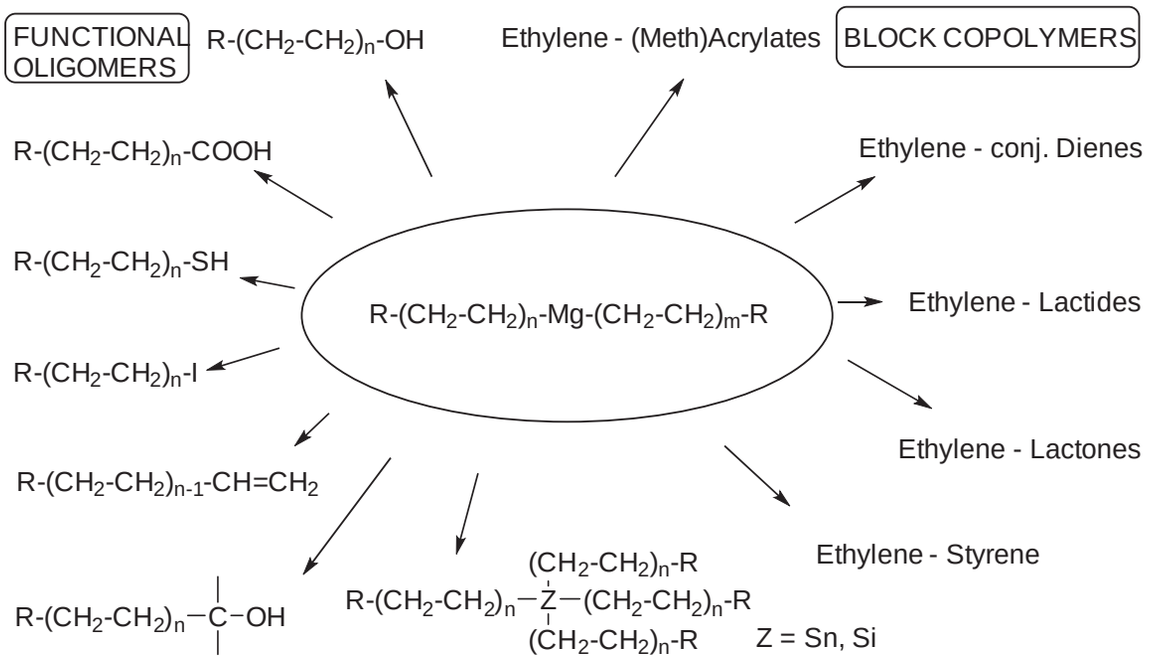
Figure 5. NMR ($CDCl_3$, 75 MHz) of an oligomer sample functionalized to primary alcohols by oxygen

second block more polar or more amorphous. From a catalytic point of view, the second step generally needs its own catalyst, which was added simultaneously to the second monomer, since different monomers require usually different catalysts. But a particularly elegant process, in terms of atom economy, should be highlighted when the magnesium atom itself was the catalytic centre of the second step. As an example of the latter case, we tested the polymerization of methyl methacrylate with magnesium end-capped macro-initiators and we obtained the corresponding PE-PMMA biblock [9]. A different situation was encountered when ε-caprolactone monomer was chosen for the second step. Indeed the traces of rare earth compounds (1 to 2 % of the magnesium amount) were found very active and compete with the magnesium activity, resulting in a polymodal distribution of PE-PCL block copolymers. A third example of block copolymerization, described recently [39], used isoprene as second monomer and needed the addition at the second step of one additional equivalent of rare earth salt per magnesium macro-initiator. The polyethylene-polyisoprene copolymers were obtained in a one-pot procedure (see scheme 8).

After several steps of functionalization as described above, the end-capped oligomers of ethylene can be designed as sophisticated macro-initiators, which were adapted to some particular polymerization mechanism. For example, RAFT or NMP mechanisms were successfully initiated with special macro-initiators based on long-chain alkyls issued from CCTP [11]. As for functionalization, the field of applications of block copolymers is largely open and new products can be synthesized purposely, depending on the precise properties required (see scheme 9).[9,11-19]



Scheme 8. Block copolymer of ethylene and isoprene with *trans* stereospecificity.



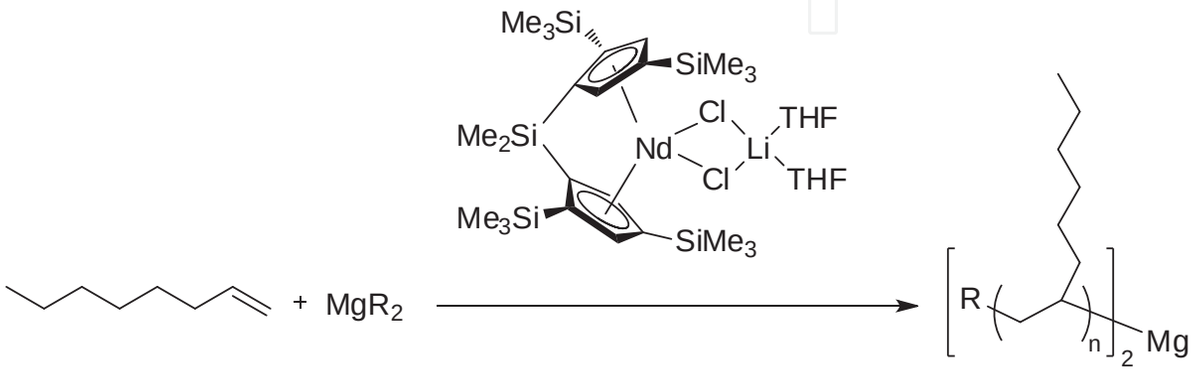
Scheme 9. Functionalization of ethylene oligomers after CCTP process.

