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Discrete iron-based complexes: applications in homogeneous coordination-insertion polymerization catalysis

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Dedicated to Professor Armando J.L. Pombeiro for his outstanding achievements in Coordination Chemistry and Catalysis.

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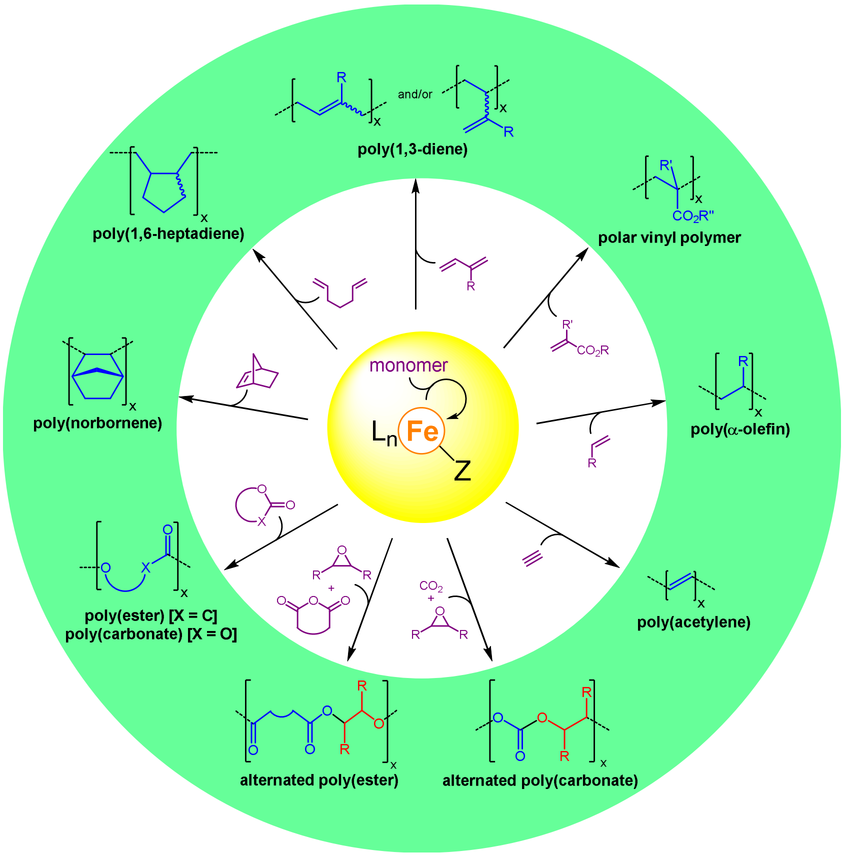
Abstract: Catalysis based on well-defined iron complexes has experienced a very strong growth over the last decade, driven by the need to develop a chemistry that is increasingly in line with environmental concerns, such as the optimization of the planet's resources and the management of the waste from any industrial transformation. The abundant and non-toxic dual character of the iron element is fully consistent with this approach. After the pioneering work of Gibson and Brookhart related to the polymerization of ethylene, which will be briefly recalled here, it appeared in the literature an increasing number of studies on the coordination-insertion polymerization of a large variety of organic monomers using iron-based catalytic systems. The purpose of this review is to provide an update in this field by examining the catalytic systems developed in recent years. Particular emphasis is placed on those involving discrete complexes through their structure and catalytic performance, in terms of both activity and selectivity (when relevant) as well as their limitations. Some key ideas on the salient aspects of this chemistry conclude the manuscript and prospective avenues are put forward.

Graphical abstract:



Contents

Abbreviations: Acetylacetonate (acac), Activated monomer mechanism (AMM), azobisisobutyronitrile (AIBN), butadiene (B), benzyl alcohol (BnOH), β-butyrolactone (BBL), bis(imino)pyridyl (BIP), butyl methacrylate (BM), 2-bromo-2-methylpropane (BMP), chlorobenzene (CB), catalyzed chain growth (CCG), coordinative chain transfer polymerization (CCTP), cyclohexene oxide (CHO), ε-caprolactone (CL), coordination-insertion mechanism (CM), chain transfer agent (CTA), dispersity (*Đ*), dichloromethane (DCM), diethyl phopshite (DEP), 2,2-dimethyltrimethylene carbonate (DMC), dimethoxyethane (DME), dimethylformamide (DMF), 2,3-dimethyl-1,3-butadiene (DMB), bis-[1,3-(diphenyl phosphate)]-2-mehtylpropane (DPPMP), diphenyl (3,5-dimethyl-1H-pyrazol-1-yl)phosphonate (DPzPP), diphenyl pyridin-2-yl phosphate (DPPyP), bis-[2,6-(diphenyl phosphate)]-pyridine [bis(DPPyP)], ethylene (E), ethyl-2-bromoisobutyrate (EBiB), ethylene carbonate (EC), glutaric anhydride (GA) γ-butyrolactone (GBL), 2-hydroxyethyl 2-bromoisobutyrate (HEBiB), isoprene (I), isobutyl vinyl ether (IBVE), *L*-lactide (*L*-LA), *rac*-lactide (*rac*-LA), methyl acrylate (MA), methylaluminoxane (MAO), methyl methacrylate (MMA), modified methylaluminoxane (MMAO), 3-methyl-1,3-pentadiene (3MP), *n*-butyl vinyl ether (NBVE), *n*-vinylcarbazole (NVC), 1,3-pentadiene (PD), pentafluorobenzoate ($OBzF_5$), propylene (P), phthalic anhydride (PA), polybutadiene (PB), polyethylene (PE), poly(*L*-Lactide) (PLLA), polyisoprene (PI), polypropylene (PP), bis(triphenylphosphino)iminium (PPN), ring-opening polymerization (ROP), *tert*-butyl acrylate (*t*-BA), tetrahydrofuran (THF), tri(2,4-difluorophenyl) phosphate (TFPP), trimethylene carbonate (TMC), triphenylphosphate (TPP), bis-[1,3-(diphenyl phosphate)]-benzene [bis(TPP)], turn-over frequency (TOF), δ-valerolactone (VL) and Ziegler-Natta (Z-N).

Keywords: iron, well-defined complexes, coordination-insertion polymerization, ring-opening polymerization, olefins, polar vinyl monomers, 1,3-dienes, cyclic esters and carbonates, CO_2/epoxides, cyclic anhydrides/epoxides.

1. Introduction

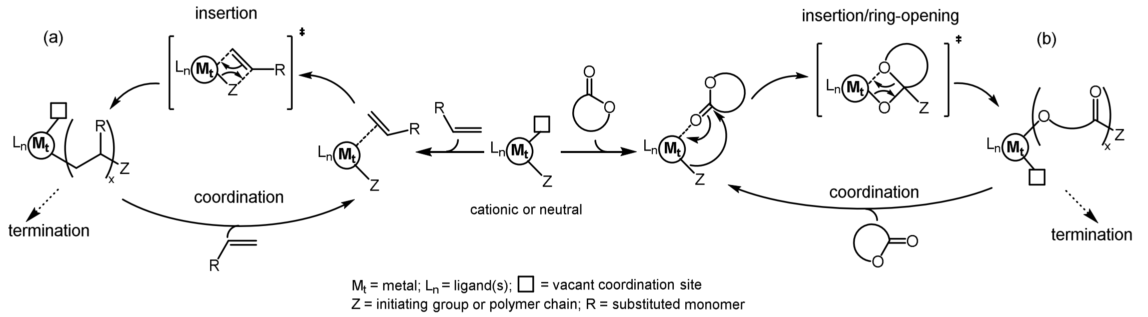
Since the initial discovery sixty years ago of Karl Ziegler and Giulio Natta [1], coordination-insertion catalysis has emerged as a preferred choice for controlling the polymerization of a wide range of unsaturated hydrocarbon monomers and many others [2]. Indeed, compared with other polymerization methodologies such as anionic or radical polymerization, the resulting microstructure of the growing chain has in this case the advantage of being dictated by the catalyst environment [3].

Conventional Ziegler-Natta (Z-N) systems are based on heterogeneous and, to a lesser extent, homogeneous catalysts, which predominantly consist in a transition or rare earth metal-based compound (pre-catalyst) in combination with a main group alkyl or a borane (or borate) co-reagent (cocatalyst) [4]. Heterogeneous Z-N catalysts dominate the industrial manufacturing of polyolefins and related polymers, however, these systems possess several active sites that make them difficult to characterize and generally lead to polymers whose microstructure may be less controlled with broad molecular weight distribution. On the other hand, homogeneous catalysts, which are represented by single-site catalysts with well-defined structures, are capable of producing polymers with a narrower molecular weight distribution and, to some extent, controlling the stereo-, regio- and chemo-selectivity according to the steric and electronic properties of the ancillary ligand(s) [5]. After the discovery of methylaluminoxane (MAO) as a cocatalyst in the late 1970s, most of the research works on homogeneous Z-N catalysts have been focused on the preparation of well-defined early transition metal-based systems, initially with Group IV metallocenes and their derivatives, followed by the development of post-metallocene catalysts [6]. Advances in this area have enabled to prepare metal-based complexes capable of polymerizing, in some cases, various monomers in a living fashion, along with efficient control over selectivity [7], molecular weight distribution and the preparation of end-functionalized polymers as well as block copolymers [8]. More recently, well-defined late-transition metal complexes have shown considerable potential as catalysts for the polymerization of unsaturated hydrocarbon monomers, allowing, *inter alia*, the preparation of polymers that display unprecedented architectures [9]. Furthermore, one of the advantages of late-transition metal-based is that they have demonstrated, in some cases, to be more tolerant toward functional groups in comparison with the more oxophilic counterparts based on early metals [10].

Among the late transition metal-based catalysts, iron is readily available, cheap with negligible environmental impact and of low toxicity [11]. This metal is an essential element of life since its presence in specific proteins helps to bind and transport oxygen through the circulatory system of all living organisms. Moreover, iron occupies an essential role in the evolution of human society as it has been widely used in the production of metal alloys for more than two millennia. At the dawn of the twentieth century, the development of catalytic systems based on iron for the production of ammonia in the Haber-Bosch process has contributed to the development of intensive agriculture and, consequently, to the support of the global population growth [12]. To date, iron has become a key metal of homogeneous molecular catalysis [13] to replace the frequent use of expensive and more toxic precious/noble metals [14].

With regard to Z-N catalytic systems, the well-accepted mechanism for the coordination-insertion polymerization of α-olefins was proposed at the beginning of the 1960s' by Cossee and Arlman [15]. In this respect, the coordination-insertion polymerization of α-olefins (and corresponding unsaturated hydrocarbon monomers) refers to a polymerization process involving the prior coordination of the double bond of the incoming monomer on the metal (M_t) active center to generate a π complex intermediate. The coordination of the monomer is then followed by its insertion into the metal-Z bond (or metal-polymer) of the propagating species, the growing chain remaining attached to the metal center (**Scheme 1a**).

Not only unsaturated hydrocarbon monomers can be polymerized by a coordination-insertion mechanism, but also, in a lower degree, several families of polar cyclic monomers such as cyclic esters or carbonates and others [16]. The coordination proceeds via σ donation of the heteroatom of the polar cyclic monomer on the metal center, which subsequently inserts into the metal-Z bond (or metal-polymer) by addition of the Z group on the carbon of the carbonyl group. This step is then followed by the ring opening of the heterocycle through the cleavage of the carbon-acyl bond (**Scheme 1b**); this polymerization process is commonly designated as coordination-insertion Ring-Opening Polymerization (ROP) [17].



Scheme 1. Mechanism of metal-catalyzed coordination-insertion polymerization of (a) unsaturated hydrocarbon monomers and (b) polar cyclic monomers.

Herein, the purpose of this literature survey is to provide an overview of well-defined single-site iron-based catalysts specifically involved in homogeneous coordination-insertion polymerization. Over the past decade, research groups working on coordination-insertion olefin polymerization using iron-based pre-catalysts have contributed to the publication of several exhaustive reviews in this field, either by focusing on a single type of monomer (mainly ethylene), or based on a family of structurally well-defined iron complexes (*vide infra*). However, to our knowledge, a full and up-to-date review that gathers polar and hydrocarbon monomers engaged in homogeneous iron-catalyzed coordination-insertion polymerization has yet not been presented. In particular, the use of discrete iron-based complexes for the ROP of cyclic esters or carbonates was only briefly reported ten years ago [18]. Hence, this review will cover advances in iron-based catalysts for the coordination-insertion (co)polymerization of monomers including ethylene, α-olefins, cyclic olefins, α,ω-dienes, polar vinyl monomers, 1,3-dienes, polar cyclic esters (or carbonates) and CO_2 (or anhydrides)/epoxides. Particular emphasis will be made on the recent developments of the polymerization of 1,3-diene and cyclic ester (or carbonate) monomers. The polymerization of ethylene with iron-based complexes has been the subject of many comprehensive review articles in the last few years (*vide infra*); it will therefore be briefly mentioned here. Moreover, the preparation of polycarbonates from the copolymerization of epoxide and CO_2 by metal coordination complexes, which was recently released by Kozak *et al.* in 2018 [19], as well as the copolymerization of epoxide with cyclic anhydride will be promptly addressed for the iron-based systems.

The catalyst performances have been converted in turnover frequencies (TOF, turnover number per time unit in h^{-1}) either from the reported activities [TOF = activity ($g_{polymer}.mol_{cat.}^{-1}.h^{-1}$)/$M_{monomer}$ ($g.mol^{-1}$)] or the isolated polymer yields {TOF = [$n_{polymer}$ (mol)/$n_{cat.}$ (mol)]/time (h)]} or the conversion of monomer {TOF = [conv. (%) * monomer/cat. (ratio)]/time (h)}. However, it should be noted that the performance of the catalytic systems is often strongly dependent on the experimental conditions, such as, for example, the nature of the monomer, the catalyst concentration, the type of solvent, the reaction time, the stirring rate and many other parameters, thus, the comparison of the different systems for a given transformation must be taken with precaution [7f].

2. Iron-catalyzed polymerization of olefins and polar vinyl monomers

2.1. α-olefin monomers

2.1.1. Ethylene – an overview

The simultaneous investigation conducted independently by the groups of V. Gibson, M. Brookhart and A. Bennett (DuPont) in the late 1990s demonstrated a very high efficiency and selectivity of the first generation iron-based complexes for the polymerization and/or oligomerization of ethylene upon activation with an excess of MAO, producing exclusively linear oligo- or polymers (**Fig. 1**, **Table 1**) [20].

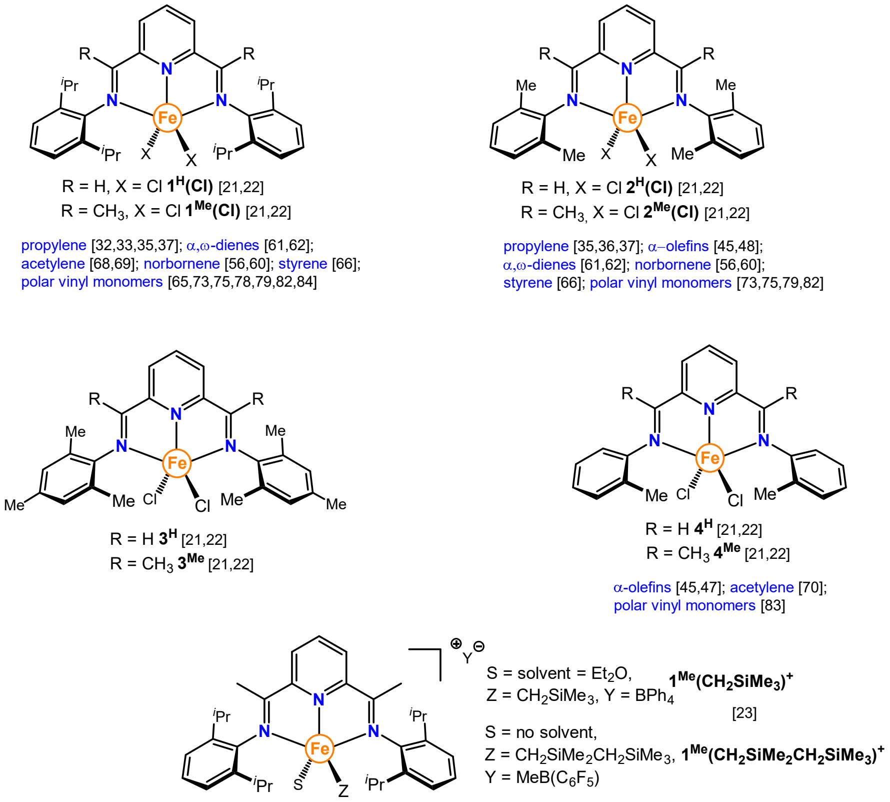


Fig. 1. Selected iron-BIP complexes used for the polymerization/oligomerization of ethylene.

Briefly, the key feature of these pre-catalysts, with respect to their reactivity with ethylene, is the presence of a bis(imino)pyridyl (BIP) tridentate pincer ligand that can produce, according to the steric hindrance of the *N*-aryl substituents, either short chain oligomers or high molecular weight polyethylene [21,22]. For example, the presence of sterically encumbered ^{i}Pr groups at both *ortho* positions of the *N*-aryl substituents of the BIP ligand promotes the formation of high M_w polyethylene [$\mathbf{1^{Me}(Cl)}$] by preventing the occurrence of chain terminations by β-H elimination. In contrast, a less congested BIP ligand bearing two Me (or one additional Me on the *para* position) at both *ortho* positions of the *N*-aryl groups produces lower M_w [$\mathbf{2^{Me}(Cl)}$, $\mathbf{3^{Me}}$]. Furthermore, the resulting M_w are dependent on the substituent on the carbon of the imino groups, with the ketimine ligand [R = Me, $\mathbf{1^{Me}(Cl)}$, $\mathbf{2^{Me}(Cl)}$] showing higher M_w than the corresponding aldimine ligand [R = H, $\mathbf{1^{H}(Cl)}$, $\mathbf{2^{H}(Cl)}$]. Subsequently, the substitution of one methyl group on the *ortho* position of both *N*-aryl substituents of the ligand leads to the generation of linear short chain oligomers ($\mathbf{4^{H}}$, $\mathbf{4^{Me}}$). Besides the resulting M_w of the polymers, the activity of the catalysts is also affected by the electronic and steric nature of the ligand framework, with the ketimine BIP ligand being more active than the aldimine counterpart ($\mathbf{1^{Me}(Cl)} > \mathbf{1^{H}(Cl)}$; $\mathbf{2^{Me}(Cl)} > \mathbf{2^{H}(Cl)}$; $\mathbf{3^{Me}} > \mathbf{3^{H}}$), while the presence of Me substituent on the *para* position of the *N*-aryl groups displays the highest activity ($\mathbf{3^{Me}}$). Independently, the group of Chirik succeeded to isolate for the first time a series of single cationic iron-based catalysts [*e.g.* $\mathbf{1Me(CH_2SiMe_3)^+}$ and $\mathbf{1Me(CH_2SiMe_2CH_2SiMe_3)^+}$], which have shown to display moderate activity for the polymerization of ethylene [23].

Table 1
Ethylene polymerization with selected (BIP)$FeCl_2$/MAO catalytic systems[a]

Complex	Activation MAO/Fe	T (°C)	p_{C2H4} (bar)	Time (min)	TOF ($10^3\,h^{-1}$)	M_w (kg/mol)	$Đ$ (M_w/M_n)	Ref.
$\mathbf{1^{H}}$ **(Cl)** (6 µmol)[a]	200	35	10	60	108	132	38.9	21
$\mathbf{1^{Me}}$**(Cl)** (0.5 µmol)[a]	1 000	50	10	60	1 920	611	9.5	21
$\mathbf{2^{H}}$**(Cl)** (6 µmol)[a]	200	35	10	60	200	108	57.3	21
$\mathbf{2^{Me}}$**(Cl)** (0.6 µmol)[a]	1 000	50	10	60	3 400	242	25.3	21
$\mathbf{3^{H}}$ (6 µmol)[a]	200	35	10	60	195	152	83.5	21
$\mathbf{3^{Me}}$ (0.6 µmol)[a]	1 000	50	10	60	7 400	148	10.7	21
$\mathbf{4^{H}}$ (6 µmol)[a]	900	50	5	60	186	1.9	2.8	22
$\mathbf{4^{Me}}$ (6 µmol)[a]	900	50	5	60	230	1.5	2.1	22
1Me($\mathbf{CH_2SiMe_3}$**)**$^+$ (10 µmol)[b]	none	23	1	30	3.0	317[c]	2.5	23
1Me($\mathbf{CH_2SiMe_2CH_2SiMe_3}$**)**$^+$ (10 µmol)[b]	none	23	1	5	7.8	199[c]	1.6	23
$\mathbf{1^{Me}}$**(Cl)** (10 µmol)[b]	600	23	1	5	33.6	172[c]	2.3	23

[a] Conditions: solvent = isobutane; [b] solvent = toluene; [c] M_n

Over the past two decades, a considerable amount of efforts has been devoted to the modification of the BIP ligand framework and the development of related architecture (**Fig. 2**), with the aim to improve the activity, the selectivity and the thermal stability of the original iron-based catalyst system. Further studies of the mechanistic aspect of the polymerization, the identification of the catalyst active species, the redox-active properties of the BIP ligand and other noticeable investigations have also been the subject of extensive researches in order to understand the structure-activity relationship of the transformation. These achievements have been gathered in several meticulous reviews and book chapters; readers are redirected to these contributions for more information [24,25].

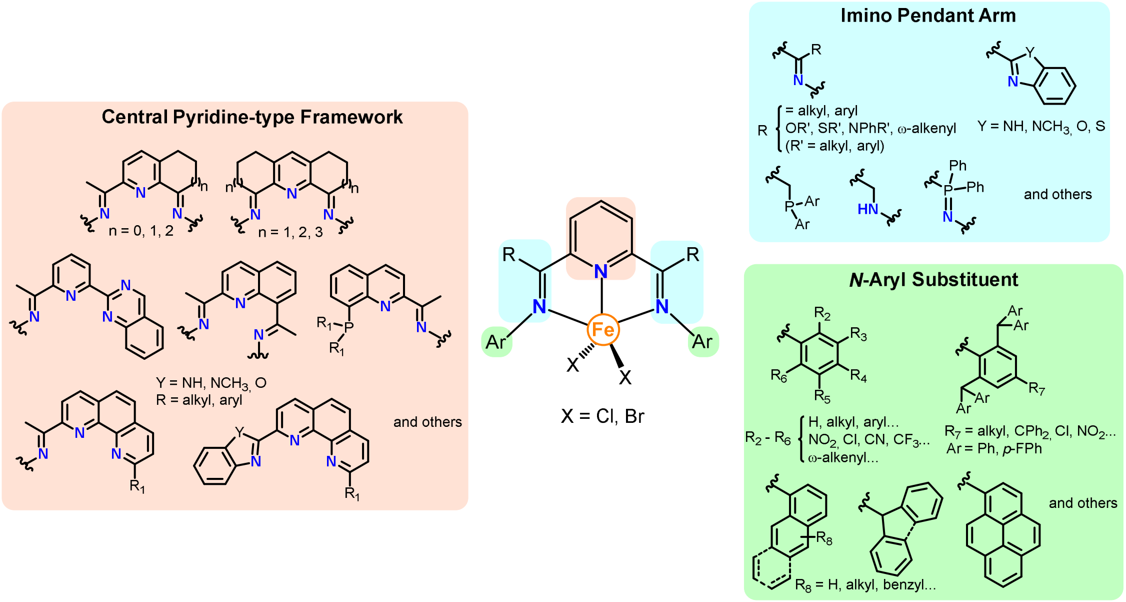
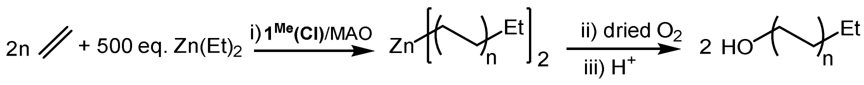


Fig. 2. Selected examples of BIP ligands with modified framework and related architectures used for iron-catalyzed polymerization/oligomerization of ethylene [24,25].

Among the modern approaches of coordinative polymerization catalysis, processes based on Coordinative Chain Transfer Polymerization (CCTP) have been developed, where the growing polymer chain is reversibly transferred, via transmetallation, from an active metal center to a dormant

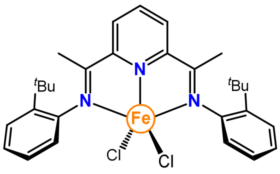
Chain Transfer Agent (CTA). This CTA is usually a main-group alkyl metal center such as Zn, Mg or Al used in large excess with respect to the catalyst [26]. If the chain transfer is fully reversible, rapid and occurs in absence of any undesired transfer/termination processes, this methodology is called Catalyzed-Chain Growth (CCG) and displays living characteristic, enabling: i) the preparation of polymer chains with narrow molecular weight distributions and ii) the functionalization of the polymer chain end [27]. Functionalized polymers offer unique features in terms of physical-chemical properties but also allow the preparation of macromolecular objects as reactive building blocks [28]. With respect to the iron-based polymerization catalysis, Gibson and coworkers described the first CCG of ethylene using $\mathbf{1^{Me}(Cl)}$/MAO in presence of 500 equiv. of $ZnEt_2$ as CTA (**Scheme 2**) [29]. In parallel, Matyjaszewki and coworkers used the same catalytic system to prepare a monohydroxy-terminated polyethylene (PE-OH) through the one-pot oxidation of the Zn-terminated polyethylene (Zn-PE) bond followed by hydrolysis [30]. More recently, Cariou *et al.* reported the *in situ* regeneration of the $ZnEt_2$ by tandem catalysis via ethyl/alkyl exchange with the use of a second Fe-alkyl catalyst [31].



