The evolution of new generation 'single-site' Ziegler–Natta polymerization catalysts

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Since the discovery of stereospecific polymerization of olefins by K. Ziegler and G. Natta in 1955, tremendous developments have occurred in the area of designing polymerization catalysts. Rapid advances in organometallic chemistry research practised both at academic and industrial laboratories throughout the world have led to the emergence of new generation olefin polymerization catalysts and polyolefin products. The purpose of this article is to highlight some of the major events that have occurred in the area of Ziegler–Natta catalysis and to illustrate the contributions of organometallic chemistry in the exciting story of the evolution of well-defined, 'single-site' metallocene catalysts. The developments in the mechanistic understanding of key steps of polymerization processes such as generation of active species, chain propagation and chain termination emerging from organometallic modeling studies are also highlighted. Also, the recent discovery of late transition metal olefin polymerization catalyst systems and its implications for further research in Ziegler–Natta catalysis is described.

Introduction

Ziegler–Natta catalysis involves the rapid polymerization of olefins under mild conditions in the presence of transition metal compounds as catalysts[1a]. This process discovered by Karl Ziegler and Giulio Natta in 1955, is an industrially important and intellectually stimulating phenomenon. They were awarded the Nobel Prize in 1963 for their landmark discovery. Over the last four decades, significant developments have occurred in the Ziegler–Natta catalysis in terms of catalyst design, process technology and mechanistic understanding of the key steps involved in the process. We are now witnessing the evolution of a new generation of catalysts and polyolefin materials, which originates from studies on homogeneous, metallocene-based and single-component polymerization catalysts. Such catalysts are also known as 'single-site' catalysts because all the active sites of these catalysts behave in the same way during polymerization, producing polymers with controlled molecular weight distributions. It is generally acknowledged that no single class of catalysts is capable of controlling all the macromolecular parameters relevant to a wide range of polyolefin products. Hence, the search for new catalyst families continues to remain an active area of research both in academic and industrial laboratories throughout the world. The objective of this article is to highlight some of the recent developments in the Ziegler–Natta catalysis and to illustrate the contribution of organometallic chemistry in the exciting story of the evolution of new generation 'single-site' olefin polymerization catalysts.

Conventional Ziegler–Natta catalysts

The early Ziegler–Natta catalysts were of two-component systems consisting of a transition metal compound (halide, alkoxide, alkyl or aryl derivative) of group 4–8 transition metals and a metal alkyl or alkyl halide of group 1–3 base metals. Transition metal compounds of group 4 (such as Ti and Zr) and aluminum alkyls (such as $AlEt_3$, Al-*i*-Bu_3, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$) have been overwhelmingly preferred. Zeigler–Natta catalysis provided for the first time stereochemical control of the olefin polymerization process. By carefully selecting the combination of catalyst and co-catalyst, one is able to produce polymers with desired structure such as isotactic, syndiotactic and atactic polyolefins (Figure 1).

The conventional Ziegler–Natta catalyst systems are heterogeneous in nature. The polymerization methods developed were mostly by trial and error approaches and the suggested mechanisms were mostly speculative in nature. As a result, fundamental questions regarding the mechanism of polymerization, origin of stereospecificity and the nature of active centers remained elusive for a long time. It is now generally believed that the non-

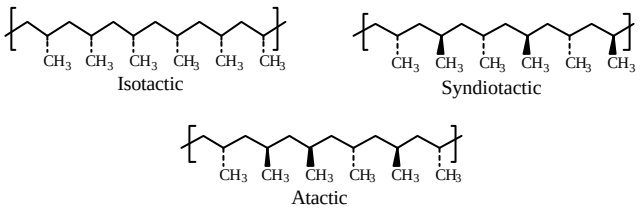

Figure 1. Structure of isotactic, syndiotactic and atactic polyolins.

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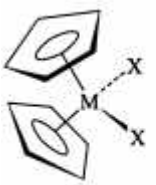
uniformity of their active centers is largely responsible for the broad molecular weight distribution of the polymers produced from these catalyst systems.

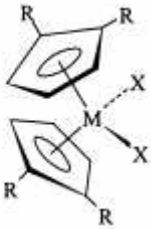
In the 1970s, 'the second generation' $MgCl_2$-supported Ziegler–Natta catalysts were discovered. These systems consisted of $MgCl_2$/Lewis base/$TiCl_4$ ternary mixture as the catalyst component and Al alkyl/Lewis base as cocatalysts and are highly active and stereospecific. The $MgCl_2$-supported catalysts brought about a remarkable simplification of polymerization and work-up processes, and led to revolutionary developments for commercial production of linear polyethylene and isotactic polypropylene. Several recent monographs address both the scientific and industrial aspects of heterogeneous supported transition metal catalysts for olefin polymerization[1b,c].

