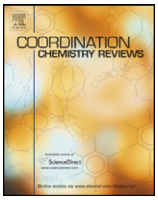
Coordination Chemistry Reviews 253 (2009) 2082–2097

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Mechanism of stereospecific polymerization of α-olefins by late-transition metal and octahedral group 4 metal catalysts

Marina Lamberti[a], Mina Mazzeo[a], Daniela Pappalardo[b], Claudio Pellecchia[a,*]

[a] Dipartimento di Chimica, Università di Salerno, Via Ponte don Melillo, I-84084 Fisciano (SA), Italy
[b] Dipartimento di Studi Geologici ed Ambientali, Università del Sannio, Via dei Mulini 59/A, I-82100 Benevento, Italy

Contents

ARTICLE INFO

Article history:
Received 24 November 2008
Accepted 10 February 2009
Available online 21 February 2009

Keywords:
Group 4 complexes
Iron complexes
Nickel complexes
Olefins
Polymerization catalysis
Stereoselectivity

ABSTRACT

In the last few years remarkable advances have been made in the field of non-cyclopentadienyl complexes as homogeneous olefin polymerization catalysts. In this paper we summarize some recent literature data concerning the stereochemical mechanism of α-olefin polymerization promoted by late transition metal systems and bi- and tetra-dentate imine phenolate group 4 metal complexes. NMR analysis of the fine structure of suitably labelled polymers, obtained by using isotopically enriched catalysts or monomers, provided valuable information on the regiochemistry and stereochemistry of the polymerization. In particular, ^{13}C was introduced in different points of the polymer chain as a sort of magnifying lens to observe fine aspects of the microstructure, and to establish a chronology in the sequence of the monomer insertions.

1. Introduction

Group 4 metallocenes and related catalytic systems (such as semi-metallocenes or constrained geometry catalysts) are an archetypal example of rationalization of the structure–reactivity relationship in homogeneous olefins polymerization catalysis [1–4].

Tailoring the coordination environment of the metal center, single-site metallocene catalysts were designed to control the molecular weight, the molecular weight distribution, the co-monomer incorporation, and the relative and absolute stereochemistry of a polymer in a way that is often forbidden by using conventional heterogeneous catalysts.

Following such examples of successful design, in the last few years non-metallocene complexes of early and late transition metals have attracted growing attention as potential catalyst precursors [5–7].

The new classes of catalysts are characterized by a large variety of structural diversity in the ancillary ligand frameworks and moreover by an easier synthetic approach compared to metallocenes.

Several important examples, including late-transition metal systems, phenoxy and amido based group 4 metal catalysts, show

---

[*] Corresponding author.
E-mail address: cpellecchia@unisa.it (C. Pellecchia).

0010-8545/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.ccr.2009.02.014

peculiar features that allow the synthesis of a remarkable variety of original homopolymer and copolymer architectures.

A precise design of microstructures of polymeric chains for a fine-tuning of physical and mechanical properties of the polymeric materials has been possible by the choice of catalysts with peculiar behaviours, in combination with novel concepts of chain growth.

For example, multi-block copolymers with sequential crystallizable and amorphous segments can be prepared using living catalysts by a pulsed introduction of the co-monomers in the feed [8–11]. A different approach consists in the use of tandem catalytic systems consisting of two metal centres which show different affinities for different co-monomers. In this case, it is possible to promote a chain growth process that occurs alternatively on the two catalytic centres, as a consequence of a “shuttling” agent which mediates the transfer of each single chain from a metal centre to the other one [12].

Moreover catalytic systems that can promote living polymerization of propylene in either atactic or highly isotactic fashion [13,14] revealed an adequate tool for the synthesis of polymers with distinctive stereochemical architectures, such as stereoblocks [15] and “stereogradient” [16] polypropylenes, by a programmed modulation of the stoichiometric ratio between the metal precursor and the co-catalyst during the polymerization reaction.

The relevant examples described above highlight the high versatility of non-metallocene catalysts and, at the same time, reveal that the effects on reactivity and stereoselectivity of the reaction conditions and structural parameters of the metal complexes are difficult to predict also for the members of a single class of catalysts.

As a consequence, a precise knowledge at the atomic level of mechanistic details regarding the selectivity of the catalytic systems is desirable.

This review is focused on different mechanistic aspects concerning the stereoselective polymerization of olefins promoted by new classes of non-metallocene catalysts.

These features have been elucidated by ^{13}C NMR analysis of the fine microstructure of the polymer whose macromolecular architecture is a “tape recorder” where the different events occurring during polymerization process are chronologically impressed.

The investigated systems include late-transition metal systems such as the Brookhart’s Ni diimine catalysts and the Fe bis(imino)pyridyl catalysts, and octahedral group 4 metal complexes supported by phenoxy-based ligands that recently emerged as very efficient catalysts receiving considerable attention both by industrial and academic researches.

In this review several mechanistic facets concerning the regio- and stereochemistry of the olefin polymerization are summarized, most of them representing an application of a method originally developed by Zambelli to investigate the behaviour of traditional homogeneous Ziegler-Natta catalysts.

2. Methods

Macromolecular microstructure is a valuable source of information for the comprehension at atomic level of many mechanistic details of the polymerization reactions.

^{13}C NMR analysis can reveal both the degree of stereoregularity and regioregularity of a poly(α-olefin), as well as the mechanisms of stereocontrol and regioselection operative during the polymerization reactions.

The relative amounts of stereosequences relative to the main chain methyl carbon atoms allow one to establish if discrimination between the faces of the inserting prochiral monomer is dictated by the chirality of the catalytic site, (*enantiomorphic site stereocontrol*), or by the chirality of the last inserted monomer unit (*chain end stereocontrol*).

According to a consolidate approach developed by Zambelli in the seventies, isotopically enriched carbon atoms ^{13}C can be introduced in different points of the polymer chain as a sort of magnifying lens to observe fine aspects of the microstructure of the polymer chain, and to establish a chronology in the sequence of the monomer insertions [17].

The regiospecificity and the mechanism of stereospecific insertion have been studied by determining the stereochemical structures of suitable ^{13}C-enriched chain end groups, that result from initiation steps when the polymerization is performed in the presence of ^{13}C-enriched aluminium alkyls. Pioneering studies performed by Zambelli et al. both on heterogeneous and homogeneous Ziegler-Natta catalytic systems afforded valuable information on clue factors governing the stereoselectivity of α-olefin polymerization [18–20]. For instance, in the case of the C_2-symmetric ethylenebis(indenyl)titanium-based catalyst stereoselectivity was shown to occur only when propylene inserts into a Ti-alkyl segment with at least two carbon atoms [21]. Consequent molecular mechanic calculations evidenced that repulsive interactions could force the entering olefin to an enantiofacial orientation in which the substituent is *trans* respect to the β-C atom of the metal-bound alkyl chain [22,23]. Also, insertion of 1-butene into a Ti–$^{13}CH_2CH_3$ bond resulted stereospecific before the formation of any chiral carbon in the growing chain, definitively demonstrating that the steric control depends on the intrinsic chirality of the metal catalysts (*enantiomorphic site* mechanism).

Analogous studies on C_s and C_2 stereorigid-bridged metallocene precursors disclosed an additional effect of direct interaction of the methyl of the incoming monomer with the substituents of the cyclopentadienyl β to the ring, which enforced (isotactic) or diminished (syndiotactic) the stereoregulation due to the growing chain [24].

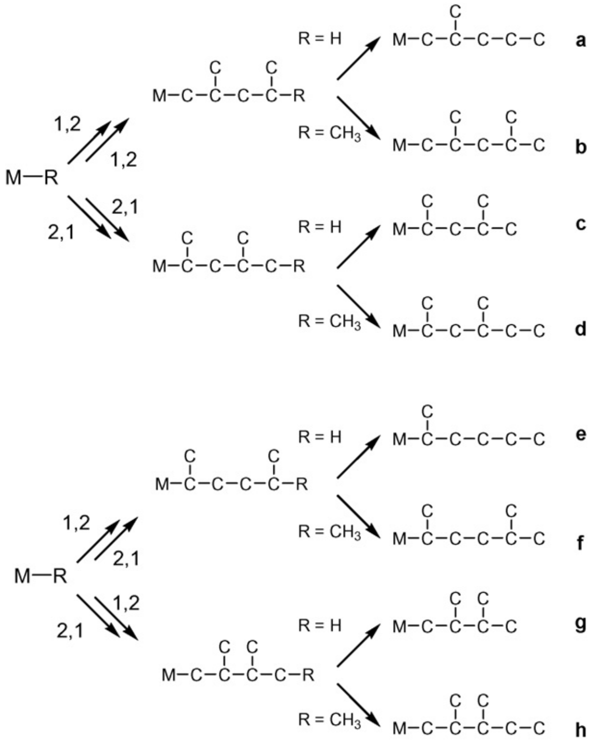
Deuterium-enriched chain end groups, formed by alcoholysis of the polymeric growing chains with deuterated alcohols, furnished additional information about the regio- and stereochemistry of the termination steps.

In Schemes 1 and 2 are presented the different chain end groups that could be formed respectively in the initiation steps and in the termination steps.

In order to investigate the chain propagation, a useful method involves the synthesis of copolymers of propylene containing isolated units of 1-^{13}C-ethylene, providing information on the regiochemistry and the stereochemistry of propylene insertion before and after ethylene (Scheme 3).

When the ethylene unit bridges regioregular, either primary or secondary, polypropylene blocks, a three-methylene sequence is formed (see Scheme 3a and b). An enriched two-methylene sequence can derive only from ethylene spanning propylene units of opposite regiochemistry, according to Scheme 3c. Finally, a four-methylene sequence can derive from the succession of insertions displayed in Scheme 3d.

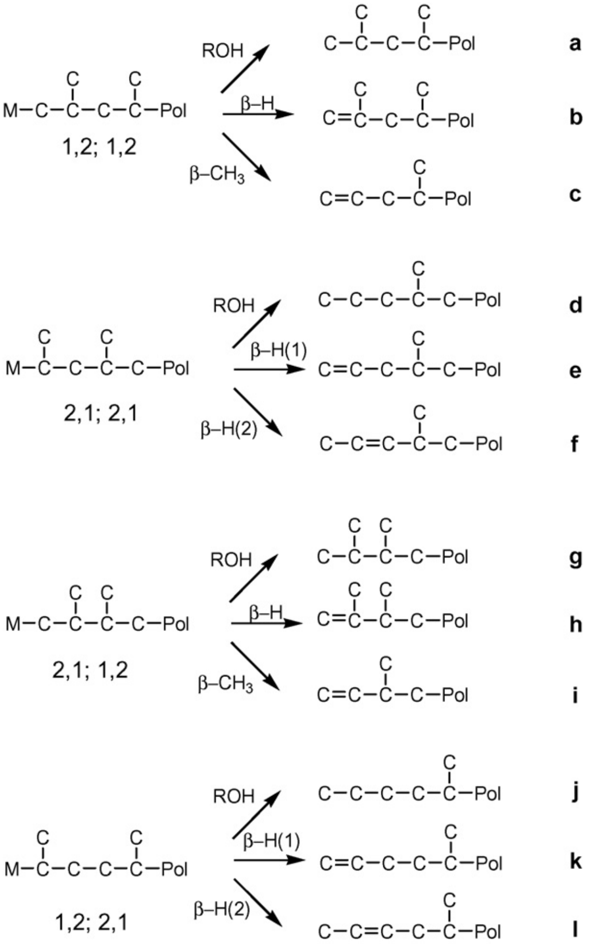
Since the chemical shifts of the enriched methylenes are affected by the stereochemical arrangements of the neighbouring propylene units, valuable information on the mechanism of steric control can be obtained. In particular, if the steric control crosses intervening ethylene units, the stereochemistry of the insertion is controlled by the chirality of the active sites (*enantiomorphic site* mechanism), while if it does not cross the intervening ethylene units, the stereospecificity of the insertion arises from the asymmetric induction by the last (propylene) unit of the growing chain (*chain end* mechanism). The whole matter has been recently revisited analysing, by high field NMR, several propylene-enriched ethylene copolymers prepared with a variety of catalysts [17,25–29].



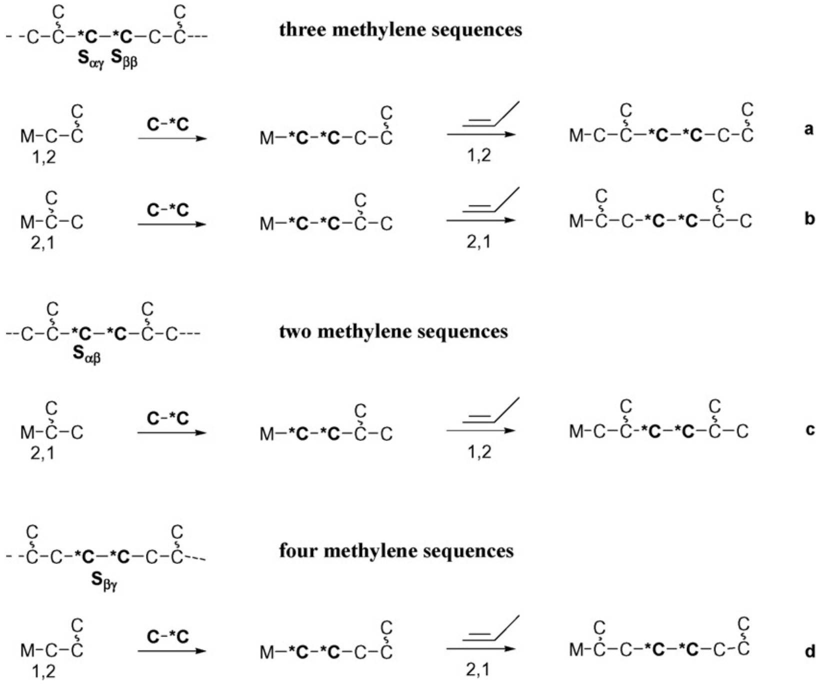
Scheme 1. Mechanisms of formation of chain end groups in the initiation steps.

3. Nickel α-diimine complexes

Late-transition metal catalysts for a long time have been known to dimerize or oligomerize olefins due to competing β-hydrogen elimination. It is enough to mention the so called "*nickel effect*" [30,31], dimerization reaction originally disclosed by Ziegler in 1953, which was then the basis of the development of the SHOP process for the production of linear α-olefins by ethylene oligomerization.