Scheme 2. Catalyzed-Chain Growth of ethylene on zinc with $\mathbf{1^{Me}(Cl)}$/MAO followed by oxidation/hydrolysis.

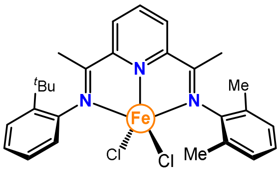
2.1.2. Propylene

Following the discovery of the highly reactive (BIP)$FeCl_2$ in ethylene polymerization, the use of this system has been subject, to a lesser extent, to additional assessments in the field of polymerization of propylene. The iron-based complexes discussed in this section are depicted in **Fig. 1** and **Fig. 3**, and the polymerization data are included in **Table 2**.

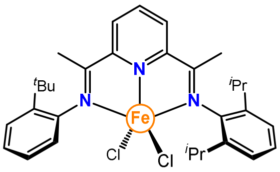


(5) [35]

α-olefins [48]; α,ω-dienes [61,62];
norbornene [56]

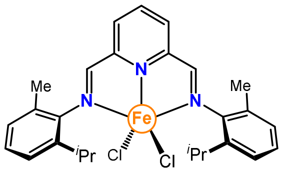


(6) [35]

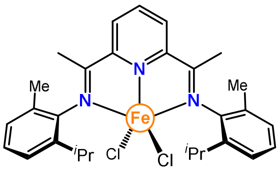


(7) [35];

α,ω-dienes [61,62]



($\mathbf{8^H}$) [48]

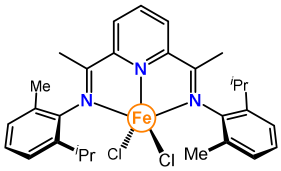


meso (C_s) ($\mathbf{8_{meso}}$)

[35,38,39,40]

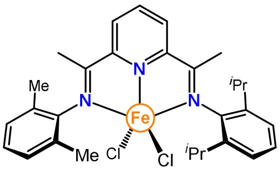
α,ω-dienes

[61,62]



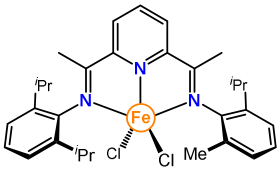
rac (C_2) ($\mathbf{8_{rac}}$)

[35,38,39,40]



(9) [35,37];

α,ω-dienes [61,62]



(10) [35]

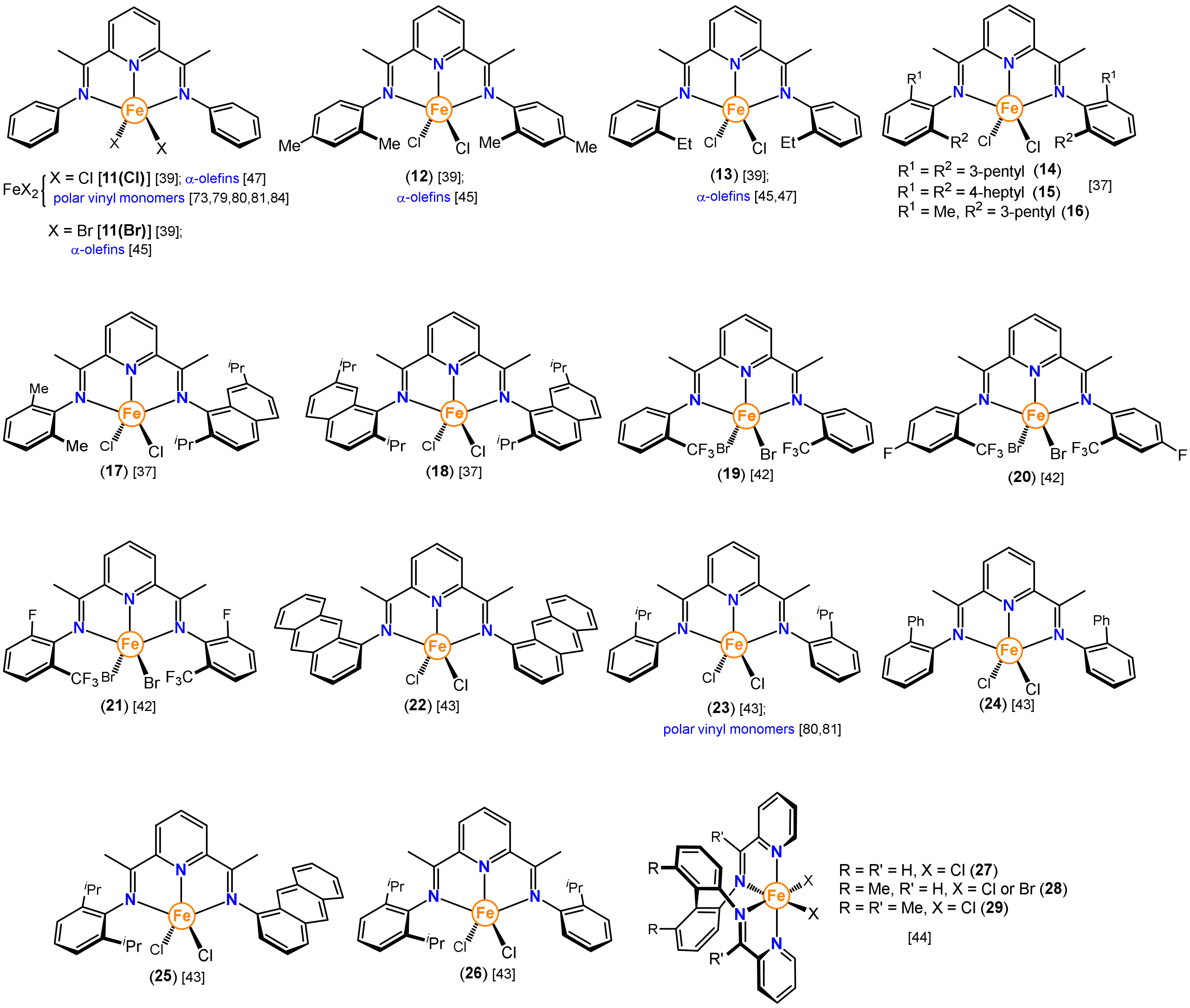


Fig 3. Bis(imino)pyridyl iron-based complexes used in propylene polymerization

Studies for the polymerization of propylene using the **1^{Me}(Cl)**/MAO system were primarily reported by Brookhart and coworkers, showing moderate activities with the formation of mainly isotactic polymers (*mmmm* > 50%) [32]. Soon after, Pellechia *et al.* studied the same system with the aim to reveal the factor that governed the regio- and stereo-selectivity of the polymerization process [33]. Polymerizations of propylene were performed at 0 °C, 20 °C and 50 °C using **1^{Me}(Cl)** in the presence of 100 equiv. of MAO, affording mainly isotactic polypropylene but in poor yields. Pentads analysis of the ^{13}C NMR spectra of the resulting polymers showed that the stereo-selectivity arose from a chain-end control mechanism with the polymers produced at low temperature exhibiting higher isotacticity [34]. Studies of the polymer chain-end with complex **1^{Me}(Cl)** in presence of an additional amount of ^{13}C-enriched $Al(Me)_3$ to the MAO cocatalyst revealed a preferential 2,1 mode of insertion of the monomer with the chain termination occurring principally through β-H elimination.

Subsequently, the group of Brookhart thoroughly investigated the influence of the steric hindrance and symmetry of a series of (BIP)$FeCl_2$ pre-catalysts for propene polymerization, through the variation of the *ortho* substituent of the *N*-aryl groups (complexes **1^{Me}(Cl)**, **2^{Me}(Cl)**, **5** –**10**) [35].

Under 1 bar of propylene at 0 or – 20 °C, these complexes combined with an excess of modified methylaluminoxane (MMAO) afforded polypropylene with low molecular masses (M_n = 600 – 7 000 g/mol) and narrow dispersity ($Đ$ = 1.8 – 2.5) in moderate yields. The most active catalyst, based on **9**, with two different *N*-aryl groups on the BIP ligand, displayed a TOF of 38 800 h^{-1}, while the less active system was found with the aldimine BIP derivative iron complex $\mathbf{8^H}$ (TOF = 700 h^{-1}). As found for ethylene polymerization, reduction of the steric bulk of the ligand framework of the iron-based catalysts lead to a decrease of the resulting molecular masses of the polymers. Examination of the ^{13}C NMR spectra of the polymers revealed that the polymerization operates via a preferential 2,1 insertion mechanism, with a decrease in regio-regularity that follows the decrease in steric hindrance of the complexes, similar to that found by Pellechia *et al.* [33]. The polypropylene obtained was highly isotactic (*mmmm* = 55 – 67%), which is consistent with a chain-end control regulated mechanism. The presence of propenyl unsaturated end groups highlights the fact that the main termination pathway proceeds through β-H elimination, while chain transfer to aluminum occurs exclusively with the primary Fe-alkyl intermediates. Similar results were obtained by the group of Zhu using the binary $\mathbf{2^{Me}(Cl)}$/MMAO catalytic systems at 25 °C, with *mmmm* content of 29% due to the presence of small substituents on the *ortho* position of the *N*-aryl groups [36]. The group of Nozaki observed the same behavior in propylene polymerization using complexes $\mathbf{1^{Me}(Cl)}$, $\mathbf{2^{Me}(Cl)}$ and **9** activated with MMAO, with the more sterically crowded complexes $\mathbf{1^{Me}(Cl)}$ and **9** affording polypropylene with higher M_n and *mmmm* pentad content than the catalyst based on the less congested complex $\mathbf{2^{Me}(Cl)}$ [37].

Independently, the group of Fink studied the polymerization of propylene using complex $\mathbf{8_{(meso/rac)}}$ in the presence of 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$ combined with 80 equiv. of $Al(^iBu)_3$ [38]. This ternary catalytic system was found to be 200 times more active (TOF = 52 300 h^{-1}) than the $\mathbf{8_{(meso/rac)}}$/MAO system (TOF = 225 h^{-1}), under these experimental conditions. In addition, the authors conducted kinetic studies by following the consumption of propylene with a mass-flowmeter in absence or presence of hydrogen. This investigation allowed the authors to propose a mechanism of propagation and termination of the polymerization reaction, which involves the presence of an active iron hydride species resulting from β-H elimination, a key intermediate engaged in the catalytic cycle. Following this study, the same group performed additional investigations on the mechanism of the propylene polymerization with the iron-based complexes $\mathbf{8_{(meso/rac)}}$, **11(Cl)** – **13** with MMAO or a combination of aluminum alkyl with $[Ph_3C][B(C_6F_5)_4]$ [39]. The resulting dimers and trimers were isolated from the polymers and were analyzed by NMR spectroscopy. The NMR spectra revealed that the more sterically bulky pre-catalyst ($\mathbf{8_{(meso/rac)}}$, **12**, **13**) follows preferentially a 2,1 monomer insertion into the Fe-alkyl bond, which in turn produces higher molar mass materials, while the absence of substituents on the *ortho* positions of the *N*-aryl groups [**11(Cl)**] slightly decreased the occurrence of the 2,1 insertion pathway. Conversely, starting from the iron hydride catalytic species, the first monomer insertion occurs preferentially in a 1,2 fashion with the more sterically hindered complexes

(**8**$_{\mathbf{(meso/rac)}}$, **12**, **13**), whereas a 2,1 insertion mode of the monomer in the Fe-H bond is preferentially observed with the less congested complex **11(Cl)**.

In 2008, the group of Càmpora succeeded to isolate the racemic mixture of the chiral *C2* diasteroisomer configuration of complex **8**$_{\mathbf{(meso/rac)}}$ by selective precipitation [40]. When compared to the performance of **8**$_{\mathbf{meso}}$ upon activation with MMAO, the *rac* diasteroisomer (**8**$_{\mathbf{rac}}$) displayed an activity three times higher than the achiral *meso* form, producing low molecular masses (M_n = 8 300 g/mol) polypropylene with narrow dispersity ($Đ$ = 1.5). Moreover, a noticeable higher amount of pentad (> 63%) was observed in the NMR spectrum of the resulting polymer sequences when compared to **8**$_{\mathbf{meso}}$ system, corroborating the presence of competitive chain growth by an enantiomorphic site control mechanism [41].

Nozaki and coworkers recently reported that the activity of complexes **14** and **15** supported by BIP ligand with 3-pentyl and 4-heptyl chains on the *ortho* positions of the *N*-aryl groups, respectively, was dramatically affected upon activation with MMAO as compared to **1**$^{\mathbf{Me}}$**(Cl)** (TOF = 4 800 h^{-1} for **1**$^{\mathbf{Me}}$**(Cl)** *vs* 20 h^{-1} for **14** and **15**) [37]. This observation implies that the long alkyl substituents within **14** and **15** prevent the coordination and insertion of the monomer into the growing chain. Investigations of the NMR spectra of the resulting polymers revealed a typical 2,1 insertion mode, producing highly isotactic materials (*mmmm* = 53 – 60%) through chain-end control mechanism with low M_n (3 400 – 4 500 g/mol) and narrow dispersity ($Đ$ = 2.1 – 2.4), in a manner similar to that observed for **1**$^{\mathbf{Me}}$**(Cl)**/MMAO. The symmetrical complex **16** bearing 2-methyl-6-(3-pentyl)-phenyl groups on the imino *N*-substituents displayed intermediate activity (TOF = 800 h^{-1}) with respect to the related complexes **2**$^{\mathbf{Me}}$**(Cl)** and **14**, while producing polymers with higher M_n under similar conditions. When compared to **1**$^{\mathbf{Me}}$**(Cl)**/MMAO, the introduction of 2,7-diisopropylnaphtyl group on one (**17**) or both imino *N*-substituents (**18**) of the (BIP)$FeCl_2$ complex did not affect the catalytic activity of the polymerization of propylene, neither the M_n of the resulting polymers. The regio-regularity and iso-selectivity of the polymerization of propylene using complexes **16** – **18**/MMAO are similar to those observed with **1**$^{\mathbf{Me}}$**(Cl)**/MMAO, with a predominant 2,1 mode of insertion of monomer that affords highly isotactic polypropylene, due to a stereo-regulation process that occurs mainly by chain-end control (*mmmm* = 52 – 59%), and chain termination step predominantly arising from β-H elimination.

In addition, the copolymerization of propylene with a series of allylic, polar and non-polar, comonomers was investigated by the same group using the binary **1**$^{\mathbf{Me}}$**(Cl)**/MMAO catalytic system [37]. No incorporation of polar units was found with allyl acetate, allyl ether and allyl methyl ethers, only the homopolymerization of propylene took place, probably due to the intermolecular interaction of the oxygen atom of the comonomer on the iron center or aluminum cocatalyst that inhibits the insertion step. Conversely, allyl benzene and allyl (triethoxy)silane were proved to be incorporated in the copolymers but exclusively at the chain end of the polypropylene chain. After analysis of the ^{1}H and ^{13}C NMR spectra of the propylene/allyl benzene copolymer, the authors suggested that the allyl comonomer followed a 2,1 regio-chemistry of insertion, similar to propylene, which undergoes direct elimination by β-H. Similarly, copolymerization of allyl (trimethyl)silane or allyl (dimethyl)(phenyl)silane with propylene using $\mathbf{1^{Me}(Cl)}$/MMAO resulted in the embedment of the allyl comonomers at the chain end, with a very small portion of in-chain incorporation (comonomer incorporations of 2.1% and 1.7%, respectively).

Surprisingly, the introduction of electron-withdrawing groups (F, CF_3) on the *N*-aryl substituents of the (BIP)$FeBr_2$ pre-catalysts (**19** – **21**) inhibits the production of polypropylene when activated by MAO, while their activity for the oligomerization of ethylene is significantly improved when compared to the non-fluorinated iron-based system ($\mathbf{4^{Me}}$) bearing one methyl group on the *ortho* position of both *N*-aryl substituents [42].

In presence of 1 000 equiv. of MMAO, the iron-based complexes supported by BIP ligand with various *N*-aryl groups (1-anthracenyl **22**; 2-isopropylphenyl **23**; 2-biphenyl **24**; 2,6-diisopropylphenyl/1-anthracenyl **25**; 2,6-diisopropylphenyl/2-isopropylphenyl **26**) have shown to display very low activity (or none for complex **24**) with poor selectivity for the oligomerization of propylene. The resulting materials displayed low molecular mass oligomers (< 600 g/mol) at 0 – 40 °C, while deactivations of the catalysts were found above 40 °C [43].

The group of Brintzinger have shown that complexes **27** – **29** were inactive for the polymerization of propylene in presence of an excess of MAO or a combination of $[Ph_3C][B(C_6F_5)_4]/Al(^{i}Bu)_3$ [44], probably due to the generation of a saturated active species with 16-electron configuration that is not capable of promoting the insertion of propylene.

Table 2

Propylene polymerization with selected iron-based catalytic systems

Complex	Activation (ratio/Fe_{cat})	T (°C)	*p* (bar)	Time (min)	TOF (10^3 h^{-1})	M_n (kg/mol)	Đ (M_w/M_n)	*mmmm* (%)	Ref.
$\mathbf{1^{Me}(Cl)}$	MAO (100 eq.)	20	6	60	0.1	7.1	nd	66	33
$\mathbf{1^{Me}(Cl)}$	MMAO	– 20	1	120	12.9	6.5	2.1	55	35
$\mathbf{1^{Me}(Cl)}$	MMAO (800 eq.)	– 20	2	60	4.8	4.7	2.5	54	37
$\mathbf{2^{Me}(Cl)}$	MMAO	– 20	1	120	3.0	1.8	2.3	-	35
$\mathbf{2^{Me}(Cl)}$	MMAO (1 000 eq.)	25	1	120	3.1	3.2	1.3	29	36
$\mathbf{2^{Me}(Cl)}$	MMAO (800 eq.)	– 20	2	120	1.7	1.6	2.1	39	37
5	MMAO	– 20	1	120	6.5	1.7	2.1	-	35
6	MMAO	– 20	1	120	7.3	2.7	1.8	-	35
7	MMAO	– 20	1	120	3.1	2.0	2.2	59	35
$\mathbf{8^{H}}$	MMAO	– 20	1	120	0.7	1.2	1.9	-	35
$\mathbf{8_{(meso/rac)}}$	MMAO	– 20	1	120	17.3	4.1	2.2	67	35
$\mathbf{8_{(meso/rac)}}$	MAO (80 eq.)	25	1.9	60	0.2	3.3	1.4	65	38
$\mathbf{8_{rac}}$	MMAO (1 000 eq.)	– 6	2.3	40-60	18.4	8.3	1.5	63	40
$\mathbf{8_{meso}}$	MMAO (1 000 eq.)	– 6	2.3	40-60	5.0	7.8	1.6	53	40
9	MMAO	– 20	1	70	38.8	5.6	2.2	56	35
9	MMAO	– 20	2	60	5.9	4.1	2.3	57	37
10	MMAO	– 20	1	120	11.8	5.7	1.8	59	35
14	MMAO (800 eq.)	– 20	2	120	0.02^{b}	3.4	2.4	60	37
15	MMAO (800 eq.)	– 20	2	120	0.02	4.5	2.1	53	37
16	MMAO (800 eq.)	– 20	2	120	0.8	6.6	2.9	54	37
17	MMAO (800 eq.)	– 20	2	60	8.3	3.2	2.6	52	37
18	MMAO (800 eq.)	– 20	2	120	1.6	3.2	4.1	59	37

2.1.3. Higher α–olefins

To date, very few examples of iron-based catalytic systems have been able to polymerize α-olefins higher than ethylene and propylene, most of the research has focused on the selective dimerization of a series of monomers. The iron-based complexes considered in this section are represented in **Fig. 1**, **Fig. 3** and **Fig. 4**; the polymerization data are summarized in **Table 3** (*vide supra* section 2.2).

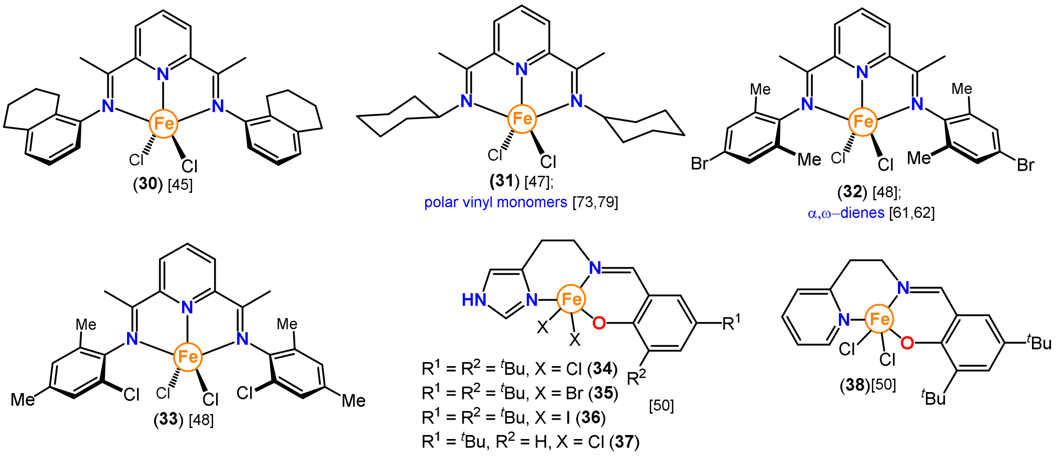


Fig. 4. Iron-based complexes used in polymerization of higher α-olefins.

Small *et al.* examined the dimerization of several α-olefins such as 1-butene, 1-hexene and 1-decene in presence of iron-based pre-catalysts bearing BIP ligands with small substituents on the *ortho* position of the *N*-aryl moiety [complexes **2**$^{\mathbf{Me}}$**(Cl)**, **4**$^{\mathbf{Me}}$, **11(Br)**, **12**, **13** and **30**]. Upon activation with MMAO (or MAO), these previously reported iron-based catalysts for ethylene and propylene polymerizations exhibited good activities (TOF < 49 000 h^{-1}) for the selective dimerization of α-olefins (up to 96%) [45]. For the complexes that bear substituents on the *N*-aryl groups of the BIP ligand [**2**$^{\mathbf{Me}}$**(Cl)**, **4**$^{\mathbf{Me}}$, **12**, **13** and **30**], investigation on the dimerization mechanism revealed that the first insertion of the α-olefin into the active iron hydride species occurs preferentially in a 1,2 fashion. This first stage is then followed by subsequent 2,1 insertion of the second α-olefin, which is more likely to be accompanied by β-H elimination rather than by the insertion of a third α-olefin. In contrast, the less congested iron-based complex **11(Br)** displays competitive 1,2/2,1 insertion mode of the primary olefin on the Fe-H species, similar to that found for the oligomerization of propylene. Further studies of the mechanism by theoretical calculations are in line with these experimental results [46].

Latterly, Berh *et al.* examined the dimerization of a series of aliphatic 1-alkene substrates by employing various iron-based complexes supported by BIP ligand (**4**$^{\mathbf{Me}}$, **11(Cl)**, **13**, **31** and 2,2'-bipyridineFeCl$_2$) [47]. In agreement with the work of Small *et al.*, activation of the iron-based pre-catalysts **4**$^{\mathbf{Me}}$ and **11(Cl)** with 500 equiv. of MAO lead to the oligomerization of linear 1-alkene substrates (1-butene, 1-pentene and 1-hexene). The formation of mainly branched dimers was achieved in low yield with the less congested **11(Cl)** catalyst, while linear dimers were obtained in moderate yields in presence of **4**$^{\mathbf{Me}}$. Moreover, dimerization of the 4-methyl-1-pentene and 4,4-dimethyl-1-pentene monomers were accomplished for the first time using complexes **4**$^{\mathbf{Me}}$ and **11(Cl)** combined with MAO. The regio-selectivity and activity of the catalysts were found to be slightly higher than that observed for the linear 1-alkenes monomers, but the activity decreases dramatically in presence of the di-substituted 4,4-dimethyl-1-pentene monomers. In contrast, aliphatic 1-alkenes bearing a methyl group on the C2 or C3 position (*e.g.* isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-1-pentene, 3-methyl-1-pentene…) were unable to be dimerized by these iron-based pre-catalysts, probably due to the steric repulsion between the substituted monomer and the catalyst that prevents its coordination on the metal center. Surprisingly, a small portion of co-dimers of propylene and isobutene (17%) were formed using the catalytic **31**/MAO system, in addition to a high ratio of dimers (63%) and small portion of trimers (20%) of homopropylene, whereas the binary 2,2'-bipyridine$FeCl_2$/MAO catalytic system afforded only traces of propylene dimers.

The iron-based complexes **2^{Me}(Cl)**, **5**, **32** and **33** proved to be inactive in the presence of 400 equiv. of MAO for the polymerization of 1-hexene [48]. The copolymerization of ethylene/1-hexene was also attempted using the **2^{Me}(Cl)**/MAO catalyst, resulting in low incorporation of hexene units into the copolymer chain (< 3.5%). Theoretical calculation studies of the copolymerization of ethylene/1-hexene with the related **1^{Me}(Cl)** complex were carried out by Ramos *et al.*, thereby revealing that the propagation step was more favorable for ethylene than for 1-hexene, in accordance with the experimental data [49].