3. Oligomers and co-oligomers of olefins and conjugated dienes

3.1. Octene

In contrast to the high activity of the rare earth / magnesium bimetallic system for ethylene polymerization, when using pentamethylcyclopentadiene Cp* ligands, the activity for other olefins such as octene was found very low. Moreover, poor selectivity hampered the propagation step by a secondary transfer reaction. This is an irreversible hydride transfer reaction, named π-allyl formation, between a living alkyl-metal catalyst and an olefin, giving rise to a dead alkane and a π-allyl-metallic complex, the latter having low, if any, catalytic ability to insert a new olefin monomer (higher activation energy of the insertion step in the catalytic

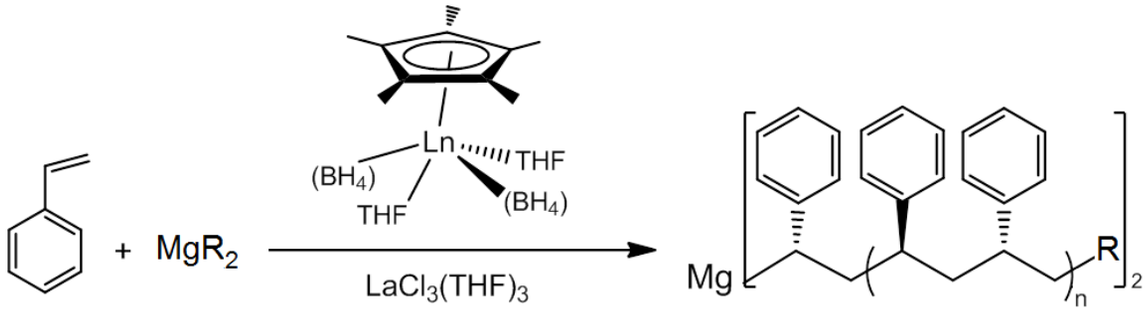
cycle). This problem was overcome by changing the ligand in the coordination sphere of the rare earth. In particular, replacement of the methyl substituents on the cyclopentadiene ring of Cp* by several crowded silyl groups fulfilled the electronic and steric requirements for a better activity and selectivity for the octene polymerization. The synthesis of a peculiar ligand (see scheme 10) and isolation of the corresponding rare earth complex represented a prerequisite to test the ability of the CCTP concept for the synthesis of magnesium end-capped oligomers of octene. Successful results were obtained, ($\overline{M}$n=400-1300 g/mol, Đ=1.11-1.65) with longer reaction times than for ethylene (24 h). [43-44]



Scheme 10. Oligomerization of octene by CCTP with neodymium / magnesium system.

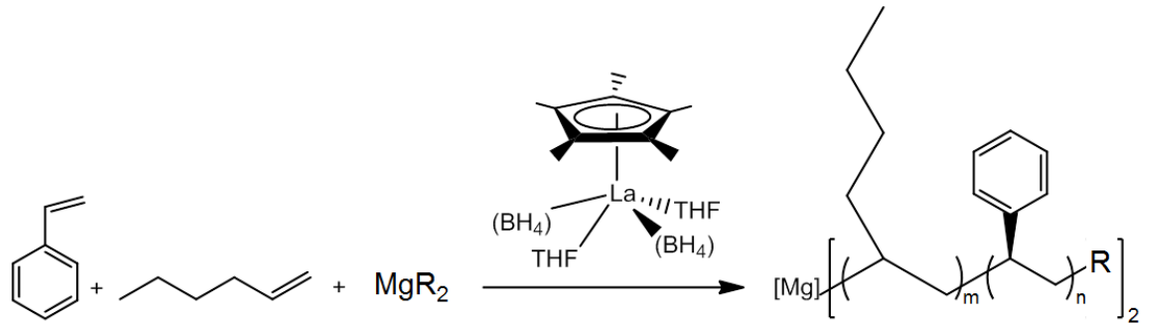
3.2. Styrene

As already mentioned for α-olefins, the activity of the decamethylmetallocene RE / Mg system was observed as negligible for the insertion step of styrene in a polymerization catalytic cycle. Higher temperature gave effective chain transfer of oligostyrene on dialkylmagnesium, but with competitive radicalar and/or anionic mechanisms besides the coordination one [45-48]. By switching from Cp* to other ligands, a stereoselective CCTP process yielded near-perfect syndiospecific and isospecific oligostyrenes end-capped with magnesium [49-51]. The use of half-metallocene systems (with only one Cp* ligand per rare earth) and even of inorganic rare earth salts like chloride, borohydride, alkoxide or phenoxide [52], gave successful results in oligomerization of styrene in a chain transfer mechanism to dialkyl magnesium. In a study centered to the structure/reactivity relationships of the pre-catalyst, it was shown that $Ln(BH_4)_3(THF)_x$ (x=3, Ln=Nd, La) as well as the mixed $La(BH_4)_2Cl(THF)_{2.6}$ led to an efficient transmetallation of the growing polystyrene chain with the Mg chain transfer agent. However, ^{1}H NMR and MALDI-TOF studies established the simultaneous occurrence of some β-H abstraction. Such uncontrolled termination reactions were absent with $LaCl_3(THF)_3$, $Cp^*Nd(BH_4)_2(THF)_2$ and $Cp^*La(BH_4)_2(THF)_2$. The quantitative transfer efficiency observed led us to conclude to a Catalyzed Chain Growth on magnesium. Moreover, the reaction remained significantly syndioselective (85 %) with the two latter ones, as observed previously when combined with only 1 equiv BEM (see scheme 11) [53-54].



Scheme 11. Oligomerization of styrene by CCTP with rare earth / magnesium system. 85% syndiotactic selectivity for $Cp^*Ln(BH_4)_2(THF)_2$, Ln=Nd, La, and atactic polystyrene for $LaCl_3(THF)_3$.

Statistical copolymerization was assessed with 1-hexene and styrene monomers in the presence of the $Cp^*La(BH_4)_2(THF)_2$/n-butylethylmagnesium (BEM) catalytic system. Poly(styrene-*co*-hexene) statistical copolymers were obtained with up to 46% yield, and 23% 1-hexene content (see scheme 12). The occurrence of chain transfer reactions in the presence of excess BEM was established in the course of the statistical co-polymerization, through significant molecular weights decrease *vs.* 1 equiv BEM, along with narrowing of the dispersities. Thanks to this transfer process, the quantity of 1-hexene in the copolymer was increased substantially, from 8.6 to 23.2 %, for 80/20 1-hexene/styrene composition in the feed and in the presence of 10 equiv. BEM versus 1 equiv. [55]. These results extend the range of CCTP concept to a chain transfer induced control of the composition of statistical copolymers to poly(styrene-co-hexene) copolymers.