Homogenous Ziegler–Natta catalysts

The development of homogenous catalysts for olefin polymerization reaction is an important stage in the evolution of Ziegler–Natta catalysts. The first homogenous Ziegler–Natta catalyst was discovered independently by Breslow and Newburg[2a], and Natta *et al.*[2b] in 1957. The catalyst bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2) activated with alkyl aluminum chloride (AlR_2Cl) exhibited low polymerization activity for ethylene. It was found later that small amounts of water were found to increase significantly the activity of the catalysts[3]. The reaction between water and aluminum alkyls was shown to produce alkyl alumoxanes. In 1980, Kaminsky and coworkers[4] used oligomeric methylalumoxane (MAO) with group 4 metallocene compounds [1] to obtain ethylene polymerization catalysts having extremely high activities. Other group 4 metallocene compounds [2] were similarly found to be highly active towards various olefins in the presence of MAO as the co-catalysts.



[1]

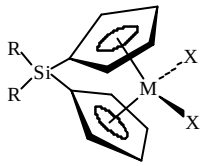


[2]

However, these metallocene catalysts are non-stereospecific producing only atactic polypropylene because of the symmetric feature of their active centres. The modified metallocenes containing stereorigid ligand systems were found to be particularly attractive for stereospecific olefin polymerization.

ansa-metallocenes

Among the modified metallocenes, *ansa*-metallocenes in which the cyclopentadienyl groups linked by short bridging groups are very important. A wide range of *ansa*-metallocenes with differing bridging groups has been reported in the literature. The synthesis, structure and reactivity of several stereorigid silyl bridged metallocene compounds of zirconium(IV) and titanium(IV) [3] have been studied[5].



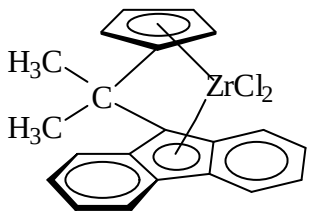
R = CH_3, C_2H_5, n-C_3H_7

X = Cl, Br, CH_3

M = Ti, Zr

[3]

In the early 1980s, Brintzinger and coworkers[6] developed racemic ethylene-bridged bis(indenyl)$ZrCl_2$, $Et(Ind)_2$ $ZrCl_2$ [4] and racemic ethylene-bridged bis(4,5,6,7-tetrahydroindenyl) zirconium dichloride, $Et(H_4Ind)_2ZrCl_2$ [5] as well as their titanium analogues which have both *meso* and racemic configurations. These chiral catalysts activated with MAO catalysed the stereoselective polymerization of propylene with very high activities. For the first time isotactic polyolefins were obtained using homogenous Ziegler–Natta catalysts. This finding demonstrated the stereochemical control by chiral *ansa*-indenyl ligands on the transition metal ion in the selection of one of the two enantiotopic faces (*re* or *si*) of prochiral monomer in the migratory insertion. As predicted, the *meso*-$Et(Ind)_2$ $TiCl_2$/MAO system only produced atactic polypropylene. Since then, a large number of *ansa*-metallocene compounds have been developed, each of them having a unique catalytic activity and stereospecificity. For example, highly syndiotactic polypropylene was prepared by Ewen and coworkers[7] using

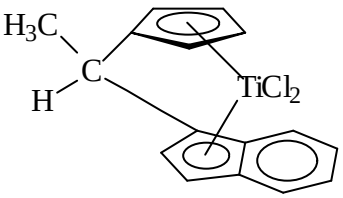


[6]

Cs symmetric $Me_2C(Cp)(Flu)ZrCl_2$ [6]. The *rrr* sequences in the polymers produced from these reactions indicated stereochemical site control with chain migratory insertion resulting in site isomerization and occasional reversal of diastereoface selectivity. Such highly syndiotactic polypropylene products are softer and tougher with excellent optical properties. These products are soon expected to replace other engineering plastics such as nylons, poly(ester)s and poly(carbonate)s. Similarly, Waymouth and Coates[8] have obtained novel optically active isotactic polymers from cyclopolymerization of 1,5-hexadiene using $Et(Ind)_2ZrCl_2$ catalysts (Scheme 1). Chein *et al.*[9]

Scheme 1.

have obtained novel thermoplastic elastomers containing alternating sequence of stereoregular–irregular polypropylene using carbon-bridged $(H)(CH_3)C(C_p)(Ind)TiCl_2$ [7].