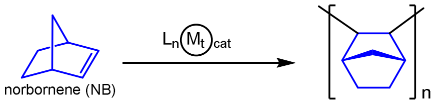
Upon activation with 400 equiv. of $EtAlCl_2$, complexes **34** – **38** are among the few that have proven effective for the polymerization of 1-hexene at 30 °C, with TOF ranging from 26 000 – 33 600 h^{-1}, producing low M_n polymers ($M_n \approx$ 1 050 g/mol) with narrow dispersity ($Đ \approx 1.2$) [50]. Microstructure analysis of the resulting atactic polymers by NMR spectroscopy showed the presence of highly branched structure with 17% of methyl, 3% of ethyl, 7% of propyl, 30% of butyl and 43% of longer chain. The presence of a high ratio of alkyl chain longer than butyl suggested that an initial 2,1 mode of insertion of the 1-hexene monomer takes place, which is followed by successive chain-walking processes that results in the formation of long branched chain in the polymer.

2.2. Iron-based complexes for the polymerization of other olefin monomers

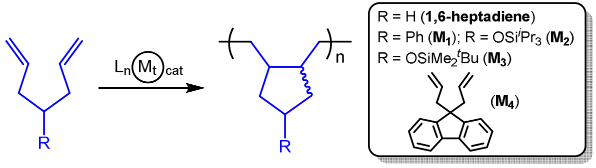
2.2.1. Norbornene and 1,6-heptadiene

Polymers containing repeated sequences of cycloalkane units have attracted great interest for designing high performance macromolecular architectures with unique physical, optical and mechanical properties [51]. Among the different methodologies, the vinyl/addition polymerization of norbornene (NB) [52] (**Scheme 3a**) and the transition metal catalyzed cyclopolymerization of α,ω-diene monomers [53] (**Scheme 3b**) are part of the processes used to prepare such types of polymers.

(a) Vinyl-/addition type of norbornene



(b) Cyclopolymerization of α,ω-dienes



Scheme 3. Metal-catalyzed (a) vinyl/addition polymerization of NB and (b) cyclopolymerization of α,ω-dienes.

To our knowledge, reports on iron-catalyzed both transformations are very limited. In this section, the iron-based complexes employed for the vinyl/addition polymerization of norbornene and the cyclopolymerization of α,ω-diene are shown in **Fig. 1**, **Fig. 3**, **Fig. 5** and **Fig. 6**, the polymerization data are depicted in **Table 3**.

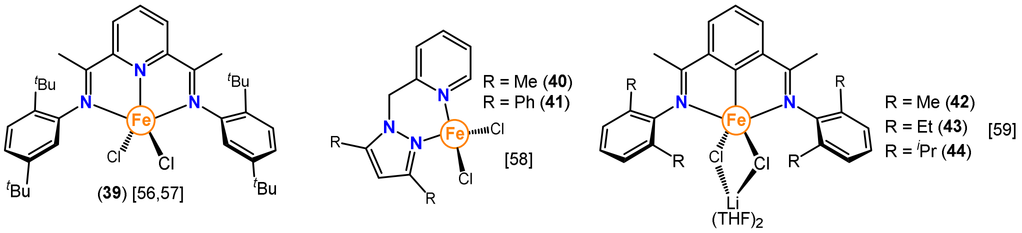
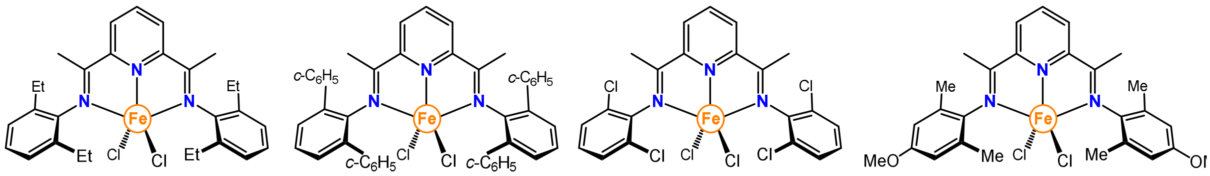


Fig. 5. Iron-based complexes used in vinyl/addition polymerization of norbornene.

A series of homo- and hetero-polynuclear cage carboxylate complexes of the type $\{[Fe_3O(OCO^tBu)_6(H_2O)_3]OCO^tBu\}$ and $[Fe_2NiO(OCO^tBu)_6(L)_3]$ (L = piperidine or morpholine) have been investigated by the groups of Janiak and Winpenny for the vinyl-addition polymerization of norbornene in presence of MAO or $AlEt_3/B(C_6F_5)_3$ combination [54]. The tri-nuclear iron cage complex $\{Fe_3O\}$ showed activity similar to that found for $Fe(acac)_3$ (TOF = 68 h^{-1}), whereas the hetero-metallic $\{Fe_2NiO\}$ displayed a much higher activity that is comparable to the binary $Ni(acac)_2$/MAO catalytic system (TOF = $10^4 – 10^5$ h^{-1}).

Homoleptic iron allyl complex, $Fe[1,3\text{-}C_3H_3(SiMe_3)_2]_2$, was found to be poorly active for the polymerization of norbornene after activation with MAO, affording only traces of polymeric materials [55]. Similarly, the group of Sacchi showed that the Fe-based complexes **1^{Me}(Cl)** and **5** combined with 880 equiv. of MAO were quasi-inactive for the polymerization of norbornene after 5 days at 50 °C [56]. In contrast, complex **39**, which bears an additional ^{t}Bu group on the *meta* position of the *N*-aryl substituents when compared to **5**, showed to display moderate activity for the polymerization of norbornene (TOF = 98 h^{-1}, M_v = 19 kg/mol) in presence of 500 equiv. of MAO at 30 °C. The obtained polymer had typical IR spectrum characteristic of a vinyl-addition type polymerization process [57]. The group of Darkwa performed the polymerization of norbornene using the iron-based complexes supported by pyrazolyl-pyridine type ligand, **40** and **41**, in combination with 1 000 equiv. of MAO [58]. Analysis of the resulting polymer was consistent with a vinyl-addition polymerization process. In addition, the authors showed that the activity of the catalytic systems was affected by the electronic and steric nature of the ligand, with complex **40** bearing methyl substituents on the pyrazolyl moiety displaying slightly higher activity (TOF ≈ 1 600 h^{-1}, M_n = 647 kg/mol) than the related phenyl analogue complex **41** (TOF ≈ 1 300 h^{-1}). In all cases, the related nickel complexes proved to be more active than the iron-based pre-catalysts under the same experimental conditions. Upon activation with 500 equiv. of MAO, both complexes **42** and **43** exhibited very low activity for the polymerization of norbornene at 15 °C, resulting in the formation of only traces of polymers. In contrast, the more sterically hindered complex **44** showed good activity (TOF = 1 400 h^{-1}), producing a high molecular weight polymer [59].

The copolymerization of norbornene and ethylene has been investigated in presence of the catalytic **1^{Me}(Cl)**/MAO system under chain transfer conditions using $ZnEt_2$ at different ratios [60]. The authors observed that the presence of $ZnEt_2$ did not influence either the catalytic activity or the copolymer composition, with only a very limited amount of norbornene comonomer incorporated into the copolymer chain (*ca* 0.7 – 1.6% of NB incorporation), in low yield. This observation is in line with the result described by Sacchi and coworkers using **1^{Me}(Cl)**/MAO catalytic system (*vide supra*).



(**45**) [61,62]
polar vinyl monomers [82,84]

(**46**) [61,62]

(**47**) [61,62]

(**48**) [61,62]

Fig. 6. Iron-based complexes used in α,ω-dienes polymerization.

Cyclopolymerization of 100 equiv. of 1,6-heptadiene monomer at room temperature was carried out by Takeuchi *et al.* using complexes **1^{Me}(Cl)**, **2^{Me}(Cl)**, **5**, **7**, **$8_{(meso/rac)}$**, **9**, **32**, **45** – **48** upon activation with 50 eq. of MMAO [61,62]. Analysis of the obtained polymers by NMR spectroscopy studies confirmed the entire cyclization of the monomer during the course of the polymerization. Pre-catalysts **$8_{(meso/rac)}$**, **32**, **47** and **48** were found to convert quasi quantitatively the monomer in 5 hours (yield up to 91%), producing polymers with relatively high M_n (11 000 – 14 000 g/mol). On the other hand, pre-catalysts **1^{Me}(Cl)**, **2^{Me}(Cl)**, **5**, **7**, **9**, **45** and **46** afforded polymers with lower M_n (2 460 – 7 500 g/mol) in good yields (62 – 89%). The polymers obtained with pre-catalysts **2^{Me}(Cl)**, **9**, **32**, **45**, **47** and **48** showed highly *cis*-fused five membered rings poly(1,6-heptadiene) microstructure (up to 90%), whereas complexes **1^{Me}(Cl)**, **5**, **7**, **$8_{(meso/rac)}$** and **46** gave rise to polymers with a mixture of *cis*/*trans* distribution. The formation of *cis*-fused cyclopentane emerges from a 2,1-insertion mode of one double bond of the monomer into the Fe-alkyl bond, resulting in an intermediate that preferentially adopts a chair conformation, which is then followed by a 1,2-insertion of the remaining double bond. Nevertheless, given that there have been only two studies described in this field, it appears rather hazardous to draw any rational conclusion about the general rules that could influence the selectivity and activity of the polymerization reaction.

Copolymerization of ethylene and 1,6-heptadiene have also been attempted using complex **1^{Me}(Cl)** and **2^{Me}(Cl)** combined with MMAO, but affords distinct homo-polymers rather than true copolymers. In addition, stereo-selective cyclopolymerization of the derived 1,6-heptadiene monomers **M$_1$**, **M$_2$** and **M$_3$** (**Scheme 3**) were also achieved using the binary **2^{Me}(Cl)**/MMAO catalytic system, affording exclusively *cis*-fused five-membered ring polymers in a similar manner to that found for the 1,6-heptadiene monomer (*cis*/*trans* ratio = >99/<1). Monomer **M$_4$** was also polymerized with the iron complex **1^{Me}(Cl)**/MMAO system, which resulted in the formation of *cis*/*trans*-fused five-membered rings mixture in the ratio of 65/35, respectively.

Table 3
Selected data for the polymerization of 1-hexene, 1,6-heptadiene and norbornene using Fe-based complexes.

Complex	Monomer (ratio/Fe)	Activation (Cocat./Fe)	T (°C)	Time (h)	Yield (%)	TOF (h^{-1})	M_n (g/mol)	$Đ$ (M_w/M_n)	Ref.
34	1-hexene (2 000)	$EtAlCl_2$ (400)	30	-	-	33 600	1 045	1.22	50
35	1-hexene (2 000)	$EtAlCl_2$ (400)	30	-	-	28 000	1 059	1.22	50
36	1-hexene (2 000)	$EtAlCl_2$ (400)	30	-	-	26 800	1 068	1.23	50
37	1-hexene (2 000)	$EtAlCl_2$ (400)	30	-	-	26 000	1 079	1.24	50
38	1-hexene (2 000)	$EtAlCl_2$ (400)	30	-	-	27 500	1 063	1.23	50
39	Norbornene (10 000)	MAO (500)	30	5	-	98	19 000[a]	-	57
40	Norbornene (2 500)	MAO (1 000)	30	1	61	610	647 000[b]	-	58
41	Norbornene (2 500)	MAO (1 000)	30	1	50	500	-	-	58
1^{Me}(Cl)	1,6-heptadiene (100)	MAO (50)	25	5	62	12.4	3 00	-	62
2^{Me}(Cl)	1,6-heptadiene (100)	MAO (50)	25	5	78	15.6	6 000	-	62
5	1,6-heptadiene (100)	MAO (50)	25	5	73	14.6	2 460	-	62
7	1,6-heptadiene (100)	MAO (50)	25	5	89	17.8	3 600	-	62
8	1,6-heptadiene (100)	MAO (50)	25	5	100	20	12 400	-	62
9	1,6-heptadiene (100)	MAO (50)	25	5	82	16.4	6 800	-	62
32	1,6-heptadiene (100)	MAO (50)	25	5	91	18.2	13 000	-	62
45	1,6-heptadiene (100)	MAO (50)	25	5	82	16.4	7 500	-	62
46	1,6-heptadiene (100)	MAO (50)	25	5	78	15.6	4 300	-	62
47	1,6-heptadiene (100)	MAO (50)	25	5	98	19.6	14 000	2.4	62
48	1,6-heptadiene (100)	MAO (50)	25	5	94	18.8	11 000	-	62

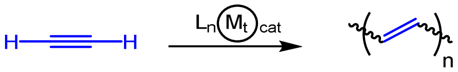
[a] M_v; [b] M_w

2.2.2. Styrene

In the 1990s, the preparation of syndiotactic polystyrenes attracted a lot of attention to achieve materials that display a high melting temperature and high chemical resistance [63]. Most of the systems used for the stereo-selective polymerization of styrene are based on group 3, 4 and rare-earth catalysts as well as few examples of complexes based on group 10 [64]. However, to our knowledge, only two examples of coordination-insertion polymerization of styrene using iron-based catalytic systems have been described in the literature, one of which failed to promote the polymerization of styrene (*vide infra* **Fig. 8**, complexes **49** and **62**) [65]. The only active iron systems were reported by Schellenberg using the complexes **1^{Me}(Cl)** and **2^{Me}(Cl)** (**Fig. 1**) in the presence of 300 equiv. of MAO, producing syndiotactic polystyrenes but with very low yields [66].

2.2.3. Acetylene

Conjugated polymers are part of a large class of materials that exhibit high electrical conductivity, after appropriate doping, for applications as organic compounds in microelectronics. Polyacetylene represents the simplest conjugated polymer that can be prepared by conventional Z-N catalysis (**Scheme 4**) [67]. However, similar to the cyclopolymerization of non-conjugated dienes, there has been very few examples of iron-based complexes reported to date for the polymerization of acetylene. The iron-based complexes used for this transformation are depicted in **Fig. 1**.



Scheme 4. Polymerization of acetylene with metal-based complexes.

The group of Britovsek has explored the polymerization of acetylene by combining pre-catalyst **1^{Me}(Cl)** and 100 equiv. MAO [68]. This system led to an extremely active catalyst (TOF up to 62 500 h^{-1}), with the formation of a polyacetylene/toluene gel in presence of [**1^{Me}(Cl)**] = 100 µM, while the production of polyacetylene film was noted at lower catalyst concentration [**1^{Me}(Cl)**] < 20 µM. The characterization of the polymers by IR spectroscopy revealed the presence of a mixture of *trans*/*cis* polyacetylene microstructure. Interestingly, the same group performed the polymerization of acetylene with **1^{Me}(Cl)**/MAO (1/100) under reversible chain transfer condition by using 500 equiv. of $Zn(Et)_2$ as chain transfer agent (*vide supra*) [69]. An even number of short-chain oligomers has been identified as the main product of the reaction. Furthermore, the absence of other irreversible chain termination has led to the quantitative production of oligomers with respect to zinc, which indicates the occurrence of a CCG process, similar to that found with ethylene. The presence of branched and cyclic oligomers has also been observed, suggesting a mechanism involving an intramolecular sigma-bond metathesis. Attempts to copolymerize ethylene and acetylene with **1^{Me}(Cl)**/MAO was unsuccessful and resulted in the formation of two disparate homopolymers. In addition, a striking variation in product selectivity was observed using the less congested pre-catalyst **4^{Me}** in presence of MAO, which led to the formation of benzene via a metallacyclic mechanism, or 1,3-hexadiene when $Zn(Et)_2$ was used as chain transfer agent [70].

2.3. Iron-based complexes for the polymerization of polar vinyl monomers.

The polymerization of polar vinyl monomers using iron-based systems has been mainly investigated through radical pathway and no control of the selectivity could be obtained [71]. On the other hand, several research groups have been interested to investigate the coordination-insertion polymerization of polar vinyl monomers [**Fig. 7**, *tert*-butyl acrylate (*t*-BA), methyl acrylate (MA), methyl methacrylate (MMA), *n*-butyl vinyl ether (NBVE), isobutyl vinyl ether (IBVE), *n*-vinylcarbazole (NVC)] and their copolymerization with olefins in presence of catalysts based on late transition metal systems. Most research in this area has focused on the use of Ni and / or Pd metal-based catalysts [72], still, several reports on iron complexes have been described in the literature (**Fig. 8**) and will be outlined here with the polymerization data gathered in **Table 4**.

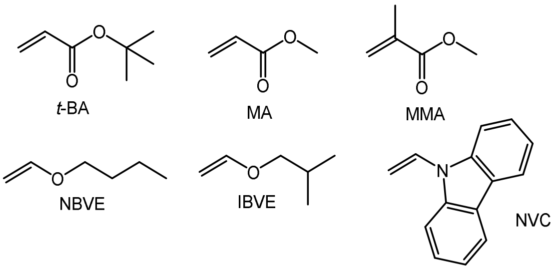


Fig. 7. Selected polar vinyl monomers used in iron-catalyzed coordination polymerization

To date, the polymerization mechanism of polar vinyl monomer with iron-based complexes activated by an excess of alkyl aluminum (or MAO, MMAO) remains unclear. Several initial studies conducted have not made it possible to decide among a radical, ionic, coordination-insertion, or group-transfer polymerization (GTP) type mechanism [73,74,75,76,77].

One of the first attempt to polymerize polar vinyl monomers in presence of an iron-based catalyst has been reported by the group of Gibson, using complex **1^{Me}(Cl)** or the related **1^{Me}(acac)$^+$** cationic species (**Fig. 8**) combined with either 100 equiv. of MAO or 1 equiv. of $B(C_6F_5)_3$/10 equiv. $AlMe_3$ [78]. With the aim to achieve the copolymerization of ethylene and polar vinyl comonomers such as methyl acrylate (MA), methyl methacrylate (MMA), 2-vinyl-1,3-dioxolane, vinyl acetate, acrolein and acrylonitrile with these catalysts systems, the authors noted that no copolymer could be produced under these experimental conditions. However, the catalyst activity with respect to ethylene polymerization was not influenced by the presence of 1 000 equiv. of MMA monomer, whereas a significant decrease in activity was observed when MA or 2-vinyl-1,3-dioxolane were used as comonomers. Moreover, in each case, only homopolymers of ethylene were formed with a negligible amount of polar vinyl homopolymer. Conversely, vinyl acetate, acrolein and acrylonitrile were found to deactivate the catalytic system. In addition, they noted that these catalytic systems did not perform the homo-polymerization of any polar vinyl monomers reported in this study.

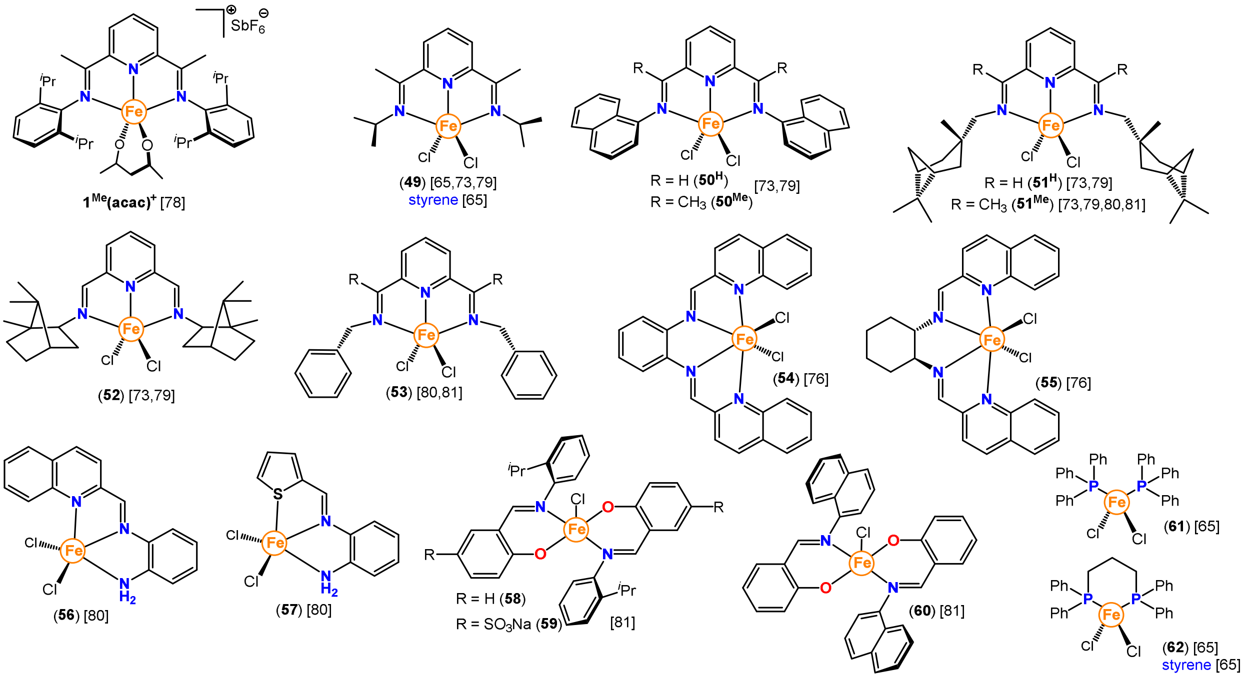


Fig. 8. Iron-based complexes used in coordination polymerization of polar vinyl monomers.

The first achievement in homopolymerization of a polar monomer with an iron catalyst was realized by the group of Repo who described the polymerization of *t*-BA with the (BIP)FeCl$_2$ complexes **1^{Me}(Cl)**, **2^{Me}(Cl)**, **11(Cl)**, **31** and **49** – **52** after activation with 250 equiv. of MAO [73, 79]. Under similar experimental conditions, the activity of the catalysts was found to be dependent on the nature of the ligand, with the *N*-alkyl substituted (BIP)FeCl$_2$ complexes being marginally more active than the *N*-aryl ones. Kinetic studies of the performance of complexes **1^{Me}(Cl)** and **49** revealed a high initial polymerization activity, which decreases with time to reach a lower steady state values (TOF = 66 – 118 h^{-1}) [65]. The polymers produced with these catalysts at 20 °C are mainly syndiotactic-enriched attatic materials (*r* dyads ranging from 42 – 67% for **1^{Me}(Cl)**, **2^{Me}(Cl)**, **11(Cl)**, **31**, **49, 50^{Me}** and *r* triads ranging from 34 – 42% for **49**, **50^{H}**, **51^{H}**, **51^{Me}**, **52**) resulting probably from a chain-end control.

In presence of 250 equiv. of MAO, the iron-based complexes **54** and **55** supported by tetradentate *N,N,N,N* ligands have shown to display low activity (TOF = 66 and 88 h^{-1}, respectively) for the polymerization of *t*-BA [76]. The polymers produced by these catalytic systems displayed similar M_n and *Đ* but lower triads percentages were observed (21 – 27%) when compared to the (BIP)FeCl$_2$/MAO systems.

The (BIP)FeCl$_2$ complexes **11(Cl)**, **23**, **51^{Me}** and **53** along with the iron-based complexes **56** – **60** have shown to display from low to moderate activity for the polymerization of *t*-BA at room temperature when activated by 2 300 equiv. of MAO [80,81]. An increase of the steric hindrance of the BIP ligand increased the performance of the catalytic systems and the molar masses of the resulting polymers. Complexes **56** and **57** showed lower activity than the substituted BIP iron-based complexes **23**, **51^{Me}**, **53** but higher than the non-substituted complex **11(Cl)**. Regarding the (bis)salicylaldiminato iron-based pre-catalysts, the presence of sulfonated substituent (**59**) or naphtyl terminal group (**60**) showed lower monomer conversions when compared to the related complex **58**.

Subsequently, the polymerization of *t*-BA was carried out in presence of iron-based complexes bearing phosphine ligand (**61**, **62**) upon activation with 250 equiv. of MAO [65]. When compared to the (BIP)FeCl$_2$ complexes **1^{Me}(Cl)** and **49**, the binary **61**/MAO and **62**/MAO catalytic systems are more active but behave similarly in term of dependence of monomer concentration and polymerization temperatures. As suggested by the authors, the higher activity of complexes **61** – **62** could emerge from i) the steric hindrance of the complexes, ii) the difference in electron density at the metal center and iii) the distinct coordination sphere around the active metal species.

One of the first attempt to polymerize MMA monomer with an iron-based catalyst has been reported by Kim *et al.* using either the complexes **1^{Me}(Cl)**, **2^{Me}(Cl)** or **45** in presence of 500 equiv. of MAO, however, these catalytic systems have proved to be poorly active (TOF $<$ 10 h^{-1}) [82]. Independently, the polymerization of MMA has also been investigated upon activation with different aluminum co-reagents at 30 °C with the (BIP)FeCl$_2$ complexes **1^{Me}(Cl)** and **2^{Me}(Cl)** [75]. Among the catalytic systems used for the polymerization of MMA, the combination of complexes **1^{Me}(Cl)** and 100 equiv. of Al^{i}Bu$_3$ exhibited the highest activity (TOF = 708 h^{-1} *vs* **1^{Me}(Cl)**/MMAO TOF = 375 h^{-1}), producing syndiotactic-rich polymer (*rr* = 54%). In this study, the presence of 50 equiv. of galvinox did not influence the activity of the binary **1^{Me}(Cl)**/Al^{i}Bu$_3$ catalytic systems as well as the tacticity, M_n and $Đ$ of the resulting polymer. Complex **51^{Me}** has been used for the polymerization of MMA at room temperature in presence of 9 000 equiv. of MAO, affording syndio-rich atactic polymer (*rrrr* = 52%) with high M_n (1 620 kg/mol) and narrow dispersity ($Đ$ = 1.5) in moderate yield (TOF = 833h^{-1}) [80]. The polymerization of MMA and MA were also attempted by the group of Repo and Abu-Surrah with complexes **54** and **55** after activation with an excess of MAO but resulted in low conversion of monomers, producing polymers with rather low molar masses, particularly for MMA [76].