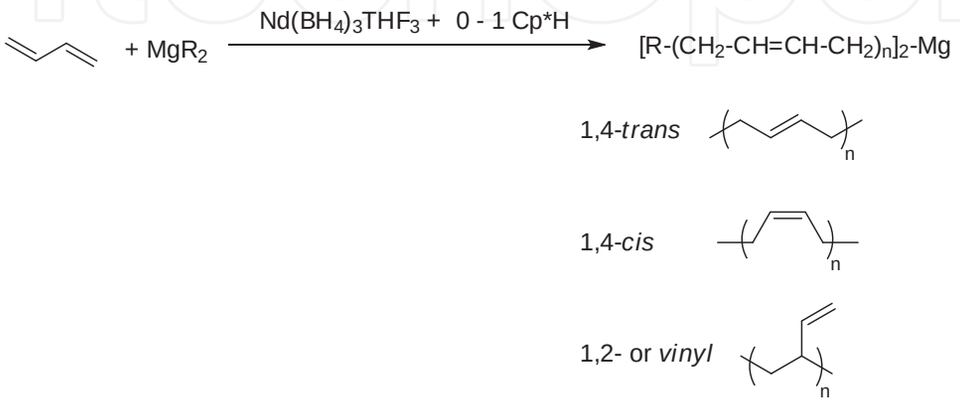


Scheme 12. Half-lanthanocene/BEM-mediated styrene-hexene Coordinative Chain Transfer co-Polymerization.

3.3. Butadiene

Polymerization of butadiene was known for a long time to be realized with catalytic systems based on rare earth salts and dialkyl magnesium [56-58]. Chain transfer efficiency to magnesium was of prime importance for example for the synthesis of functionalized polybutadienes with applications in the tyre industry [20]. Another striking point of this polymerization was the regioselectivity of the reaction which, in principle, can afford three kinds of sequences named 1,2-(or vinyl), 1,4-*trans* and 1,4-*cis* (see scheme 13). Using dialkyl magnesium in combination with rare earth salts was most generally effective for 1,4-*trans* selectivity [59], but

1,4-*cis* sequences have been obtained in some cases [60]. We recently established that the selectivity shifted slightly from high 1,4-*trans* (up to 97%) to more 1,2-regular (17%) simply by increasing from 1 to 10 the ratio of magnesium transfer agent relative to rare earth amounts. [61]. A chain transfer induced control of regioselectivity was hence evidenced (see table 1). Decrease of molar masses with increase of magnesium amounts was observed, delineating the transfer efficiency, although with a moderately controlled character (moderate dispersity). The magnesium presence at the tips of oligomer chains was attested by further functionalization, as mentioned below.



Scheme 13. Oligomerization of butadiene by CCTP with rare earth / magnesium catalytic system.

Run [a]	[Mg]/[Nd]	Time (h)	Isolated Yield (%)	Selectivity [b] (%)			$\bar{M}$ n [c] (kg.mol^{-1})	Đ [d]
				1,4-trans	*1,4-cis*	*1,2*		
1	1	2	96	95.0	3.5	1.5	49	1.29
2[e]	1	2	43	96.7	1.9	1.4	47	1.38
3	2	2	54	95.5	2.4	2.1	19	1.28
4	3	2	16	93.0	2.4	4.6	5.5	1.20
5	5	2	8	88.0	3.1	8.9	3.9	1.24
6	5	8	20	89.9	2.1	8.0	3.9	1.43
7	5	20	37	90.4	1.3	8.3	5.5	3.00
8	10	20	18	80.7	3.5	15.8	3.8	2.90

a: Reactions at 50 °C, in 10 mL of toluene; pre-catalyst: $Nd(BH_4)_3(THF)_3$ 20 µmol; co-catalyst: BEM; [butadiene]/[Nd]=1000

b: Determined by ^1H and ^{13}C NMR spectroscopy in $CDCl_3$

c: Number-average molecular weight measured by SEC with reference to PS standards. No correction factor applied.

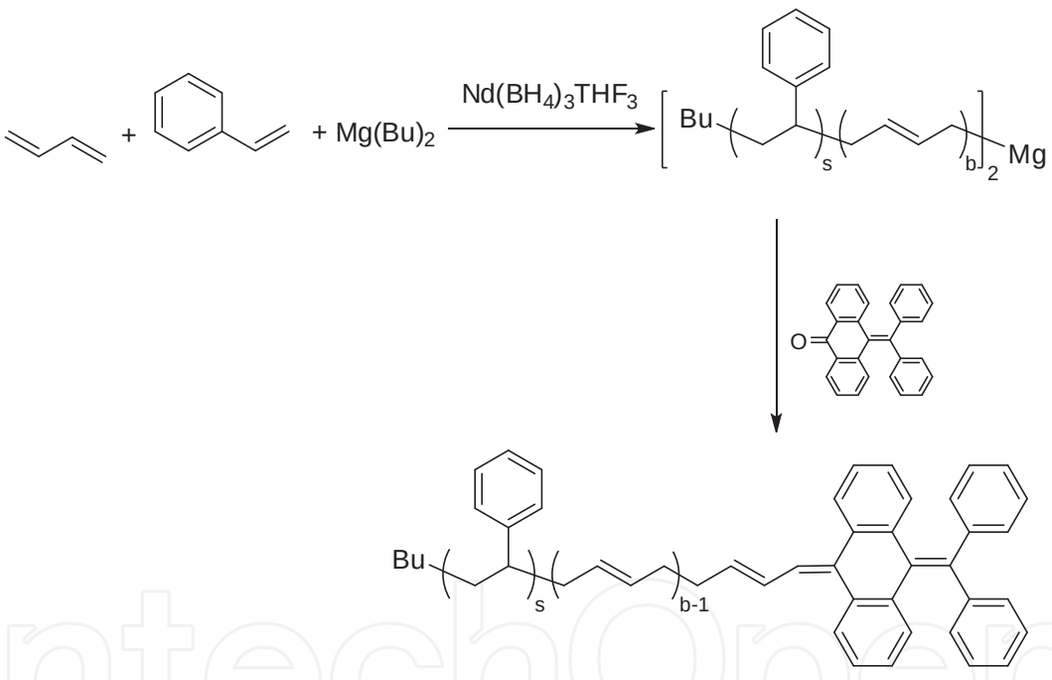
d: Dispersity measured by SEC: Đ=$\bar{M}$ w / $\bar{M}$ n

e: With addition of Cp*H (20 µmol) and supplementary BEM (10 µmol) in order to have an in situ prepared half-metallocene Cp^*NdX_2.

Table 1. Butadiene polymerization with Nd $(BH_4)_3(THF)_3$ and chain transfer with dialkyl magnesium.