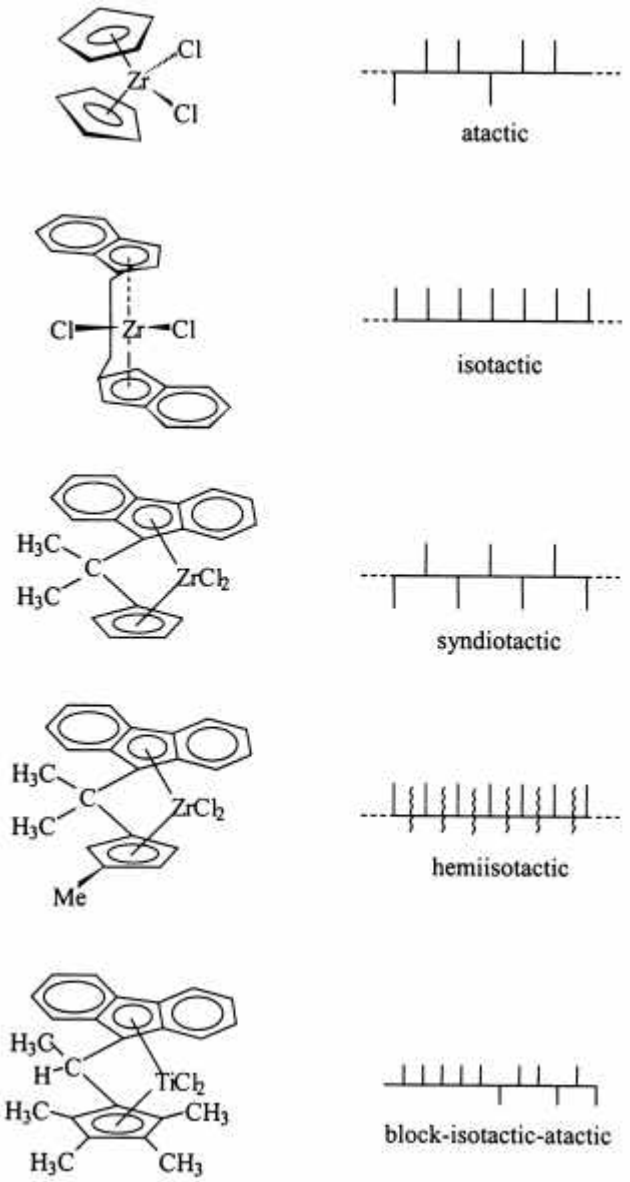
[7]

Thus, the discovery of *ansa*-metallocene catalysts is believed to be of immense significance in catalysis, organometallic and polymerization chemistry. The modifications of catalysts by variations of the ligands surrounding the active centre permit correlation of catalyst structure with catalytic activity and stereospecificity. A correlation of various metallocene structures to polypropylene structure is given in Scheme 2.

The studies made on *ansa*-metallocenes have increased our understanding of the molecular mechanism of the stereochemical control in α-olefin polymerization and helped rationalize catalyst structure–polymer property relations. The power of 'rational catalyst design' has been recently demonstrated by Spaleck and coworkers[10a,b] who have systematically investigated the effect of substitution in bridged bis(indenyl)zirconium systems. The high activities of the catalysts are explained on the basis of the electronic effects whereas, the steric effects are attributed to high stereospecificity and high molecular weights of the polymer. More detailed description of the scope of metallocene catalysts for olefin polymerization can be found in several recent publications[1b,11a–c].

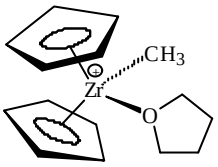
Single-component catalysts

The homogenous Ziegler–Natta catalyst systems discussed above invariably employed MAO as cocatalysts. The requirements of large amounts of expensive MAO together with low efficiency of the corresponding catalysts at high temperatures and incorporation of small amounts of the comonomer are some of the drawbacks of the metallocene/MAO catalyst systems. Also, the poorly characterized cocatalyst structures have made the mechanistic studies of these systems very difficult. For these reasons,



Scheme 2. Relationship of catalyst structure and symmetry to polymer stereochemistry.

the nature of active species in these two-component Ziegler–Natta catalyst systems was not understood for a very long time. Therefore, studies on MAO-free, alternate catalyst systems have received much attention during the 1980s. The search for alternate MAO-free catalyst systems began with the work of Jordan *et al.*[12] who discovered the synthesis of group 4 cationic metallocene alkyl systems. The complex $[Cp_2ZrMe(THF)]^+[BPh_4]^-$ [8]



[8]

obtained by the oxidative cleavage of M-R bonds of Cp_2MR_2 complexes was the first example of a structurally well-characterized cationic metallocene alkyl compound (Scheme 3).

$$Cp_2MR_2 + Ag^+BPh_4^- \rightarrow Cp_2MR^+\ BPh_4^- + ½\ RR + Ag^0$$
$$Cp_2Fe^+BPh_4^- \rightarrow Cp_2MR^+\ BPh_4^- + Cp_2Fe + ½\ RR$$

Scheme 3.

This compound polymerizes olefin in the absence any co-catalysts. Subsequently, a 'nacked benzyl' compound $Cp_2Zr(\eta^2CH_2Ph)$, was directly observed by low temperature ^1H NMR spectroscopy. Several other routes for the synthesis of such cationic complexes are also available. The protonolysis route[13] involves the use of bulkier ammonium reagents (Scheme 4).

$$Cp_2MR_2 + [HNR_3]^+\ [BPh_4]^-\ ([Cp_2MR]^+[BPh_4]^- + NR_3 + RH$$

Scheme 4.

Marks *et al.*[14] have used a strong Lewis acid $B(C_6F_5)_3$ to generate the cations (Scheme 5).

$$Cp_2MR_2 + B(C_6F_5)_3 \rightarrow [Cp_2MR]^+\ [B(C_6F_5)_3(R)]^-$$

Scheme 5.

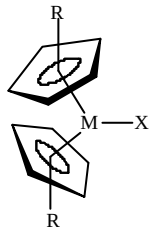
Chien *et al.*[15] have employed $[Ph_3C]^+\ [B(C_6F_5)_4]^-$ salts for the generation of cationic complexes (Scheme 6).

$$Cp_2MR_2 + [Ph_3C]^+\ [B(C_6F_5)_4]^- \rightarrow [Cp_2MR]^+B(C_6F_5)_4]^- + Ph_3CCR$$

Scheme 6.