In 2008, the group of Miri described the homopolymerization of MA and its copolymerization with ethylene using the binary **4^{Me}**/MAO catalytic systems [83]. In presence of MAO cocatalyst, the activity of complex **4^{Me}** for the homopolymerization of MA has shown to decrease dramatically within the initial hour, until reaching a steady state value that continues to decline slightly in 18 hours. The polymers produced with complex **4^{Me}** in presence of 100 equiv. of MAO have moderately high M_n, while an increase of the amount of MAO led to the formation of lower M_n, probably due to the occurrence of chain transfer reaction with the aluminum co-reagent. In a similar manner to that found by the group of Gibson (*vide supra*), the copolymerization of MA and ethylene in presence of **4^{Me}**/MAO resulted in the formation of two homopolymers rather than a true copolymer.

The iron-based phosphine supported complexes (**61**, **62**) have been found to promote the polymerization of MA in the presence of 250 equiv. of MAO at 25 °C with substantially similar activity (TOF = 2 900 h^{-1} for complex **61** and TOF = 2 100 h^{-1} for complex **62**), while affording polymers with higher M_n for complex **62** (460 kg/mol) compared to complex **61** (110 kg/mol). Upon increasing the temperature of the polymerization to 70 °C, the activity of both catalysts increased in the same order of magnitude (two times higher than that found at 25 °C) and the resulting M_n reached a comparable value of *ca* 450 kg/mol [77].

The polymerization of vinyl ethers (NBVE and IBVE) have been carried out by the group of Kim using the (BIP)FeCl$_2$ complexes **1^{Me}(Cl)**, **2^{Me}(Cl)**, **45** and **11(Cl)** combined with 100 equiv. of MAO [84]. Complex **11(Cl)** with no substituent on the *ortho* positions showed much lower activity than the other complexes **1^{Me}(Cl)**, **2^{Me}(Cl)** and **45**, while affording the highest polymer M_n for both monomers. In all cases, the poly(vinyl ether) were mainly syndio-rich atactic materials. Overall, no specific relationship between the steric hindrance of the catalyst and the resulting molecular weight and tacticity of the polymer could be drawn.

The binary **51^{Me}**/MAO catalytic system has been shown to promote the polymerization of *n*-vinylcarbazole (NVC) (TOF = 115 h^{-1}), producing poly(*n*-vinylcarbazole) with high M_n (128 kg/mol) and narrow molecular weight distribution (*Đ* = 1.8) [80].

Table 4
Polar vinyl monomer coordination polymerization with selected iron-based catalytic systems

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (h)	Conv. (%)	TOF (h^{-1})	M_n (kg/mol)	*Đ* (M_w/M_n)	*r dyads* (%)	Ref.
1^{Me}(Cl)	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	48	66	34.4	2.9	54	73
2^{Me}(Cl)	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	70	96	98.4	1.9	55	73
11(Cl)	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	63	87	67.7	2.0	53	73
11(Cl)	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	72	46.1	2.3	-	80
23	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	213	46.8	2.5	-	80
31	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	68	94	61.8	2.4	42	73
49	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	86	118	63.7	2.2	59	73
50^{Me}	*t*-BA (1.1 M) 3 300	MAO (250)	20	24	65	89	83.4	2.0	65	73
50^{H}	*t*-BA (1.1 M)	MAO (250)	20	24	-	67	59.1[a]	2.3	34	79
51^{H}	*t*-BA (1.1 M)	MAO (250)	20	24	-	102	63.5[a]	2.3	36	79
51^{Me}	*t*-BA (1.1 M)	MAO (250)	20	24	-	86	95.7[a]	2.1	37	79
51^{Me}	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	428	95.9[a]	2.1	-	80
52	*t*-BA (1.1 M)	MAO (250)	20	24	-	96	70.4[a]	2.3	42	79
53	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	272	86[a]	2.0	-	80
54	*t*-BA (1.1 M)	MAO (250)	20	24	-	66	76	1.9	27[b]	76

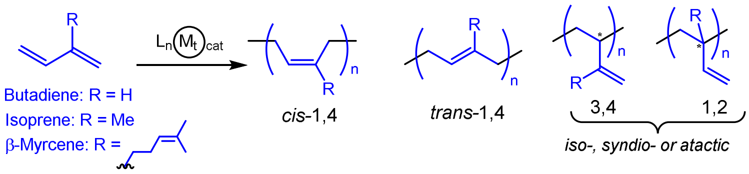
Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (h)	Conv. (%)	TOF (h^{-1})	M_n (kg/mol)	*Đ* (M_w/M_n)	*r dyads* *(%)*	Ref.
55	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	88	82	1.9	21[c]	76
56	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	152	-	-	-	80
57	*t*-BA (1.1 M)	MAO (2 300)	20	24	-	96	-	-	-	80
58	*t*-BA (2.0 M) 11 430	MAO (2 300)	25	12	-	546	45.9	1.1	-	81
59	*t*-BA (2.0 M) 11 430	MAO (2 300)	25	12	-	163[b]	41.8	1.1	-	81
60	*t*-BA (2.0 M) 11 430	MAO (2 300)	25	12	-	124	-	-	-	81
51^{Me}	MMA (148 500)	MAO (9 000)	20	12	-	833	1 620	1.5	52[d]	80
54	MMA (3.0 M)	MAO (250)	20	24	-	27	2.0	1.7	-	76
55	MMA (3.0 M)	MAO (250)	20	24	-	42	4.3	3.2	-	76
1^{Me}(Cl)	MMA (2 000)	MMAO (200)	30	24	-	375[b]	8.1[a]	2.1	55[d]	75
1^{Me}(Cl)	MMA (2 000)	$AlEt_3$ (50)	30	24	-	625	13.9[a]	2.5	69[d]	75
1^{Me}(Cl)	MMA (2 000)	Al^iBu_3 (100)	30	24	-	708	9.0[a]	2.5	54[d]	75
2^{Me}(Cl)	MMA (2 000)	MMAO (200)	30	24	-	333	9.5[a]	2.0	67[d]	75
2^{Me}(Cl)	MMA (2 000)	$AlEt_3$ (50)	30	24	-	292	12.9[a]	2.1	66[d]	75
2^{Me}(Cl)	MMA (2 000)	Al^iBu_3 (100)	30	24	-	333	14.7[a]	2.4	66[d]	75
54	MA (3.0 M)	MAO (250)	20	24	-	157	35.7	1.6	-	76
55	MA (3.0 M)	MAO (250)	20	24	-	171	41.0	2.2	-	76
4^{Me}	MA (5.55 M) (35 000)	MAO (100)	60	1	-	139	279	2.4	54	83
4^{Me}	MA (5.55 M) (35 000)	MAO (425)	60	1	-	534	179	2.3	53	83
4^{Me}	MA (5.55 M) (35 000)	MAO (1 850)	60	1	-	278	56.5	1.9	51	83
61[g]	MA (7.4 M) (27 500)	MAO (250)	25	3	-	2 900[e]	110[e]	3.6	51[e]	77
61[g]	MA (7.4 M) (27 500)	MAO (250)	70	3	-	5 500[e]	425[e]	2.4	52[e]	77
62[g]	MA (7.4 M) (27 500)	MAO (250)	25	3	-	2 100[e]	460[e]	1.9	50[e]	77
62[g]	MA (7.4 M) (27 500)	MAO (250)	70	3	-	5 000[e]	375[e]	1.7	49[e]	77
1^{Me}	NBVE (2 700)	MAO (100)	30	24	-	14	61	2.4	51	84
2^{Me}	NBVE (2 700)	MAO (100)	30	24	-	21	49	4.0	56	84

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (h)	Conv. (%)	TOF (h^{-1})	M_n (kg/mol)	*Đ* (M_w/M_n)	*r dyads* (%)	Ref.
11(Cl)	NBVE (2 700)	MAO (100)	30	24	-	6	81	2.7	56	84
45	NBVE (2 700)	MAO (100)	30	24	-	24	79	3.0	56	84
1^{Me}	IBVE (2 700)	MAO (100)	30	24	-	25	27	2.5	53	84
2^{Me}	IBVE (2 700)	MAO (100)	30	24	-	22	9	2.5	55	84
11(Cl)	IBVE (2 700)	MAO (100)	30	24	-	4	87	2.6	58	84
45	IBVE (2 700)	MAO (100)	30	24	-	27	62	2.3	54	84

[a] extracted from M_w; [b] [*t*-BA] = 0.6 mol/L, 12 h; [c] [*t*-BA] = 1.6 mol/L, 12 h; [d] r triads; [e] extracted from figure

3. Iron-catalyzed polymerization of 1,3-diene monomers

The polymerization of 1,3-dienes has seen a considerable surge of interest over the past two decades, due to the wide range of industrial applications of the resultant polymers that can display different thermal, mechanical and physical properties depending on its chain microstructures (*e.g. cis*-1,4, *trans*-1,4, iso-, syndio-, atactic-3,4 and/or -1,2 vinyl arrangements, **Scheme 5**) [85]. Over the different polymerization methodologies (*e.g.* radical [86], cationic [87], or anionic [88] processes), the fine control of the stereo/regio-regularity of the chain microstructure can be reached, to some extent, only through coordination-insertion polymerization using Ziegler-Natta type catalysts.

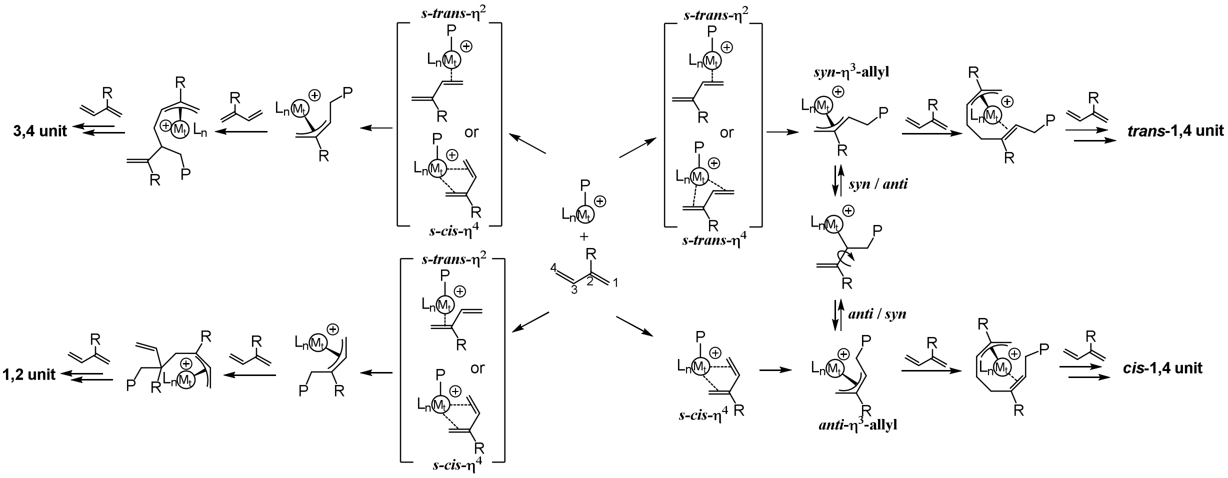


Scheme 5. Polymer microstructures from the polymerization of 1,3-dienes (limited to mono-substituted dienes for clarity)

For many years, most of the research works have been focusing on the synthesis of *cis*-1,4 polydienes, which is one of the major component used state in the tire manufacturing and elastomer industry. More recently, *trans*-1,4 polydienes have shown to display excellent anti-fatigue properties, among others, that can be used in long durability “green” tires. On the other hand, the selective crosslinking of the pendant vinyl-groups in 1,2- (or 3,4-) polydiene can improve the performance of the material with wet-skid and low rolling resistance tread [89].

Several single-site metal-based systems of rare earth [90] (mainly neodymium) and transition [91] metals (mainly titanium, nickel and cobalt) have shown to be highly active for the polymerization of 1,3-dienes, affording simultaneously high molar masses and control over the microstructure. It is generally accepted that the stereo- and regio-selectivity of 1,3-dienes polymerization depend on the mode of coordination of the incoming diene monomer (*s*-η^2-*trans*, *s*-η^4-*trans* or *s*-η^4-*cis*) and the conformation of the terminal η^3-allyl unit of the growing polymer chain that is bound to the metal center in *anti* or *syn* fashion, which are exchangeable (**Scheme 6**) [92]. In that context, it was shown that stereo- and regio-control can be attained providing that suitable ligand design (steric and electronic) and/or appropriate alkylating agent are combined.

In the case of iron-based catalysts, coordinative polymerization of 1,3-dienes has not been intensively investigated when compared to the field of ethylene polymerization. A majority of the works related to this topic have been reviewed in 2010 by Ricci *et al.* [93,94] and in a book chapter by Olivier-Bourbigou and coworkers (2015) [25c]. Several research works focusing on well-defined iron-based catalysts have been published since these last bibliographic surveys; therefore, we will present (as far as possible) a comprehensive coverage of the literature in this field. The first section will deal with iron complexes supported by bidentate ligands, the second part will be devoted to iron-based counterparts bearing tridentate ligands and, finally, the last section will briefly present studies on the use and impact of phosphorous additives to the catalytic behavior.



Scheme 6. Proposed mechanism of coordinative 1,3-diene polymerization, relevant step for the formation of 1,2/1,4/3,4 microstructure.

The first report on the use of an iron complex for the polymerization of 1,3-dienes was described in 1964 by Noguchi *et al.* [95]. Polymerization of butadiene (B) and isoprene (I) were performed at 30 °C for 20 hours using a combination of $Fe(dmg)_2$ (dmg = dimethylglyoximate) and $AlEt_3$ (Al/Fe = 4). Polybutadiene with content mixture of 1,2/*trans*-1,4/*cis*-1,4 units = 63/13/24 and polyisoprene with a quasi-equal amount of 3,4-/*cis*-1,4 units = 45/54 along with a very small portion of 1,2 content (1%) were obtained.

In 1970, Swift *et al.* [96] studied various cyano-substituted pyridine ligands in combination with $Fe(acac)_3/AlEt_3$ (or Al^iBu_3) for the polymerization of I and B, most of them exhibiting very low activity or none. The best result was obtained with $Fe(acac)_3$/phenyl-2-pyridylacetonitrile/$AlEt_3$ (1/1/3) system, with a TOF of 21 h^{-1} at 25 °C, affording polyisoprene of composition *cis*-1,4/3,4/1,2 units ≈

48/50/2. In parallel, butadiene polymerization was carried out using Fe(acac)$_3$/2-cyanopyridine/AlEt$_3$ (1/1/3) producing polybutadiene (TOF = 17 h^{-1}) with an equal fraction of *cis*-1,4 and 1,2 structures.

3.1. Iron-based catalysts bearing bidentate ligand for the polymerization of 1,3-dienes

The molecular structures of the iron complexes bearing bidentate ligand discussed in this section are depicted in **Fig. 9** and the polymerization data are gathered at the end of this section in **Table 5**.

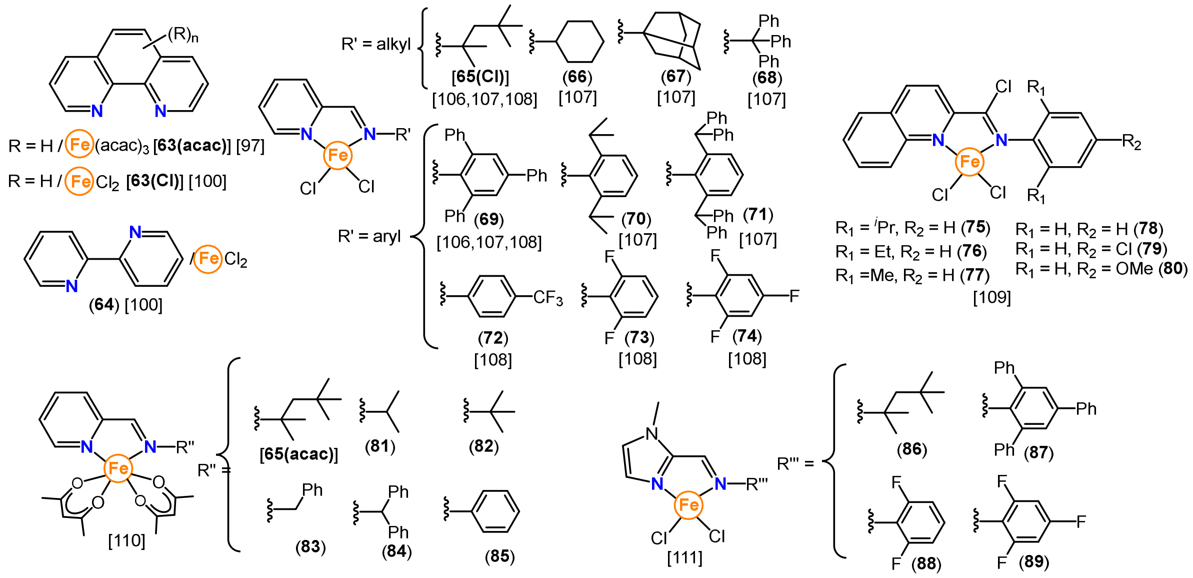


Fig. 9. Iron-based complexes (bidentate ligands) for the polymerization of 1,3-dienes.

The group of Wu described in 1982 the polymerization of butadiene using a catalytic system based on Fe(acac)$_3$/Al^{i}Bu$_3$ (1/50) in presence of 1 equiv. of 1,10-phenanthroline ligand [**63(acac)**] [97]. Butadiene was found to be converted in high yield at 18 °C in toluene (TOF = 1 668 h^{-1}), with a *cis*-1,4/1,2/*trans*-1,4 = 50/46/4 microstructure of the resulting polybutadiene. In addition, the authors suggested that Fe(III)(acac)$_3$ was probably reduced to Fe(II) after reacting with Al^{i}Bu$_3$ and in presence of 1,10-phenanthroline, producing a putative Fe(1,10-phenanthroline)(^{i}Bu)$_2$ complex. Using the same catalytic system, Xie *et al.* showed that the polymerization of isoprene in toluene was able to provide polymer in high conversion, with microstructure consisting of 3,4/*cis*-1,4 units of *ca* 30/70, while in apolar hexane solvent, much lower yield was observed [98]. Independently, Hsu *et al.* showed that an additional amount of water (H$_2$O/Al^{i}Bu$_3$ = 0.064) was needed to afford polyisoprene with excellent yield at 10 °C in hexane. The resulting microstructure of the polymer revealed a content mixture of 3,4/*cis*-1,4 units of 81/19 with no trace of 1,2 and *trans*-1,4 fractions [99]. The author suggested that the generation of "*a more electron accepting bridged alkyl aluminoxane*" could be accountable for this high activity.

After these primarily reports, it was only at the beginning of the 21st century that Ricci and coworkers revitalized the field of coordinative 1,3-dienes polymerization with iron-based catalysts. Several catalytic systems have been studied by combining $FeCl_2$ with various aromatic and aliphatic nitrogen ligands, as well as phosphine bidentate ligands, in presence of alkyl aluminum cocatalysts (Al^iBu_3, $AlEt_3$ and MAO) [100]. The authors found that most of the active Fe-based catalysts consist of complexes bearing bidentate aromatic nitrogen ligands when activated with an excess of MAO, whereas the use of Al^iBu_3 or $AlEt_3$ as cocatalysts was less effective in term of activity and control over the selectivity. Conversely, the use of aliphatic nitrogen bidentate ancillary ligands displays very low activities and regio-/stereo-selectivities, while iron complexes bearing bidentate phosphine ligands were essentially inactive. In this study, $FeCl_2$/MAO system with 1,10-phenanthroline [**63(Cl)**] or 2,2'-bipyridine (**64**) have shown to exhibit very high catalytic activities for the polymerization of 1,3-dienes at 20 °C when activated with 1000 equiv./Fe of MAO. For example, the system **63(Cl)**/MAO enabled the polymerization of butadiene with a TOF of *ca* 2.73×10^6 h^{-1}, affording polymer with a mixed structure of *cis*-1,4/1,2 content = 30/70. Moreover, the resulting polymer had a high molecular weight (M_w = 1 517 kg/mol) with narrow molecular weight distribution (M_w/M_n = 1.2), which indicated the presence of a single-site active species. Various substituted-1,10-phenanthroline ligands combined with $FeCl_2$ were also screened for the polymerization of butadiene, after activation with MAO, and proved to be less active when compared to the system bearing unsubstituted 1,10-phenanthroline ligand. In particular, the use of 2,9-dimethyl-1,10-phenanthroline ligand showed lower catalytic activity with respect to the polymerization of butadiene (TOF = 340 h^{-1} at 20 °C), probably because of an increase of the steric hindrance around the coordination sphere of the metal catalyst that could disrupt the coordination of the incoming monomer.

Using **64**/MAO catalytic system at 20 °C, polybutadiene (TOF = 2.73×10^6 h^{-1}) with *cis*-1,4/1,2 structures (33/67) and syndiotactic sequence (*rrrr* = 36.9%) was obtained. As noted above, the use of **64**/Al ^{i}Bu$_3$ or $AlEt_3$ exhibited lower catalytic activity (TOF ≈ 49×10^3 and 25×10^3 h^{-1}, respectively) as well as a slight decrease of 1,2 selectivity, emphasizing the role of the cocatalyst toward the selectivity of the polymerization [100]. In addition, it was shown that the selectivity was dependent on the reaction temperature, with low temperature leading to a high increase content of 1,2 units at – 78 °C (content of 1,2 fraction = 91% and *rrrr* = 52.5%), while the activity of the catalysts decreased drastically (TOF = 18 h^{-1}). Similar results were obtained using $(2,2'\text{-bipyridine})_2FeEt_2$ complex when activated with MAO[101].

In the case of isoprene, high activity was observed using **64**/MAO (TOF ≈ 800×10^3 h^{-1}) [100], affording polyisoprene with a microstructure containing *cis*-1,4/3,4 units = 33/67. As in butadiene polymerization, a significant increase of 3,4-selectivity was noticed at – 78 °C (*cis*-1,4/3,4 units = 7/93), likely corresponding to syndiotatctic polyisoprene sequence, although in this case the yield was poor (TOF = 14 h^{-1}). Since the binary **64**/MAO produces stereo-regular 3,4-polyisoprene, Rosa *et al.* used this recipe at – 30 °C to prepare a syndiotactic-rich polyisoprene with *cis*-1,4/3,4 contents of 15/85 and *rrrr* = 53%, which, after hydrogenation, gave for the first time a syndiotactic-rich poly(3-methyl-1-butene) [102].

Polymerization of 1,3-pentadiene (PD) and 2,3-dimethyl-1,3-butadiene (DMB) was also undertaken with **64**/MAO catalytic system at 20 °C, yielding quantitatively poly(1,3-pentadiene) (TOF = 79 x 10^3 h^{-1}) with structure content of *cis*-1,4/1,2 units (30/60) and highly stereo-regular poly(2,3-dimethyl-1,3-butadiene) (TOF = 703 x 10^3 h^{-1}) with *cis*-1,4 units = 99%), respectively.

Later, the same group reported the polymerization of 3-methyl-1,3-pentadiene (3-MP) using **64**/MAO at – 30 °C affording, for the first time, highly crystalline poly(3-methyl-1,3-pentadiene) with syndiotactic 1,2 sequence (1,2 content of 99% and *rrrr* $\geq$ 99%) [103]. However, the activity of the catalyst was found to be very low under these conditions (TOF = 3 h^{-1}).

The origin of the regio-selectivity of the **64**/MAO catalytic system toward the polymerization of I and 3-MP has been recently investigated by DFT calculation by the group of Luo [104]. The authors started their studies by representing the active species in the form of the cationic complex $[(2,2'\text{-bipyridine})_2\text{FeMe}]^+$. The calculation revealed that in this active species, the 2,2'-bipyridine is a redox-inert ligand that contrasts with that observed in related redox-active iminopyridine and bis(imino)pyridine ligands [105]. More importantly, calculation of the insertion pathway suggested that the 3,4-regio-selectivity of isoprene was favored over the 1,4-insertion, similarly, it appears that the steric factor also governs the 1,2-regio-regularity of the polymerization of 3-MP with the $(2,2'\text{-bipryidine})_2\text{FeCl}_2$/MAO.