Scheme 2. Mechanisms of formation of chain end groups in the termination steps.



Scheme 3. Methylene sequences formed by the insertion of a single ethylene unit between blocks of polypropylene chains.

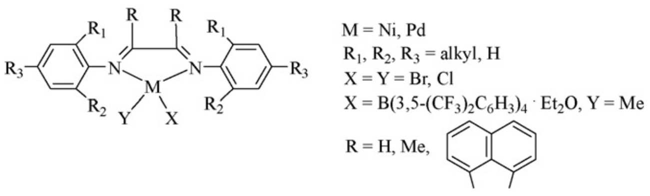


Fig. 1. Schematic representation of Ni(II) and Pd(II) α-diimine complexes.

Ni(II) and Pd(II) α-diimine complexes (Fig. 1), bearing bulky aryl groups at the N-imine, after activation with MAO or other ionizing reagents, were discovered by Brookhart to efficiently promote ethylene and α-olefin polymerization [32–34]. In these complexes a crucial role is played by the bulky *ortho*-substituents on the aryl rings, which strongly retard associative chain transfer or chain transfer to the monomer. Related Ni(II) or Pd(II) complexes, lacking such bulky substituents, produced instead only dimers or oligomers [35–37].

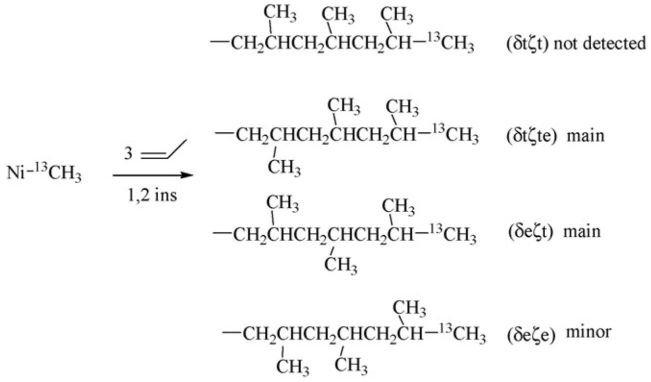
Since the first observation, α-diimine ligands attracted great interest for the advantageous feasibility and flexibility in design to introduce sterically and electronically demanding features. As a consequence, a large number of structural variations have been reported in the academic and patent literature, and have been the subject of several reviews. The Ni(II) and Pd(II) α-diimine systems exhibited several unique features, including the copolymerization of ethylene with functionalized olefins, the living polymerization of ethylene and α-olefins, the homopolymerization of cyclic and internal acyclic olefins [5,6,38,39].

As far as polymerization of ethylene is concerned, a careful tuning of the ligands can be used to vary product composition from oligomers to polymers, and from linear to highly branched products [40]. Spectroscopic and computational studies both converged to the conclusion that a cationic alkyl ethylene complex is the resting state of the catalyst system; the branching are formed through a series of β-hydrogen eliminations and re-insertion reactions *via* a β-agostic cationic alkyl intermediate [41,42]. The degree of branching and the polymer architecture depend on a number of factors: the metal, the steric bulk of the diimine ligand and the reaction conditions. In this regard we ourselves also reported a study on the polymerization of ethylene with nickel α-diimine catalysts, and disclosed a dependence of the degree of branching of the obtained polyethylenes not only on the ligand environment at the Ni centre but also on the type of co-catalyst [43].

Our main contribution in this field was the achievement of stereospecific polymerization of propylene and the elucidation of the mechanism involved. As matter of fact, polymerization of propylene at sub-ambient temperature in the presence of the homogeneous catalytic system (1,2-bis(2,6-diisopropylphenyl)ethylenediimine)nickel dibromide (**1**)-MAO afforded prevailingly syndiotactic crystalline polypropylene with a *rr* triad content up to 80% at −78 °C [44].

Analysis of the pentad region of the ^{13}C NMR spectrum indicated a polymer microstructure mainly consisting of blocks of *r* diads bridged by isolated *m* dyads. This microstructure is that expected for a "*chain end*" mechanism of steric control, i.e., the enantioface selectivity of the monomer insertion is controlled by the configuration of the methine carbon of the last unit of the growing chain (*unlik*e-1,3 asymmetric induction) [45]. A significant amount of regioirregular monomer units was also detected (about 12%), the regioirregular sequence consisted of blocks of monomer units with opposite regiochemistry. A similar microstructure was observed in syndiotactic polypropylene first obtained by Natta et al. in the presence of homogeneous vanadium-based catalysts [25,46].

A significant difference from the vanadium-based systems emerged from investigation of the regiochemistry of the monomer insertion in the initiation step. By using a ^{13}C-enriched catalyst, the resonances due to ^{13}C-enriched end groups obtained by propylene insertion into the Ni–$^{13}CH_3$ bond were observed in the ^{13}C NMR spectrum of the polymer. These resonances were attributed to the enriched CH_3's of the diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups, generated by primary (1,2) monomer insertion into the Ni–$^{13}CH_3$ bond of the active species (initiation step), followed by further primary insertion of two monomer units (Scheme 4). Interestingly, of the four possible diastereoisomers only two (δtζe and δeζt) were detected with comparable intensities, so indicating that steric control becomes active when the first chiral carbon was generated in the growing chain [47]. On the contrary, in the case of vanadium-based catalysts all the four possible diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups were observed, indicating therefore that primary insertion of monomer in the initiation and in the first two propagation steps is stereoirregular. In this latter case, in fact, the steric control was effective only when the monomer insertion turned from primary to secondary [48].



Scheme 4. Mechanism for formation and Fischer projections of the four possible diastereomeric [7-^{13}C]-2,4,6-trimethylheptyl end groups. The diastereotopic placements of $^{13}CH_3$ are indicated by using Greek letters to denote the number of bonds between the enriched CH_3 and the methyl backbone substituents, followed by the symbol e (*erythro*) or t (*threo*), giving the steric relationship between the same methyl carbon atoms.

A primary (1,2) monomer insertion as the main propagation mode was confirmed by analyzing the end groups formed in the termination step, where deuteriolysis was performed by quenching the polymerization with deuteriated trifluoromethanol [49]. The formation of a deuteriated methyl group belonging to an isobutyl chain end ($CH_2DCH(CH_3)CH_2$–) was confirmed by ^{13}C and ^{2}H NMR analysis, while in the case of vanadium catalyst the same experiment led to a deuteriated methylene belonging to a *n*-propyl chain end [50].

A copolymer of propylene with trace amounts of ^{13}C-enriched ethylene was prepared with the nickel catalyst (see the ^{13}C NMR spectrum in Fig. 2).

In this case sequences of two, three and also four methylene were observed in comparable amount, in agreement with the poor regioregularity of the system. The resonances relative to $S_{\alpha\gamma}$ carbon atoms (Scheme 3a) are influenced by the stereochemistry of the adjacent propylene dyads and furnish additional information. The *r*-$S_{\alpha\gamma}$ amount is about 60%, indicating that the ethylene units spanning regioregular blocks of polypropylene are more often bordered by syndiotactic (*r*) than by isotactic (*m*) stereochemical dyads. Interestingly, the ratio *r*-$S_{\alpha\gamma}$/*m*-$S_{\alpha\gamma}$ (6:4) was lower than the *r*/*m* ratio in the main chain (∼8:2): this is not surprising considering that, since the propagation is prevailing 1,2, the $S_{\alpha\gamma}$ is diagnostic of the two propylene units incorporated after the enriched ethylene unit, and that the *chain end control* can be affected by the presence of a less bulky chain. The region of $S_{\beta\beta}$ carbon atoms is less informative; in fact, a sharp peak at 22.50 ppm emerges from a broad

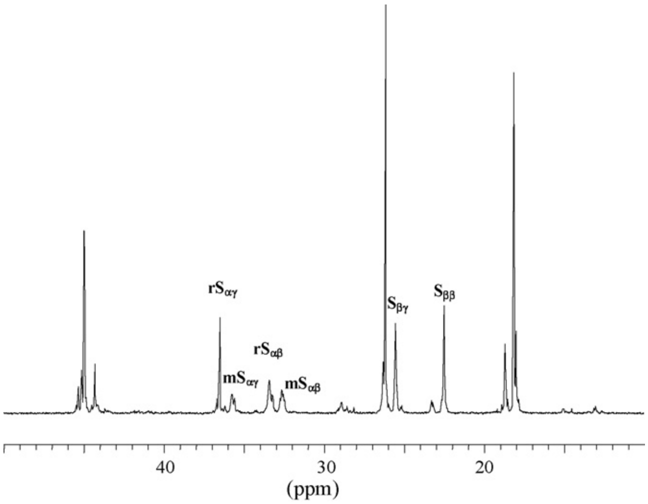


Fig. 2. 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propylene with a little amount of 1-^{13}C-ethylene prepared with (**1**)-MAO. δ in ppm from hexamethyldisiloxane.

band of resonances. This is the same resonance found in the case of a copolymer prepared with a highly syndiospecific C_s symmetric metallocene [26], but splitting of the resonances for the *rrRrr* and *rrMrr* pseudohexads, which would allow one to establish if the steric control crosses or not the intervening ethylene unit, was not detected.

A theoretical QM/MM study of propylene polymerization suggested that the mechanism of *unlike* chain end controlled stereoselectivity for 1-alkene primary insertion is a sub-case of the more general mechanism of *chiral orientation of the growing chain*. The chirality (*si* or *re*) of the tertiary carbon of the growing chain nearest to the metal determines, in the α-agostic-assisted transition state for monomer insertion, the preferential chain orientation around the metal-carbon bond. This chiral orientation of the chain, in turn, discriminates by non-bonded repulsive interactions between propylene enantiofaces (*re* or *si*, respectively). Calculations showed that the preference for syndiospecific propagation is entropy-driven, since three isoenergetic transition states have been located for propylene insertion of a given chirality, two corresponding to the unlike (syndiotactic) enchainment, and only one for the like (isotactic) enchainment [51].

Some efforts were directed by ourselves [52] and by others [53,54] in order to prepare C_2-symmetric α-diimine Ni catalysts which might turn the α-olefins polymerization from *unlike* to *like* through an *enantiomorfic site control* mechanism and might induce isotacticity in these systems. Therefore we synthesized several nickel diimine compounds having various *ortho*-substituents on the aromatic rings and tested them in the polymerization of propylene (Fig. 3). Variation of the coordination environment at the metal centre significantly affected the microstructure of the resulting polypropylene. Comparison of the performances of C_2-symmetric precatalysts with those of C_{2v}- and C_s-symmetric ones suggested that a dual mechanism of steric control (i.e., an *enantiomorphic site* type isospecific steric control counterbalancing the syndiospecific *chain end* steric control) could be operative for the former.

Complex	R1	R2	R3
2	iPr	iPr	H
3	Me	Me	H
4	Me	iPr	H
5	Me	tBu	H
6	Me	tBu	tBu

Fig. 3. Schematic representation of catalysts **2**–**6**.

Later on, this approach was successfully pursued by Coates, who reported a chiral C_2-symmetric Ni(II) catalyst that exhibits both living behaviour and isospecificity in the polymerization of propylene. Very interestingly, this complex produced polypropylenes with microstructures ranging from highly isotactic at low temperature to regiorandom at high temperature. Therefore, by changing temperature during propylene polymerization, regioblock copolymers were also prepared [55].

A remarkable result in this framework was also the preparation of a cyclophane-based Ni(II) α-diimine complex, which was highly active and robust at elevated temperatures. The living polymerizations of propylene and 1-hexene were obtained for the first time for a late-transition metal system at high temperature. The thermal stability of the complexes was attributed to the unique cyclophane structure that keeps the axial sites for the metal centre fully blocked even at high temperature [56,57].

4. Iron bis(imino) pyridine catalysts

Iron and cobalt complexes with bulky bis(imino)pyridine ligands were independently reported by Brookhart [58–61] and Gibson [62,63] as ethylene polymerization catalysts for the production of strictly linear, high-molecular weight polymers. These catalysts, activated by MAO, exhibit productivities that rival the most efficient group 4 metallocene catalysts and, as a result, received considerable attention by both industrial and academic scientists. A systematic evaluation of the substituent effect established structure–reactivity relationships that allow a fine-tuning of the polymerization activity by modifying the ligand structural design [36–38,64,65]. In particular, changes to the basic bis(imino)pyridine ligand motif have been targeted, with modifications to the N-imine substituents, the C-imino substituents, and the central pyridine substituents at the forefront. The steric bulk on the imino nitrogen seems to prevent the formation of bis-chelate complexes and control the rates of propagation and chain termination, thus influencing the activity of the catalysts and the molecular weight of the polymers [64].

Bis(arylimino)pyridyl Fe(II) and Co(II) complexes bearing a single *ortho*-substituent on the aryl rings promote selective ethylene oligomerization to linear α-olefin with a Schultz-Flory distribution. Moreover, they have been used as oligomerization catalysts in combination with various early and late metal complexes in tandem catalytic systems for the production of branched polyethylene.

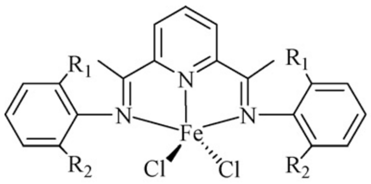
The absence of branches in the polymer chains indicates that these catalysts do not polymerize *via* a *chain-walking* mechanism as it occurs for Ni(II) and Pd(II) α-diimine [5,6,32–42] neither incorporate significantly the produced α-olefins into the growing polymer chain.

These catalysts resulted also moderately active in the polymerization of propylene to isotactic polymers "ostensibly due to a *chain end* control mechanism" as reported by Small and Brookhart [58–61].

In connection with our interest in exploring the factors leading to stereospecific polymerization with late-transition metal catalysts, we studied the stereochemical mechanism of propylene polymerization promoted by the iron-based catalysts complexes **7** and **8** (Fig. 4) and the regiochemistry of propagation elucidated by end group analysis.

Complex **7**, with bulky isopropyl *ortho*-substituents on the arylimino moieties, produced regioregular isotactic polypropylene with a 69% *mm* triad content at 0 °C.