Organometallic modelling studies for olefin polymerization

The discrete, structurally well-characterized, cationic, group 4 metal alkyls Cp_2MR^+ and $[CpM(R)L]^+$ (L = labile ligand) have been demonstrated as useful model systems for studies on olefin polymerization. The reactions of these compounds with various olefins, H_2 and with other ligand systems have greatly helped to understand the key steps of Zeigler–Natta catalysis such as the initiation, chain propagation and chain termination steps[16]. It is now generally agreed that the catalytically active species in olefin polymerization is a co-ordinatively unsaturated cationic alkyl complex $[L_mMR]^+$ that is stabilized by several other ligands. The cationic species are generated during the interaction of the cocatalyst with the catalyst. The cocatalyst initially alkylates the catalyst and subsequently abstracts an anionic ligand (halide or alkyl) to generate the cationic species. Theoretical and spectroscopic studies have given strong evidence that the highly electrophilic, d^0, 14-electron Cp_2MR^+ are indeed the active species in most metallocene-based olefin polymerization catalysis. It is believed that the high polymerization activity of these complexes is due to the high co-ordinative unsaturation of the 14-electron, three-coordinate metal centres. Whether the positive charge of the species Cp_2MR^+ is critical is not yet known. The electron-counting constraints however, simply dictate that for group 4 metal, a d^0 Cp_2MR fragment must be cationic. With this in view, Jordan *et al.*[17] prepared neutral analogues of the cations by the replacement of a Cp^- ligand by the dianionic, 6-electron donor $C_2B_9H_{11}^{2-}$ ligand (dicarbollide). Indeed, the corresponding compound $[Cp^*(C_2B_9H_{11})M(Me)]_n$ showed moderate ethylene polymerization activity in the absence of aluminum cocatalysts. Similarly, several neutral, group 3, alkyls and hydride complexes [9, 10] of scandium and yttrium which are iso-electronic with group 4 cationic alkyl complexes also have been shown to be active towards olefin polymerization[18a,b].



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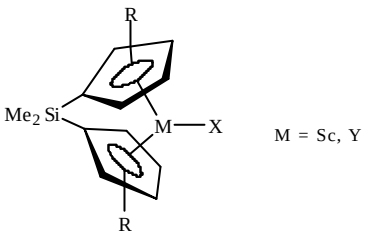


[10]

The reactions of these cationic complexes with a variety of olefins have shown that these complexes exhibit a strong tendency to co-ordinate with weak Lewis base olefin molecules. Organometallic models for the elusive $Cp_2(R)(olefin)^+$ are also now available. Such studies have provided indirect evidences for olefin co-ordination to active species in Ziegler–Natta catalysis and theoretical calculations have supported this view.

The repetitive insertion of olefin into the active M-R bond leading to the chain growth is the key step in olefin

polymerization. It is strongly believed that the stereospecificity of the polymer formed greatly depends on this step. The present knowledge of the mechanistic details on the chain propagation has reached a high degree of accuracy due to the extensive ^{13}C NMR analysis of the polymers produced and the modelling studies carried out using the single-component cationic systems.

The chain termination/transfer is the key step for controlling the molecular weight of a polymer. Modelling studies using several well-defined catalyst systems have established that chain termination/transfer occurs via facile β-hydrogen or β-alkyl elimination. The studies on the ligand effects on β-hydrogen or β-alkyl processes using these model compounds have greatly helped to understand the relations between the catalyst structure and polymer properties. The studies on M-R bond hydrogenolysis in $[Cp_2MR]^+$ complexes have provided fundamental information on H_2-terminated chain termination/transfer mechanisms relevant to olefin polymerization catalysis[16].

Group 4 non-metallocene systems

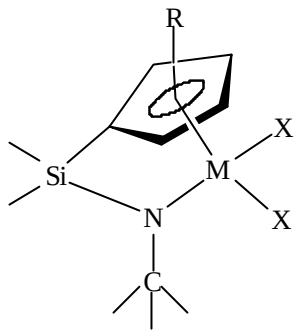
Thus, fundamental organometallic studies on group 4, group 3 and f-element metallocene systems in recent years have provided a working rationale for catalyst design in olefin polymerization reactions. On the basis of these studies, the following steric and electronic properties have been recognized as important factors in the catalyst design:

(i) d^0, 14-electron metal system;
(ii) highly unsaturated metal centre;
(iii) availability of vacant orbital sites *cis* to alkyl ligands;
(iv) positively charged metal centre.

The current challenge is therefore, to exploit the general insights gained from Cp_2MR^+ systems to develop new classes of 'tunable' catalysts with improved and/or complementary properties. Keeping these views in mind, several new types of metal alkyl complexes in non-metallocene environments have been studied. Among them, the mono-Cp systems or 'constrained geometry catalysts', alkoxy/phenoxy systems and chelating diamides are very important and will be briefly discussed in the following sections.