Subsequently, Ritter and coworkers [106] have described the selective polymerization of isoprene with high catalytic activity using well-defined substituted iminopyridyl iron-based complexes [**65(Cl)** and **69**], upon activation with $AlEt_3$ or Al^iBu_3 and $[Ph_3C][B(C_6F_5)_4]$. In this study, the authors found that an inversion of selectivity of the polymerization could be reached depending on the nature of the substituent attached to the imino group. Using an octyl-substituted iminopyridyl iron complex **65(Cl)** with $Fe/Al^iBu_3/[Ph_3C][B(C_6F_5)_4]$ = 1/3/1, polyisoprene with microstructure containing *trans*-1,4/*cis*-1,4/3,4 units = 91/1/8 was quantitatively achieved at 23 °C (TOF = 500 h^{-1}). On the other hand, *cis*-1,4 polyisoprene with *trans*-1,4/*cis*-1,4/3,4 content = 1/66/33 was obtained, to some extent, after 1 hour at 23 °C (TOF = 1 x 10^3 h^{-1}) with supermesityl-substituted iron complex **69** using $Fe/AlEt_3/[Ph_3C][B(C_6F_5)_4]$ = 1/3/1. Moreover, the *cis*-1,4% of polyisoprene could be improved up to 85% at lower temperature with content of 3,4 decreasing to 14% (TOF = 246 h^{-1} at – 78 °C). With these catalytic systems, the M_n were as expected for one polymer chain per Fe metal, with relatively narrow molecular weight distributions ($Đ$ = 1.7 – 2.0, M_w = 62.5 – 75 kg/mol). It should be noted that the replacement of the alkyl group of the aluminum agent (^{i}Bu *vs* Et) has little influence on the selectivity of the polymerization. In addition, the authors conducted the polymerization of bio-sourced 1,3-diene monomers, β-myrcene and farnesene isomers (mixture of α and β isomers), and they have shown that only the β isomers could be polymerized with pre-catalyst **65(Cl)** and **69**. As for isoprene, the selectivity of the polymerization of both monomers, after activation with $AlR_3/[Ph_3C][B(C_6F_5)_4]$ (R

= ^{i}Bu for **65(Cl)** and R = Et for **69**), strongly depends on the nature of the imino group, with complex **65(Cl)** producing poly-β-myrcene or poly-β-farnesene with high content of *trans*-1,4 units (88 and 87%, respectively), while complex **69** yields polymers consisting of large amount of *cis*-1,4 units (76 and 71%, respectively).

In 2016, Chen and coworkers [107] expanded this work by using iron-based complexes supported by various alkyl- (**65(Cl)** – **68**) and aryl- (**69** – **71**) substituted-iminopyridyl for the polymerization of isoprene. Different alkylaluminum reagents were assessed in presence of pre-catalyst **66**. Only an excess of MAO (500 equiv./Fe) was capable of producing polyisoprene in high yield (TOF = 804 h^{-1} at 25 °C) and high M_n (> 60 kg/mol), while the use of 150 equiv. of $AlEt_2Cl$ gave polymer in high yield but with low molar masses, and Al^iBu_3 or $AlEtCl_2$ were not efficient. After 2 hours at 25 °C in presence of 500 equiv. of MAO, the aryl-substituted-iminopyridine iron based complexes **69** – **71** afforded polymers with higher M_n = 103 – 182 kg/mol and TOF = 1 038 – 1 224 h^{-1} than the related alkyl-substituted Fe pre-catalysts **65(Cl)** – **68** (M_n = 61 - 79 kg/mol and TOF = 726 – 1 038 h^{-1}). The authors suggested that the electron-withdrawing aryl group could enhance the electrophilicity at the metal center, which in turn lead to stronger monomer coordination and faster chain propagation. In addition, the steric hindrance around the metal center, conferred by the presence of bulky aryl group, could reduce the appearance of chain transfer, thereby producing a polyisoprene with a higher M_n. However, in contrast to the work of Ritter and coworkers, the *trans*/*cis* ratio was scarcely affected by the nature of the substituent on the imino group (alkyl *vs* aryl) when an excess of MAO was used as the alkylating agent. In fact, polyisoprenes with high *cis*-1,4 content (*ca* 63 – 78%) and low *trans*-1,4 (*ca* 3 – 9%) units were produced with all pre-catalyst **65(Cl)** – **71**, emphasizing that the alkylating agent/cocatalyst couple plays an important role in controlling the stereo-selectivity. It is noteworthy that the nature of the imino substituent slightly influence the regio-selectivity with a larger amount of 3,4 content, at the expense of mainly *cis*-1,4 units, for the alkyl-substituted Fe complexes **65(Cl)** – **68** with *cis*-1,4/3,4 content ≈ 77.5/15, when compared to the aryl-substituted pre-catalysts **69** – **71** that displayed a microstructure consisting of *cis*-1,4/3,4 units ≈ 66/30. As previously seen in Ritter's work, the activity of the pre-catalysts **65(Cl)** and **69** decreases at – 25 °C and the resulting polymers display higher M_n when compared to the polymerization conducted at room temperature, most likely due to a decrease of chain transfer at lower temperature. Interestingly, the resulting polyisoprene microstructure was not affected by the reaction temperature.

Very recently, further investigations have been described by the group of Wang's regarding the nature of the imino substituent using fluorinated-aryl iminopyridine ligands (**72** – **74**) as well as complexes **65(Cl)** and **69** [108]. These complexes have been employed for the polymerization of isoprene, in combination with an excess of MAO and in absence or presence of 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$. The authors showed that under the same experimental condition, the incorporation of fluorinated aryl moiety on the imino group of the iron complexes **72** – **74** provided polyisoprene in higher yield than complexes **65(Cl)** and **69**. Using an excess of MAO, the activities were in the order

72 > **73** >> **74** > **69** > **65(Cl)**, which followed the trend observed previously with electron-withdrawing substituents leading to higher activity of the catalyst due to an increase of Lewis acid character at the iron metal center. In presence of 500 equiv. of MAO, complexes **72** and **73** produced polyisoprene with relatively low M_n (*ca* 90 kg/mol) and broad $Đ$ (3.5 – 4.3), while complex **74** afforded polymers with high M_n (190 kg/mol) and narrow molecular weight distribution ($Đ$ = 2.1); this differences are, to date, not completely rationalized. The microstructure of the polymers resulting from the polymerization of isoprene with catalysts **72** –**74** were not impacted by the nature of the fluorinated substituent, with a quasi-equal content of *cis*-1,4 and 3,4 units. However, when the polymerization of isoprene was conducted with complexes **65(Cl)**, **72** –**74** in presence of 5 equiv. of MAO and 1 equiv. of $[Ph_3C][B(C_6F_5)_4]$, preferential *trans*-1,4 selectivity (up to 95%) was observed with total absence of *cis*-1,4 units, again indicating that the cocatalyst plays a significant part in the control of stereo-selectivity. In contrast to the binary **72** –**74**/MAO system, the resulting polyisoprenes displayed narrow molecular weight distribution and low M_n (M_n = 1.4 – 1.6 kg/mol and $Đ$ = 1.7 – 2.2), probably due to an increase of chain transfer when the ternary **72** –**74**/MAO/$[Ph_3C][B(C_6F_5)_4]$ system was used. Surprisingly, the polymerization of isoprene using the binary **65(Cl)** or **69**/MAO (MAO/Fe = 500) catalyst behaved very differently in comparison with the study of Chen *et al.* Firstly, the activity of the catalysts proved to be very low at 25 °C and, secondly, the polymers did not exhibit the same microstructure as previously described. The authors have shown that preferential *trans*-1,4 stereo-selective polymerization of isoprene was achieved using **65(Cl)**/MAO (*trans*-1,4/3,4 units = 90/10, with TOF = 138 h^{-1}), with polymer displaying bimodal molecular weight distribution. This is very different from the work of Chen *et al.* who showed that the same system produced polyisoprene in high yield featuring a narrow molecular weight distribution with a slight preference for *cis*-1,4 units (*cis*-1,4 = 77.5%). When compared to the work of Chen *et al.* using **69**/MAO, a fairly similar microstructure content of the resulting polyisoprene was obtained (*cis*-1,4/3,4 with ratio = 65/35 *vs* 63/34), but the polymer was produced in lower yield (TOF = 264 *vs* 1 224 h^{-1}) with lower M_n. The introduction of dealkylating agent $[Ph_3C][B(C_6F_5)_4]$ in presence of 5 equiv. of MAO and complex **65(Cl)** enhanced the *trans*-1,4 stereo-selectivity of isoprene polymerization (98%), despite the production of polymer in low yield and low M_n, in contrast to the work of Ritter and coworkers. Conversely, the combination of **69**/MAO/$[Ph_3C][B(C_6F_5)_4]$ has proved ineffective with respect to the polymerization of isoprene.

Independently, Liu *et al.* have modified the iminopyridine skeleton by replacing the pyridine ring with a quinoline moiety and by introducing an additional chloride substituent on the carbon of the imino group [109]. Thus, several iron-based complexes supported by 2-(*N*-arylcarboximidoylchloride)-quinoline ligands, bearing different substituents on the aryl group (**75** – **80**), were used for the polymerization of butadiene after activation with 100 equiv. of MAO. In contrast to the related highly active (1,10-phenanthroline)$FeCl_2$ [**63(Cl)**] and (2,2'-bipyridine)$FeCl_2$ (**64**) pre-catalysts, complexes **75** – **80** associated to MAO display low activities in butadiene polymerization (TOF < 60 h^{-1} at 20 °C) and poor selectivity (63 – 78/8 – 20/13 – 17 for *cis*-1,4/*trans*-1,4/1,2 units, respectively).

The group of Wang's has further investigated the effect of the auxiliary ligands in the iron-based iminopyridyl complexes [*e.g.* **65(Cl)** – **76**], for the polymerization of isoprene [110], by replacing both chloride anions with two acetylacetonato groups [**65(acac)**, **81** – **85**]. Upon treatment with 500 equiv. of MAO, complexes **65(acac)** and **81** – **85** displayed good activities, the binary **85/**MAO, **83**/MAO, **84/**MAO and **81**/MAO systems being the most effective catalysts (TOF up to 12 000 h^{-1}) that also afforded polyisoprene with the highest M_n (43 000 – 67 000 g/mol). The authors suggested that the catalytic performances were related to the electronic effect of the substituent on the imino group, with complexes bearing electron-withdrawing group exhibiting the highest activity. The microstructure of the resulting polyisoprene, produced with the pre-catalysts **81** and **83** – **85**, showed poor selectivity with an almost equal content in *cis*-1,4 and 3,4 units (*cis*-1,4 = 36 – 55% *vs* 3,4 = 42 – 54 %). In contrast, the binary **65(acac)**/MAO and **82**/MAO catalytic systems generated polymers with high *trans*-1,4 content (> 74 %). When compared to the related iron-based iminopyridyl **65(Cl)** complex, the polymer produced in this study afforded similar microstructure than the previous investigation performed by the same group [108] but, in this case, with an activity 5 times higher (TOF = 590 h^{-1} vs 138 h^{-1}, respectively). However, the resulting selectivity found with the binary **65(acac)**/MAO catalytic system (*trans*-1,4 content = 87 %) or **65(Cl)**/MAO (*trans*-1,4 content = 90 %) [108] is in sharp contrast with the result reported by the group of Chen using **65(Cl)**/MAO (*cis*-1,4 content = 78 %) [107], under the same experimental conditions. The origin of the selectivity is still unclear but, as suggested by the authors, this behavior may be related to the nature of the counter anion ($acac^-$ vs Cl^-). Increasing the temperature of the polymerization from – 30 °C to 50 °C using complexes **65(acac)** or **83**, combined with MAO, resulted in a significant increase of *trans*-1,4 contents (*trans*-1,4 = 36% *vs* 86% for **65(acac)** and 0% *vs* 13% for **83**), suggesting that higher temperature favor the *trans*-1,4 selectivity.

In parallel, the same group described the polymerization of isoprene using the akin iron-based iminoimidazole pre-catalysts **86** – **89** (replacement of the pyridyl moiety in complexes **65**, **69**, **73** and **74** by an imidazole group) [111]. Studies of various cocatalyst systems have shown that only the combination of 10 equiv. of $AlEtCl_2$ and 1 equiv. of $[CPh_3][B(C_6F_5)_4]$ allowed the formation of polymers. In all case, high *trans*-1,4 polyisoprenes were obtained with complexes **86** – **89** (*trans*-1,4 units > 96%), but, no correlation between the nature of the substituent on the imino group and the catalytic activity (TOF ≈ 500 h^{-1}) and selectivity of each complex as well as the molecular characteristic of the resulting polymers ($M_n \approx 1\,800$ g/mol) could be drawn.

Independently, the polymerization of isoprene has been successfully achieved in a hybrid material constituted of carbon nanotubes (CNTs) and iron nanoparticules (NPs). Specifically, the system consists of an iron-based pre-catalyst supported by a bidentate 2-[1-(1-naphthalenylimino)ethyl]-pyridyl ligand immobilized on the iron NPs through π interactions, themselves confined in CNTs [112]. Upon activation with a combination of Al(^{i}Pr)$_3$/[CPh$_3$][B(C$_6$F$_5$)$_4$], this hybrid system was able to produce a CNT-confined Fe NPs covered with a polyisoprene (stereoregularity not specified) air barrier.

Table 5
Selected data for the polymerization of 1,3-dienes with iron complexes bearing bidentate ligands.

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
63(acac)	B (5 000)	$Al(^iBu)_3/Fe = 50$	18	180	100	1 670	50	4	-	46	-	-	-	97
63(Cl)	B (22 740)	MAO/Fe = 1 000	20	0.5	100	2 728 800	30	-	-	70	-	1 517	1.2	100
64	B (22 740)	MAO/Fe = 1 000	20	0.5	100	2 728 800	33	-	-	67	36.9	1 400	1.3	100
64	B (7 580)	MAO/Fe = 1 000	- 78	4 200	17	18	9	-	-	91	52.5	-	-	100
64	B (4 547)	$Al(^iBu)_3/Fe = 30$	20	5	90	49 080	55	-	-	45	-	-	-	100
64	B (4 547)	$Al(Et)_3/Fe = 30$	20	10	91	24 780	54	-	-	46	-	-	-	100
64	I (6 665)	MAO/Fe = 1 000	20	0.5	100	800 000	33	-	67	-	-	-	-	100
	PD (6 635)	MAO/Fe = 1 000	20	5	100	79 620	30	-	-	70	-	-	-	100
	DMB (5 860)	MAO/Fe = 1 000	20	0.5	100	703 200	>99	-	-	-	-	-	-	100
	3-MP (888)	MAO/Fe = 100	-30	14 400	78	3	-	-	-	>99	95	94	2.1	103
65(Cl)	I (1 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe = 3/1/1$	23	120	>99	498	1	91	8	-	-	62.5[a]	2.0	106
65(Cl)	I (2 500)	MAO/Fe = 500	25	120	83.1	1 038	78	8	14	-	-	61	1.6	107
65(Cl)	I (2 500)	MAO/Fe = 500	25	120	10.9	138	-	90	10	-	-	627/4	2.1/1.7	108
65(Cl)	I (1 250)	$MAO/[Ph_3C][B(C_6F_5)_4]/Fe = 5/1/1$	25	120	30.2	192	-	98	2	-	-	15	1.8	108
65(acac)	I (2 000)	MAO/Fe = 500	25	120	55	590	3	87	10	-	-	12	2.0	110

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
65(acac)	I (2 000)	MAO/Fe = 50	25	300	92	440	5	86	9	-	-	19	1.9	110
65(acac)	I (2 000)	MAO/Fe = 50	- 30	120	2.5	30	32	36	32	-	-	6	1.4	110
65(acac)	I (2 000)	MAO/Fe = 50	50	120	20	150	7	80	13	-	-	7	1.9	110
65(Cl)	β-My (2 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 5/1/1	23	720	91	150	4	88	8	-	-	125 [a]	2.1	106
65(Cl)	α and β-Fa (2 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 30/1/1	23	1 440	90	78	5	87	8	-	-	55 [a]	1.5	106
66	I (2 500)	MAO/Fe = 500	25	120	64.1	804	77	9	14	-	-	60	2.1	107
67	I (2 500)	MAO/Fe = 500	25	120	58.2	726	77	8	15	-	-	70	1.8	107
68	I (2 500)	MAO/Fe = 500	25	120	61.3	768	78	8	14	-	-	61	2.1	107
69	I (1 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 3/1/1	23	60	>99	1 002	66	1	33	-	-	75 [a]	1.9	106
69	I (1 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 3/1/1	– 78	240	>99	246	85	1	14	-	-	70 [a]	1.7	106
69	I (2 500)	MAO/Fe = 500	25	120	98.1	1 224	63	3	34	-	-	103	2.1	107
69	I (2 500)	MAO/Fe = 500	25	120	21.1	264	65	-	35	-	-	61	1.5	108
69	I (1 250)	$MAO/[Ph_3C][B(C_6F_5)_4]/Fe$ = 5/1/1	25	120	Trace	-	-	-	-	-	-	-	-	108
69	β-My (2 000)	$AlEt_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 5/1/1	23	720	87.0	144	76	4	20	-	-	115 [a]	2.2	106
69	α and β-Fa (2 000)	$Al^iBu_3/[Ph_3C][B(C_6F_5)_4]/Fe$ = 30/1/1	23	1 440	84	72	71	4	25	-	-	50 [a]	1.4	106
70	I (2 500)	MAO/Fe = 500	25	120	83.2	1 038	70	5	25	-	-	180	1.8	107

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
71	I (2 500)	MAO/Fe = 500	25	120	85.7	1 074	71	5	24	-	-	182	1.6	107
72	I (2 500)	MAO/Fe = 500	25	120	>99.0	1 236	54	-	46	-	-	91	4.3	108
72	I (1 250)	MAO/[Ph_3C][$B(C_6F_5)_4$]/Fe = 5/1/1	25	120	52.8	330	-	95	5	-	-	14	1.7	108
73	I (2 500)	MAO/Fe = 500	25	120	85.3	1 068	54	-	46	-	-	97	3.5	108
73	I (1 250)	MAO/[Ph_3C][$B(C_6F_5)_4$]/Fe = 5/1/1	25	120	76.3	474	-	98	2	-	-	15	2.1	108
74	I (2 500)	MAO/Fe = 500	25	120	32.7	408	56	-	44	-	-	190	2.1	108
74	I (1 250)	MAO/[Ph_3C][$B(C_6F_5)_4$]/Fe = 5/1/1	25	120	64.8	408	0	96	4	-	-	16	2.2	108
75	B (2 000)	MAO/Fe = 100	20	240	10.5	53	78	9	-	13	-	20	3.4	109
76	B (2 000)	MAO/Fe = 100	20	240	8.6	43	77	10	-	13	-	10	1.8	109
77	B (2 000)	MAO/Fe = 100	20	240	10.3	52	73	12	-	15	-	9	2.0	109
78	B (2 000)	MAO/Fe = 100	20	240	11.4	57	64	19	-	17	-	13	3.0	109
79	B (2 000)	MAO/Fe = 100	20	240	7.2	38	72	13	-	15	-	9	2.1	109
80	B (2 000)	MAO/Fe = 100	20	240	5.9	29	72	13	-	15	-	10	2.3	109
81	I (2 000)	MAO/Fe = 500	25	10	>99	12 000	39	16	45	-	-	58	2.7	110
82	I (2 000)	MAO/Fe = 500	25	120	>99	1 000	12	74	14	-	-	17	3.0	110
83	I (2 000)	MAO/Fe = 500	25	10	>99	12 000	36	10	54	-	-	67	2.2	110

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	$Đ$ (M_w/M_n)	Ref.
83	I (2 000)	MAO/Fe = 50	25	10	>99	12 000	39	9	52	-	-	115	1.9	110
83	I (2 000)	MAO/Fe = 50	- 30	10	>99	12 000	45	0	55	-	-	107	2.3	110
83	I (2 000)	MAO/Fe = 50	50	10	>99	12 000	38	13	49	-	-	86	2.1	110
84	I (2 000)	MAO/Fe = 500	25	10	>99	12 000	55	3	42	-	-	65	2.7	110
85	I (2 000)	MAO/Fe = 500	25	10	>99	12 000	51	-	49	-	-	43	3.3	110
86	I (1250)	$AlEtCl_2/[Ph_3C][B(C_6F_5)_4]/Fe$ = 10/1/1	25	120	81	500	-	98	2	-	-	1.6	2.8	111
87	I (1250)	$AlEtCl_2/[Ph_3C][B(C_6F_5)_4]/Fe$ = 10/1/1	25	120	88	540	-	96	4	-	-	1.8	4.4	111
88	I (1250)	$AlEtCl_2/[Ph_3C][B(C_6F_5)_4]/Fe$ = 10/1/1	25	120	76	470	-	97	3	-	-	2.0	3.3	111
89	I (1250)	$AlEtCl_2/[Ph_3C][B(C_6F_5)_4]/Fe$ = 10/1/1	25	120	80	500	-	97	3	-	-	1.5	3.1	111

B = butadiene ; I = isoprene ; EP = (E)-1,3-pentadiene ; DMB = 2,3-diemthyl-1,3-butadiene ; 3-MP = 3-methyl-1,3-pentadiene ; My = Myrcene ; Fa = Farnesene; ^{a} calculated from $M_n = M_w/Đ$

3.2. Iron-based catalysts bearing tridentate ligand for the polymerization of 1,3-dienes

In this section, iron-based pre-catalysts supported by tridentate ligands are illustrated in **Fig. 10** and the polymerization data are disclosed in **Table 6**.

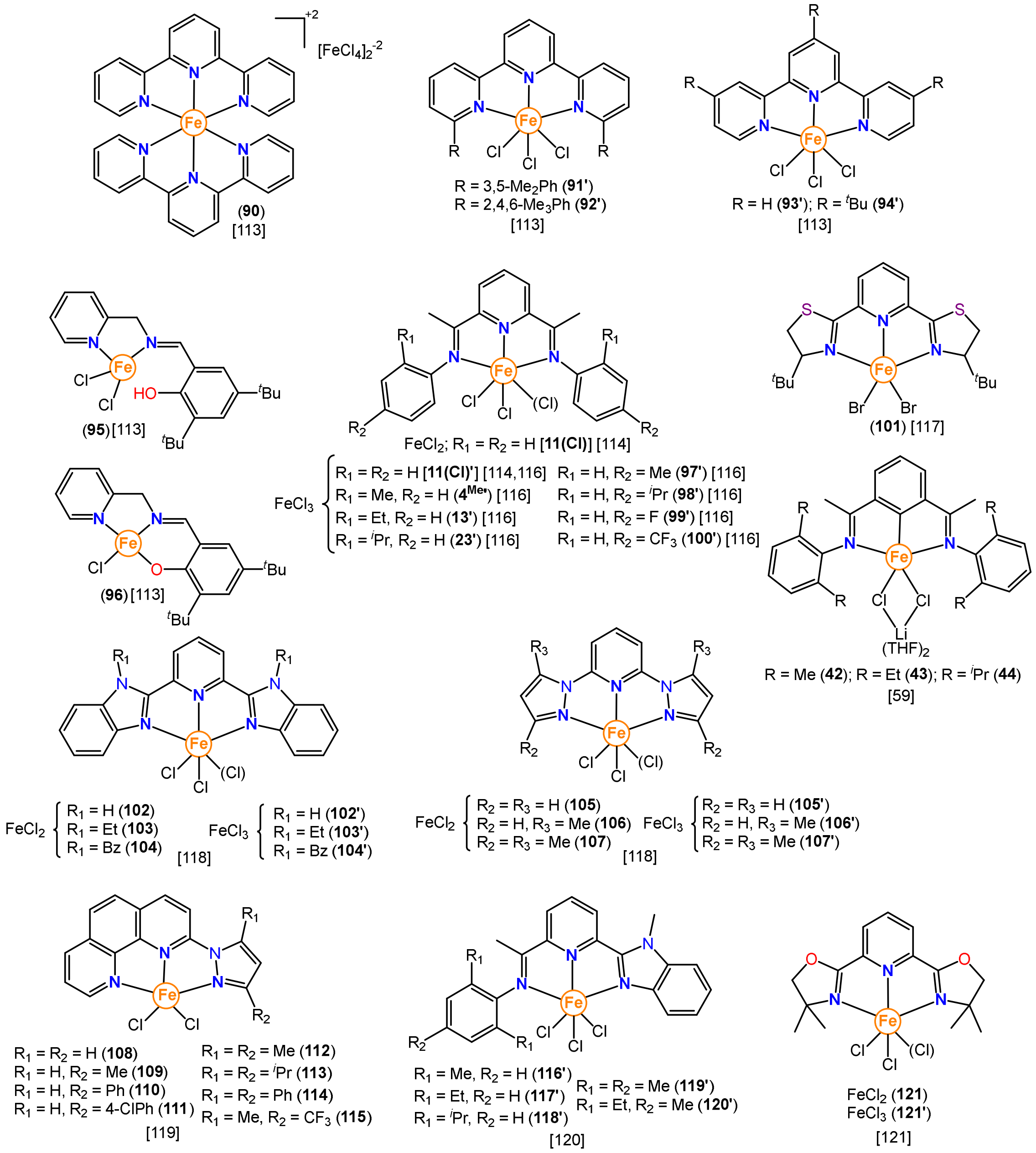


Fig. 10. Iron-based complexes (tridentate ligands) used for the polymerization of 1,3-dienes.