NMR analysis of the polypropylene microstructure suggested that a *chain end* mechanism of steric control was operative. Interestingly, this steric control was still effective above room temperature,



Complex	R_1	R_2
7	iPr	iPr
8	Me	iPr

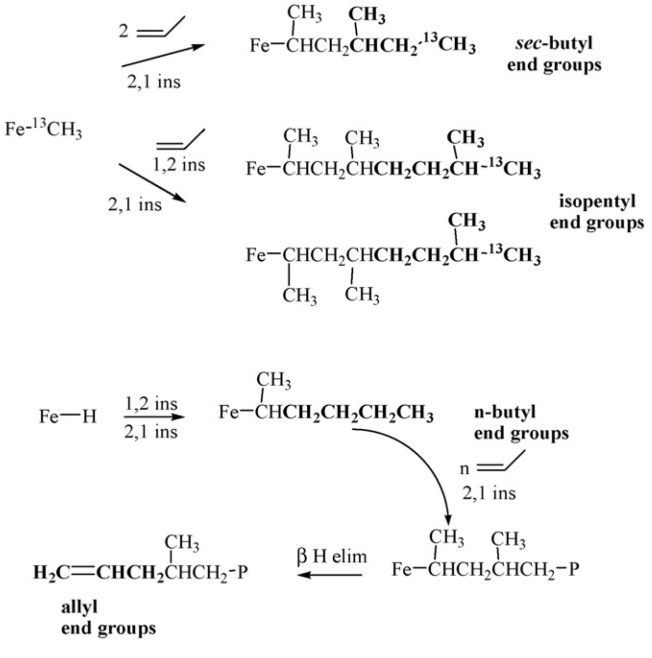
Fig. 4. Schematic representation of catalysts **7**–**8**.

e.g., at 50 °C (*mm* = 60%) [66]. The isotactic-specific polymerization catalyst Cp_2TiPh_2-MAO, disclosed by Ewen [67], operated through a *chain end* control mechanism only at sub-ambient temperatures. A possible explanation for this peculiar behaviour comes from the study of the regiochemistry of monomer insertion. A polymer sample bearing ^{13}C-enriched end groups was prepared by adding some ^{13}C-enriched $Al(CH_3)_3$ to the iron catalyst. The major ^{13}C-enriched end groups observed were *sec*-butyls, deriving from 2,1 insertions of propylene into *in situ* generated Fe-$^{13}CH_3$ bonds. Isopentyl end groups were also detected, deriving from initiation *via* 1,2 insertion followed by 2,1 insertion (Scheme 5).

Analysis of the natural abundance end groups showed the presence of unsaturated allyl groups deriving from β-H-elimination at the methyl of a secondary growing chain (Scheme 5) and *n*-butyl end groups, originating from 1,2 insertion of propylene into Fe–H bonds followed by a 2,1 insertion (Scheme 5).

Since the polymer backbone is highly regioregular, the above end group analysis indicated that primary insertion is favoured into Fe–H bond, primary and secondary insertion have comparable probabilities into Fe–CH_3 bonds, while secondary insertion is preferred into Fe-alkyl bonds (for alkyl > CH_3). In conclusion secondary insertion is the most probable event during the propagation.

Complex **8** afforded a polypropylene with a similar content of *mm* triads, although the polymer microstructure slightly deviates from the composition expected for a simple *chain end* mechanism. Thus, a copolymer of propylene containing about 1% of 1-^{13}C-enriched ethylene was prepared with complex **8**. NMR analysis of the copolymer did not show any detectable methylene pair sequences, thus indicating that 2,1 propylene insertion is preferred also after ethylene insertion and remains the main propagation mode. Further information came from close examination of the fine structure of the enriched carbon atoms (Fig. 5). As expected, the relative areas of the resonances of the *m*-$S_{\alpha\gamma}$- and *r*-$S_{\alpha\gamma}$-enriched methylenes were the same as the molar fraction of *m* and *r* dyads inside the polypropylene blocks, determined from the methyl pentad resonances. In fact, for a secondary mode of propagation, the $S_{\alpha\gamma}$ is diagnostic of the stereochemical arrangement of the two propylene units incorporated *before* the insertion of enriched ethylene (see Scheme 3b).



Scheme 5. Mechanisms for initiation and termination in the polymerization of propylene for the catalytic system based on complex **7**.

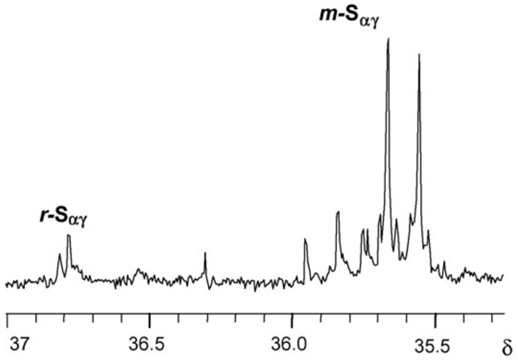


Fig. 5. $S_{\alpha\gamma}$ region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propylene with a little amount of 1-^{13}C-ethylene prepared with complex **8**-MAO. δ in ppm from hexamethyldisiloxane.

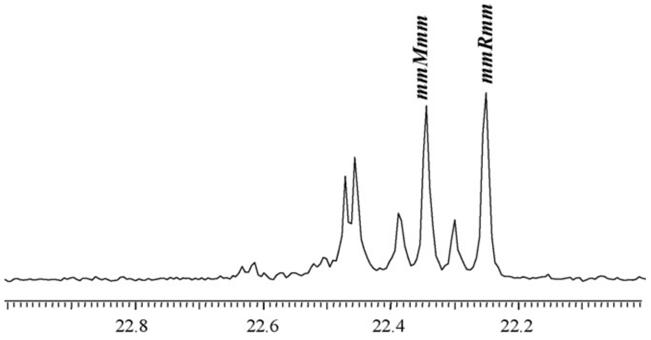
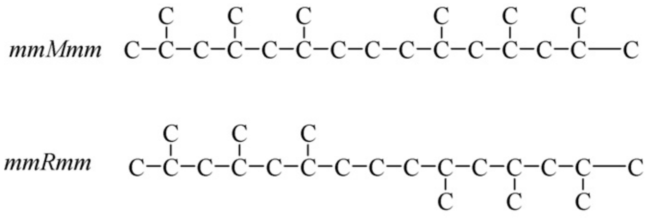


Fig. 6. $S_{\beta\beta}$ region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propylene with a little amount of 1-^{13}C-ethylene prepared with complex **8**-MAO. δ in ppm from hexamethyldisiloxane.

In the $S_{\beta\beta}$ region of the spectrum (Fig. 6) two major resonances attributable to *mmMmm* and *mmRmm* pseudohexads were detected, confirming a *chain end* mechanism of steric control, i.e., the steric control does not cross the intervening ethylene unit (see Scheme 6).

A similar spectrum was observed for a copolymer prepared with the Ewen's achiral Cp_2TiPh_2-MAO catalyst which affords isotactic



Scheme 6. Stereosequences of regioregular pseudohexads.

polypropylene *via chain end* control at low temperature [67]. On the contrary, only the *mmMmm* pseudohexad was observed for an isospecific C_2-symmetric *ansa*-zirconocene such as *rac*-$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}Ind)_2ZrCl_2$ [68] in agreement with an *enanthiomorfic-site* mechanism of steric control [26].

5. Octahedral complexes of group IV metals with phenoxy-based ligands

Group IV metal complexes in octahedral environments could offer, depending on the structural properties of the coordinated ligands, the appropriate symmetry and the steric and electronic characteristics at the metal centre necessary to promote stereospecific polymerization.

The attention paid to these systems was principally due to the similarity of their structures with that of the heterogeneous catalysts based on both $TiCl_3$ and $MgCl_2/TiCl_n$ system, with the role of the surface being played by the ligand framework. Respect to group 4 metallocene complexes which are pseudo-tetrahedral, a more crowded coordination sphere could better satisfy, in principle, the steric requirements for a high regio- and enantioselectivity.

In particular, ligands containing monoanionic phenoxide donors and neutral additional donors efficiently stabilize the complexes of electropositive early transition metals forming strong metal-oxygen bonds [5,6,69,70], and allow one to obtain a stereochemically rigid framework for the metal centre for stereoselective polymerizations of prochiral olefins [71–74].

The large choice of different additional neutral donors has allowed the synthesis of numerous families of non-metallocene catalysts and offered the possibility of a rational design of catalytically active site by easily modifying of the electronic character, geometry, and steric hindrance of the coordination environment.

Octahedral group 4 metal complexes supported by two bidentate monoanionic (NO) ligands or by a single tetradentate dianionic (ONNO) ligand, in which the additional donors are neutral nitrogen atoms, revealed to be among the most interesting classes of polymerization catalysts.

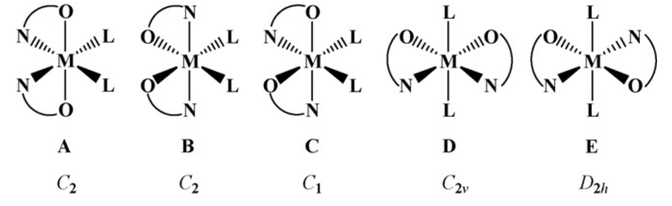
In the following sections we describe our research focused on some remarkable examples of these classes.

5.1. Octahedral complexes bearing bidentate phenoxy-imine ligands

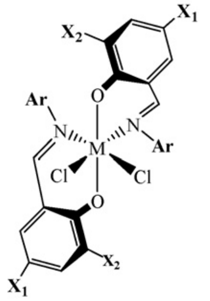
A structural requirement for olefin polymerization catalysts is that co-ligands occupy mutually *cis* coordination sites. For this reason the stereochemistry of the MX_2 group of octahedral complexes is an important feature of the overall structure with respect to catalytic activity.

In particular, bidentate ligands can organize around the metal centre according to five different configurations (see Scheme 7) while only structures A–C satisfy the above requirement.

The first studies concerning the use of phenoxyimine-based catalysts for olefin polymerization involved group 4 metal complexes bearing two hydroxyphenyloxazoline ligands synthesised by Floriani et al.; however they showed very low catalytic activities [75,76].



Scheme 7. Possible stereoisomers in octahedral complexes with two bidentate ligands.



Complex	M	Ar	X₁	X₂
9	Ti	C_6H_5	H	tBu
10	Ti	3,5-F_2-C_6H_3	H	tBu
11	Ti	C_6F_5	H	tBu
12	Ti	C_6F_5	Br	Br
13	Ti	C_6F_5	Cl	Cl
14	Ti	C_6F_5	I	I
15	Zr	C_6F_5	H	Me
16	Ti	C_6F_5	H	Me
17	Zr	C_6F_5	Br	Br
18	Zr	C_6F_5	Cl	Cl

Fig. 7. Schematic representation of catalysts **9**–**18**.

More recently complexes containing Schiff bases have been widely investigated because of their ease of preparation and modification of both steric and/or electronic properties. One of the most significant examples are octahedral bis(phenoxy-imine) group 4 complexes developed at Mitsui Chemicals [69,77–79] which were revealed to be extremely efficient catalysts for ethylene polymerization [80], with activities comparable, or even exceeding, those of metallocene catalysts. The numerous studies performed on these systems as catalysts for homo- and co-polymerization of α-olefins revealed an extremely versatile catalytic behaviour that offered the possibility to afford a wide variety of olefin-based polymers with unique and distinctive architectural features [79].

As for the polymerization of propylene, Coates [81,82] and Fujita [83,84] have independently reported that titanium complexes bearing fluorinated N-aryl groups and bulky *ortho*-phenol substituents, promote syndiospecific polymerization of propylene in a living manner. The mechanism of syndiospecific polymerization has been largely investigated by both experimental [85–88] and theoretical techniques [89,90].

Numerous experimental studies have evidenced that the stereoselectivity of these systems can be suitably modified by opportune variations of the precatalyst structure [77,91–95] or by the choice of adequate polymerization conditions [96,97].

In the following paragraphs some mechanistic aspects of the polymerization of propylene promoted by bis(phenoxy-imine) titanium and zirconium complexes (see Fig. 7) will be discussed with particular attention to the regiochemistry and stereochemistry of the monomer insertion elucidated by NMR analysis.

5.1.1. Bis(phenoxy-imine) titanium complexes

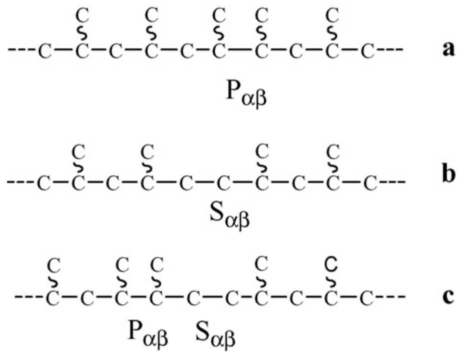
The titanium complexes **9**–**14** (Fig. 7) were prepared, in moderate to high yields, by metathesis reaction between $TiCl_4$ and 2 equivalents of the lithium salt of the opportune ligand according to literature procedures [98].

For the titanium complexes **12**–**14** ^1H, ^{13}C and ^{19}F NMR spectra showed the presence of a single isomer (compatible with isomers A and B of Scheme 7) in solution at room temperature. In agreement with the observed structures of previously reported analogous titanium complexes [95] and on the basis of NMR data it is reasonable to assume a C_2-symmetry for these complexes.

The polypropylene obtained by **9** activated by MAO was prevailingly syndiotactic with a content of *rr* triads of 80% and with a distribution of methyl pentads in agreement with a *chain end* mechanism of steric control.

An accurate ^{13}C NMR analysis of the polypropylene microstructure showed the presence of a few regioirregularly arranged monomer units (<2%), as indicated, e.g., by the methyl resonances ($P_{\alpha\beta}$ carbon atoms) [99] of the tail-to-tail units (see Scheme 8a and c).

NMR analysis of the polymer end groups allowed one to establish their structures: allylic unsaturated end groups flanked by an



Scheme 8. Fischer projections of chain segments containing blocks with different regioregularity (a and b) or isolated regioinverted units (c).

rr triad and, in equal amount, saturated chain end groups (*n*-propyl and *n*-butyl end groups) (Scheme 9). Allyl end groups were originated in the termination steps from a β-hydrogen elimination at the methyl of the growing chain end after a 2,1 insertion (see Scheme 2e). Consequently, in the initiation steps, saturated chain end groups were generated by 1,2 propylene insertion into Ti–H bonds, followed, either immediately or after a few insertion steps, by inversion of the regiochemistry to 2,1 (see Scheme 1a and e).

Experiments of alcoholysis of the polymeric chains, performed with suitable deuteriated alcohols, ruled out the possibility that the saturated chain end groups were formed during the termination steps.