Constrained geometry catalysts

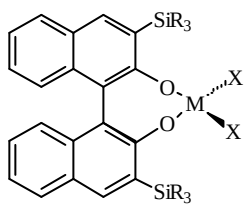
The development of 'half metallocene' or 'constrained geometry catalysts' containing dialkylsilyl-bridged alkylimido Cp ligand framework by Dow and Exxon during the late 1980s is yet another significant event in the history of the evolution of Ziegler–Natta catalysts[19a,b]. The characteristic feature of the structure of the constrained geometry catalyst is the short bond angle (less than 115^0) between Cp, M and N atoms. This arrangement allows the metal centres to be more open for monomer and comonomer incorporation. New families of ethylene-α-olefin copolymers have now been prepared using these catalyst systems by Dow under the trade name 'INSITE'. This technology allows the manufacture of both polyolefin plastomers and polyolefin elastomers through the controlled incorporation of comonomers concentration respectively. The polymers obtained from this catalyst systems [11] show excellent physical and mechanical properties due to narrow molecular weight distribution. Such catalysts produce copolymers with long-chain branching (LCB) in contrast to LLDPE copolymers produced by other metallocene catalysts. As a result, polyolefins produced by INSITE technology exhibit unusually good processability with enhanced shear thinning and allow the synthesis of polymers previously unknown.



[11]

Alkoxy systems

Terminal oxygen donors such as phenoxide ligands have been used successfully in olefin polymerization catalysis. In 1995, Schaverien *et al.*[20] presented a study using various sterically hindered chelating phenoxide complexes of titanium and zirconium as olefin polymerization catalysts. Ethylene polymerization tests with complexes [12, 13] have shown only moderate activities, whereas, complex [14], with a methylene group has given higher activity. Okuda and coworkers[21a,b] have successfully used ethylene-bridged bis(alkoxide) complexes [15], in the copolymerization of ethylene with styrene. Theoretical calculations on these systems have been performed by



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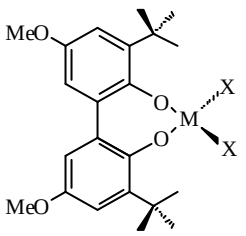

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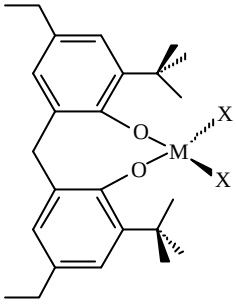

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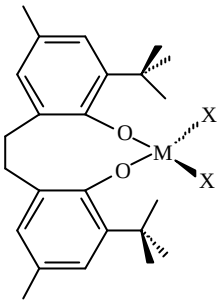
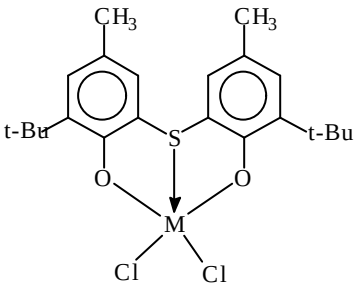


[15]

Morokuma *et al.*[22]. Kakugo and coworkers[23] have reported that titanium alkoxides in combination with MAO are highly active catalysts for ethylene and propylene polymerization. Similarly, the titanium complex [16] with a bidentate 2,2′-thiobis(6-tert-butyl-4-methylphenoxy) ligand has produced stereoregular polypropylene with very high molecular weight and highly syndiotactic polystyrene.



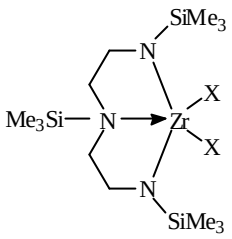
M = Ti, Zr

[16]

These catalysts are also active towards both conjugated and nonconjugated dienes. An ethylene-styrene copolymer with significant amount of styrene incorporation was reported by Kakugo and coworkers[24]. Further work by Schaverien *et al.*[20] and Okuda *et al.*[21] has shown the importance of the additional intramolecular sulphur donor for high catalytic activity. An alternating ethylene–styrene copolymer together with syndiotactic polystyrene was obtained using 2,2′-thiobis(4-methyl-6-tert-butylphenoxy) titanium isopropoxide (SPP) or dichloride with MAO. Also, mono-aryloxy or mono-alkoxy zirconium complexes/ MAO catalysts were reported for ethylene polymerization. It was found that the bulkiness around the zirconium atom in the complexes is significant to achieve high activity of polymerization.

Chelating diamide complexes

Three different systems have been reported to date of a group 4 bis(amido)complex with an additional donor Y – that is an amine, pyridyl or ether donor – incorporated in the ligand systems. The ligand system *trig*-[N⁻,N,N⁻] [17] developed by Horton *et al.*[25] and *planar*-[N⁻,O,N⁻] [18] developed by Bochmann and coworkers[26] have given moderate activity in the polymerization of ethylene. McConville and coworkers[27,a,b] synthesized several chelating diamide complexes [$ArN(CH_2)_3NAr$] – TiR_2(Ar = 2,6-$iPr_2C_6H_3$; R = Me, CH_2Ph) and found them to polymerize 1-hexene. The titanium dimethyl complex when activated with $B(C_6F_5)_3$ catalyses the living polymerization of α-olefins at room temperature[28]. This is the first example of living polymerization of an α-olefin.