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Statistical copolymerizations were achieved with styrene and butadiene monomers under conditions similar to previous experiments in table 1. Corresponding oligomers were obtained with $\overline{M}$n ranging from 4.4 to 240 kg/mol, for Mg / Nd from 10 to 1, respectively, and styrene incorporation up to 16.9%. Regioselectivity was 1,4-*trans* sequences for butadiene and isolated styrene units inserted statistically in the chains, as identified by ^{13}C NMR. Insertion rates for butadiene were found higher than for styrene. Among these copolymerization experiments, one was short stopped by quenching with a ketone (benzhydrylidene anthrone, Sigma-Aldrich, see scheme 14) in order to have light oligomers, end-capped with a functional group. Analysis by MALDI-TOF mass spectrometry gave a detailed snapshot of the growing chains, evidencing the C-Mg reactivity of the magnesium end-capped oligomers (see figure 6). Statistical distributions of styrene and butadiene monomers were observed, that follow exactly the Poisson probability. The lower styrene insertion rate, as compared to the butadiene one, was clear: the average degree of polymerization, after a 15-minute reaction, was between 17 and 18 for butadiene monomer whereas it was between 1 and 2 for styrene monomer.



Scheme 14. Statistical copolymerization of butadiene and styrene under CCTP conditions and further functionalization with benzhydrylidene anthrone.

3.4. Isoprene

In the presence of 1 to 10 equiv alkyl magnesium as chain transfer agent, combined to $Cp^*Ln(BH_4)_2(THF)_n$ (Ln=La, n=2.5; Ln=Nd, n=2), the observed molecular weight distributions are monomodal, and the number average molecular weight is close to the calculated one considering two growing chains per magnesium atom. This, along with reasonable dispersities (Đ 1.3–1.9), highlights a rare earth catalyzed polyisoprene chain growth on magnesium (see scheme 15). With $Ln(BH_4)_3(THF)_3$ (Ln=La, Nd) in the same conditions transfer efficiency is

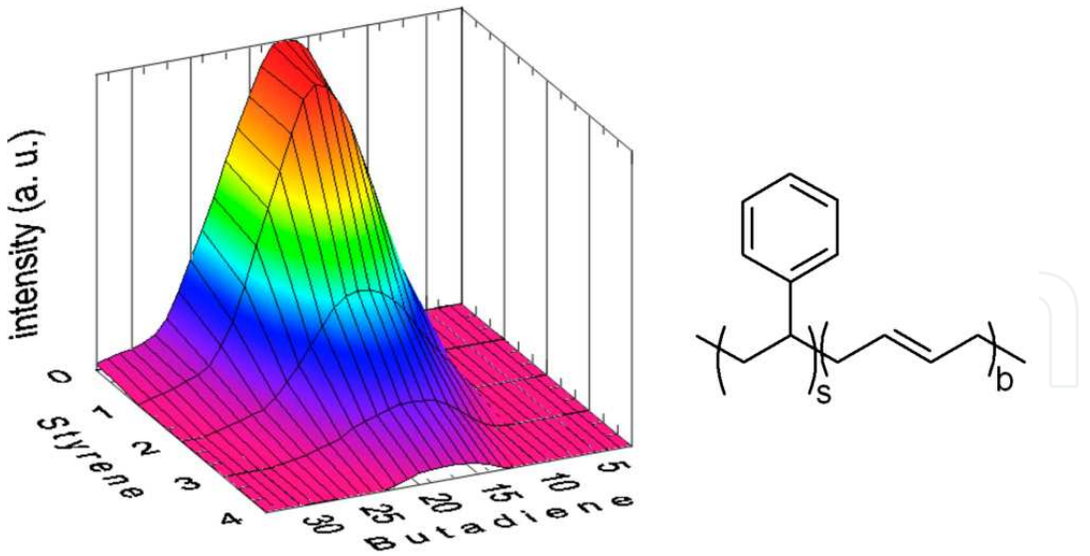
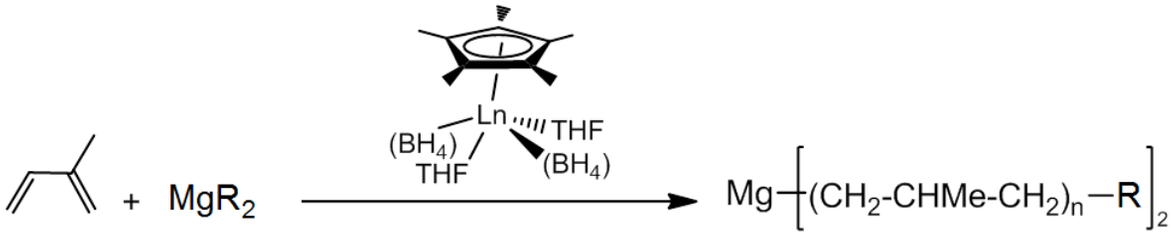


Figure 6. MALDI-TOF cumulative diagram of a poly(butadiene-*co*-styrene) oligomer initiated with butyl groups and functionalized with benzhydrylidene anthrone.

around 50–60%. With all the catalysts, the polymerization is significantly slowed down with BEM excesses *vs* 1 equiv. magnesium dialkyl, as observed for butadiene [62]. The excess of BEM has another consequence to the polymerization process: the transmetalation is accompanied by a modification of the selectivity of the reaction, from 98.5% 1,4-*trans* with 1 BEM to up to 46% 3,4-polyisoprene using 10 equiv. chain transfer agent. This simply appears as a way to tune the microstructure of the polyisoprene just by adjusting the quantity of chain transfer agent [63]. Actually, a gradual decrease of the 1,4-*trans* stereoselectivity of the reaction, leading to a great variety of poly(1,4-*trans*-isoprene) based materials, is observed at the benefit of 3,4-selectivity with increasing quantities of magnesium dialkyl. By combining dialkylmagnesium and trialkylaluminum, we disclosed that the *trans*-selectivity can be preserved: a 1,4-*trans* stereoselective oligomerization of isoprene with a CCTP character leading to the growth of several poly(1,4-*trans*-isoprene) chain per catalyst metal is reached using the half-lanthanocene $Cp^*La(BH_4)_2(THF)_2$ in combination with BEM and Al^iBu_3 in 1/1/9, 1/1/19, or 1/1/39 quantities, respectively [64].