In 2003, well-defined iron(II) and iron(III)-based complexes supported by tridentate ligands (*N,N,N*-terpyridine-type and *N,N,O*-pyridyloxy-benzaldimine) (**90** – **96**), have been studied for the polymerization and copolymerization of 1,3-dienes in presence of 100 equiv. of MMAO [113]. Only the pre-catalysts **90** and **93’** – **96** exhibited some activity for the polymerization of butadiene and isoprene with TOF ranging from 17 to 132 h^{-1}. Complexes **91’** and **92’** were not efficient even in the presence 1 000 equiv. of MMAO, probably due to the presence of bulky substituents on the 6 and 6’’ position of the terpyridine skeleton disfavoring the coordination of the incoming monomer, which in turn inhibits the insertion/propagation steps. Complex **90** afforded polybutadiene and polyisoprene with a content mixture of *cis*-1,4/*trans*-1,4/1,2 = 20/51/29 and *cis*-1,4/1,2/3,4 = 14/36/50 units, respectively, indicating the poor stereo- and regio-selectivity of the catalyst. Interestingly, the polymerization of isoprene in the presence of complex **93’** showed low stereo- and regio-selectivity (content of *cis*-1,4/1,2/3,4 = 12/27/61), whilst high *trans*-1,4 polybutadiene was obtained under the same experimental conditions (*trans*-1,4 units > 95%). This control of selectivity as function of monomers was also observed, in some extent, with complex **94’**, which afforded polyisoprene with high content of 3,4-units (> 81%) while a low selectivity was observed for the polymerization of butadiene (mixture of *cis*-1,4/*trans*-1,4/1,2 units = 31/23/46). In this study, the highest activity for the polymerization of 1,3-dienes was observed with complexes **95** and **96** bearing *N,N,O*-pyridyloxy-benzaldimine type ligand, despite producing polymers with uncontrolled microstructure. Additionally, the authors performed the statistical copolymerization of butadiene and isoprene in presence of the binary **93’** or **94’**/MMAO systems. At the early stage of the polymerization, it was found that complex **93’** favored the incorporation of butadiene while complex **94’** embeds preferentially isoprene, producing probably tapered rather than statistical copolymers. The authors suggested that an increase of electronegativity on the ligand of complex **94’** was responsible for the higher insertion rate of isoprene, due to the inductive effect of the ^{t}Bu substitutents on the terpyridine backbone. The microstructure of the butadiene and isoprene repeat units obtained in the copolymers are in accordance with the homopolymerization data. However, using complex **94’**, a decrease of 3,4-polyisoprene relative to *cis*-1,4-polyisoprene units was observed (homo-polyisoprene 3,4/*cis*-1,4 = 82/15 *vs* isoprene units in copolymer 3,4/*cis*-1,4 = 40/46).

Independently, Tobisch explored the mechanism of the *trans*-1,4-selective polymerization of butadiene with complex **93’** by DFT method [92]. From this study, it was proposed that the (terpyridine)Fe(III)Cl_3 complex **93’** could be reduced to [(terpyridine)Fe(II)Me]$^+$ in presence of MMAO, which generates, after insertion of butadiene, the active species of the form [(terpyridine)Fe(II)(η^2-C_4H_6)(η^3-RC_3H_4)]$^+$. Moreover, the author suggested that the chain growth was preferentially governed by π-allyl-insertion mechanism with the *trans*-1,4 selectivity occurring through *trans*-η^2-butadiene insertion into the *syn*-η^3-butenyl-Fe(II) bond, whereas the *cis*-1,4 pathway was, unusually, kinetically disfavored.

The discovery of highly active ethylene polymerization catalysts, (BIP)FeCl_2/MAO, prompted some research groups to study their catalytic potential in the polymerization of 1,3-diene monomers. An early report claimed that this catalytic system was inactive toward the polymerization of 1,3-dienes, presumably due to the presence of bulky substituents on the *N*-aryl ring of the BIP ligand that could be detrimental to the coordination of the 1,3-diene monomer on the metal center, as compared to the less congested ethylene monomer [113]. The group of Zhang re-examined the use of the iron-based complex supported by the BIP ligand for the 1,3-dienes polymerization, but this time using a BIP ligand that did not incorporate a substituent on the *N*-aryl moiety in order to facilitate the coordination of the monomer [114]. Complexes (BIP)$FeCl_2$ [**11(Cl)**] and (BIP)$FeCl_3$ [**11(Cl)'**] were evaluated in butadiene polymerization in presence of 100 equiv. of MAO. Complex **11(Cl)'** quantitatively produced polymers (TOF = 250 h^{-1} at 20 °C) with high content of *trans*-1,4 units (> 94%), whereas the $FeCl_2$ counterpart **11(Cl)** was less active with mixture of microstructure consisting of *cis*-1,4/*trans*-1,4/3,4 units ≈ 35/55/10. The high *trans*-1,4 selectivity using **11(Cl)'**/MAO was attributed to the preferential *single*-η^2 coordination mode of butadiene on the metal center due to the tridentate BIP ligand, which could generate a metal-alkyl active species with one less coordination site than that of the corresponding metal with bidentate nitrogen ligand (*vide supra*). The higher activity of complex **11(Cl)'** in comparison with **11(Cl)** was ascribed, by the authors, to a higher electrophilicity of the Fe(III) center than its Fe(II) counterpart. Though, the divergence in activity (and selectivity) of both complexes may also stem from the distinct nature of the pre-catalysts, with the solid-state structure of **11(Cl)** being isolated [115] as an ion pair $[(BIP)_2Fe][FeCl_4]$ while complex **11(Cl)'** is under monomeric form $[(BIP)FeCl_3]$.

The same research group carried out further investigations in the field by varying the steric and electronic effect of the BIP ligand [116]. Seven iron(III)-based complexes (**4^{Me}'**, **13'**, **23'** and **97'** – **100'**) supported by different BIP ligands have been evaluated toward the polymerization of butadiene in presence of 40 equiv. of Al^iBu_3 and compared with the former complex **11(Cl)'**. Activation of pre-catalyst **11(Cl)'** with an excess of Al^iBu_3 showed similar activity and afforded polybutadiene having identical M_n and microstructure content to that using excess MAO. However, the activity and selectivity of the polymerization were greatly influenced by the substituent on the aryl ring of the BIP ligand. It was noticed that an increase of the steric bulkiness at the 2-position of each *N*-aryl group decreases both the activity and the *trans*-1,4 selectivity, with the activity of the catalysts being in the order **11(Cl)'** > **4^{Me}'** > **13'** > **23'** and the composition of the *trans*-1,4 units varying as **11(Cl)'** (95%) > **4^{Me}'** (43%) > **13'** (30%) > **23'** (10%). In contrast, a significant increase of M_n of the resulting polymer was observed for complexes **4^{Me}'**, **13'** and **23'** (M_n > 250 kg/mol) compared to complex **11(Cl)'** (M_n = 29 kg/mol). The authors suggested that the decrease of activity could be attributed to the difficulty of the incoming monomer to coordinate to the iron center, due to the presence of sterically hindered substituent at the 2-position of each *N*-aryl group for **4^{Me}'**, **13'** and **23'**. Conversely, the presence of a congested iron center is able to delay the appearance of chain transfer with respect to chain propagation, resulting in higher M_n for the polymers produced with complexes **4^{Me}'**, **13'** and **23'**. At this stage, the reason for the decrease in *trans*-1,4 selectivity observed for **11(Cl)'**, **4^{Me}'**, **13'** and **23'** could not be explained. It is noteworthy that the authors prepared an iron complex bearing a BIP ligand with cyclohexyl-substituent instead of aryl-substituent on the imino group, which proved to display very low activity after activation with Al^iBu_3 (TOF = 12.5 h^{-1} at 20 °C). Regarding the modification at the 4-position of each *N*-aryl group of the BIP structure, it was found that the presence of an electron-donating alkyl substituent in **97'** (Me) and **98'** (^{i}Pr) had essentially no effect on the activity and the *trans*-1,4 selectivity of the catalyst. However, an electron-withdrawing group, F in **99’** and CF_3 **100’**, disrupts the active species by increasing the Lewis acidity of the iron metal center, which, in contrast to bidentate pyridine-imine ligand, reduces the catalytic activity that followed the order **11(Cl)’** > **99’** > **100’**, while keeping the same *trans*-1,4 selectivity. Overall, the authors concluded that modification at the 2-position of the *N*-aryl group of the BIP ligand influences both the activity and the selectivity, whereas the 4-positions altered only the catalytic performance.

Britovsek and his collaborators have studied other variants of BIP ligand architecture by introducing a thiazoline moiety on the imino carbon atom. After activation by 500 equiv. of MAO, the iron complex **101** showed good activity toward the polymerization of butadiene (TOF = 16 266 h^{-1}), producing polymer of high M_n (110 000 g/mol) and narrow dispersity (1.77) with a microstructure consisting of high *cis*-1,4 content (74%) as well as a mixture of *trans*-1,4 (17%) and 1,2 units (10%) [117].

Iron-based complexes supported by bis(imino)aryl NCN pincer ligand have also been investigated for the polymerization of butadiene by the group of Mu [59]. Three iron-based pre-catalysts bearing different *N*-aryl substituents on the imino group (**42**, **43** and **44**) were evaluated in butadiene polymerization, after activation with 25 equiv. of $AlMe_3$, and showed moderate catalytic activities (TOF = 714 – 852 h^{-1}). In contrast to the (BIP)$FeCl_2$ complexes **11(Cl)’**, **4^{Me}’**, **13’** and **23’**, the presence of the sterically bulky substituent on the 2- and 6-position of the *N*-aryl group increases the catalytic activity [**42** (H) < **43** (Et) < **44** (^{i}Pr)] while affording polymers with lower M_n [M_n = 860 kg/mol for **42** *vs* M_n = 55.4 kg/mol for **44**], with broad molecular weight distribution ($Đ$ = 3 – 7.2). Additionally, these catalytic systems display a slight preference for the production of *cis*-1,4 polybutadiene, with a microstructure of the resulting polymer consisting of *cis*-1,4 (*ca* 73%) and 1,2 units (*ca* 27%) without any trace of *trans*-1,4.

Following the work of Britovsek, iron(II)- and iron(III)-based derivatives supported by tridentate 2,6-bis(2-benzimidazolyl)pyridyl (**102** – **104**, **102’** – **104’**) and 2,6-bis(pyrazol)pyridine (**105** – **107**, **105’** – **107’**) ligands have been studied toward the polymerization of butadiene in presence of MMAO [118]. Under the same polymerization conditions, the catalytic performances and the polymer microstructures were identical for the iron(II)- and iron(III)-based pre-catalysts when supported by the same ligand, indicating that the same active species was likely generated upon activation with MMAO despite a divergence in the initial oxidation states of the iron center. In presence of 200 equiv. of MMAO, complexes **102** and **102’** displayed moderate catalytic activity for the polymerization of butadiene (TOF ≈ 234 h^{-1} at 20 °C) with the resulting polybutadiene microstructure having a high M_n (*ca* 147 kg/mol) along with *cis*-1,4 content (*ca* 80 – 81%) and a small amount of *trans*-1,4/1,2 units = 12/7 – 8. However, under the same conditions, complexes **103** and **103’**, and in more extent complexes **104** and **104’**, exhibited very low activity (TOF < 30 h^{-1}) and selectivity. The authors suggested that the N-H functionality in **102** and **102’** could be deprotonated upon activation with MMAO, resulting in the formation of an anionic amide ligand (free or in the form of anionic-cationic N-Al ion-pairs) that could increase the catalytic performances. Thus, substitution of the N-H functionality by ethyl (**103** and **103'**) or benzyl group (**104** and **104'**) results in a decrease of activity and selectivity. Moreover, this hypothesis could explain the relatively high *cis*-1,4 selectivity for the polymerization of butadiene using complexes **103** and **103'**, which is in stark opposition to the usual high *trans*-1,4 selectivity found for complexes **93'** and **11(Cl)'** supported by related tridentate terpyridine or BIP ligand, respectively. Regarding the iron-based pre-catalysts **105** – **107** and **105'** – **107'** bearing 2,6-bis(pyrazol)pyridine ligand, it was found that an increase of the steric hindrance around the active metal center was detrimental to the catalytic performance [activity in the order **105** (or **105'**) >> **106** (or **106'**) > **107** (or **107'**)], which inversely produced polymer with higher M_n, consistent with the results obtained with complexes **11(Cl)'**, **4^Me^'**, **13'** and **23'**. Polybutadiene with high *trans*-1,4 enchainment (> 90%) was isolated from the binary system **105** (or **105'**)/MMAO, similarly to the akin complexes **93'** and **11(Cl)'**. However, a mixture of *cis*-1,4/*trans*-1,4/1,2 units was obtained in a ratio of *ca* 23/46/31 for **106** (or **106'**) and **107** (or **107'**)/MMAO, highlighting the important role of the steric bulkiness of the ligand in the control of the selectivity.

Well-defined iron(II)-based complexes supported by tridentate 2-pyrazolyl-1,10-phenanthroline (**108** – **115**) have been investigated for the polymerization of butadiene by varying the ligand structure and the polymerization conditions [119]. The authors found that the optimum catalytic performance was reached at a temperature of 40 °C using the binary system **109**/Al^iBu_3 (Al/Fe = 40), affording quantitative conversion of butadiene in 4 hours (TOF = 495 h^{-1}) with the resulting polymer consisting of high *trans*-1,4 (91%) and 1,2 units (9%). The *trans*-1,4 selectivity of the catalytic system increased as a function of the temperature (> 95% at 60 °C), while significant loss of *trans*-1,4 character was obtained below 20 °C with the resulting polymer displaying a mixture of *trans*-1,4/*cis*-1,4/1,2 content. All the complexes (**108** – **115**) exhibited the same tendency of selectivity of the polymerization as a function of the temperature. This result is in agreement with the proposed polymerization mechanism of 1,3-dienes where the formation of the *trans*-1,4 units is favored at high temperature since it derives from the *syn*-η^3-allyl intermediate, which is thermodynamically more stable than the *anti* isomer. Moreover, the use of different alkyl-aluminum cocatalysts highlighted the importance of the nature of the alkyl reagent toward the activity and selectivity of the polymerization, with Al^iBu_3 displaying the highest activity and selectivity when compared to $AlMe_3$, $AlEt_3$, $AlOct_3$, MAO or MMAO. It was also observed that an increase of the bulkiness of the alkyl group of the aluminum co-reagent leads to higher *trans*-1,4 selectivity. The authors suggested that this effect was due to a more congested counter-anion, stemming from AlR_3, around the active iron species, which probably favors the insertion at the C1 position rather than the more hindered C3 position. Upon activation with 40 equiv. of Al^iBu_3, the iron-based pre-catalyst **108**, with no substituent on the pyrazolyl framework, displayed slightly lower catalytic activity at 60 °C but with a dramatic loss in stereo-selectivity when compared to the corresponding complex **109** with methyl group at the 3-

position of the pyrazolyl ring (TOF = 458 h^{-1} and *cis*-1,4/trans-1,4/1,2 content = 16/62/22 *vs* TOF = 495 h^{-1} and *cis*-1,4/trans-1,4/1,2 content = 0/96/4, respectively). The presence of phenyl substituents at the 3-position (**110**) decreased the catalytic performance of the iron-based complex (TOF = 396 h^{-1}), while producing stereo-regular *trans*-1,4 polybutadiene (> 96%), similar to complex **109**. Conversely, the introduction of *para*-chlorophenyl substituent at the 3-position (**111**) had a negative effect on the activity and the stereo-selectivity of the butadiene polymerization. Regarding the addition of alkyl or aryl-substituent on both the 3- and 5-position of the pyrazolyl ring, complexes **112** (Me, Me), **114** (Ph, Ph) and **115** (Me, CF_3) exhibited much lower activity (TOF = 59 – 113 h^{-1}) than complex **109**, with the resulting polybutadiene displaying non-stereoregular microstructure. In contrast, the presence of ^{i}Pr group on the 3- and 5-position in complex **113** resulted in an increase of the catalytic performance (TOF = 467 h^{-1}) when compared to pre-catalysts **112** and **114** – **115**, with a marginal preference for the formation of *trans*-1,4 polybutadiene (> 73%). Surprisingly, the catalytic activity of pre-catalyst **113** showed a unique dependence toward the polymerization temperature, with respect to the other related complexes **109** – **112** and **114** – **115**, with a decrease of activity of the binary **113**/$Al^{i}Bu_3$ catalytic system from 60 °C to 20 °C (TOF = 98 h^{-1} at this temperature).

The iron(III)-based complexes supported by 2-(methyl-2-benzimidazolyl)-6-(1-arylimino)-ethyl)-pyridine ligand (**116’** – **120’**), which can be seen as an hybrid of the ligands supported complexes **112’** – **114’** and (BIP)$FeCl_2$, displayed very low activity for the isoprene polymerization at 40 °C after activation with 400 equiv. of $Al^{i}Bu_3$ [120]. No dependence regarding the nature of the substituent of the *N*-aryl moiety was found for the resulting polyisoprene microstructure, which consisted of mainly 1,4-content (≥ 78%) with 7 – 8% of 3,4 and 10 – 12% of 1,2-units. Morevover, the authors showed that the addition of a third external donor component, triphenyl phosphate $(C_6H_5O)_3P(O)$, had a slight impact on the polymerization behavior. The catalytic performances of **117’** increased as the amount of triphenyl phosphate increased from 2 to 160 equiv./Fe, while the stereo- and regio-regularity of the resulting polyisoprene decreased. Nevertheless, in the presence or absence of triphenyl phosphate, pre-catalysts **116’** – **120’** afforded poylisoprene with bimodal distribution after activation with an excess of $Al(^{i}Bu)_3$, suggesting the presence of more than one active iron species.

Recently, Gong *et al.* have reported that well-defined iron(II)- (**121**) and iron(III)- (**121’**) based pre-catalysts bearing 2,6-bis(oxazolin-2-yl)pyridine ligand showed moderate activity and poor stereo-selectivity in the polymerization of butadiene in presence of 300 equiv. of MAO [121]. The binary **121**/MAO and **121’**/MAO systems exhibited identical behavior in the butadiene polymerization, indicating the presence of a similar active species. Moreover, the obtained polymers displayed narrow molecular weight distribution (2 – 3), which implied that a single-site active species was probably generated upon activation with MAO.

Table 6.
Selected data for the polymerization of 1,3-dienes with iron complexes bearing tridentate ligands.

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
90	B (200)	MMAO/Fe = 100	25	360	99	33	20	51	-	29	-	12	1.3	113
90	I (200)	MMAO/Fe = 100	25	720	99	17	14	-	50	36	-	632	1.7	113
93'	B (200)	MMAO/Fe = 100	25	240	99	50	-	96	-	4	-	5	1.1	113
93'	I (200)	MMAO/Fe = 100	25	360	99	33	12	-	61	27	-	1 468	1.4	113
94'	B (200)	MMAO/Fe = 100	25	180	99	66	31	23	-	46	-	621	1.7	113
94'	I (200)	MMAO/Fe = 100	25	180	99	66	15	3	82	-	-	470	2.1	113
95	B (200)	MMAO/Fe = 100	25	60	99	198	26	39	-	38	-	80	1.7	113
95	I (200)	MMAO/Fe = 100	25	180	99	66	25	-	53	22	-	358	2.1	113
96	B (200)	MMAO/Fe = 100	25	180	99	66	25	37	-	38	-	759	2.9	113
96	I (200)	MMAO/Fe = 100	25	180	99	66	37	0	46	17	-	563	2.9	113
11(Cl)	B (1 000)	MAO/Fe = 100	20	240	82	205	35	55	-	10	-	35	1.7	114
11(Cl)'	B (1 000)	MAO/Fe = 100	20	240	100	250	0	95	-	5	-	27	2.7	114
11(Cl)'	B (1 000)	$Al^{i}Bu_3$/Fe = 40	20	240	99	248	0	95	-	5	-	29	2.0	116
4^{Me}'	B (1 000)	$Al^{i}Bu_3$/Fe = 40	20	240	25	62	14	43	-	43	-	253	2.9	116
13'	B (1 000)	$Al^{i}Bu_3$/Fe = 40	20	240	8	20	30	30	-	40	-	295	2.6	116

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* *(%)*	M_n (kg/mol)	*Đ* *(M_w/M_n)*	Ref.
23’	B (1 000)	Al^{i}Bu$_3$/Fe = 40	20	240	10	25	44	10	-	46	-	278	2.7	116
97’	B (1 000)	Al^{i}Bu$_3$/Fe = 40	20	240	99	248	< 1	95	-	5	-	37	2.2	116
98’	B (1 000)	Al^{i}Bu$_3$/Fe = 40	20	240	97	242	< 1	97	-	3	-	31	2.0	116
99’	B (1 000)	Al^{i}Bu$_3$/Fe = 40	20	240	64	160	< 1	93	-	6	-	30	2.1	116
100’	B (1 000)	Al^{i}Bu$_3$/Fe = 40	20	240	43	108	< 1	93	-	7	-	33	2.0	116
101	B (-)	MAO/Fe = 500	25	30	-	16 266	73	17	-	10	-	110	1.8	117
42	B (500)	AlMe$_3$/Fe = 25	25	30	71.1	711	-	73	-	27	-	860	5.0	59
43	B (500)	AlMe$_3$/Fe = 25	25	30	78.9	789	-	73	-	27	-	1 160	7.2	59
44	B (500)	AlMe$_3$/Fe = 25	25	30	85.2	852	-	74	-	26	-	55.4	3.0	59
102	B (1 000)	MMAO/Fe = 200	20	240	95	238	81	12	-	7	-	142	2.5	118
103	B (1 000)	MMAO/Fe = 200	20	240	11	28	57	31		12	-	88	3.1	118
104	B (1 000)	MMAO/Fe = 200	20	240	trace	-	-	-	-	-	-	-	-	118
102’	B (1 000)	MMAO/Fe = 200	20	240	91	228	80	12	-	8	-	153	2.7	118
103’	B (1 000)	MMAO/Fe = 200	20	240	15	38	56	34	-	10	-	94	3.3	118
104’	B (1 000)	MMAO/Fe = 200	20	240	trace	-	-	-	-	-	-	-	-	118
105	B (1 000)	MMAO/Fe = 200	20	240	78	195	2	90	-	8	-	42	1.6	118

Complex	Monomer (Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* *(%)*	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
106	B (1 000)	MMAO/Fe = 200	20	240	38	95	27	45	-	28	-	101	2.5	118
107	B (1 000)	MMAO/Fe = 200	20	240	31	78	19	47	-	34	-	144	2.0	118
105’	B (1 000)	MMAO/Fe = 200	20	240	74	185	2	91	-	7	-	55	1.9	118
106’	B (1 000)	MMAO/Fe = 200	20	240	37	93	25	45	-	30	-	115	2.2	118
107’	B (1 000)	MMAO/Fe = 200	20	240	26	65	21	47	-	32	-	141	2.1	118
108	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	91.6	458	16	62	-	22	-	21	2.8	119
109	B (2 000)	$Al^{i}Bu_3$/Fe = 40	20	240	94.3	472	21	58		21	-	82	3.0	119
110	B (2 000)	$Al^{i}Bu_3$/Fe = 40	40	240	99	495	0	91	-	9	-	45	3.0	119
110	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	99	495	0	96	-	4	-	18	1.9	119
110	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	79.2	396	0	96	-	4	-	25	2.9	119
111	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	16.8	84	42	24	-	34	-	88	1.9	119
112	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	11.7	59	35	41	-	24	-	23	2.4	119
113	B (2 000)	$Al^{i}Bu_3$/Fe = 40	20	240	19.5	98	27	12	-	61	-	93	2.9	119
113	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	93.4	467	14	73	-	13	-	24	2.6	119
114	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	22.5	113	39	30	-	31	-	98	2.3	119
115	B (2 000)	$Al^{i}Bu_3$/Fe = 40	60	240	14.5	73	24	57	-	19	-	51	2.7	119

Complex	(Monomer/Fe)	Activation	T (°C)	Time (min)	Conv. (%)	TOF (h^{-1})	*cis* -1,4 (%)	*trans*-1,4 (%)	3,4 (%)	1,2 (%)	*rrrr* (%)	M_n (kg/mol)	*Đ* (M_w/M_n)	Ref.
116’	I (10 000)	Al^{i}Bu$_3$/Fe = 400	40	1440	4.0	17	81		9	10	-	5.2/0.44	2.2/1.2	120
117’	I (10 000)	Al^{i}Bu$_3$/Fe = 400	40	1440	4.1	17	79		10	11	-	8.5/0.44	3.3/1.3	120
117’	I (10 000)	Al^{i}Bu$_3$/Fe = 400 + PO(OPh)$_3$ (20 eq./Fe)	40	1440	8.9	37	78		12	10	-	277/0.98	3.0/1.9	120
117’	I (10 000)	Al^{i}Bu$_3$/Fe = 400 + PO(OPh)$_3$ (160 eq./Fe)	40	1440	11.6	49	41		47	12	-	112/1.44	2.5/1.7	120
118’	I (10 000)	Al^{i}Bu$_3$/Fe = 400	40	1440	3.9	16	82		7	11	-	4.5/0.47	1.8/1.2	120
119’	I (10 000)	Al^{i}Bu$_3$/Fe = 400	40	1440	4.5	19	78		10	12	-	8.9/0.46	3.7/1.2	120
120’	I (10 000)	Al^{i}Bu$_3$/Fe = 400	40	1440	4.8	20	83		7	10	-	2.8/0.45	1.4/1.3	120
121	B (2 000)	MMAO/Fe = 300	25	240	56.9	285	56	33	-	11	-	31	2.9	121
121’	B (2 000)	MMAO/Fe = 300	25	240	37.0	185	30	60	-	10	-	29	2.5	121

B = butadiene ; I = isoprene ; PD = (E)-1,3-pentadiene ; DMB = 2,3-dimethyl-1,3-butadiene ; 3-MP = 3-methyl-1,3-pentadiene ; My = Myrcene ; Fa = Farnesene;

3.3. Iron precursors with phosphorous additives for the polymerization of butadiene

In parallel with the development of well-defined iron-based pre-catalysts for the polymerization of butadiene, the group of Zhang and Dong investigated the effect of electron donor phosphorous additives in combination with Fe(acac)$_3$/AlR$_3$ or Fe(2-ethylhexanoate)$_3$/AlR$_3$ [Fe(2-EHA)$_3$]. These catalysts are systematically generated by mixing all the reagents *in situ*, which implies that the mechanism of formation of the active species and its structure remain, until now, unclear. Nevertheless, it has been found that some of these systems display a high tolerance to the polymerization temperature and produce highly regular syndiotactic 1,2-polybutadiene under appropriate conditions. Herein, some of these catalytic systems, where the additives are illustrated in **Fig. 11** and the polymerization data in **Table 7**, will be described.