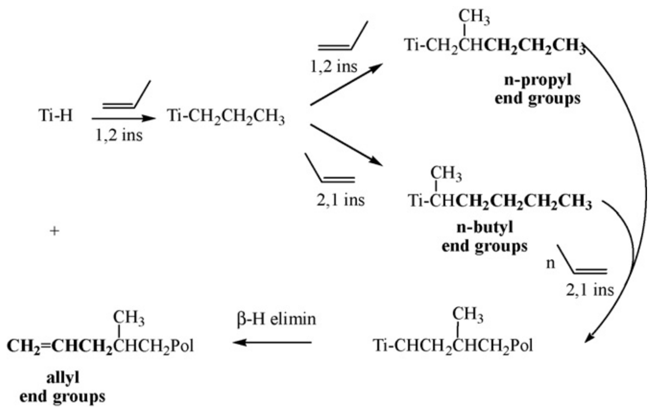
The whole picture described above suggests that β-hydrogen elimination is the main termination process, generating allyl-terminated macromolecules and Ti–H bonds into which a primary insertion of propylene is favoured, which can be followed either by a primary (60%) or a secondary (40%) propylene insertion (see Scheme 9).

Similar conclusions were subsequently reported by Coates [87] from end group analysis of a syndiotactic polypropylene sample produced with complex **10** and also on the basis of the mechanistic studies on the cyclopolymerization of 1,6-heptadiene.

The regiochemistry of polymerization for the living catalytic system based on the perfluorinated complex **11** was previously reported by Fujita [88] by the analysis of low molecular weight polymer samples.

A deeper insight in the stereochemical polymerization mechanism was obtained by preparing a propylene-1-^{13}C-enriched ethylene copolymer with catalyst **11**-MAO [85,86].

The ^{13}C NMR spectrum (Fig. 8) indicated that the methylene pairs outnumber the three-methylene sequences (see Scheme 2).



Scheme 9. Mechanisms for initiation and termination in the polymerization of propylene by the catalytic system **9**/MAO.

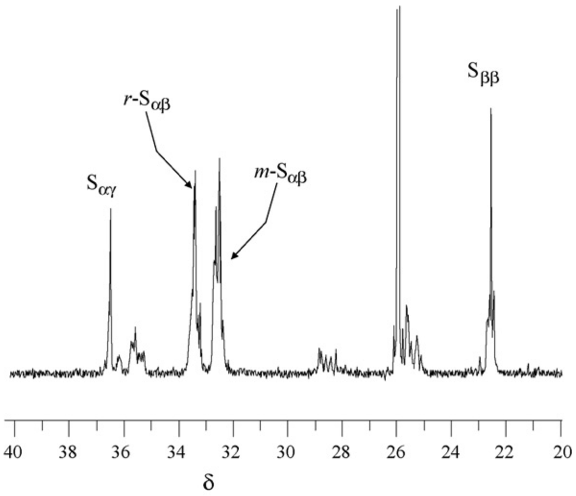
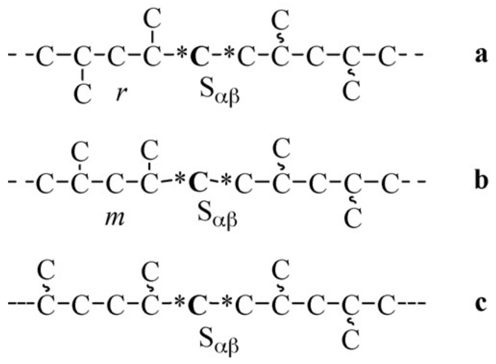


Fig. 8. Aliphatic region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propylene with a little amount of 1-^{13}C-ethylene prepared with **11**-MAO. δ in ppm from hexamethyldisiloxane.

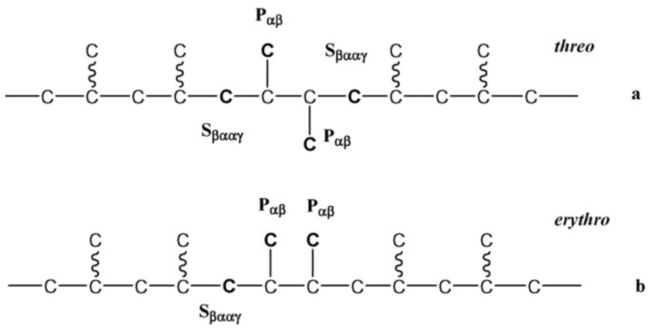
In other words, ethylene units more often bridge blocks of propylene units with opposite regiochemistry than blocks of regioregularly arranged propylene units. This agrees with the previous observations: 2,1 insertion of propylene is favoured during the “*normal*” propagation, but 1,2 insertion becomes slightly favoured into metal-primary carbon bond formed after the insertion of an ethylene unit. In addition the fraction of the r-$S_{\alpha\beta}$-enriched carbon atoms was unexpectedly low (45%) if compared to the *r* diad content inside the polypropylene blocks (98%). On the basis of literature data [100–102], the m-$S_{\alpha\beta}$ (Scheme 10b) resonance probably overlapped with the $S_{\alpha\beta}$ carbon flanking a regioirregular propylene diad (Scheme 10c). Since two methylene sequences can derive only from a ^{13}C-enriched ethylene inserted after a secondary polypropylene block and followed by a primary propylene insertion (see Scheme 3c), and since the secondary block is highly syndiotactic, one may conclude that either 1,2 insertion is highly isotactic or that it is prevailingly followed by a 2,1 insertion, ruling out the presence of significant amount of primary blocks.

Analogues studies were recently extended to bis(phenoxy-imine) titanium complexes (**12**–**14**) bearing ligands with halide substituents in the *ortho*- and *para*-positions of the phenolate rings [93].

The NMR analysis of the polypropylene samples showed that, at low temperature (<0 °C), these catalytic systems produce prevailing isotactic polypropylenes ([*mm*] ~ 64%) with a microstructure compatible with an “enantiomorphic sites” mechanism of steric control and characterized by a considerable amount of regioin-



Scheme 10. Regioregular (a and b) and regioirregular (c) propylene-1-^{13}C ethylene-propylene sequences.



Scheme 11. Fischer projections of vicinal *threo* (a) and *erythro* (b) methyls bringing blocks of different regiochemistry.

versions (10%). A comparison of the catalytic behaviour of the titanium complexes (**12**–**14**) revealed that, increasing the steric bulk of the halogen substituents, the catalytic activity decreases while the stereospecificity increases. Such complexes revealed a catalytic behaviour different from that of all the previously discussed complexes which afford prevailingly syndiotactic polypropylene whatever the size of the *o*-phenoxy alkyl substituents and also in the absence of substituents [97,103,104], but quite similar to that described for the isospecific phenoxy-ketimine titanium complexes [91,92].

To investigate the origin of this behaviour a more detailed analysis of the microstructure of the produced polypropylenes by **12**–**14**/MAO was performed.

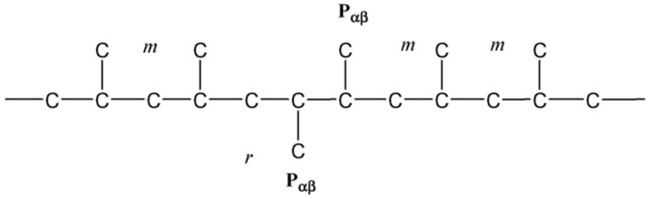
In particular the resonances relative to the methyl carbon atoms ($P_{\alpha\beta}$) of tail-to-tail junctions and to the methylene carbon atoms ($S_{\alpha\beta}$) [99] of head-to-head junctions of the regiomistakes abundantly present within the polymer chains were discussed. The resonances relative to the $S_{\alpha\beta}$ carbon atoms [100,105] indicated that the polymer chains are prevailing formed by segments generated by consecutive 2,1 insertions and 1,2 insertions (Scheme 8b).

The analysis of the resonances of $S_{\beta\alpha\alpha\gamma}$ carbon atoms [106] and of the resonances of the *threo* $P_{\alpha\beta}$ carbon atoms (see Scheme 11a), which are much more intense of the resonances diagnostic of *erythro* $P_{\alpha\beta}$ carbon atoms (see Scheme 11b), indicated that the regiodefects occur, prevailingly, with the same enantiofacial selectivity of the precedent monomer insertion.

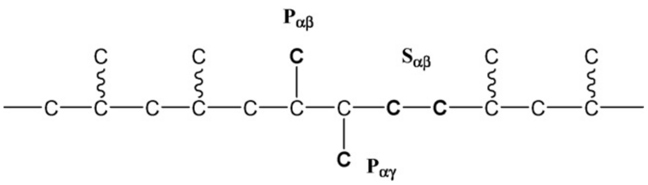
The structure of most abundant diastereoisomeric regioirregular sequence [105,107] (Scheme 12) showed that the most frequent stereochemical arrangement of the monomeric units adjacent to the regioirregular junctions of the polypropylene chains is meso indicating that both regiochemical propagation modes are preferentially isospecific.

Less frequent stereomistakes, formed by insertion of a single monomeric unit with opposite regiochemistry and with the same enantioface, are also observed (see Scheme 13) [29,108].

These microstructural data revealed that during the polymerization reaction a regiomistake occurs initially with the insertion of the monomeric unit with same enantioface of the previous inserted monomer unit but, if the new propagation mode is preserved, the subsequent insertions occur with the opposite enantioface. This behaviour is quite different from that observed for the chiral group 4 metallocene catalysts for which it was clearly established that the infrequent secondary single insertions of propylene occur preferably with the opposite enantioface with respect to the preferred 1,2 mode of insertion [109,110].



Scheme 12. Fischer projection of the most frequent stereochemical arrangement of the monomer units adjacent to the vicinal *threo* methyls.



Scheme 13. Fischer projections of vicinal *threo* methyls of isolated regioinverted units.

The NMR end group analysis allowed one to establish their structures: a single diastereoisomer of the isobutyl end groups [111–113] with a percentage of 54% (Schemes 1b and 2a) and *n*-propyl end groups 46% (Scheme 2d) [114].

These data suggested that the polymerization is prevailingly initiated by some consecutive 1,2-insertions of the propylene into a $Ti–CH_3$ bond (generating the isobutyl end groups) and that the chirality of the titanium centre is effective in controlling the stereochemistry of the insertion already in the second propagation step.

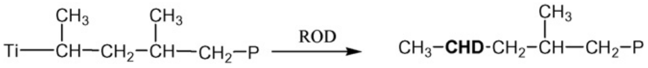
The hypothesis that *n*-propyl groups are formed in the termination steps by hydrolysis of titanium-bound secondary growing chains (see Scheme 2) was corroborated by deuterium labelling experiments that clearly showed the presence of a single type of isotopically enriched $CH_3CHDCH_2–$ end group, that is expected for deuterolysis of a secondary polymer chain bound to titanium (Scheme 14).

The fine analysis of the stereochemical structure of *n*-propyl groups [114] indicated that these ends groups were adjacent, prevailingly, to an isotactic *mm* stereochemical triad, and, with a lower frequency, to a *mr* stereochemical triad. This suggested that secondary propylene insertion is less isospecific than primary propylene insertion.

Since the amount of isobutyl end groups exceeds slightly that of *n*-propyl, some hydrolysis of titanium-bound primary growing chains also occur in the termination steps. The mechanism hypothesized on the basis of the detected end groups is described in Scheme 15.

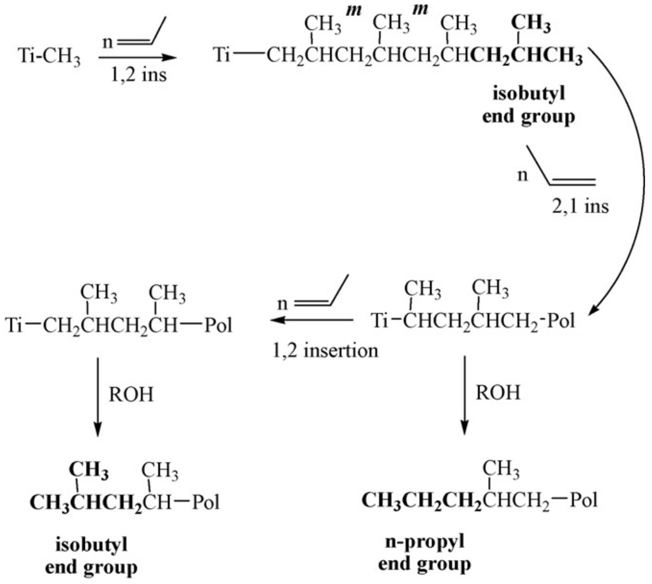
A copolymerization of propylene with a low amount of ethylene showed that the isolated ethylene units [115] were located between blocks of polypropylene chains leading to either a two-methylene sequence or a three-methylene sequence (Scheme 3), no resonances attributable to four-methylene sequences were observed in the spectrum (Fig. 9). The methylene pairs outnumber the three-methylene sequences (70% vs. 30%) suggesting that the ethylene units bridge blocks of propylene units with opposite regiochemistry more frequently than blocks of regioregularly arranged propylene units (see Scheme 3).

The *m*-$S_{\alpha\gamma}$ abundance was about 61%, indicating that the ethylene units spanning regioregular blocks of polypropylene were more often bordered by isotactic (*m*) than by syndiotactic (*r*) stereochemical dyads. Moreover, considering that the primary propylene insertion (1,2) is highly isospecific, as observed by the end groups formed in the initiation steps, it can be reasonably excluded that the above three methylene sequences are flanked by regioregular blocks deriving exclusively by primary insertions.



$$Ti{-}\overset{CH_3}{CH}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}P \xrightarrow{ROD} CH_3{-}\mathbf{CHD}{-}CH_2{-}\overset{CH_3}{CH}{-}CH_2{-}P$$

Scheme 14. Deuteriolysis of a secondary polymer chain.



Scheme 15. Mechanisms for initiation and termination in the polymerization of propylene by the catalytic systems **12**–**14**/MAO.

The data of the ^{13}C NMR spectrum of the copolymer support the hypothesis that the highly isospecific propylene primary insertion is not the prevalent mode of propagation, while the moderate isotacticity of the polymer would be due to the presence of a conspicuous fraction of less stereoregular blocks derived from secondary insertions.

In conclusion the catalysts **12**–**14** produce, at low temperature, a prevailing isotactic polypropylene *via* an *enantiomorphic sites* mechanism of steric control and with a microstructure consisting of shorter primary, highly isotactic blocks and longer, secondary, poorly isotactic blocks.