Scheme 15. Rare earth catalyzed polyisoprene chain growth on magnesium. Ln=Nd, La

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An example of functionalization has been assessed on magnesium end-capped oligomers of isoprene, by oxidation with oxygen and hydrolysis to primary alcohols. Analysis by MALDI-TOF mass spectrometry (see figure 7) was in accordance with the expected structure for half of the observed peaks. The other half witnessed the presence of unfunctionalized species which may arise from difficulties to avoid hydrolysis or coupling reactions, before or during the oxidation.

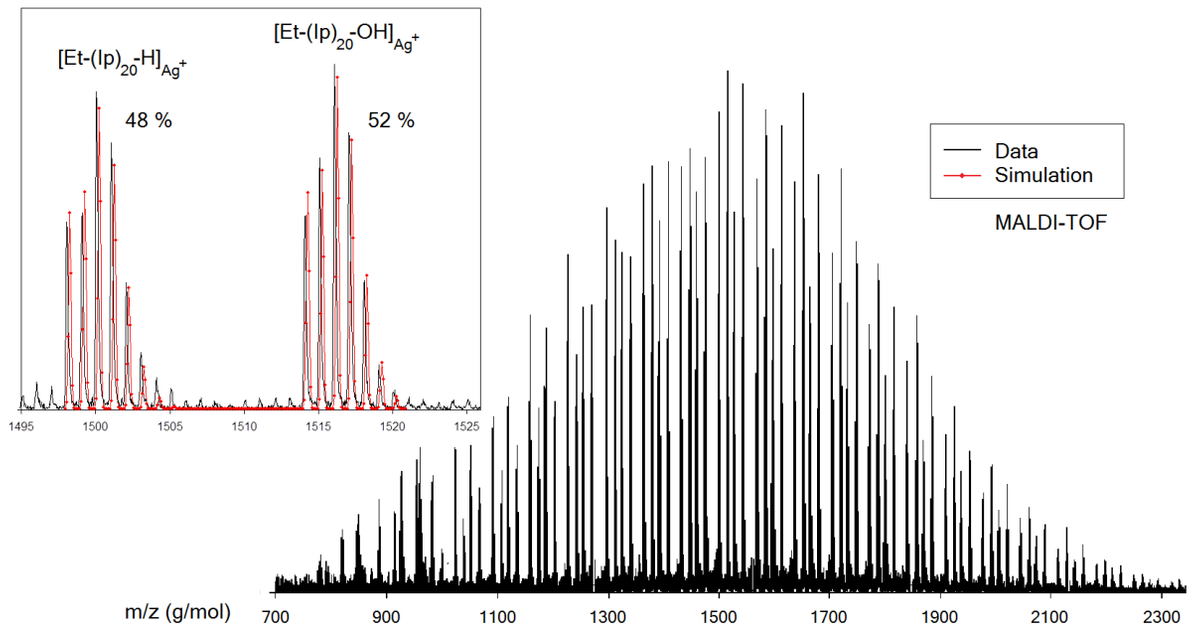
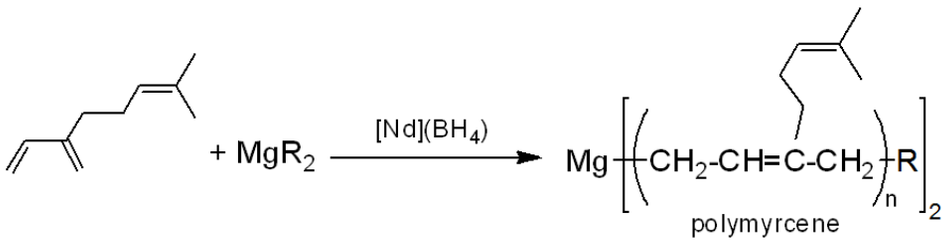


Figure 7. MALDI-TOF spectrum of isoprene oligomers functionalized in primary alcohols.

3.5. Myrcene

As expected from our previous results with isoprene and butadiene, polymerization of β-myrcene with neodymium borohydride-based coordination catalysts ($Cp^*Nd(BH_4)_2(THF)_2$ and $Nd(BH_4)_3(THF)_3$) in the presence of gradual excesses of BEM (1 to 20 equiv) shows high level of transfer reactions efficiency between neodymium and magnesium [65]. For 1-5 Mg co-catalyst equiv, the measured molecular weights (by SEC and end-group integration NMR) match quite well with calculated values for the growth of two chains per magnesium atom. As the BEM quantity increase, dispersities become more narrow, which accounts for rapid and reversible polymer chain transfer. In addition, the selectivity turns from > 90 %-1,4-*trans*[1] (1 BEM) to 3,4-rich (64%, 20 BEM), thus illustrating the "tuning ability" of the BEM concentration in such processes, as already observed with isoprene and butadiene (see scheme 16).

1 The selectivity was initially claimed as cis but recent additional experiments led us to reconsider it as trans. This will be published soon.



Scheme 16. Oligomerization of myrcene by CCTP with rare earth / magnesium system. [Nd](BH$_4$)=Nd(BH$_4$)$_3$(THF)$_3$, Cp*Nd(BH$_4$)$_2$(THF)$_2$, MgR$_2$=BEM.

4. Conclusion

Readily applicable syntheses of magnesium end-capped oligomers of olefinic unsaturated monomers leading to tailor-made macromolecular objects were proposed. The strategy implemented to achieve this goal consisted in Coordinative Chain Transfer Polymerization involving rare earths precatalysts combined to a dialkylmagnesium reagent. After work-up, organo-functionalized oligomers bearing an hydroxyl, anthrone, rhodamine group, etc, or a second polymer sequence could be prepared.

The rare earth precatalyst was unprecedentedly and advantageously prepared via an *in situ* methodology, which allowed to start with basic compounds as dialkylmagnesium, commercial rare earth salts, and a cyclopentadiene (typically the permethylated one C_5Me_5H), to afford a highly efficient metallocene-based catalytic combination.

A complete panel of analyses was carried out on the oligomer samples, thus allowing a well-defined knowledge of the mechanism of reaction and of the active species involved, along with the ideal operative conditions in order to accurately monitor the process, in particular in the case of ethylene monomer. Basically, the growing length of these oligomers could be tuned all along the reaction just by checking the ethylene intake. After consumption of the monomer, the reaction was stopped by addition of a functionalization reagent, affording a rich variety of end-capped oligomers of ethylene. Similar processes were applied to others monomers including olefins, styrene, conjugated dienes, and including also copolymers of these monomers.