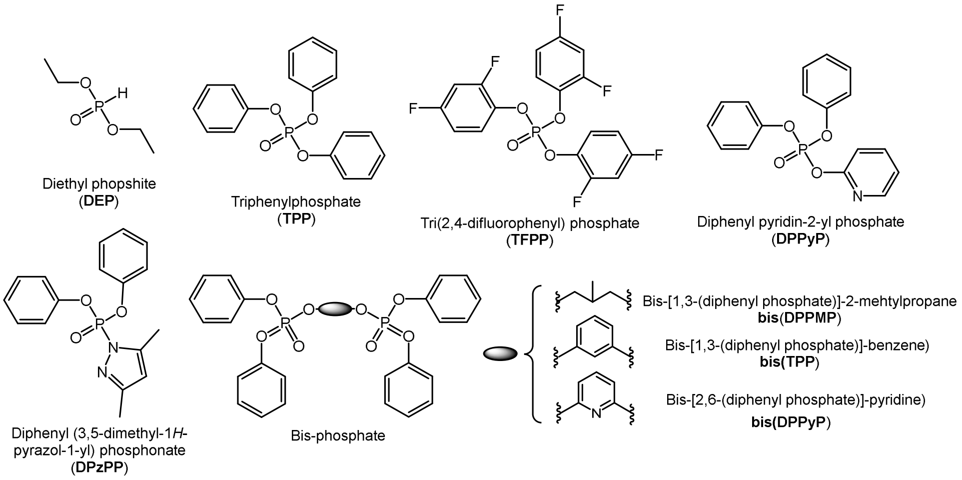


Fig. 11. Phosphorous additives used in combination with Fe precursors for the polymerization of butadiene.

As previously mentioned, iron-based complexes supported by bidentate phosphine ligands in presence of alkyl aluminum activators are not effective for the polymerization of 1,3-dienes (see section 3.1.). In sharp contrast, the use of diethyl phosphite (**DEP**) [122] as additive in a ratio of [**DEP**]/[Fe] = 2 – 6, when combined with Fe(2-EHA)$_3$/Al*i*Bu$_3$, exhibited living character [123] and afforded polybutadiene with a prominent content of 1,2-units (> 85%) under appropriate conditions. By applying the ternary Fe(2-EHA)$_3$/Al^{i}Bu$_3$/**DEP** catalytic system, the regio-regularity of the resulting polymer was found to be strongly influenced by the amount of aluminum cocatalyst. When the [Al]/[Fe] ratio was less than 10, amorphous polybutadiene consisting of a mixture of 1,2- and *cis*-1,4 units with a very small portion of *trans*-1,4 was produced, while increasing the ratio above 10, polybutadiene with both high content of 1,2-units (> 85%) and syndiotacticity (*rrrr* > 81%) was obtained [124]. The preparation of butadiene-based block copolymers have been further investigated by taking advantage of the living character of this ternary catalytic system [123]. Butadiene was first completely polymerized at 40 °C for 24 hours with Fe(2-EHA)$_3$/**DEP**/Al^{i}Bu$_3$ (BD/Fe/**DEP**/Al = 1 000/1/3/6), which was then followed by the *in situ* addition of 860 equiv. of isoprene to yield a block copolymer of poly(butadiene-*b*-isoprene). In a similar manner, stereoblock copolymer with an amorphous polybutadiene block segment comprised of a mixture of *cis*-1,4/1,2 content and a crystalline syndiotactic segment was prepared by sequential polymerization using Fe(2-EHA)$_3$/**DEP** in presence of different amounts of cocatalyst. The first stage of the copolymerization was performed using 5 equiv. of Al^{i}Bu$_3$, producing the first amorphous polybutadiene block with 52% of 1,2 content. Subsequently, *in situ* addition of an excess of Al^{i}Bu$_3$ (30 equiv.) and butadiene resulted in a change of selectivity of the catalytic system, providing a second crystalline polybutadiene block [124].

With the aim to enhance both the catalytic performances and the regio-selectivity of the ternary catalytic system, the same group has pursued studies on the modification of the phosphorous additive. It was shown that the use of the ternary Fe(2-EHA)$_3$/Al^{i}Bu$_3$/di(aryl) phosphite [(ArO)$_2$(H)P(O)] or tri(aryl) phosphate [(ArO)$_3$P(O)] [122] or diethyl acetylphosphonate (EtO)$_2$(COMe)P(O) [125] catalytic systems displayed good catalytic activity and 1,2 regio-selectivity for the polymerization of butadiene at 50 °C. For example, 4 equiv. of triphenylphosphate (**TPP**) in combination with Fe(2-EHA)$_3$/Al^{i}Bu$_3$ (Fe/Al = 1/30) for butadiene polymerization produced high syndiotactic 1,2-polybutadiene (1,2 units = 91.5%; *rrrr* = 94.5%, TOF = 362 h^{-1} at 50 °C) [126]. Introduction of electron-withdrawing group on the *O*-aryl moiety of the phenyl groups, tri(2,4-difluorophenyl) phosphate (**TFPP**), greatly enhances the performance of the catalytic system (TOF = 2 910 h^{-1} at 50 °C), with a marginal loss of selectivity (1,2 units = 89.0%; *rrrr* = 92.9%). Unprecedentedly, the ternary Fe(2-EHA)$_3$/Al^{i}Bu$_3$/(**TFPP**) catalytic system was found to be highly tolerant to the polymerization temperature, producing syndiotactic 1,2-polybutadiene (1,2 units = 88.9%; *rrrr* = 88.7%) with high activity (TOF = 11 760 h^{-1}) even at 80 °C. Replacement of one phenyl group of the triphenylphosphate additive by one pyridine substituent, diphenyl pyridin-2-yl phosphate (**DPPyP**), resulted in higher catalytic activity and 1,2-regio-selectivity at 50 °C for the ternary Fe(acac)$_3$/Al^{i}Bu$_3$/additive system, but with a loss of syndiotacticity of the resulting polybutadiene [127]. An increase of crystallinity of the resulting polybutadiene could be obtained at elevated temperature (80 °C). On the other hand, substitution of more than one phenyl group by pyridine substituent was detrimental to both activity and selectivity. In a similar manner, the replacement of one phenyl group by one pyrazolyl substituent, diphenyl (3,5-dimethyl-1H-pyrazol-1-yl)phosphonate (**DPzPP**), enhanced the activity (TOF = 2 980 h^{-1} at 80 °C) of the ternary system and preserved the selectivity (1,2 units = 93.3%; *rrrr* = 91.7%) [128]. However, the presence of more than one pyrazolyl group was found to be unfavorable, as for the pyridine substituent. Further studies have shown that the use of bis-phosphate additives such as bis-[1,3-(diphenyl phosphate)]-2-mehtylpropane [**bis(DPPMP)**], bis-[1,3-(diphenyl phosphate)]benzene [**bis(TPP)**] and bis-[2,6-(diphenyl phosphate)]-pyridine [**bis(DPPyP)**] were also efficient to promote the polymerization of butadiene even at 80 – 100 °C, producing polymers with high 1,2-regio-regularity and syndiotacticity (1,2 units > 93%; *rrrr* > 91%).

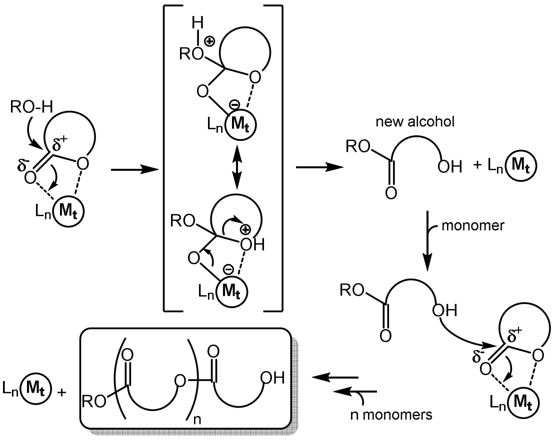
Table 7
Selected polymerization data for the polymerization of 1,3-dienes with Fe precursors and phosphorous additives.

Pre-catalytic system	Butadiene/Fe	Activation	T (°C)	Time (min)	TOF (h^{-1})	1,2 (%)	*rrrr* *(%)*	M_n (kg/mol)	Đ *(M_w/M_n)*	Ref.
DEP + $Fe(2\text{-}EHA)_3$ (3/1)	1 000/1	$Al(^iBu)_3/Fe$ (5/1)	50	120	485	52.4	46.9	78	1.7	124
DEP + $Fe(2\text{-}EHA)_3$ (3/1)	1 000/1	$Al(^iBu)_3/Fe$ (30/1)	50	120	492	91.7	82.5	163	2.2	124
TPP + $Fe(2\text{-}EHA)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (30/1)	50	240	362	91.5	94.5	58	2.5	126
TFPP + $Fe(2\text{-}EHA)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (30/1)	50	30	2 910	89.0	92.9	63	2.7	126
TFPP + $Fe(2\text{-}EHA)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (30/1)	80	8	11 760	88.9	88.7	68	2.2	126
TPP + $Fe(acac)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	50	460	160	88.2	95.7	74	3	127
DPPyP + $Fe(acac)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	50	460	200	94.2	72.7	37	5.5	127
DPzPP + $Fe(acac)_3$ (4/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	80	40	2 980	93.3	91.7	79	2.8	128
DPPMP + $Fe(acac)_3$ (2/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	80	40	2 600	93.5	91.1	72	2.3	128
Bis(TPP) + $Fe(acac)_3$ (2/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	80	40	2 760	94.0	94.2	78	2.2	128
Bis(DPPyP) + $Fe(acac)_3$ (2/1)	2 000/1	$Al(^iBu)_3/Fe$ (40/1)	80	40	2 850	94.1	93.8	94	2.3	128

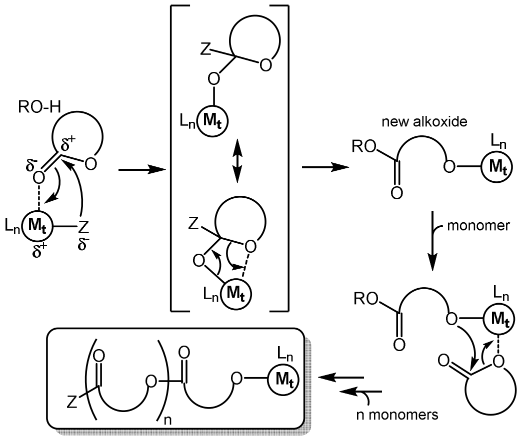
Diethyl phopshite (**DEP**) ; Triphenylphosphate (**TPP**) ; Tri(2,4-difluorophenyl) phosphate (**TFPP**) ; diphenyl pyridin-2-yl phosphate (**DPPyP**) ; diphenyl (3,5-dimethyl-1H-pyrazol-1-yl)phosphonate (**DPzPP**) ; bis-[1,3-(diphenyl phosphate)]-2-mehtylpropane (**DPPMP**), bis-[1,3-(diphenyl phosphate)]-benzene [**bis(TPP)**] and bis-[2,6-(diphenyl phosphate)]-pyridine [**bis(DPPyP)**]

4. Iron-catalyzed ring-opening polymerization of cyclic ester and carbonate monomers

The ROP of cyclic esters and related monomers by means of iron catalysts takes place by activation of the monomer by the metal, similarly as it proceeds with many elements of the periodic table [129]. This will obviously be dependent on the Lewis acid character of the cation, itself being related to the set of ligands in a given complex and also to the formal oxidation state of the metal (generally +II or +III for iron). In absence of any active ligand bound to the metal and in presence of an additional (generally protic) nucleophile, the mechanism of the reaction is expected to be of Activated Monomer Mechanism (AMM) type (**Scheme 7**). Such polymerization process is operating with most inorganic salts, the nucleophile being in most cases an alcohol that was added intentionally, or impurities present in the mixture like typically residual water. When the complex comprises an active ligand, typically alkoxide (phenoxide), in a well-defined purposely synthesized compound or resulting from the reaction of any alkyl/amido precursor with an alcohol (phenol) molecule, the polymerization reaction is expected to undergo through a Coordination-insertion Mechanism (CM) process (**Scheme 8**).



Scheme 7. ROP by Activated Monomer Mechanism [130].



Scheme 8. ROP by Coordination-insertion mechanism [131].

4.1. Iron-based inorganic salts / coordination catalysts for ROP.

Relevant catalysts in this section are inorganic salts of FeX_2 or FeX_3 formula (X = Cl, Br, ClO_4), carboxylates, diketonate (acac and related) complexes, homo- or hetero-metallic alkoxides/phenoxides that are under the form of a discrete compound or *in situ* generated from metal/reagent combination and amido derivatives. Their chemical structures are represented in **Fig. 12**. When considered as significant, the ROP data of selected experiments are gathered in **Table 8** at the end of the ROP section.

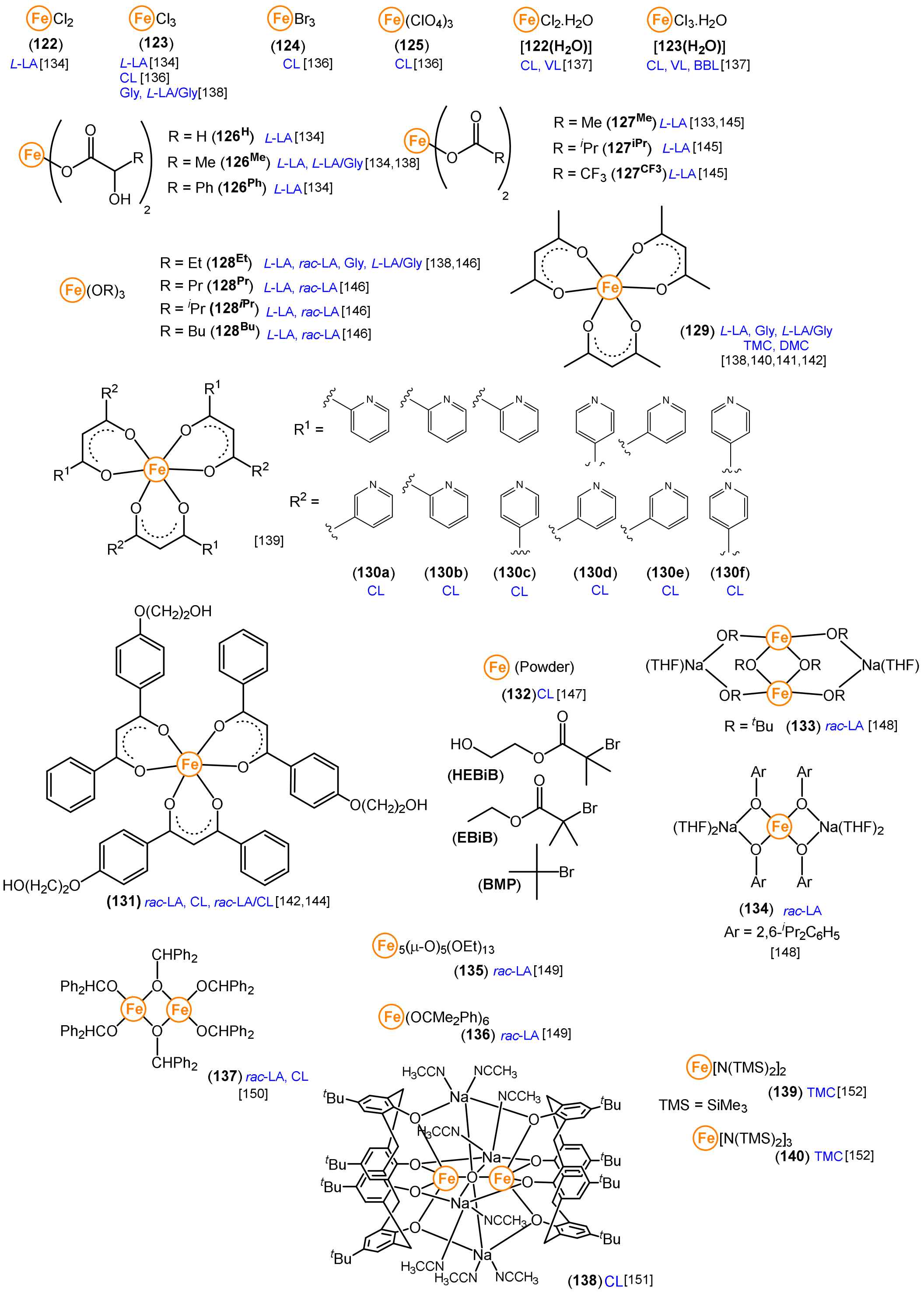


Fig. 12. Iron-based inorganic salts / coordination catalysts for the ROP of cyclic esters or carbonates.

The first study involving an iron derivative was published in 1985. In this study, iron oxide Fe_2O_3 was used to polymerize *L*-lactide (*L*-LA) under melt conditions at 180 °C (monomer to catalyst ratio of 100) [132]. A 48 hours period was required to reach conversion of 91% (TOF = 1.9 h^{-1}). Racemization of the polymerization product, due to transesterification reactions, was observed. The exact nature of the initiator was not discussed. A decade later, in turn, Södergård and Stolt used commercially available iron oxides and chlorides to polymerize *L*-LA under melt conditions (210 °C)

[133] and they found that the chlorides were more efficient than the oxides. The monomer conversion exceeded 90% (1 000 equiv. of monomer) after three hours under their conditions for both Fe(II) and Fe(III) chlorides (**122** and **123**, respectively), resulting in a maximum of M_w = 18 kg/mol in the case of **122**. Some racemization due to transesterification was noticed. With these compounds, the oxidation state of the iron metal did not affect the efficiency of the catalytic systems. At lower temperature in bulk (150 °C), Kricheldorf and coworkers had just before shown that commercial $FeCl_2$ (**122**) was a sluggish initiator (TOF less than 10 h^{-1}) toward the ROP of *L*-LA [134]. Interestingly however, the isolated poly(*L*-lactide) (PLLA) did not display, in this case, any racemization. Therefore, undesired transfer reactions resulting from H-abstraction in the α-position, as encountered with more basic alkaline-earth compounds [135], were considered as negligible. At 120 °C, **122** failed to yield PLLA, as same as observed previously with Fe_2O_3 [132].

It is only recently that commercial Fe(III) salts **123** – **125** (specified here as anhydrous) were revisited as potential ROP catalysts for cyclic esters, in combination with alcohols as initiators [136]. Among the three salts tested, iron perchlorate **125** was the best catalyst (highest activity – TOF = 210 h^{-1} – along with narrowest dispersity). Linear increase of M_n with time argued for controlled polymerization under such conditions of polymerization. Under their hydrated form, the iron chlorides were found to be efficient ROP catalysts in bulk (27 °C) for ε-caprolactone (CL), δ-valerolactone (VL) and β-butyrolactone (BBL) [137]. In particular, the Fe(III) chloride **123(H_2O)** displayed an extremely high activity toward BBL with TOF values up to 66 700 h^{-1}. It is worth mentioning that **123(H_2O)** was found to be much more active than its Fe(II) congener **122(H_2O)** toward the ROP of CL and VL. However, with both catalysts, poor control over molecular weights (experimental values >> theoretical ones) and dispersity (often approaching the value of 2) were observed. In the presence of alcohols, for all three monomers, the activity was enhanced and the dispersity was slightly narrowed, but no reversible transfer was clearly detected. The authors concluded that the rate of initiation and propagation were much superior to the rate of transfer. It was proposed that initiation proceeds via an AMM, which agrees well with the much higher activity of the most acidic Fe(III) catalyst compared to the Fe(II) catalyst. The authors noted in general a low level of transesterification, providing that both monomer and solvent were highly purified.

The iron(II) carboxylates: $FeGlyc_2$ (**126^{H}**), $FeLac_2$ (**126^{Me}**), $FeMand_2$ (**126^{Ph}**) (glycolate, lactate, mandelate, respectively) were assessed as catalysts by Kricheldorf *et al.* [134]. At 150 °C in bulk, the yields with **126^{H}** and **126^{Ph}** resembled to those found with $FeCl_2$ (**122**) as initiator (TOF < 10 h^{-1}) toward the ROP of *L*-LA, although **126^{Me}** could convert higher amounts of monomer (monomer to catalyst ratio up to 8 000), whereas complex **126^{Ph}** was found to be less efficient. The authors showed that undesired transfer reactions were taking place with these catalysts, which limit the molecular weights. Later on, various iron carboxylates were evaluated by Södergård and Stolt for *L*-LA polymerization under melt conditions (210 °C) [133]. The best results were obtained with the commercial iron(II) acetate $FeOAc_2$ (**127^{Me}**) (*i.e.* TOF = 960 h^{-1}). Some racemization due to transesterification was identified. Ferrocene has also been evaluated in the same study; it was found as very poorly efficient under the same conditions.

In 2002, $Fe(OEt)_3$ (**128^{Et}**), $Fe(acac)_3$ (**129**), $FeCl_3$ (**123**) and $Fe(lactate)_2$ (**126^{Me}**) were used as initiators to statistically copolymerize glycolide with *L*-lactide, at 100 – 150 °C in bulk [138]. The resulting copolymers obtained with complexes **128^{Et}** and **129** displayed high molecular weights, similarly to copolymers prepared under the same conditions with $Sn(oct)_2$, while complexes **123** and **126^{Me}** produced low molecular weight copolymers. All copolymers exhibited *quasi*-segmental chain microstructure due to transesterification reactions. As for them, complexes **128^{Et}**, **129** and **123** were found efficient toward the homo-ROP of glycolide in bulk. Substituted-diketonate Fe(III) complexes **130a-f** were synthesized and assessed for the ROP of CL [139]. The experiments were carried out at 110 °C in toluene in the presence of an excess of benzyl alcohol (BnOH). All complexes were active, complex **130a** being the most efficient among the series (TOF = 20.4 h^{-1}). The molecular weights were found close to the expected values considering benzyl alcohol as chain transfer agent, and they increased linearly with monomer conversion. Initiation was proposed to occur through a Fe-OR moiety resulting from dissociation of at least one diketonate ligand in the presence of alcohol. Regarding the ROP of *L*-LA, the homoleptic $Fe(acac)_3$ derivative **129** [140,138] showed low activity (TOF = 63 h^{-1}) at 130 °C in toluene as single component catalyst [141]. Concerning the reaction mechanism, the authors advanced cautiously by proposing the formation of an active cationic species by loss of an acetylacetonate ligand or by splitting into two ionic mononuclear entities. The same compound had been previously shown to be much more active (TOF = 684 h^{-1}) with additional BnOH (3 equiv) *vs. rac*-LA polymerization at 130 °C in bulk [142]. The ROP process was well controlled in this case (narrow *Đ*, M_n close to theoretical value). This catalyst behavior compared well with that of complex $Fe(dbmOH)_3$ (dbm = dibenzoylmethane) (**131**) under the same experimental conditions, which was found even more active (TOF = 891 h^{-1}). In this homoleptic tris(β-diketonate) derivative, the ligand bears an additional hydroxyl function so as to include within the same molecule the catalyst and the initiator. The ROP reaction afforded an iron-star $Fe(dbmPLA)_3$ which was further easily demetalated into dbmPLA macroligand. Noteworthy, chain extension was noted with additional *rac*-lactide in the presence of $Fe(dbmPLA)_3$. Ligand exchange between the β-diketonate ligand in the iron catalyst and the alcohol as CTA was proposed to take place, on the basis of kinetic studies [143]. Complex **131** also enabled, in a similar way, the ROP of ε-CL (in bulk at 110 °C) and of sequentially added CL and *rac*-LA to afford $Fe(dbmPLA)_3$ and Fe(dbmPCL-*b*-PLA)$_3$, respectively, which were further demetalated into functionalized dbmPLA and dbmPCL-*b*-PLA [144]. ^{1}H NMR and kinetic studies established a slight tendency to transesterification for such polymerizations conducted under harsh conditions, especially at high monomer conversions (conv. > 70%).