5.1.2. Bis(phenoxy-imine) zirconium complexes

The mechanistic investigations regarding the stereospecific polymerization of propylene promoted by (bis-phenoxy-imine) catalysts were extended to the analogous zirconium complexes displayed in Fig. 7.

Ligands [85,93,94] and complexes **15**, **17**, and **18** were prepared, according to literature procedures [80,116], by reaction of 2 equivalents of the ligand lithium salt with $ZrCl_4 \cdot 2THF$ in tetrahydrofuran.

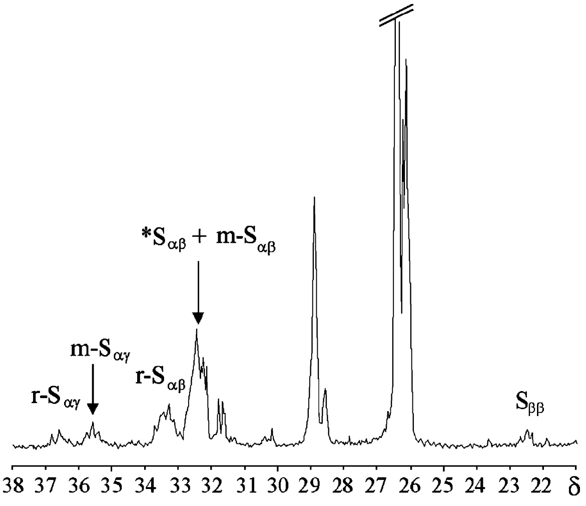


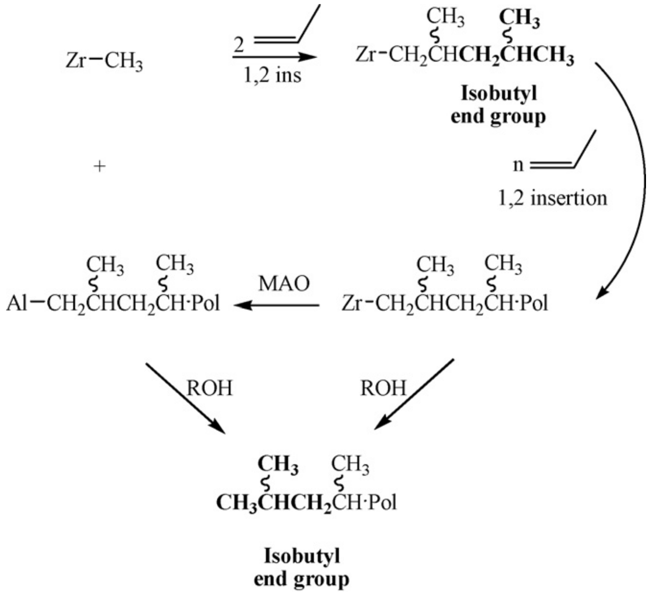
Fig. 9. Aliphatic region of the 100.6 MHz ^{13}C NMR spectrum ($C_2D_2Cl_4$, 100 °C) of a copolymer of propylene with a little amount of ethylene prepared with **12**-MAO. δ in ppm from hexamethyldisiloxane.

Polymerization of propylene at room temperature in the presence of **15** resulted in the production of a poor stereoregular, prevailingly syndiotactic polypropylene ($P_r = 0.67$). The polymer microstructure is in agreement with a *chain end* mechanism of steric control. End group analysis showed the almost exclusive presence of isobutyl end groups, indicative of a primary (1,2) propylene insertion operating both in the initiation and the termination steps. The formation of isobutyl end groups during the termination step was confirmed by the presence of $CH_2DCH(CH_3)CH_2-$ end groups in the ^2H NMR spectrum of a polypropylene sample prepared with the same deuterium labelling technique used in the case of the nickel catalyst (see above, Scheme 4).

The reasonable polymerization mechanism (see Scheme 16) involves primary propylene insertion into Zr–CH_3 bonds, followed by prevailingly primary insertions during the propagation, and termination *via* chain transfer of the primary growing chain to MAO (or to $Al(CH_3)_3$ present in the MAO solution) generating a new Zr–CH_3 bond for re-initiation.

Further support to the whole picture came from copolymerization of propylene with a small amount of 1-^{13}C-enriched ethylene (see the spectrum in Fig. 10a). In this case the three methylene sequences outnumber the methylene pairs (79% vs. 21%), in agreement with a prevailingly primary regiochemistry: this result is unexpected in view of the opposite regiochemistry observed for related bis(phenoxy-imine)titanium catalysts. In order to discriminate the role played by the nature of the metal in determining the regiochemistry of propylene insertion from any ligand effect, we tested the titanium complex (complex **16** in Fig. 7) bearing the same ligands. The polypropylene produced was very similar to that obtained with the corresponding Zr compound [117]. End groups analysis, also confirmed by deuterium labelling data, revealed in this case the presence of *n*-propyl and isobutyl end groups. As discussed above, these data suggest that the polymerization is prevailingly initiated by at least two consecutive 1,2-insertions into a Ti–CH_3 bond (generating the isobutyl end groups), while the main termination step is the hydrolysis of titanium-bound secondary growing chains generating *n*-propyl end groups (see Scheme 17).

Conclusive results came from the structure of a copolymer of propylene with a low amount of 1-^{13}C-ethylene. NMR analysis (see the spectrum in Fig. 10b) showed that in this case methylene pairs



Scheme 16. Cycle of propylene polymerization for catalyst **15**.

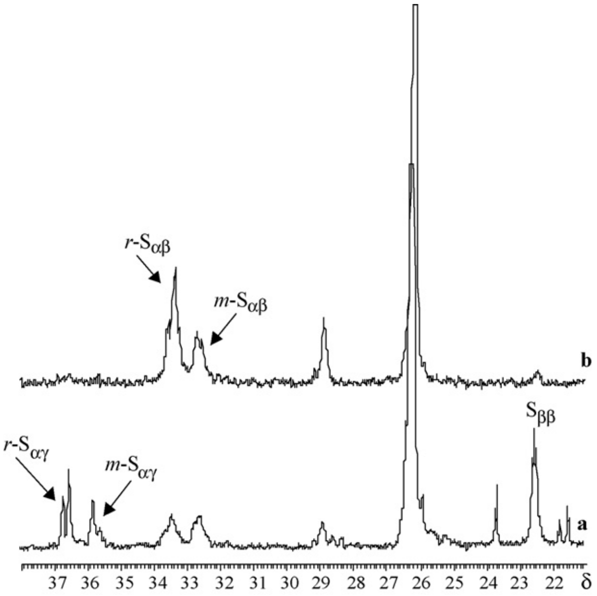


Fig. 10. Aliphatic regions of the 100.6 MHz ^{13}C NMR spectra ($C_2D_2Cl_4$, 100 °C) of copolymers of propylene with a little amount of ethylene prepared with **15**-MAO (a) and **16**-MAO (b). δ in ppm from hexamethyldisiloxane.

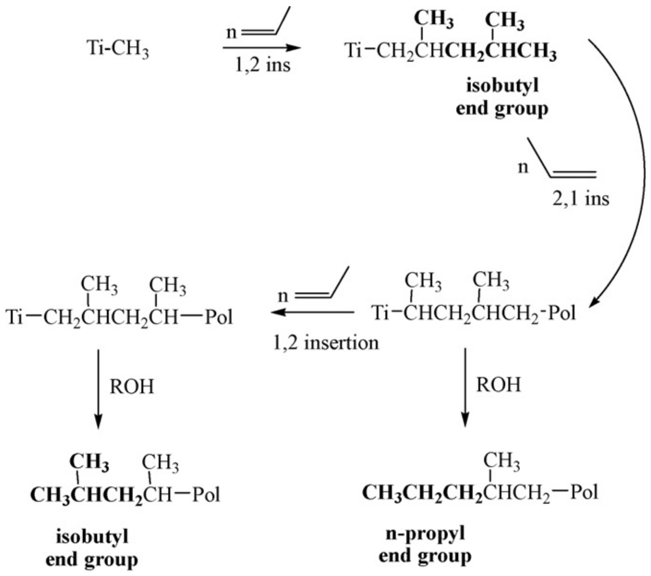
outnumber the three methylene sequences (90% vs. 10%), suggesting that 2,1 insertion of propylene is the "normal" mode of propagation, and that 1,2 insertion becomes preferred after the insertion of an ethylene unit, which generates a metal-primary carbon bond.

In conclusion, zirconium and titanium complexes bearing the same ligands afford prevailingly syndiotactic polypropylenes having very similar structures, but *via* opposite regiochemistries [94].

Analogous studies were extended to zirconium complexes supported by phenoxyimine ligands with halogen substituent in the *ortho*- and *para*-position of the phenolate rings.

Polymerization of propylene with complexes **17**–**18** using dried methylaluminoxane [118] produced slightly syndiotactic-enriched polypropylenes ([*rr*] ~ 40%) with a small amount of regioirregularly arranged monomer units (<1%).

The comparison between the polymerization results obtained with **17**–**18** and those obtained with an analogous phenoxyimine catalyst bearing methyl substituents on the phenol rings (complex **15**) provided evidence that the introduction of halogen substituents on the ligand skeleton has beneficial effects on the catalytic activity and on the regioselectivity of the catalytic systems (% of vicinal methyl: <1% for **17**–**18** and 3.5% for **15**, respectively). The improved propensity of catalysts **17** and **18** to polymerize propylene with primary regiochemistry has important consequences on the structures of the chain end groups. In fact the polymers produced with these systems with *ortho*-phenol alkyl substituents show a mixture of different unsaturated end groups formed mostly by a β-H transfers following a 2,1 insertion (>90%) [117]. Differently, as a consequence of the increased regioselectivity, catalysts **17** and **18**, when activated by dried MAO or Al(^{i}Bu)$_3$ and $Ph_3CB(C_6F_5)_4$, produce, selectively, vinyl-terminated low molecular weight polypropylenes which are interesting precursors for synthesis of the terminally functionalized polypropylenes.



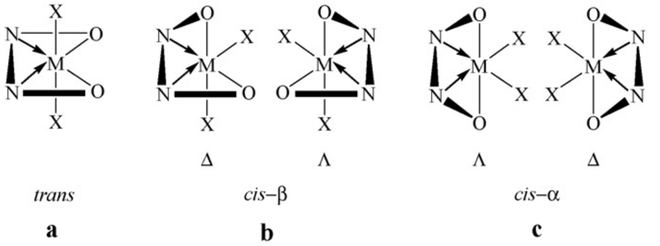
Scheme 17. Cycle of propylene polymerization for catalyst **16**.

5.2. Octahedral complexes bearing tetradentate ligands

Linear tetradentate phenolate ligands bind strongly to oxophilic group 4 metal, possibly generating chirality at a metal center and hence have a big potential for stereoselective polymerization of prochiral olefins. In this respect, they are more promising than the bidentate ones.

The interest toward this new class of complexes as stereospecific polymerization catalysts was initially inspired by the pioneering work of Kol and co-workers who reported the first example of a non-metallocene C_2-symmetrical zirconium complex, bearing a tetradentate diamine-diphenolate ligand (*salan*), active in living and isospecific polymerization of high-olefins at room temperature [119]. The mechanism of propylene polymerization promoted by this class of catalysts was studied by Busico et al. [120]. He showed that, depending on the steric hindrance at the active metal, isotactic site-controlled or weakly syndiotactic chain end controlled polymers could be obtained, in both cases *via* highly regioselective 1,2 monomer insertion.

A strictly related class of ligands is represented by *salen* [*N*,*N*′-ethylenebis(salicylidenaminate)] compounds and *salen*-type ligands have emerged as one of the most important ligand systems in asymmetric catalysis [121,122]. Nevertheless the investigation of the potential of complexes of this class of ligands as olefin polymerization catalysts has been limited. An early study by Repo et al. [123] explored the performances of simple salen Zr complexes, in which the tetradentate Schiff-base ligand coordinates the metal in a substantially planar fashion, resulting in poor catalytic activity in the polymerization of ethylene and in lack of activity in the polymerization of propylene. Related acen and hexafluoroacen Zr alkyl complexes, displaying non-planar Schiff-base ligands, were previously investigated by Jordan and co-workers [124,125] who reported low to moderate ethylene polymerization activities after activation with $[HNMe_2Ph][B(C_6F_5)_4]$ and Al^{i}Bu$_3$. C_2-symmetric Zr complexes [126] of biaryl-bridged *salen*-type ligands displaying non-planar coordination of the Schiff-base were also reported to be inactive in ethylene polymerization in the presence of methylalumoxane (MAO) co-catalyst [127]. This observation was traced to the well known [124,125] reactivity of the imine functionality vs. the intramolecular reduction *via* 1,2-migratory insertion of metal-bound alkyl ligands [126]. As a matter of fact, introduction of a methyl group at the *meta* position of the phenolate ring (shielding the imine functionality) afforded a modified Zr complex which, activated by MAO, was moderately active in the polymerization of ethylene at room temperature [127]. However, a closely related Zr complex bearing a cyclohexyl-bridged *salen* ligand without any substituent at the *meta* position of the phenolate ring was recently reported to polymerize ethylene and copolymerize ethylene with propylene and 1-hexene with moderate activity in the presence of MAO or $Ph_3CB(C_6F_5)_4$/Al(^{i}Bu)$_3$ co-catalyst [128,129].



Scheme 18. Possible stereoisomers in octahedral complexes with tetradentate ligands.

We have studied quadridentate *salen*- and related *salan*-type complexes to compare these two classes of strictly related complexes and to obtain a better understanding of their behaviour in α-olefin polymerization.

Tetradentate ligands can wrap around an octahedron according to three different configurations (see Scheme 18) and the desirable structure for potential precatalysts are the stereoisomers b and c.

5.2.1. Binaphthyl-bridged bis(phenolate) zirconium complexes

We chose a binaphthyl bridge which provides conformationally constrained backbones inducing non-planar co-ordination and favouring *cis* structures b (*cis*-β) and c (*cis*-α). Moreover, the use of chiral non-racemic ligands can result in the preferential formation of “chiral-at-metal” complexes, which are of great potential interest for enantioselective catalysis.

Ligands were obtained by condensing binaphthyl diamine and salicylaldehydes under standard condensation conditions [130]. Complex **19** (Fig. 11) was synthesized according to a literature procedure [131] by reacting the sodium salt of the salen proligand with [$ZrCl_4(THF)_2$]. It was characterized by ^1H and ^{13}C NMR analysis. NMR spectra suggested that this complex has at least a C_2-symmetry in solution, so that it could have either a *cis*-α or a *trans*-configuration. A single crystal X-ray analysis indicated the selective formation of the *cis*-α isomer.