Applications of these compounds include copolymers and formulation additives for fine chemistry, plasturgy and electronics, pharmaceutics and cosmetics, dyes and adhesives etc.

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References

[1] Gladyz J. A. Frontiers in Metal-Catalyzed Polymerization: Designer Metallocenes, Designs on New Monomers, Demystifying MAO, Metathesis Déshabillé. Chem. Rev., 2000, 100(4), 1167-1168, and all articles in this special issue.

[2] Coates, G. W.; Hustad, P. D.; Reinartz, S. Catalysts for the Living Insertion Polymerization of Alkenes: Access to New Polyolefin Architectures Using Ziegler–Natta Chemistry. Angew. Chem., Int. Ed., 2002, 41, 2236-2257.

[3] Guan, Z; Cotts, P. M.; McCord, E. F.; McLain, S. J. Chain Walking: A New Strategy to Control Polymer Topology. Science, 1999, 283, 2059-2062.

[4] Arriola, D. J.; Carnahan, E. M.; Hustad, P. D.; Kuhlman, R. L.; Wenzel, T. T. Catalytic Production of Olefin Block Copolymers via Chain Shuttling Polymerization. Science, 2006, 312, 714-719.

[5] Britovsek, G. J. P.; Cohen S. A.; Gibson V. C.; van Meurs M. Iron Catalyzed Polyethylene Chain Growth on Zinc: A Study of the Factors Delineating Chain Transfer versus Catalyzed Chain Growth in Zinc and Related Metal Alkyl Systems. J. Am. Chem. Soc., 2004, 126, 10701-10712.

[6] Chenal, T.; Mortreux, A.; Visseaux, M. Method for Preparing Dialkyl Magnesium Compounds by Ethylene Polymerization and Uses Thereof. Patent WO2013/014383A1.

[7] Pelletier, J. F.; Bujadoux, K.; Olonde, X.; Adisson, E.; Mortreux, A.; Chenal, T. Long-Chain Dialkylmagnesium, its Preparation Process and Applications. Patent US005779942A, 1996.

[8] Pelletier, J. F.; Mortreux, A.; Olonde, X.; Bujadoux, K. Synthesis of New Dialkylmagnesium Compounds by Living Transfer Ethylene Oligo-and Polymerization with Lanthanocene Catalysts. Angew. Chem. Int. Ed. Engl., 1996, 35(16), 1854-1856.

[9] Chenal, T.; Olonde, X.; Pelletier, J. F.; Bujadoux, K.; Mortreux, A. Controlled polyethylene chain growth on magnesium catalyzed by lanthanidocene: A living transfer

polymerization for the synthesis of higher dialkyl-magnesium. Polymer, 2007, 48, 1844-1856.

[10] Carpentier, J.-F.; Sarazin, Y. Alkaline-earth metal complexes in homogeneous polymerization catalysis. Topics in Organometallic Chemistry, 2013, 45, 141-189.

[11] Mazzolini, J.; Espinosa, E.; D'Agosto, F.; Boisson, C. Catalyzed Chain Growth (CCG) on a Main Group Metal: an Efficient Tool to Functionalize Polyethylene. Polym. Chem., 2010, 1, 793-800.

[12] German, I.; Kelhifi, W.; Norsic, S.; Boisson, C.; D'Agosto F. Telechelic Polyethylene from Catalyzed Chain-Growth Polymerization. Angew. Chem. Int. Ed., 2013, 52(12), 3438-3441.

[13] Espinosa, E.; Charleux, B.; D'Agosto, F.; Boisson, C.; Tripathy, R.; Faust, R.; Soulié-Ziakovic C. Di-and Triblock Copolymers Based on Polyethylene and Polyisobutene Blocks. Toward New Thermoplastic Elastomers. Macromolecules, 2013, 46, 3417-3424.

[14] Bieligmeyer, M.; Mehdizadeh Taheri, S.; German, I.; Boisson, C.; Probst, C.; Milius,W.; Altstadt, V.; Breu,J.; Schmidt, H.-W.; D'Agosto, F.; Forster, S. Completely Miscible Polyethylene Nanocomposites. J. Am. Chem. Soc., 2012, 134, 18157-18160.

[15] Mazzolini, J.; Boyron, O.; Monteil, V.; D'Agosto, F.; Boisson, C.; Sanders, G. C.; Heuts, J. P. A.; Duchateau, R.; Gigmes, D.; Bertin D. Polyethylene End Functionalization using Thia-Michael Addition Chemistry. Polym. Chem., 2012, 3, 2383-2392.

[16] Lefay, C.; Glé D.; Rollet, M.; Mazzolini, J.; Bertin, D.; Viel, S.; Schmid, C.; Boisson, C.; D'Agosto, F.; Gigmes, D.; Barner-Kowollik, C. Block Copolymers via Macromercaptan Initiated Ring Opening Polymerization. J. Polym. Sci. Part A: Polym. Chem., 2011, 49(3), 803-813.

[17] Akbar, S.; Beyou, E.; Chaumont, P.; Mazzolini, J.; Espinosa, E.; D'Agosto F.; Boisson C. Synthesis of Polyethylene-Grafted Multiwalled Carbon Nanotubes via a Peroxide-Initiating Radical Coupling Reaction and by Using Well-Defined TEMPO and Thiol End-Functionalized Polyethylenes. J. Polym. Sci. Part A: Polym. Chem., 2011, 49(4), 957-965.

[18] Espinosa, E.; Glassner, M.; Boisson, C.; Barner-Kowollik, C.; D'Agosto, F. Synthesis of Cyclopentadienyl Capped Polyethylene and Subsequent Block Copolymer Formation Via Hetero Diels-Alder (HDA) Chemistry. Macromol. Rapid Commun., 2011, 32, 1447-1453.

[19] Mazzolini, J.; Mokthari, I.; Briquel, R.; Boyron, O.; Delolme, F.; Monteil, V.; Bertin,D.; Gigmes, D.; D'Agosto, F.; Boisson, C. Thiol-End-Functionalized Polyethylenes. Macromolecules, 2010, 43, 7495-7503.

[20] Cortial, G.; Le Floch, P.; Nief, F.; Thuilliez, J. Novel Organometallic Compounds Containing a Metal Belonging to the Second Column of the Periodic Table, and Method for Preparing Same. Patent WO2010/139449A1.