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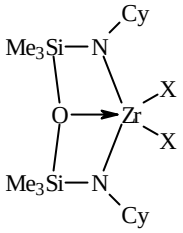

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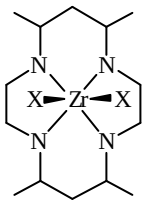
β-diketimate ligands

In 1993 Jordan and coworkers reported the synthesis of cationic d^0 group 4 metal alkyl complexes incorporating tetraaza macrocyclic ligands and their applications as olefin polymerization catalysts[29]. The corresponding zirconium complexes [19] are about 30 times less active than Cp_2ZrCl_2-based catalysts. Well-defined cationic complexes of the type [20] have been reported recently as olefin polymerization catalysts[30].

Bis(salicylaldiminato) ligands

A new series of non metallocene bis(salicyladiminato) ligands has been reported by workers from Mitsui Chemicals which polymerize ethylene in conjunction with MAO[31]. The catalyst [21] produces 3800 kg PE/mol Ti^{-1} h^{-1}



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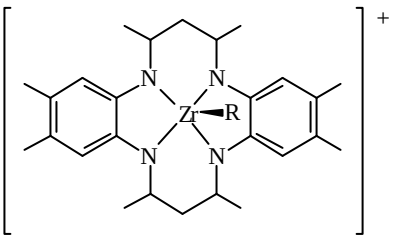
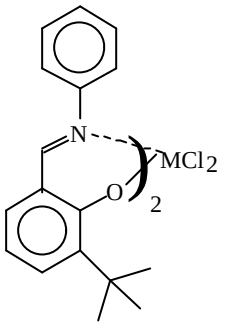
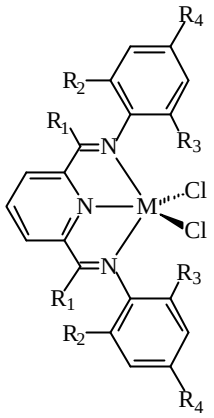


[20]



M=Ti,Zr

[21]



M = Fe(II), Co(II)
R_1 = H, Me
R_2 = R_3 = iPr, R_4 = H
R_2 = R_3 = Me, R_4 = H, Me
R_2 = R_4 = Me, R_3 = H

[22]

at 75°C/0.1 MPa pressure. A linear polyethylene with a Mw = 440,000 and polydispersity of 2.0 was formed.

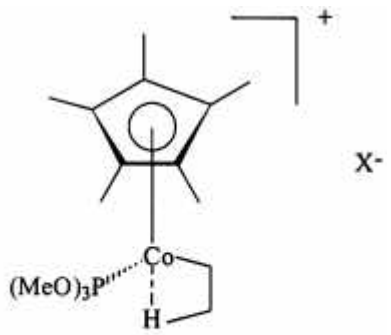
The corresponding zirconium complexes are also active for ethylene polymerization (25°C, 1 bar, 116 kg PE/mol Zr.h against a value of 27 (10^3 kg PE/mol Zr.h under similar conditions for Cp_2ZrCl_2. At a reduced catalyst concentration, the activity was 519 × 10^3 kg PE/mol Zr.h, one of the highest activities ever obtained amongst not only post-metallocenes but also Group IV metallocenes. However, the obtained molecular weight of PE was low, ca 10,000. Using $Ph_3C^{(+)}B^{(-)}(C_6F_5)_4$ as the activator, poly(ethylene)s of Mw as high as 5 million could be obtained.

Late transition metal catalysts

It is evident from the above discussions that the olefin polymerization activity is mostly dominated by the early transition metal systems. The electron-deficient nature of their metal centres has been thoroughly exploited over the years to develop more active catalysts for the polymerization of olefins. The late transition metal catalysts, on the other hand, are less electrophilic and exhibit greater tendency to undergo b-hydride elimination and, therefore, were best known for oligomerization of olefins. But, recently, late transition metal complexes containing neutral bis-imine ligands have been recognized as the latest addition to the small but significantly growing number of highly active polymerization catalysts. Bennett and coworkers[32a,b] and Gibson and coworkers[33a–c] reported the first iron-based olefin polymerization catalysts [22] containing 2,6-bis(imino)pyridine ligands. These complexes when activated with MAO polymerize ethylene with exceptionally high activities comparable to the most active Ziegler–Natta catalyst systems. The complexes show a pseudo square pyramidal geometry and the aryl groups on the imine nitrogen are perpendicular to the square plane and the bulky ortho substituents provide the necessary steric protection around the metal.

Aryl substitutents with only one small *ortho* substituent give highly active oligomerization catalysts with exceptionally high selectivity for the production of a-olefins[34]. These iron catalysts produce broad polydispersity linear polyethylene. Depending upon experimental conditions, the polyethylene prepared by iron catalysts has even bimodal distribution. ^{13}C NMR analysis of these polymers reveals saturated end groups. The broad molecular weight distribution is explained as due to chain transfer to aluminum co-catalysts. However, by appropriate choice of the organoaluminum activator, it has been shown recently, that even iron (II) catalyst can produce narrow molecular weight distribution poly(ethylene)s[35].