Tetradentate ligands can afford chiral-at-metal octahedral complexes having Δ- or Λ-configuration (except in the case of the *trans*-isomer) (see Scheme 18). In the case of *cis*-α isomer, two enantiomeric couples of diastereoisomers are possible: R-Δ/S-Λ and S-Δ/R-Λ, but the presence of just one pattern of signals in the NMR spectra suggested that only one enantiomeric couple was selectively formed, indicating that chirality at the metal was perfectly induced by the ligand chirality. The same feature was recently observed in the case of analogous *salan* zirconium complexes reported by Kol and co-workers [132,133].

Testing complex **19** in ethylene polymerization, we demonstrated the importance of the co-catalyst choice for this type of complexes [134]. In fact the activation of complex **19** for ethylene polymerization was achieved by several combinations of aluminium alkyls and MAO or boron compounds, while MAO alone was not able to generate a catalytic active species. On the basis of hydrolysis experiments performed on different catalytic combinations (i.e., **19**/MAO and **19**/AliBu$_3$) we concluded that some aluminium alkyls are able to reduce the imine bonds, *in situ*, generating catalytic active species which have a binaphthyl-amine ligand while MAO is not able to perform the same reduction.

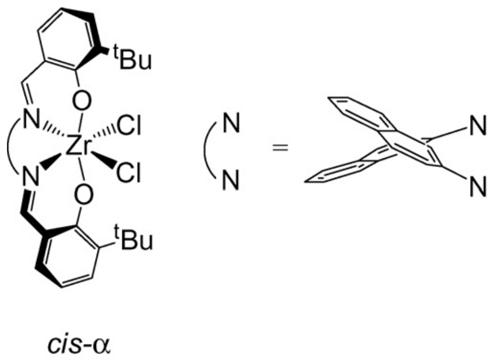


Fig. 11. Schematic representation of complex **19**.

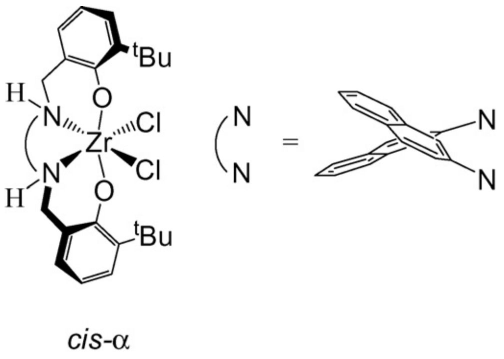


Fig. 12. Schematic representation of complex **20**.

We decided to synthesize an authentic binaphthyl-amine-bridged bis(phenolate)zirconium complex (*Salan* complex **20**, Fig. 12) and to test its behaviour as precatalyst in the polymerization of α-olefins [135].

Salan ligand was synthesized, in good yield, by reduction of the related *salen* ligand according to a standard procedure reported in the literature [136]. Ligand deprotonation and reaction with $ZrCl_4(THF)_2$, followed by recrystallization gave pure complex **20**. Both ^{13}C and ^1H NMR analysis suggested that this complex has at least a C_2-symmetry in solution. By analogy with complex **19**, we supposed the formation of the *cis*-α isomer.

Complex **20** was then used as precatalyst in the polymerization of ethylene [135]. As expected, MAO resulted an effective activator of **20**. In fact, when activated with MAO ([Al/Zr] = 500:1), complex **20** showed a fair activity in the polymerization of ethylene (activity = 60 $Kg_{polymer}/mol_{Zr}$ h atm), similar to that of complex **19** activated with $Al(^iBu)_3/Ph_3CB(C_6F_5)_4$ (activity = 40 $Kg_{polymer}/mol_{Zr}$ h atm).

Complexes **19** and **20** were also tested in the polymerization of propylene and higher α-olefins, i.e., 1-butene, 1-pentene and 1-hexene, using the appropriate co-catalytic system for each catalyst [134,135].

Unlike the previously reported *salen* complexes, which are substantially inactive in the polymerization of propylene and higher α-olefins, polymers were obtained from all the monomers with significant productivities (activities range from 100 to 1500 $g_{polymer}/mol_{Zr}$ h [monomer]).

In particular, we obtained ultrahigh-molecular weights polypropylenes (e.g., for a PP sample produced with complex **19**, M_w = 1.280.000 with M_w/M_n of 4.4, triad analysis was [*mm*]:[*mr*]:[*rr*] ≈ 34.6:37.3:28.1). The production of regioregular atactic polypropylene with such a high molecular weight has few precedents in the literature [97,137]. The molecular weights of the higher poly(α-olefins) resulted lower than that of a polypropylene sample produced under comparable conditions, but significantly high [138].

The molecular weights of polymers produced by complex **20** are lower than that produced by complex **19** because of more frequent termination reactions occurring by chain transfer to residual $Al(CH_3)_3$ in dried MAO.

For the polymer obtained with complex **19**, for which the active species is prepared in situ, the molecular weight distributions range from rather broad in the case of poly-(1-butene) (6.0) to the value expected for a single-site catalyst in the case of poly-(1-hexene) (2.1). On the contrary, in the case of complex **20**, the values expected for a single-site catalyst are observed for all the monomers (PDI ≈ 2).

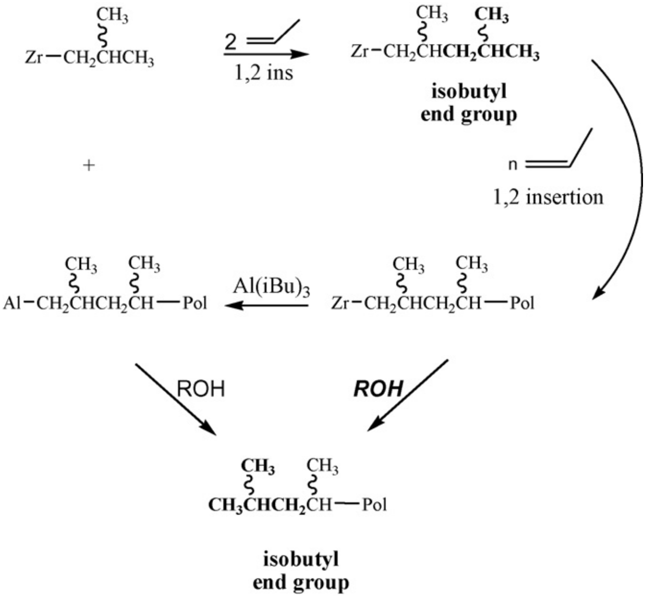
The most intriguing result was the unexpected different stereospecificities observed for the polymerization of propylene, affording an ultrahigh molecular weight atactic polymer, and for the polymerization of higher α-olefins, affording highly isotactic poly-(1-butene), poly-(1-pentene) and poly-(1-hexene). The content of isotactic pentads of poly-(1-butene), poly-(1-pentene) and poly-(1-hexene), evaluated from the intensity of the α-CH_2 carbon in the ^{13}C NMR spectra, increased while the size of the reacting monomer increased. Such unusual result pointed to an effect of the size of the substituent of the monomer on the steric control [135].

The comparable activities and the very similar microstructures of the polymers obtained by **19** and **20** confirmed the hypothesis that binaphthyl-amine bis(phenolate) complexes are the true active species for both the catalytic systems.

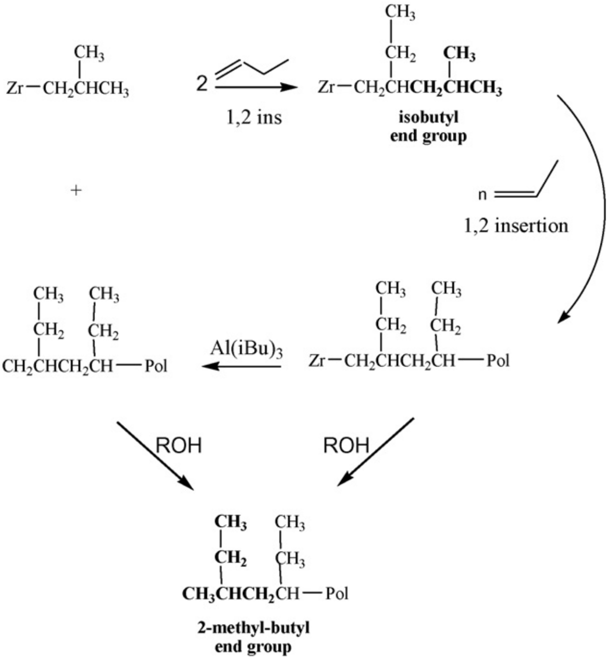
In an effort to elucidate the mechanistic details by which catalysts **19** and **20** produce highly regioregular and almost completely atactic polypropylenes, and highly isotactic poly-(1-butene), -(1-pentene) and -(1-hexene), the regiochemistry of propylene and 1-butene polyinsertion in the presence of both the catalysts was investigated [135]. In order to detect the natural abundance end groups formed by initiation and termination processes, we prepared low M_n polypropylene and poly-1-butene samples, under proper polymerization conditions.

The ^{13}C NMR spectrum of a polypropylene sample obtained with complex **19** shows, in addition to resonances due to the main-chain carbon atoms, resonances attributable to carbon atoms of isobutyl end groups [111,139]. The exclusive presence of isobutyl end groups suggests a primary (1,2) propylene insertion in both the initiation and the termination steps (see Scheme 1b and Scheme 2a). This observation suggests that the probable polymerization mechanism involves primary propylene insertion into Zr-(*i*-Bu) bonds (generated by treatment of **19** with Al(^{i}Bu)$_3$), followed by prevailingly primary insertion during the propagation, and termination *via* hydrolysis of zirconium- or aluminium-bound primary growing chains (see Scheme 19).

In the ^{13}C NMR spectrum of a polypropylene sample obtained with complex **20** we observed isobutyl end groups and *n*-butyl [140] (the molar ratio isobutyl:*n*-butyl was 2:1) indicating that, in this case, the main termination step was the hydrolysis of the polymer chain soon after an isolated (2,1) monomer insertion into a Zr-bound primary growing chain (see Scheme 2j).



Scheme 19. Cycle of propylene polymerization for catalyst **19**.



Scheme 20. Cycle of 1-butene polymerization for catalyst **19**.

Nevertheless, the fact that the insertion in the initiation steps is primary and the absence of regiomistakes in the main chain suggested a prevailing primary insertion mode of propylene also in this case.

The ^{13}C NMR spectrum of poly-1-butene obtained with complex **19** displayed peaks attributable to isobutyl end groups, that are consistent with a 1,2 insertion of 1-butene into a Zr-(i-Bu) bond. Moreover the presence of the 2-methyl-butyl [21] end groups suggested that the main termination step was the alcoholysis of zirconium-bound primary growing chains. Since the molar ratio isobutyl/2-methyl-butyl was 1:1, the active mechanism was so summarizable: the polymerization was initiated by primary 1-butene insertion into Zr-(*i*-Bu) bonds, and was terminated by alcoholysis of zirconium- or aluminium-bound primary growing chains (see Scheme 20).

The ^{13}C NMR spectrum of poly-1-butene obtained with complex **20** displayed peaks attributable [21] to 2-methyl-butyl end groups. The exclusive presence of this kind of end groups is indicative of primary (1,2) 1-butene insertion in both the initiation (1,2 insertion of 1-butene into Zr–CH_3 bonds generated by treatment of **20** with MAO) and the termination steps (alcoholysis of zirconium-bound primary growing chain).

Also in this case, the polymer microstructure and the absence of regioinversions are in agreement with a prevailingly primary regiochemistry for 1-butene polymerization promoted by complex **20**.

In brief, end groups analysis indicates for both catalysts a prevailing primary insertion for both propylene and 1-butene. Thus, the different stereospecificities observed for the polymerization of propylene and of higher α-olefins do not depend on different regiochemistries.

In the case of poly-(1-butene) obtained by both **19** and **20**, the exclusive presence of a single diastereoisomer for the 2-methyl-butyl end groups [135] indicates that the 1,2 insertion is highly isospecific, already after the first monomer insertion. On the contrary, a poorly stereospecific initiation has been generally observed for 1-butene insertions into M–CH_3 bonds for metallocene catalysts [21] as well as for heterogeneous Ziegler-Natta catalysts [18].

The ability of this class of complexes to promote isospecific polymerization of higher α-olefins, in addition to the possibility to obtain easily the same type of complex in its optically active form, make it a good candidate to pursue enantioselective polymerization of chiral racemic α-olefins.

Various strategies have been reported to obtain chiral catalysts able to promote enantioselective polymerization of chiral racemic α-olefins. For example: (i) optically active Lewis bases were added to conventional and supported heterogeneous Ziegler-Natta catalysts [141,142]; (ii) homogeneous enantiomeric metallocenes have been obtained through the formation of diastereomeric derivatives and their separation by use of their differing solubilities [143]; (iii) optically active doubly bridged ansa-zirconocene catalysts have been synthesized by introducing enantiopure substituents on cyclopentadienyl ligands [144,145].

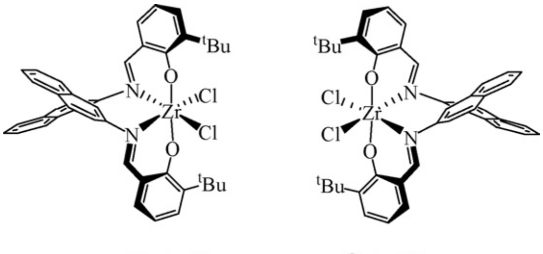
Sulfur-bridged bis(phenolate) group 4 metal catalyst precursors, that efficiently polymerize styrene to give isotactic polymers [146] have been recently obtained in a chiral form by using a 1,2-*trans*-dithiocyclohexanediyl bridge [147]. These complexes, properly activated, have been shown able to produce optically active isotactic oligostyrenes, demonstrating that the insertion of styrene in such post-metallocene catalyst occurs stereospecifically.

For the *cis*-α configuration of complex **19**, we observed that only one enantiomeric couple was selectively formed owing to a perfect induction of chirality from the ligand to the metal. This observation suggested that the use of a chiral diamine fragment should result in the selective formation of one enantiomeric complex. Actually, the enantiomeric binaphthyl-bridged salen dichlorozirconium (IV) complexes, S-Δ-**19** and R-Λ-**19** (see Fig. 13) were easily obtained by a two steps synthesis starting, respectively, from (S) and (R) ligands [148]. ^1H and ^{13}C NMR spectra showed patterns perfectly superimposable to those of the racemic complex.