[21] Jeske, G.; Lauke, H.; Mauermann, H.; Swepston, P. N.; Schumann, H.; Marks T. J. Highly Reactive Organolanthanides. Systematic Routes to and Olefin Chemistry of Early and Late Bis(pentamethylcyclopentadienyl) 4f Hydrocarbyl and Hydride Complexes. J. Am. Chem. Soc., 1985, 107, 8091-8103.

[22] Watson, P.L.; Herskovitz, T. Homogeneous Lanthanide Complexes as Polymerization and Oligomerization Catalysts: Mechanistic Studies. ACS Symposium Series., 1983, 459-479

[23] Cendrowski-Guillaume, S.M.; Le Gland, G.; Nierlich, M.; Ephritikhine, M. Lanthanide Borohydrides as Precursors to Organometallic Compounds. Mono(cyclooctatetraenyl) Neodymium Complexes. Organometallics, 2000, 19(26), 5654-5660.

[24] Ballard, D.G.H.; Courtis, A.; Holton, J.; McMeeking, J.; Pearce, R. Alkyl bridged complexes of the group 3A and lanthanoid metals as homogeneous ethylene polymerisation catalysts. Journal of the Chemical Society, Chemical Communications., 1978, 22, 994-995

[25] Olonde, X.; Bujadoux, K.; Mortreux, A.; Petit, F. Catalysts and Process for the Preparation of Same for Use in the Polymerization of Ethylene. Patent WO 93/07180.

[26] Pettijohn, T. M. Olefin Polymerization Process and Polymer Produced. Patent US005350816A, 1994.

[27] Zinck, P.; Valente, A.; Terrier, M.; Mortreux, A.; Visseaux, M. Half-Lanthanidocenes Catalysts via the ''Borohydride/Alkyl'' Route: A simple Approach of Ligand Screening for the Controlled Polymerization of Styrene. C. R. Chimie, 2008, 11, 595-602.

[28] Visseaux, M.; Terrier, M.; Mortreux, A.; Roussel, P. Facile Synthesis of Lanthanidocenes by the "Borohydride/Alkyl Route" and Their Application in Isoprene Polymerization. Eur. J. Inorg. Chem., 2010, 2867-2876.

[29] Ziegler, K.; Gellert, H. G.; Külhorn, H.; Martin, H.; Meyer, K.; Nagel, K.; Sauer, H.; Zosel, K. Aluminium-organische Synthese im Bereich olefinischer Kohlenwasserstoffe. Angewandte Chemie, 1952, 64(12), 323-329.

[30] Bergbreiter, D. E.; Blanton J. R.; Chandran R.; Hein, M. D.; Huang, K.-J.; Treadwell, D. R.; Walker, S. A. Anionic Syntheses of Terminally Functionalized Ethylene Oligomers. J. Polym. Sci. Part A: Polym. Chem., 1989, 27(12), 4205-4226.

[31] Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Coordinative Chain Transfer Polymerization. Chem. Rev., 2013, 113, 3836-3857.

[32] Sita, L. R. Ex Uno Plures ("Out of One, Many"): New Paradigms for Expanding the Range of Polyolefins through Reversible Group Transfers. Angew. Chem. Int. Ed., 2009, 48, 2464-2472.

[33] Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. Chain Walking: A New Strategy to Control Polymer Topology Science, 1999, 283, 2059-2062.

[34] D'Agosto, F.; Boisson, C. A RAFT Analogue Olefin Polymerization Technique using Coordination Chemistry. Australian Journal of Chemistry, 2010, 63(8), 1155-1158.

[35] Makio, H.; Ochiai, T.; Mohri, J.-I.; Takeda, K.; Shimazaki, T.; Usui, Y.; Matsuura,S.; Fujita, T. Synthesis of Telechelic Olefin Polymers via Catalyzed Chain Growth on Multinuclear Alkylene Zinc Compounds. J. Am. Chem. Soc., 2013, 135, 8177-8180.

[36] Kretschmer, W. P.; Meetsma, A.; Hessen, B.; Schmalz, T.; Qayyum, S.; Kempe, R. Reversible Chain Transfer between Organoyttrium Cations and Aluminum: Synthesis of Aluminum-Terminated Polyethylene with Extremely Narrow Molecular-Weight Distribution. Chem. Eur. J., 2006, 12, 8969-8978.

[37] Ganesan, M.; Gabbaï, F. P. [Cp*Cr(C_6F_5)(Me)(Py)] as a Living Chromium(III) Catalyst for the "Aufbaureaktion". Organometallics, 2004, 23 (20), 4608-4613.

[38] Bazan, G. C.; Rogers, J. S.; Fang C. C. Catalytic Insertion of Ethylene into Al−C Bonds with Pentamethylcyclopentadienyl−Chromium(III) Complexes. Organometallics, 2001, 20 (10), 2059-2064.

[39] Chenal, T.; Visseaux, M. Combining Polyethylene CCG and Stereoregular Isoprene Polymerization: First Synthesis of Poly(ethylene)-b-(trans-isoprene) by Neodymium Catalyzed Sequenced Copolymerization. Macromolecules, 2012, 45, 5718-5727.

[40] Lin-Gibson, S.; Brunner, L.; Vanderhart, D. L.; Bauer, B. J.; Fanconi, B. M.; Guttman, C. M.; Wallace W. E. Optimizing the Covalent Cationization Method for the Mass Spectrometry of Polyolefins. Macromolecules, 2002, 35(18), 7149-7156.

[41] Lennon, P. J.; Mack D. P.; Thompson Q. E. Nucleophilic Catalysis of Organosilicon Substitution Reactions. Organometallics, 1989, 8, 1121-1122

[42] Amin, S. B.; Marks T. J. Versatile Pathways for In Situ Polyolefin Functionalization with Heteroatoms: Catalytic Chain Transfer. Angew. Chem. Int. Ed., 2008, 47, 2006-2025.

[43] Bogaert, S.; Chenal, T.; Mortreux, A.; Nowogrocki, G.; Lehmann, C. W.; Carpentier, J. –F. ansa-Bis(cyclopentadienyl) Ligands: Synthesis and Use in Olefin Oligomerization. Organometallics, 2001, 20, 199-205.

[44] Bogaert, S.; Chenal, T.; Mortreux, A.; Carpentier, J.-F. Unusual product distribution in ethylene oligomerization promoted by in situ ansa-chloroneodymocene-dialkylmagnesium systems. Journal of Molecular Catalysis A: Chemical, 2002, 190(1-2), 207-214.