The most extensively studied example of the group 9 catalyst is the Co(III) complex [23][36]. This cationic compound shows a b-agostic interaction and inserts ethylene in a living fashion to form high molecular weight polymers with narrow polydispersity. The activities are low and a most active catalyst is obtained when non-co-ordinating counterions are employed. Higher olefins are



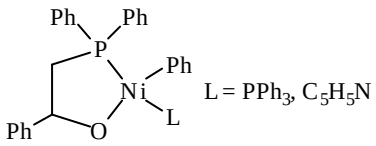
X = BF_4

= $B[3,5\text{-}(CF_3)_2C_6H_3]_4$

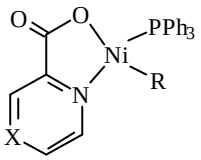
[23]

only oligomerized, but end functionalized polyethylene materials have been successfully synthesized with these systems. The Co(II) complex [22] also has been shown to be an active olefin polymerization catalyst in the presence of MAO.

Many group 10 compounds with anionic P,O ligands are well-known to oligomerize ethylene. They play a central role in the Shell Higher Olefin Process (SHOP). There have also been reports that SHOP-type oligomerization catalysts can polymerize ethylene under certain conditions. Compound [24], for example, where L = PPh_3 shows very high polymerization activity[37]. Similarly, complex [25], based on mixed donor chelates, has been shown to be active towards olefin polymerization[38].



L = PPh_3, C_5H_5N



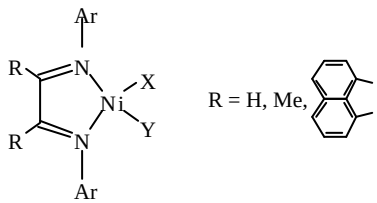
X = N, C-NO_2

R = *o*-$CH_3C_6H_4$

[24] [25]

The nickel(II) and Pd(II) systems reported by Brookhart and coworkers[39a,b], based on square planar cationic alkyl compounds supported by bulky diimine (N,N) ligands, were the first examples of late transition metal catalysts capable of polymerizing higher α-olefins as well as ethylene to high molecular weight polymers.

When treated with MAO, the nickel dibromide derivatives of the compound [26] show very high activity, up to 11000 g mol^{-1} h^{-1} bar^{-1} and the corresponding well-defined cationic alkyl species is also active. β-elimination from the growing polymer chain leads to chain branching or chain transfer. The formation of high molecular weight polymers is possible because the steric protection of the vacant axial coordination sites reduces the rate of associative displacement from β-eliminated olefin-hydride complexes and thus reduces chain transfer rates. A range of polyethylene materials with molecular weights up to 1×10^6 and degrees of branching from linear to over 70 branches per 1000 carbon atoms is accessible by simple variation of temperature, pressure and ligand architecture. At low temperature, the polymerization is living, and di and tri block ethylene/α-olefin copolymers can be synthesized[40]. Also, at low temperature, propylene is polymerized to syndiotactic polypropylene by chain-end control[41]. At higher temperature, α-olefins are polymerized to give more linear materials than expected because of β-elimination reinsertion mechanisms leading to chain straightening.



R = H, Me,

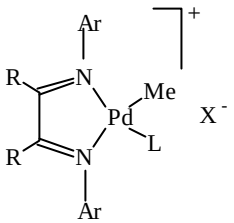
X = Y =Br

X = B[3,5-$(CF_3)_2C_6H_3]_4$.Et_2O, Y = Me

Ar = 2,6-*i*$Pr_2C_6H_3$, 2,6-$Me_2C_6H_3$, 2-*t*BuC_6H_4

[26]

The analogous Pd(II) compounds [27] show more moderate activity to produce highly branched amorphous polyethylene, with a range of molecular weights and up to 100 branches per 1000 carbon atoms. The mechanism of polymerization with these catalysts has been studied and the alkyl–olefin catalyst resting state has been characterized by NMR technique. These catalysts are able to copolymerize α-olefins with functionalized comonomers such as methyl acrylate, resulting in highly branched random copolymers with ester groups on some chain ends[42]. The mechanism for copolymerization is by 2,1-insertion of acrylate and chelate ring expansion, followed by insertion of ethylene units. Activities, however, are found to be much lower than for homopolymerization.



R = H, Me,

Ar = 2,6-*i*$Pr_2C_6H_3$

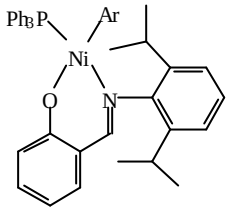
X = B[3,5-$(CF_3)_2C_6H_3]_4$, SbF_6

L = Et_2O, MeCN

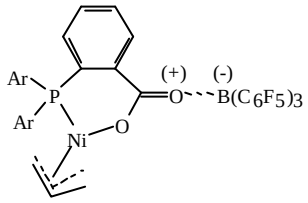
[27]

Theoretical calculations have been performed on both nickel and palladium systems[43]. These studies corroborate the crucial role of axial steric protection in the formation of high molecular weight polymers. The development of these catalysts, both in terms of ligand modification and new activation pathways is still continuing[44].