The synthesized complexes were analysed by optical rotation measurements. As expected, complex **19** was not optically active, while S-Δ-**19** and R-Λ-**19** showed an equal but opposite [α] value. Moreover the measured [α] value for each complex had the opposite sign with respect to that of the corresponding chiral ligand.

Complex **19** and the enantiomeric complexes S-Δ-**19** and R-Λ-**19** were tested in the polymerization of *rac* 4-methyl-1-hexene (4MH) at room temperature by using $Al(^iBu)_3$ and $[CPh_3][B(C_6F_5)_4]$ as co-catalyst resulting in significant activities (activity ≈ 1600 $g_{polymer}/mol_{Zr}$ [4MH] h), very similar to that obtained for 1-hexene polymerization.

The PDI is always lower than 2 indicating the single-site nature of this catalyst. We previously observed [134] that PDI decreases changing from poly-(1-butene) to poly-(1-hexene), suggesting that the larger is the monomer the lower is the chain transfer rate. It is reasonable that the larger steric encumbrance of 4MH, due to its C4 substituent, enhances this effect.



R-Λ-**19** S-Δ-**19**

Fig. 13. Schematic representation of complexes R-Λ-**19** and S-Δ-**19**.

The polymers obtained were analysed by optical rotation measurement. As expected, poly-(4MH) obtained with complex **19** was not optically active, whereas polymeric samples obtained with the two antipodes of the chiral catalyst showed an equal but opposite [α] value.

In more detail, poly-(4MH) obtained with R-Δ-**19** had positive [α] which means that the S-antipode is preferentially polymerised, coherently the recovered monomer resulted enriched in the R-antipode.

For this polymerization experiment we calculated $s = 1.1$ (s = (rate of fast reacting monomer)/(rate of slow reacting monomer) valuable by Kagan's equation). This value indicates a poor resolution for 4MH; this could be explained considering that the stereogenic center of 4MH is separated from the olefin moiety by a methylene unit. Very similar values of s parameter were obtained polymerising 4MH by using optically active doubly bridged ansa zirconocene catalysts [144]; and higher values (up to 1.4) were reached with a pure diastereomer of the metallocene catalyst derivatised with *O*-acetyl-*R*-mandelic acid [149].

Poly-(4MH) obtained with racemic complex **19**, S-Δ-**19** and R-Λ-**19** was also analysed by ^{13}C NMR. The assignment of the resonances, made on the basis of literature data [150,151], revealed an essentially isotactic microstructure.

In conclusion, the synthesized chiral catalyst R-Λ-**19** is able to polymerise 4-methyl-1-hexene to an isotactic polymer with a good yield. It is also able to discriminate between the two monomeric antipodes and to give the preferential polymerization of (S)-4MH. Accordingly, the chiral catalyst S-Δ-**19** is able to polymerize 4-methyl-1-hexene to an isotactic polymer incorporating preferentially the (R)-4MH monomer antipode.

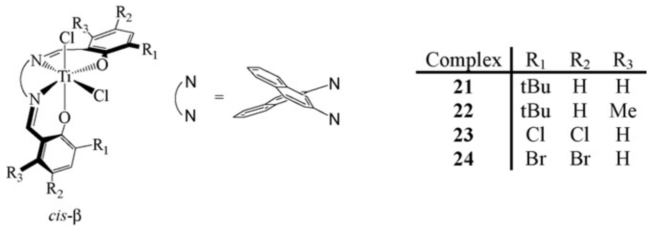
While the enantioselectivity is poor, the results nonetheless demonstrate that the resolution of chiral olefins *via* stereoselective polymerization with this readily synthesized class of catalyst is possible.

5.2.2. Binaphthyl-bridged bis(phenolate) titanium complexes

We also explored the behaviour of titanium complexes of this class of tetradentate ligands as precatalysts for ethylene and propylene polymerization.

We synthesized four new binaphthyl-bridged Schiff base complexes of titanium (complexes **21**–**24** in Fig. 14) [152,153]. In particular, methyl groups at the *meta* position of the phenolate ring (complex **22**) were introduced in order to evaluate the effect of shielding of the imine functionality. Chlorine and bromine substituents at the *ortho*- and *para*-positions of the phenolate ring (complexes **23** and **24**) were introduced to evaluate the effect of electron-withdrawing groups [138].

^1H and ^{13}C NMR spectra supported the presence of two isomers, the C_1-symmetric *cis*-β and either the C_2-symmetric *cis*-α or the C_{2v}- symmetric trans. In all the cases the *cis*-β isomer was the more abundant one, with a ratio between the observed isomers depending on the substituents on the ligands (it ranged from 20:1 for complex **22** to 3:1 for complex **23**).



Complex	R_1	R_2	R_3
21	tBu	H	H
22	tBu	H	Me
23	Cl	Cl	H
24	Br	Br	H

Fig. 14. Schematic representation of binaphthyl-bridged *salen* dichlorotitanium complexes **21**–**24**.

The presence of just one pattern of signals in the ^1H NMR spectra for the *cis*-β configuration, which is the predominant one in our case, suggested that only one enantiomeric couple was formed selectively, implicating that chirality at metal was induced by the ligand chirality.

X-ray analysis of single crystals of **21** revealed that the coordination environment of the Ti atom was a distorted octahedral with two *cis* chlorine atoms and two nitrogen atoms in the equatorial plane, thus indicating the selective formation of *cis*-β isomer in the solid state.

As previously reported for a similar zirconium complex [127,154], replacement of H atoms with Me groups in the *meta* position of the phenolate rings leads to an imine steric protection towards the alkyl migration from the metal to the imino carbon resulting in a catalytically active complex **21** for ethylene polymerization both using MAO and $Al(^iBu)_3/Ph_3CB(C_6F_5)_4$ as activators.

On the other hand complexes **21**, **23** and **24** bearing H atoms in *meta* positions of the phenolate rings, need a pretreatment with $Al(^iBu)_3$ to result in reasonable polymerization activity. As we have just observed for the zirconium analogue, $Al(^iBu)_3$ or aluminum hydride compounds, contaminants in $Al(^iBu)_3$, act as reducing agents affording diamine bis(phenolate) complexes which are the true catalytic species, as also confirmed by hydrolysis experiments.

Moreover a positive effect of *ortho*- and *para*-phenolate halides on the polymerization activity of the corresponding complexes **23** and **24** was demonstrated.

Finally, polymerization of propylene resulted in the production of an isotactic polymer in the case of complex **22**, and of substantially atactic samples in the case of complexes **21** and **24** suggesting that *salen* complexes are able to afford isotactic-specific propylene polymerization, while the *salan* complexes are not stereospecific.

6. Conclusions

Research activity in the field of metal-catalyzed olefin polymerization, an area considered “mature”, is still experiencing a significant growth, attracting scientists working in inorganic, organic, organometallic, industrial, theoretical and polymer chemistry. The huge number of new catalysts introduced in the last years has provided important developments in the coordination chemistry of transition metals throughout the Periodic Table.

Successful new classes of highly active non-metallocene catalysts include late-transition metal systems such as the Ni and Pd diimine catalysts, the Fe bis(imino)pyridyl catalysts, and the group 4 metal bis(phenoxy-imine) and diaminodiphenolate catalysts, all of them showing a number of interesting peculiar features. Notwithstanding the high number of ligand–metal combinations tested allowed one to address many structural features relevant for catalysis, the capability to predict catalyst–polymer structure relationships is much lower than in the case of metallocenes, e.g., while polymerization of propylene by metallocene catalysts invariably involves primary (1,2) monomer insertion as the preferential mode of propagation, practically all possible combinations of regiochemistries and stereochemistries have been observed in propylene polymerization by non-metallocene catalysts. Moreover, the larger variety of electronic and steric parameters that can be modulated in the case of non-metallocene catalysts results in some unexpected change of stereospecificity following even subtle ligand structure modifications.

Finally, an issue which is still far from being clarified for all kinds of polymerization catalysts is the capability to predict the catalyst activity on the basis of a rational design. For this reason, especially in industrial research laboratories, an alternative has recently involved use of high throughput screening (HTS) methodologies, an extension of the combinatorial chemistry techniques widely used in the pharmaceutical research.

References

[1] H.H. Brintzinger, D. Fischer, R. Muelhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Eng. 34 (1995) 1143.
[2] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.
[3] G.W. Coates, Chem. Rev. 100 (2000) 1223.
[4] L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, Chem. Rev. 100 (2000) 1253.
[5] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. 38 (1999) 428.
[6] V.C. Gibson, S.K. Spitzmesser, Chem. Rev. 103 (2003) 283.
[7] K.P. Bryliakov, Russ. Chem. Rev. 76 (2007) 253.
[8] G.W. Coates, P.D. Hustad, S. Reinartz, Angew. Chem., Int. Ed. 41 (2002) 2236.
[9] G.J. Domski, J.M. Rose, G.W. Coates, A.D. Bolig, M. Brookhart, Prog. Polym. Sci. 32 (2007) 30.
[10] V. Busico, R. Cipullo, N. Friederichs, S. Ronca, G. Talarico, M. Togrou, B. Wang, Macromolecules 37 (2004) 8201.
[11] A. Hotta, E. Cochran, J. Ruokolainen, V. Khanna, G.H. Fredrickson, E.J. Kramer, Y.-W. Shin, F. Shimizu, A.E. Cherian, P.D. Hustad, J.M. Rose, G.W. Coates, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 15327.
[12] D.J. Arriola, E.M. Carnahan, P.D. Hustad, R.L. Kuhlman, T.T. Wenzel, Science 312 (2006) 714.
[13] Y. Zhang, R.J. Keaton, L.R. Sita, J. Am. Chem. Soc. 125 (2003) 9062.
[14] Y. Zhang, L.R. Sita, J. Am. Chem. Soc. 126 (2004) 7776.
[15] M.B. Harney, Y. Zhang, L.R. Sita, Angew. Chem., Int. Ed. 45 (2006) 2400.
[16] M.B. Harney, Y. Zhang, L.R. Sita, Angew. Chem., Int. Ed. 45 (2006) 6140.
[17] M. Lamberti, M. Mazzeo, D. Pappalardo, A. Zambelli, C. Pellecchia, Macromol. Symp. 213 (2004) 235.
[18] A. Zambelli, M.C. Sacchi, P. Locatelli, G. Zannoni, Macromolecules 15 (1982) 211.
[19] P. Locatelli, M.C. Sacchi, I. Tritto, Macromolecules 19 (1986) 305.
[20] A. Zambelli, P. Ammendola, A. Grassi, P. Longo, A. Proto, Macromolecules 19 (1986) 2703.
[21] P. Longo, A. Grassi, C. Pellecchia, A. Zambelli, Macromolecules 20 (1987) 1015.
[22] P. Corradini, G. Guerra, M. Vacatello, V. Villani, Gazz. Chim. Ital. 118 (1988) 173.
[23] L. Cavallo, G. Guerra, M. Vacatello, P. Corradini, Macromolecules 24 (1991) 1784.
[24] P. Longo, A. Proto, A. Grassi, P. Ammendola, Macromolecules 24 (1991) 4624.
[25] A. Zambelli, I. Sessa, F. Grisi, R. Fusco, P. Accomazzi, Macromol. Rapid Commun. 22 (2001) 297.
[26] I. Sessa, D.R. Ferro, F. Grisi, D. Liguori, G. Milano, A. Zambelli, Macromol. Chem. Phys. 203 (2002) 2604.
[27] V. Busico, J.C. Chadwick, R. Cipullo, S. Ronca, G. Talarico, Macromolecules 37 (2004) 7437.
[28] V. Busico, R. Cipullo, S. Ronca, Macromolecules 35 (2002) 1537.
[29] V. Busico, R. Cipullo, C. Polzone, G. Talarico, J.C. Chadwick, Macromolecules 36 (2003) 2616.
[30] K. Ziegler, H.G. Gellert, E. Holzkamp, G. Wilke, E.W. Duck, W.R. Kroll, Justus Liebigs Ann. Chem. 629 (1960) 172.
[31] K. Ziegler, Brennst. Chem. 35 (1954) 321.
[32] L.K. Johnson, C.M. Killian, M. Brookhart, J. Am. Chem. Soc. 117 (1995) 6414.
[33] L.K. Johnson, S. Mecking, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 267.
[34] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664.
[35] W. Keim, Angew. Chem. 102 (1990) 251.
[36] R. Abeywickrema, M.A. Bennett, K.J. Cavell, M. Kony, A.F. Masters, A.G. Webb, J. Chem. Soc., Dalton Trans. (1993) 59.
[37] S.J. Brown, A.F. Masters, J. Organomet. Chem. 367 (1989) 371.
[38] S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169.
[39] S. Mecking, Angew. Chem., Int. Ed. 40 (2001) 534.
[40] Z. Guan, P.M. Cotts, E.F. McCord, S.J. McLain, Science 283 (1999) 2059.
[41] S.A. Svejda, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 121 (1999) 10634.
[42] M.D. Leatherman, S.A. Svejda, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 125 (2003) 3068.
[43] D. Pappalardo, M. Mazzeo, C. Pellecchia, Macromol. Rapid Commun. 18 (1997) 1017.
[44] C. Pellecchia, A. Zambelli, Macromol. Rapid Commun. 17 (1996) 333.
[45] F.A. Bovey, G.V.D. Tiers, J. Polym. Sci. 44 (1960) 173.
[46] G. Natta, I. Pasquon, A. Zambelli, J. Am. Chem. Soc. 84 (1962) 1488.
[47] C. Pellecchia, A. Zambelli, L. Oliva, D. Pappalardo, Macromolecules 29 (1996) 6990.
[48] P. Locatelli, M.C. Sacchi, E. Rigamonti, A. Zambelli, Macromolecules 17 (1984) 123.
[49] C. Pellecchia, A. Zambelli, M. Mazzeo, D. Pappalardo, J. Mol. Catal. A: Chem. 128 (1998) 229.
[50] A. Zambelli, P. Longo, S. Terenghi, D. Recupero, G. Zannoni, J. Mol. Catal. A: Chem. 152 (2000) 25.
[51] G. Milano, G. Guerra, C. Pellecchia, L. Cavallo, Organometallics 19 (2000) 1343.
[52] D. Pappalardo, M. Mazzeo, S. Antinucci, C. Pellecchia, Macromolecules 33 (2000) 9483.
[53] M. Schmid, R. Eberhardt, M. Klinga, M. Leskelae, B. Rieger, Organometallics 20 (2001) 2321.
[54] T. Schleis, J. Heinemann, T.P. Spaniol, R. Mulhaupt, J. Okuda, Inorg. Chem. Commun. 1 (1998) 431.
[55] A.E. Cherian, J.M. Rose, E.B. Lobkovsky, G.W. Coates, J. Am. Chem. Soc. 127 (2005) 13770.
[56] D.H. Camacho, Z. Guan, Macromolecules 38 (2005) 2544.