[45] Bogaert, S.; Carpentier, J. –F. Chenal, T.; Mortreux, A.; Ricart, G. Chlorolanthanocene-dialkylmagnesium systems for styrene bulk polymerization and styrene-ethylene block copolymerization. Macromolecular Chemistry and Physics, 2000, 201(14), 1813-1822.

[46] Sarazin, Y.; Chenal, T.; Mortreux, A.; Vezin, H.; Carpentier, J.-F. Binary cerium(IV) tert-butoxides-dialkylmagnesium systems: Radical versus coordinative polymerization of styrene. Journal of Molecular Catalysis A: Chemical, 2005, 238, 207-214.

[47] Menoret, S.; Carlotti, S.; Fontanille, M.; Deffieux, A.; Desbois, P.; Schade, C.; Schrepp, W.; Warzelhan, V. Retarded anionic polymerization, 5 influence of the structure of dialkylmagnesium additives on the reactivity of polystyryllithium species. Macromolecular Chemistry and Physics, 2001, 202(16), 3219-3227.

[48] Carlotti, S.; Desbois, P.; Warzelhan, V.; Deffieux, A. Retarded anionic polymerization (RAP) of styrene and dienes. Polymer, 2007, 48(15), 4322-4327.

[49] Sarazin, Y.; de Fremont, P.; Annunziata, L.; Duc, M.; Carpentier, J.-F. Syndio-and Isoselective Coordinative Chain Transfer Polymerization of Styrene Promoted by ansa-Lanthanidocene/Dialkylmagnesium Systems. Advanced Synthesis & Catalysis, 2011, 353(8), 1367-1374.

[50] Annunziata, L.; Duc, M.; Carpentier, J.-F. Chain Growth Polymerization of Isoprene and Stereoselective Isoprene-Styrene Copolymerization Promoted by an ansa-Bis(indenyl) allyl-Yttrium Complex. Macromolecules, 2011, 44(18), 7158-7166.

[51] Rodrigues, A.-S.; Kirillov, E.; Vuillemin, B.; Razavi, A.; Carpentier, J.-F. Binary ansa-lanthanidocenes/dialkylmagnesium systems versus single-component catalyst: Controlled synthesis of end-capped syndiotactic oligostyrenes. Journal of Molecular Catalysis A: Chemical, 2007, 273(1-2), 87-91.

[52] Gromada, J.; le Pichon, L.; Mortreux, A.; Leising, F.; Carpentier, J.-F. Neodymium alk(aryl)oxides-dialkylmagnesium systems for butadiene polymerization and copolymerization with styrene and glycidyl methacrylate. Journal of Organometallic Chemistry, 2003, 683(1), 44-55.

[53] Zinck, P.; Valente, A.; Mortreux, A.; Visseaux, M. In situ generated half-lanthanidocene based catalysts for the controlled oligomerisation of styrene: Selectivity, block copolymerization and chain transfer. Polymer 2007, 48, 4609-4614.

[54] Zinck, P.; Valente, A.; Bonnet, F.; Violante, A.; Mortreux, A.; Visseaux, M.; Ilinca, S.; Duchateau, R.; Roussel, P. Reversible coordinative chain transfer polymerization of styrene by rare earth borohydrides, chlorides/dialkylmagnesium systems. J. Polym. Sci. Part A: Polym. Chem., 2010, 48, 802-814.

[55] Valente, A.; Zinck, P.; Mortreux, A.; Bria, M.; Visseaux, M. Half-lanthanocene/dialkylmagnesium-mediated coordinative chain transfer copolymerization of styrene and hexane. J. Polym. Sci. Part A: Polym. Chem., 2011, 49, 3778-3782.

[56] Jenkins, D. K. Polymerization of Conjugated Dienes. Patent US004619982, 1986.

[57] Jenkins, D. K. Butadiene polymerization with a rare earth compound using a magnesium alkyl cocatalyst: 1. Polymer, 1985 26(1), 147-151.

[58] Jenkins, D. K. Butadiene polymerization with a rare earth compound using a magnesium alkyl cocatalyst: 2. Polymer, 1985 26(1), 152-158.

[59] Monakov, Y..B.; Duvakina, N.V.; Ionova, I.A. Polymerization of Butadiene with a Halogen-containing Trans-regulating Neodymium-magnesium Catalytic System in the Presence of Carbon Tetrachloride. Polymer Science-Series B, 2008, 50 (5-6), 134-138.

[60] Jenkins, D. K. Sequential Formation of Trans and Cis Butadiene Homopolymers with One Catalyst System. Polymer, 1994, 35(13), 2897-2898.

[61] Ventura, A.; Chenal, T.; Bria, M.; Bonnet, F.; Zinck, P.; Ngono-Ravache, Y.; Balanzat, E.; Visseaux, M. Trans-stereospecific polymerization of butadiene and random copolymerization with styrene using borohydrido rare earths / magnesium dialkyl catalysts. European Polymer Journal, 2013, 49, 4130-4140.

[62] Terrier, M.; Visseaux, M.; Chenal, T.; Mortreux, A. Controlled Trans-stereospecific Polymerization of Isoprene with Lanthanide(III) Borohydride/Dialkylmagnesium Systems: the Improvement of the Activity and Selectivity, Kinetic Studies, and Mechanistic Aspects. Journal of Polymer Science, Part A: Polymer Chemistry, 2007, 45 (12), 2400-2409.

[63] Valente, A.; Zinck, P.; Mortreux, A.; Visseaux, M. Catalytic Chain Transfer (co-)Polymerization: Unprecedented Polyisoprene CCG and a New Concept to Tune the Composition of a Statistical Copolymer Macromol. Rapid Commun., 2009, 30, 528-531.

[64] Valente, A.; Zinck, P.; Vitorino, M.J.; Mortreux, A.; Visseaux, M. Rare earths/main group metal alkyls catalytic systems for the 1,4-trans stereoselective coordinative chain transfer polymerization of isoprene. Journal of Polymer Science, Part A: Polymer Chemistry., 2010, 48 (21), 4640-4647.

[65] Loughmari, S.; Hafid, A.; Bouazza, A.; El Bouadili, A.; Zinck, P.; Visseaux, M. Highly Stereoselective Coordination Polymerization of β-Myrcene from a Lanthanide-based Catalyst: Access to Bio-sourced Elastomers. Journal of Polymer Science, Part A: Polymer Chemistry, 2012, 50 (14), 2898-2905.