More recently, a nickel (II) complex has been reported which produces linear poly(ethylene)s *in the absence of* an organoaluminum coactivator[45]. The complex resembles the SHOP catalyst, except that the P-O chelate is replaced with a 'harder' nitrogen-based ligand with an increasing steric demand [28]. The catalyst has moderate activity (16 kg/g Ni), produces high molecular weight PE (Mw 236,000) and possesses 5 branches/1000 carbons atoms. Use of a pair of nickel (II) catalyst and mono



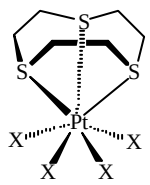
[28]



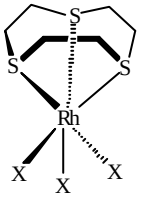
[29]

Cp-Ti catalyst can lead to 'tandem catalysis', namely *in situ* dimerization of ethylene to butene-1 followed by copolymerization of ethylene and butene-1 to form a linear low density polyethylene[46]. The catalyst pair employed was a mixture of [11] and [29].

One example of a Pt(IV) catalyst [30] has been reported.[47] Tri thiacyclononane-supported complex shows a moderate activity of 12 g mol^{-1} h^{-1} bar^{-1} for the polymerization of ethylene with MAO activation. The related rhodium [31] was also found to be active towards olefin polymerization.

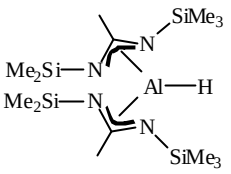


[30]

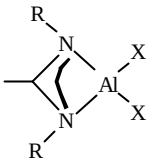


[31]

More recently, there are reports in the literature describing several homogenous aluminum compounds exhibiting olefin polymerization activity. Teuben and cowork ers[48] have reported that an aluminum hydride complex [32] containing two benzamidnate ligands under moderate conditions initiates polymerization of propylene. Also, it has been recently reported by Jordan and Coles[49] that another aluminum catalyst [33], when activated with $[Ph_3C][B(C_6F_5)_4]$ polymerizes olefin under moderate conditions. Gibson *et*

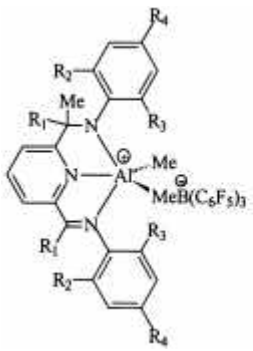


[32]

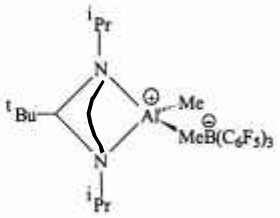


[33]

al.[50] have further reported the preparation of cationic aluminum complexes [34] bearing a monoanionic, tridentate N,N,N-chelating ligand derived from the neutral 2,6-bis(imino) ligand. These cationic complexes have been shown to polymerize ethylene in the absence of any cocatalysts. These complexes are similar to the transition metal-free cationic aluminum alkyl complexes previously reported by Jordan and coworkers [35].



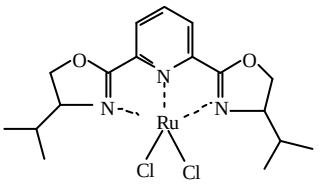
[34]



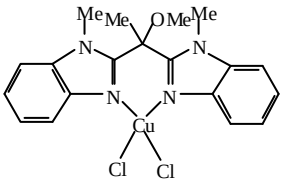
[35]

Several other late transition metal catalysts have appeared recently. These include a Ru (II) complex [36] and even a Cu (II) complex [37].

The ruthenium catalyst [36] with MAO as the coactivator exhibits moderate activity for ethylene polymeriza-



[36]



[37]

tion (8 bar, 50°C, 1.34 kg PE/mol Ru.h, Mw = 2,080,000, polydispersity 2.93)[51]. The copper (II) catalyst [37], on the contrary, shows very high polymerization activity in the presence of MAO as the activator (8 bar, 60°C, 610 kg PE/mol Cu.h)[52]. The Cu (II) catalyst also promotes copolymerization of ethylene with *t*-butylacrylate, methyl methacrylate and other polar monomers. Compatibility with polar comonomers is a unique feature of many less oxophilic late transition metal catalysts.

Conclusions

Thus, remarkable developments have occurred during the last 15 years in the evolution of Ziegler–Natta catalysts leading to the design and application of a variety of olefin polymerization catalyst systems. This trend clearly reflects the attention given to this area both in academic and industrial laboratories throughout the world. The explosion of interest in this area has already yielded a large number of research publications, reviews and patents granted to major chemical industries. This is perhaps one of the few areas where key ideas originated in academic laboratories, basically as scientific curiosities, have quickly emerged as a dominant force in the industry. The role of organometallic and co-ordination chemists is particularly significant in the evolution of the new generation 'single site' olefin polymerization catalysts. It is obvious that the search for new polymerization catalysts is not yet over and the topic will continue to provide a fertile ground for organometallic, co-ordination and polymer scientists in the future.

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