[57] D.H. Camacho, E.V. Salo, J.W. Ziller, Z. Guan, Angew. Chem., Int. Ed. 43 (2004) 1821.
[58] B.L. Small, M. Brookhart, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 39 (1998) 213.
[59] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049.
[60] B.L. Small, M. Brookhart, Macromolecules 32 (1999) 2120.
[61] B.L. Small, M. Brookhart, J. Am. Chem. Soc. 120 (1998) 7143.
[62] G.J.P. Britovsek, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S.J. McTavish, G.A. Solan, A.J.P. White, D.J. Williams, Chem. Commun. (1998) 849.
[63] G.J.P. Britovsek, M. Bruce, V.C. Gibson, B.S. Kimberley, P.J. Maddox, S. Mastroianni, S.J. McTavish, C. Redshaw, G.A. Solan, S. Stroemberg, A.J.P. White, D.J. Williams, J. Am. Chem. Soc. 121 (1999) 8728.
[64] V.C. Gibson, C. Redshaw, G.A. Solan, Chem. Rev. (Washington, DC, United States) 107 (2007) 1745.
[65] C. Bianchini, G. Giambastiani, I.G. Rios, G. Mantovani, A. Meli, A.M. Segarra, Coord. Chem. Rev. 250 (2006) 1391.
[66] C. Pellecchia, M. Mazzeo, D. Pappalardo, Macromol. Rapid Commun. 19 (1998) 651.
[67] J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355.
[68] W. Spaleck, F. Kueber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle, E.F. Paulus, Organometallics 13 (1994) 954.
[69] Y. Suzuki, H. Terao, T. Fujita, Bull. Chem. Soc. Jpn. 76 (2003) 1493.
[70] H. Kawaguchi, T. Matsuo, J. Organomet. Chem. 689 (2004) 4228.
[71] M. Kakugo, T. Miyatake, K. Mizunuma, Chem. Express 2 (1987) 445.
[72] T. Miyatake, K. Mizunuma, Y. Seki, M. Kakugo, Makromol. Chem., Rapid Commun. 10 (1989) 349.
[73] T. Miyatake, K. Mizunuma, M. Kakugo, Makromol. Chem., Macromol. Symp. 66 (1993) 203.
[74] C.J. Schaverien, A.J. Van Der Linden, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.) 35 (1994) 672.
[75] P.G. Cozzi, E. Gallo, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Organometallics 14 (1995) 4994.
[76] P.G. Cozzi, C. Floriani, A. Chiesi-Villa, C. Rizzoli, Inorg. Chem. 34 (1995) 2921.
[77] H. Makio, T. Fujita, Bull. Chem. Soc. Jpn. 78 (2005) 52.
[78] Y. Suzuki, H. Tanaka, T. Oshiki, K. Takai, T. Fujita, Chem. Asian J. 1 (2006) 878.
[79] T. Matsugi, T. Fujita, Chem. Soc. Rev. 37 (2008) 1264.
[80] S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, H. Tanaka, T. Fujita, Chem. Lett. (1999) 1263.
[81] J. Tian, G.W. Coates, Angew. Chem., Int. Ed. 39 (2000) 3626.
[82] J. Tian, P.D. Hustad, G.W. Coates, J. Am. Chem. Soc. 123 (2001) 5134.
[83] J. Saito, M. Mitani, J.-I. Mohri, S.-I. Ishii, Y. Yoshida, T. Matsugi, S.-I. Kojoh, N. Kashiwa, T. Fujita, Chem. Lett. (2001) 576.
[84] H. Makio, N. Kashiwa, T. Fujita, Adv. Synth. Catal. 344 (2002) 477.
[85] M. Lamberti, D. Pappalardo, A. Zambelli, C. Pellecchia, Macromolecules 35 (2002) 658.
[86] M. Lamberti, D. Pappalardo, A. Zambelli, C. Pellecchia, Macromolecules 35 (2002) 6478.
[87] P.D. Hustad, J. Tian, G.W. Coates, J. Am. Chem. Soc. 124 (2002) 3614.
[88] J. Saito, M. Mitani, M. Onda, J.-I. Mohri, S.-I. Ishii, Y. Yoshida, T. Nakano, H. Tanaka, T. Matsugi, S.-I. Kojoh, N. Kashiwa, T. Fujita, Macromol. Rapid Commun. 22 (2001) 1072.
[89] G. Milano, L. Cavallo, G. Guerra, J. Am. Chem. Soc. 124 (2002) 13368.
[90] P. Corradini, G. Guerra, L. Cavallo, Acc. Chem. Res. 37 (2004) 231.
[91] A.F. Mason, G.W. Coates, J. Am. Chem. Soc. 126 (2004) 16326.
[92] J.B. Edson, Z. Wang, E.J. Kramer, G.W. Coates, J. Am. Chem. Soc. 130 (2008) 4968.
[93] M. Mazzeo, M. Strianese, M. Lamberti, I. Santoriello, C. Pellecchia, Macromolecules 39 (2006) 7812.
[94] M. Lamberti, R. Gliubizzi, M. Mazzeo, C. Tedesco, C. Pellecchia, Macromolecules 37 (2004) 276.
[95] M. Mitani, R. Furuyama, J.-I. Mohri, J. Saito, S. Ishii, H. Terao, N. Kashiwa, T. Fujita, J. Am. Chem. Soc 124 (2002) 7888.
[96] M. Lamberti, D. Pappalardo, M. Mazzeo, C. Pellecchia, Macromol. Chem. Phys. 205 (2004) 486.
[97] J. Saito, M. Onda, S. Matsui, M. Mitani, R. Furuyama, H. Tanaka, T. Fujita, Macromol. Rapid Commun. 23 (2002) 1118.
[98] M. Mitani, J. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S.-I. Kojoh, T. Matsugi, N. Kashiwa, T. Fujita, J. Am. Chem. Soc. 124 (2002) 3327.
[99] C.J. Carman, C.E. Wilkes, Rubber Chem. Technol. 44 (1971) 781.
[100] A. Zambelli, G. Bajo, E. Rigamonti, Makromol. Chem. 179 (1978) 1249.
[101] A. Grassi, P. Ammendola, P. Longo, E. Albizzati, L. Resconi, R. Mazzocchi, Gazz. Chim. Ital. 118 (1988) 539.
[102] P. Ammendola, X. Shijing, A. Grassi, A. Zambelli, Gazz. Chim. Ital. 118 (1988) 769.
[103] Y. Tohi, H. Makio, S. Matsui, M. Onda, T. Fujita, Macromolecules 36 (2003) 523.
[104] R. Furuyama, J. Saito, S.-I. Ishii, M. Mitani, S. Matsui, Y. Tohi, H. Makio, N. Matsukawa, H. Tanaka, T. Fujita, J. Mol. Catal. A: Chem. 200 (2003) 31.
[105] A. Zambelli, G. Gatti, Macromolecules 11 (1978) 485.
[106] T. Asakura, N. Nakayama, M. Demura, A. Asano, Macromolecules 25 (1992) 4876.
[107] T. Asakura, Y. Nishiyama, Y. Doi, Macromolecules 20 (1987) 616.
[108] J.C. Stevens, D.D. Vanderlende, (The Dow Chemical Company, USA). Wo 2003040201, (2003).
[109] A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, Macromolecules 21 (1988) 617.
[110] A. Mizuno, T. Tsutsui, N. Kashiwa, Polymer 33 (1992) 254.
[111] A. Zambelli, P. Locatelli, E. Rigamonti, Macromolecules 12 (1979) 156.
[112] A. Zambelli, M.C. Sacchi, P. Locatelli, Macromolecules 12 (1979) 783.
[113] T. Hayashi, Y. Inoue, R. Chujo, T. Asakura, Macromolecules 21 (1988) 2675.
[114] L. Resconi, F. Piemontesi, G. Franciscono, L. Abis, T. Fiorani, J. Am. Chem. Soc. 114 (1992) 1025.
[115] H.N. Cheng, Macromolecules 17 (1984) 1950.
[116] S. Matsui, Y. Tohi, M. Mitani, J. Saito, H. Makio, H. Tanaka, M. Nitabaru, T. Nakano, T. Fujita, Chem. Lett. (1999) 1065.
[117] H. Makio, Y. Tohi, J. Saito, M. Onda, T. Fujita, Macromol. Rapid Commun. 24 (2003) 894.
[118] MAO*=dried MAO obtained by distilling off the solvent by the commercial solution.
[119] E.Y. Tshuva, I. Goldberg, M. Kol, J. Am. Chem. Soc. 122 (2000) 10706.
[120] V. Busico, R. Cipullo, S. Ronaca, P.H.M. Budzelaar, Macromol. Rapid Commun. 22 (2001) 1405.
[121] P.D. Knight, P. Scott, Coord. Chem. Rev. 242 (2003) 125.
[122] U. Knof, A. Von Zelewsky, Angew. Chem., Int. Ed. 38 (1999) 303.
[123] T. Repo, M. Klinga, P. Pietikaeinen, M. Leskelae, A.-M. Uusitalo, T. Pakkanen, K. Hakala, P. Aaltonen, B. Loefgren, Macromolecules 30 (1997) 171.
[124] E.B. Tjaden, D.C. Swenson, R.F. Jordan, J.L. Petersen, Organometallics 14 (1995) 371.
[125] E.B. Tjaden, R.F. Jordan, Macromol. Symp. 89 (1995) 231.
[126] P.D. Knight, P.N. O'Shaughnessy, I.J. Munslow, B.S. Kimberley, P. Scott, J. Organomet. Chem. 683 (2003) 103.
[127] P.D. Knight, A.J. Clarke, B.S. Kimberley, R.A. Jackson, P. Scott, Chem. Commun. (2002) 352.
[128] C. Cuomo, M. Strianese, T. Cuenca, M. Sanz, A. Grassi, Macromolecules 37 (2004) 7469.
[129] R.L. Jones, N. Seidel, M. Elder, J.A. Ewen, Basell Polyolefine G.m.b.H., Germany, Wo 2004069881 (2004).
[130] X.-G. Zhou, J.-S. Huang, P.-H. Ko, K.-K. Cheung, C.-M. Che, J. Chem. Soc., Dalton Trans. (1999) 3303.
[131] P.R. Woodman, I.J. Munslow, P.B. Hitchcock, P. Scott, J. Chem. Soc., Dalton Trans. (1999) 4069.
[132] A. Yeori, I. Goldberg, M. Shuster, M. Kol, J. Am. Chem. Soc. 128 (2006) 13062.
[133] A. Yeori, I. Goldberg, M. Kol, Macromolecules (Washington, DC, United States) 40 (2007) 8521.
[134] M. Lamberti, M. Consolmagno, M. Mazzeo, C. Pellecchia, Macromol. Rapid Commun. 26 (2005) 1866.
[135] M. Strianese, M. Lamberti, M. Mazzeo, C. Pellecchia, Macromol. Chem. Phys. 209 (2008) 585.
[136] M. Shi, W.-L. Duan, G.-B. Rong, Chin. J. Chem. 20 (2002) 1319.
[137] L. Resconi, R.L. Jones, A.L. Rheingold, G.P.A. Yap, Organometallics 15 (1996) 998.
[138] S. Segal, I. Goldberg, M. Kol, Organometallics 24 (2005) 200.
[139] A. Zambelli, P. Locatelli, G. Bajo, Macromolecules 12 (1979) 154.
[140] A. Carvill, L. Zetta, G. Zannoni, M.C. Sacchi, Macromolecules 31 (1998) 3783.
[141] F. Ciardelli, C. Carlini, A. Altomare, Ziegler Catal. (1995) 455.
[142] J. Vizzini, F. Ciardelli, J.C.W. Chien, Macromolecules 25 (1992) 108.
[143] A. Schaefer, E. Karl, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 328 (1987) 87.
[144] C.R. Baar, C.J. Levy, E.Y.J. Min, L.M. Henling, M.W. Day, J.E. Bercaw, J. Am. Chem. Soc. 126 (2004) 8216.
[145] J.A. Byers, J.E. Bercaw, Proc. Natl. Acad. Sci. U.S.A. 103 (2006) 15303.
[146] C. Capacchione, A. Proto, H. Ebeling, R. Muelhaupt, K. Moeller, T.P. Spaniol, J. Okuda, J. Am. Chem. Soc. 125 (2003) 4964.
[147] K. Beckerle, R. Manivannan, B. Lian, G.-J.M. Meppelder, G. Raabe, T.P. Spaniol, H. Ebeling, F. Pelascini, R. Muelhaupt, J. Okuda, Angew. Chem., Int. Ed. 46 (2007) 4790.
[148] M. Strianese, M. Lamberti, M. Mazzeo, C. Pellecchia, Macromol. Rapid Commun. 28 (2007) 1912.
[149] J.C.W. Chien, J.C. Vizzini, W. Kaminsky, Makromol. Chem., Rapid Commun. 13 (1992) 479.
[150] A. Zambelli, A. Grassi, M. Galimberti, G. Perego, Makromol. Chem., Rapid Commun. 13 (1992) 269.
[151] F. Conti, L. Acquaviva, E. Chiellini, F. Ciardelli, M. Delfini, A.L. Segre, Polymer 17 (1976) 901.
[152] A. Soriente, M. De Rosa, M. Lamberti, C. Tedesco, A. Scettri, C. Pellecchia, J. Mol. Catal. A: Chem. 235 (2005) 253.
[153] M. Strianese, M. Lamberti, M. Mazzeo, C. Tedesco, C. Pellecchia, J. Mol. Catal. A: Chem. 258 (2006) 284.
[154] P.D. Knight, G. Clarkson, M.L. Hammond, B.S. Kimberley, P. Scott, J. Organomet. Chem. 690 (2005) 5125.