Iron(II) carboxylates: acetate (**127^{Me}**), isobutyrate (**127^{iPr}**) and trifluoroacetate (**127^{CF3}**) were intentionally synthesized as anhydrous compounds by Södergård and Stolt with the aim to use them for the ROP of *L*-LA [145]. This study was the first one involving well-defined iron(II) complexes as

ROP catalysts *vs.* *L*-LA. The polymerization reactions were performed in the melt at elevated temperatures (170 – 210 °C), a mandatory criteria to obtain a high conversion. Uncontrolled polymerization was observed due to transfer reactions and racemization. The authors proposed that a coordination-insertion polymerization mechanism (CM) was taking place, for the first time in the case of an iron-ROP catalyst.

The ROP of lactides (*L*-LA and *rac*-LA) was performed with various ferric alkoxides **128** under bulk conditions at 130 – 150 °C [146]. TOF values were comparable for all alkoxides (*ca* 20 h^{-1}) and transesterification reactions were noticed. Of the four compounds evaluated, the ethoxide **128**$^{\mathbf{Et}}$, which had been evaluated toward ROP of glycolide and its ROcoP (Ring-Opening coPolymerization) with *L*-LA [138], afforded polylactide having the highest M_n and the narrowest dispersity. NMR experiments established a coordination-insertion mechanism and it was proposed that each alkoxide group initiated a growing PLA chain.

The Fe(0)/hydroxyalkylbromide/BnOH combinations were assessed for CL polymerization (HEBiB = 2-hydroxyethyl 2-bromoisobutyrate, EBiB = Ethyl-2-bromoisobutyrate, BMP = 2-bromo-2-methylpropane) [147]. The resulting iron(II) catalyst **132** formed *in situ* with HEBiB, presumably of ferrous-alkoxide ROFeBr nature, afforded at 110 °C in toluene living and controlled polymerization, although with sluggish activity.

Hetero-bimetallic iron(II) complexes $[(THF)NaFe(OtBu)_3]_2$ (**133**) and $[(THF)_4Na_2Fe(2,6\text{-diisopropylphenolate})_4]$ (**134**) both polymerized *rac*-lactide efficiently (TOF up to 700 h^{-1}) at room temperature in dichloromethane (also at 60 °C in toluene for **133**), with complex **133** affording better control over the macromolecular data, albeit with transesterification observed at conversions > 70%. Addition of several equivalents of EtOH promoted a certain amount of chain transfer but also broadening the molecular weights distribution [148].

The first study with structurally characterized iron complexes used as catalysts for the ROP of lactide have been based on iron(III) alkoxides $Fe_5(\mu\text{-}O)(OEt)_{13}$ (**135**) and $Fe_2(OCMe_2Ph)_6$ (**136**) [149]. Complex **135** (under the form of a cluster) was found to be very active (TOF = 1 250 h^{-1}). The authors established the living character of the polymerization and two chains growing per metal, with possibly little transesterification. A coordination-insertion mechanism was proposed with the absence of epimerization of the monomer. Catalyst **136** (as a dimer) had similar behavior, although slightly less active (TOF = 950 h^{-1}). The iron(III) alkoxide of formula $[Fe(OR)_3]_2$ (**137**) (R = $CHPh_2$) was synthesized by the same group and characterized by X-ray diffraction studies [150]. This homoleptic alkoxide, which was found dimeric in the solid state, was ten times more active than the monoalkoxide **151** (see further, section 4.3.) for the ROP of CL, and enabled more controlled polymerization with initiation efficiency evaluated at 100%. This difference in reactivity was less pronounced for the ROP of *rac*-LA but the process was again in favor of **137**. This latter complex is a rare example of compounds displaying higher activity toward LA than CL (also observed with complex **138**). Sequential CL/LA copolymerization could then *de facto* be obtained successfully with complex **137**.

In terms of activity/control of the ROP of LA, complex **137** compares well with the behavior of very active catalysts **135** and **136**. However, a certain lack of reproducibility due to high sensitivity to impurities was noticed.

Some years ago, a series of structurally characterized calixarene iron(III) complexes were screened as catalysts for the ROP of CL [151]. These heteromultimetallic iron aryloxides contain calixarene ligands with methylene ($-CH_2-$) or dimethyleneoxa ($-CH_2OCH_2-$) bridges. They were found to be moderately active, yielding low M_n polycaprolactones with broad dispersity due to uncontrolled transfer resulting from prolonged reaction times. Among them, complex $[Na_4-(CH_3CN)_8(L^1Fe)_2(\mu-O)]$ **138** (L^1 = *p-tert*-Butylcalix[4]arene) displayed the best capacity to polymerize CL *via* a proposed coordination-insertion mechanism.

To date, the ROP of cyclic carbonate monomers were scarcely examined with iron-based catalyst. In 2004, Dobrzynski *et al.* studied the ROP of trimethylene carbonate (TMC) and 2,2-dimethyltrimethylene carbonate (DMC) using the iron(III) $Fe(acac)_3$ (**129)** as single initiator at 110 °C [140b]. A good activity was noticed in the case of TMC (TOF up to *ca* 65 h^{-1}), although significantly lower than that observed in the presence of an additional alcohol (*vide infra*). The authors found that the conversion increases linearly with time at 110 °C, while at 160 °C degradation is observed. High conversion of DMC was also achieved but the reaction was much slower. Poor control over molecular masses was noted at prolonged reaction times and at high monomer to initiator ratios. The mechanism of initiation in absence of exogenous alcohol was not given.

Some years later, the group of Carpentier carried out the immortal ROP of TMC with a two-component catalyst system based on the iron(III) salt **129** with an alcohol as co-initiator and chain transfer agent [140a]. Experiments were conducted in bulk at 110 – 150 °C and the catalytic activities were multiplied by a factor of more than ten by comparison with the results in absence of alcohol. A mechanism of AMM type was established, along with low percentage of transesterification. However, complex **129** was significantly less active than the homoleptic iron(II) silylamido complex **139**, and only little more active than its iron(III) homolog **140** that has been assessed earlier under the same conditions [152].

4.2. Iron-based complexes supported by neutral ligands for ROP.

Relevant catalysts in this section are coordination complexes comprising neutral nitrogen-based heterocyclic ligands. The oxidation state of the iron element is formally +II or +III, with the exception of low valent (0 or +I) iron complexes where the ligand displays a non-innocent behavior. Their chemical structure is represented in **Fig. 13.** When considered as significant, the ROP data of selected experiments are gathered in **Table 8** at the end of the ROP section.

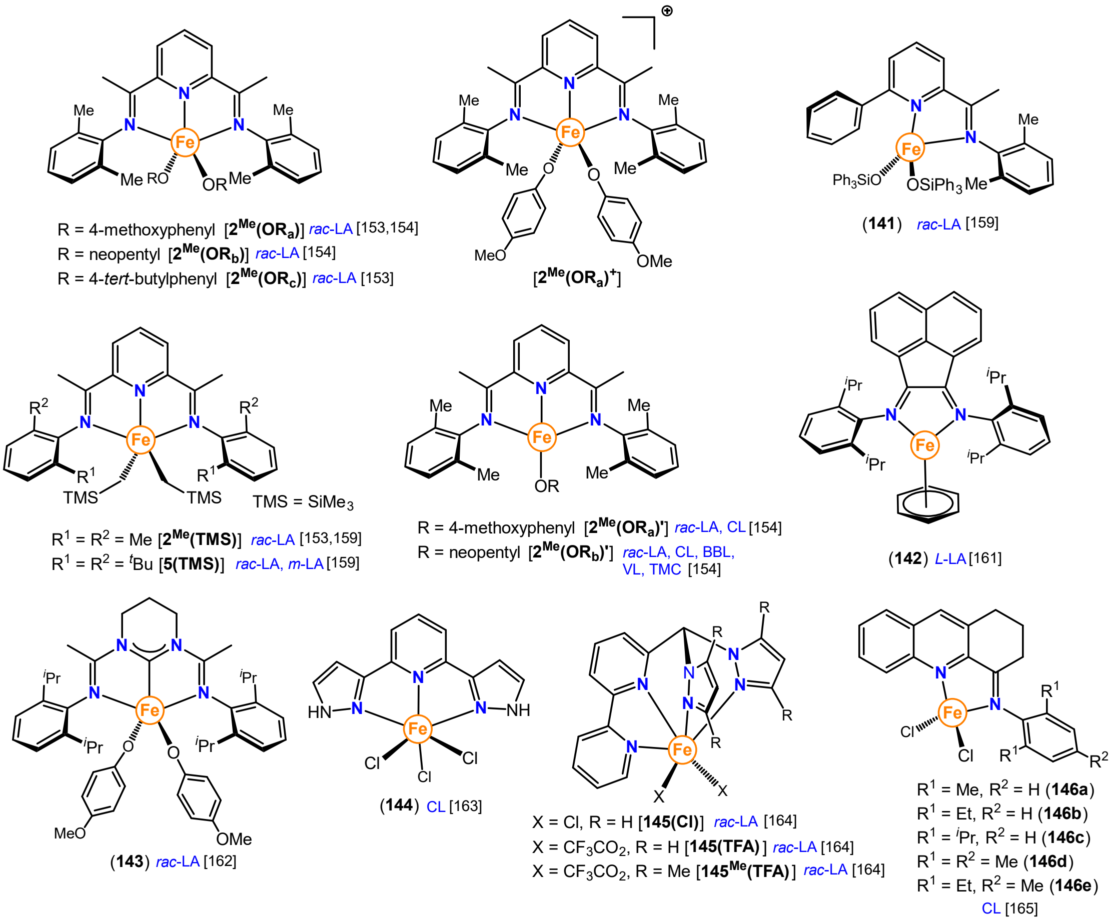


Fig. 13. Iron-based complexes bearing neutral ligands for the ROP of cyclic esters or carbonates.

In contrast to their thorough and long-time use in olefins polymerization (see section 2), the iron complexes bearing a neutral heterocyclic BIP or related ligand, which possesses a high potential of electronic/steric variations, have been only recently studied in the frame of ROP of polar cyclic monomers.

It was not until 2013 that he group of Byers investigated a series of iron(II)-BIP alkoxide/aryloxide complexes as initiators in the ROP of *rac*-LA at room temperature in dichloromethane [153]. The complex **$2^{Me}(OR_a)$**, which was isolated by reacting the alkyl precursor **2^{Me}(TMS)** with two equiv. of 4-methoxy-phenol, exhibited moderate activity (TOF = *ca* 15 h^{-1}). The analogs complexes **$2^{Me}(OR_b)$** and **$2^{Me}(OR_c)$** were *in situ* formed in the same way (but not isolated) and have shown to exhibit similar reactivity and results for the ROP of *rac*-LA, whereas complex **2^{Me}(TMS)** was sluggishly active on its own. The performances of these catalysts were optimized a few years later [154] with TOF values up to 2 820 h^{-1} in toluene at room temperature, which competes with the best metal-based catalysts towards the ROP of lactide [155,129]. With such complexes [**$2^{Me}(OR_{a-c})$**], the process was found living and operating according to a coordination-insertion mechanism, the number of growing chain per metal being dependent on the aryloxide (one chain)/alkyloxide (two chains) nature of the initiating group. The use of a chiral alcohol did not allow the control of the stereo-selectivity of the transformation. In the same study, the iron(III) complex $\mathbf{2^{Me}(OR_a)^{+}}$, which resulted from the oxidation of its iron(II) congener $\mathbf{2^{Me}(OR_a)}$, was found to be inactive for the ROP of LA. This difference in behavior was exploited to produce a redox-controlled catalytic system with switch on/off of the polymerization ability, depending on the oxidation state of the iron metal center (a recent study including theoretical support was published by the same group with CL [156]). Subsequently, the authors found that the iron(III) complex $\mathbf{2^{Me}(OR_a)^{+}}$ was able to polymerize cyclohexene oxide, whereas the iron(II) counterpart [$\mathbf{2^{Me}(OR_a)}$] was inactive. The distinct monomer selectivity of this iron-based catalyst, as a function of its oxidation state, allowed the authors to elegantly prepare a PLA-*b*-PCHO block copolymer by *in situ* switching from one species to another, using an appropriate oxidizing or reducing agent [157]. Another paper from the same authors exploited the same features to propose a way of elaborating innovative redox crosslinking of PLA from intentionally synthesized epoxy-grafted lactide monomer [158].

The first stereo-selective ROP of LA with an iron-based catalyst was achieved in a smart study by the same group, using *in situ* generated chiral iron (II) catalysts based on BIP complexes $\mathbf{2^{Me}(TMS)}$ and **5(TMS)** in the presence of silanols [159]. With *rac*-LA at room temperature in THF solution, the polymerization exhibited a living character and heterotactic PLA with P_r up to 75% was obtained (P_r probability of racemic linkages). However, deviations from the theoretical M_n values were observed, due to slow initiation. Syndiotactic PLA with P_r up to 92% was achieved from the polymerization of *meso*-LA with **5(TMS)** combined with selected silanols. The iron bis(siloxide) complex **141** containing a bidentate iminopyridine ligand was then intentionally prepared (and characterized by X-ray diffraction studies) as a model for the η^2 coordination mode of BIP. This complex behaved similarly as the binary **5(TMS)**/silanol catalytic system, affording slightly lower stereo-selectivity. Enantiomorphic-site control was advanced to explain these results, with DFT calculations as support. According to the authors, these iron-catalyzed reactions benefit from synergistic effect involving silanol and BIP ligands bound to the metal.

With the aim to focus on the impact of the oxidation state of the metal, Byers and coworkers prepared a family of formally iron(I)-(BIP) alkoxide complexes that have been involved in the ROP of a a variety of cyclic polar molecules: LA, CL, VL, γ-butyrolactone (GBL), BBL, TMC, ethylene carbonate (EC) and cyclohexene oxide [154]. Complex $\mathbf{2^{Me}(OR_a)'}$ exhibited similar activity as the iron(II) $\mathbf{2^{Me}(OR_a)}$ in ROP of *rac*-LA, but slow initiation rates were advanced to explain the higher than expected molecular weights. Faster polymerization resulted from the use of the neopentyl alkoxide complexes $\mathbf{2^{Me}(OR_b)'}$ and $\mathbf{2^{Me}(OR_b)}$, as already observed [153], the process being additionally living. Surprisingly, complex $\mathbf{2^{Me}(OR_a)}$ was found inactive toward the ROP of CL at room temperature, whereas complex $\mathbf{2^{Me}(OR_a)'}$ was found fairly active. With complex $\mathbf{2^{Me}(OR_b)'}$ as catalyst, very high activity was obtained (TOF = 11 880 h^{-1}, the best one up to now for an iron catalyst) and the process was better controlled than with $\mathbf{2^{Me}(OR_a)'}$. The complex $\mathbf{2^{Me}(OR_b)'}$ exhibited the best ROP catalyst performances among the studied series of catalysts with other monomers like BBL (but with uncompleted conversion), VL and TMC. Remarkably, the alkoxide catalyst **$2^{Me}(OR_b)$'** displayed much higher reactivity and control of the polymerisation process than its phenoxide analog **$2^{Me}(OR_a)$'**. However, GBL was not homo-polymerized by **$2^{Me}(OR_b)$'** but it could be incorporated into polymers of CL (up to 33 mol%). Poly(CL*co*VL) were also prepared by means of **$2^{Me}(OR_b)$'**. However, the combination of *rac*-LA and CL did not produce statistical copolymers, but only PLA. This trend, *a priori* surprising, considering that the homoROP of CL is much faster than that of LA, follows in fact a general behavior that is well documented [160]. Block copolymers could however be prepared. On the basis of a set of specific analyses (X-ray, Mössbauer, SQUID magnetometry) completed with theoretical (DFT) investigations, the authors concluded that the bis(imino)pyridine Fe(I) complexes **$2^{Me}(OR)$'** can rather be seen as iron(II) derivatives surrounded by a one-electron reduced ligand. The iron (III) cationic analogues were found inactive toward the same ROP processes, but they were capable of performing the ROP of epoxides.

In an interesting contribution from Findlater and coworkers, the α-diimine iron (0) complex **142** was synthesized and used for the ROP of *L*-Lactide in benzene (and in C_6D_6 solutions in the case of ^{1}H NMR monitoring) at 90 °C [161]. In the presence of **142** alone, the polymerisation was effective, probably operating *via* an activated monomer mechanism [130] with potential initiation of trace amounts of residual water considering the very high M_n obtained. Precise control over molecular weights was further obtained when an additional phenol molecule was added to the catalytic system. ^{1}H NMR analysis showed the presence of the phenol residue at the end-groups of the PLA. Despite ^{1}H NMR experiments carried out under the conditions of polymerization, the authors could not decide between an AMM and CM pathway involving a putative Fe-phenoxide (I) species, while thorough characterization of **142** suggested redox non-innocent properties of the ligand. Byers *and coll.* synthesized and used for *rac*-LA polymerization a bis(amidinato)-NHC supported bis(alkoxide) iron complex (**143**), with the aim to compare its behavior with that of bis(imino)pyridine (BIP) complexes **2^{Me}(TMS), 5(TMS)** and **$2^{Me}(OR_{a\text{-}c})$** [162]. With this more electron-releasing ligand as compared to BIP, the initiator was found to display slow initiation followed by fast propagation, affording high M_n polylactide. Very efficient catalytic behavior was observed at high catalyst ratios (TOF = 1 417 h^{-1}), largely competing with the analogous iron-BIP complexes, while maintaining narrow molecular weight distributions ($Đ$ = 1.2 – 1.3).

Another study by the group of Lang concerns the redox-control in iron-mediated ROP of cyclic esters. The iron(III) $(bppyH_2)FeCl_3$ complex **144** ($bppyH_2$ = 2,6-di(pyrazolyl)pyridine), which was structurally characterized by single crystal X-ray analysis, was found efficient to initiate the ROP of CL in the presence of alcohol at 100 °C in toluene [163]. Among the different experiments, the binary **144**/isopropanol systems exhibited the highest catalytic activity (TOF = 14.6 h^{-1}, which remains modest by comparison with the best iron catalysts described in this review) and the process was found to be living. A coordination-insertion process was proposed, on the basis of polymer alkyl end-groups signals found in the ^{1}H NMR spectrum and a discussion based on experimental M_n (although not corrected by a 0.58 factor) concludes that two PCL chains are growing per metal. In contrast to the observations of Byers in the BIP series (complexes $\mathbf{2}^{\mathrm{Me}}$, *vide supra*), the iron(II) complex (bppyH_2)$FeCl_2$ resulting from reduction of complex **144** was found inactive for the ROP of CL under the same conditions. A redox-control of the process was then implemented by reversibly switching upon *in situ* redox reversible transformation between the Fe(III) and Fe(II) species.

The bis(pyrazolyl)bipyridinylmethane supported iron(II) mononuclear complexes **145** were synthesized by Herber *et al.* and used as catalysts for the ROP of *rac*-LA under harsh conditions, *i.e.* in the melt at 150 °C [164]. The activity was rather low (TOF < 15 h^{-1}) and poorly controlled with molecular weights differing from theoretical values and, in some cases, displaying multimodal distributions. This behavior was attributed to the nature of the initiating group, chloride or trifluoroacetate, as no alcohol molecule was added to activate the initiation. Mass spectroscopy analyses did not allow to clearly establish the initiation reaction mechanisms when dry sublimed lactide was used, whereas cyclic oligomers and polymer chains with hydroxyl (from residual water initiation) end-groups were identified with unsublimed monomer. A coordination-insertion mechanism was postulated.

A recent study was reported by the group of Sun and Zhang using a series of iron(II) dichloride complexes supported by *N,N'*-bidentate 4-arylimino-1,2,3-trihydroacridine ligands (**146a-e**) for the ROP of CL [165]. The catalytic systems were generated *in situ* with 2 equiv. of $LiCH_2SiMe_3$ followed by the addition of tetradecanol as co-initiator. In the absence of alcohol co-reagents, complex **146a** was not able to promote the initiation of the polymerization. In that respect, the combination of tetradecanol and **146a-e/**2$LiCH_2SiMe_3$ displayed good activity for the ROP of CL even at room temperature (TOF = 296 – 376 h^{-1}). The catalytic activity was dependent on the *N*-aryl substituent with complex **146a** bearing a small methyl group on both ortho position showing the highest activity (TOF = 376 h^{-1}) whereas the presence of electron donating methyl group on the para position of the *N*-aryl (complex **146d**) slightly lowers the efficiency of the catalytic systems (TOF = 296 h^{-1}). Analysis of the polymer chain end revealed the presence of teradecylalkoxy terminal group, indicating that the initiation of the ROP occurs with the Fe-O$(CH_2)_{13}$-CH_3 species and that the polymerization proceeds *via* a coordination-insertion mechanism.

4.3. Iron-based complexes supported by anionic ligands for ROP.

Relevant catalysts in this section are obtained from complexes, all of iron(II) or iron(III), containing one or two bulky mono or di(anionic) nitrogen-ligands. Their chemical structures are represented in **Fig. 14.** When considered as significant, the ROP data of selected experiments are gathered in **Table 8** at the end of the ROP part.

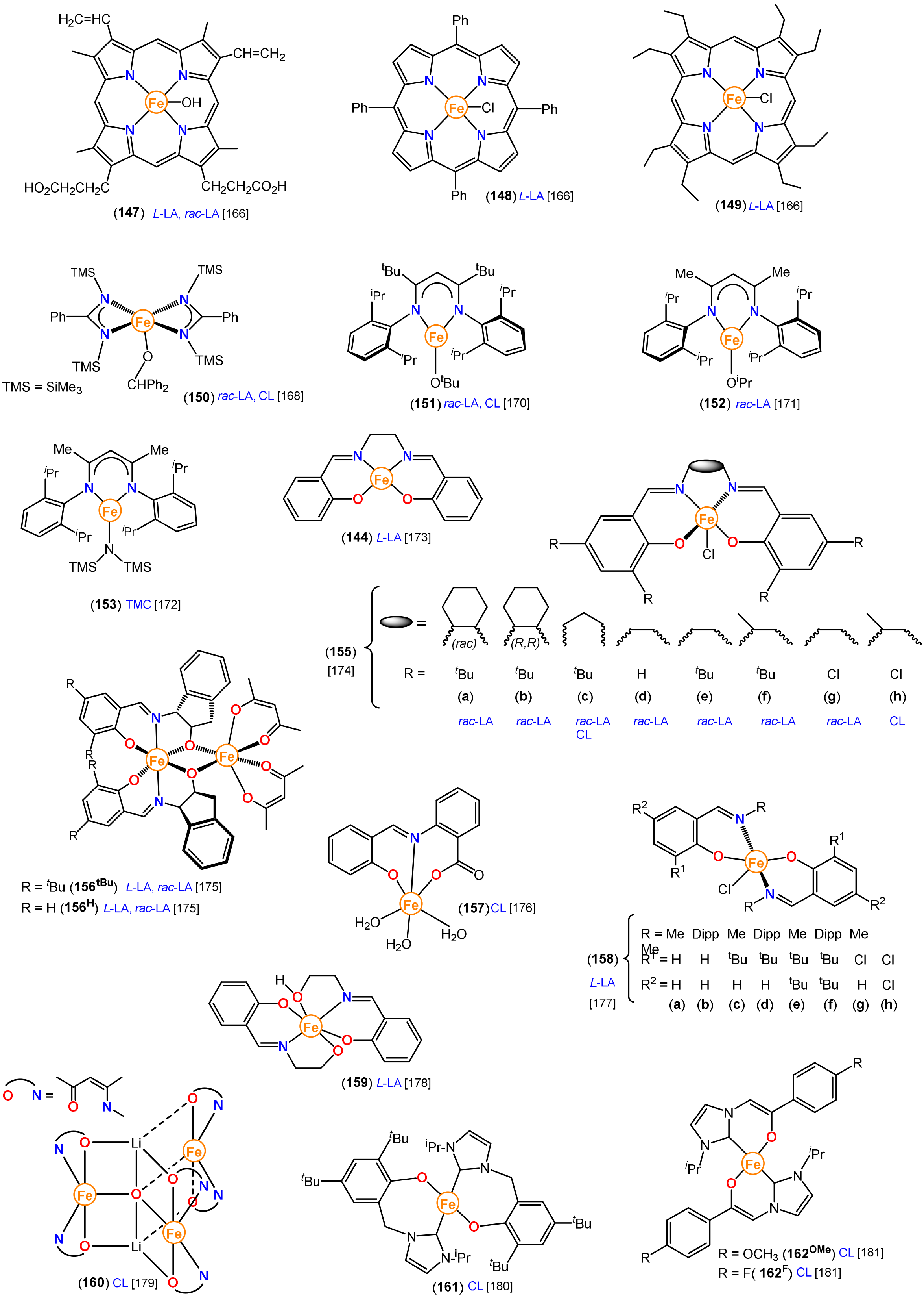


Fig. 14. Iron-based complexes bearing anionic ligands for the ROP of cyclic esters or carbonates

As soon as 1993, Kricheldorf *et al.* had assessed nitrogen-macrocyclic supported complexes of iron: hematin (**147**), tetraphenylporphyrinFeCl (**148**) and octaethylporphyrinFeCl (**149**), as ROP catalysts [166]. In contrast to recent developments involving aluminum porphyrins as ROP catalysts [167], all three iron(III) porphyrins in the present case were found poorly effective: high temperatures and bulk conditions were necessary to polymerize *L*-LA or *rac*-LA, and total conversions remained far from being achieved.

The iron(III) alkoxide of formula L_2FeOR (R = $CHPh_2$, **150**, L = *N,N*'-bis(trimethylsilyl)benzamidinate) was synthesized and characterized by X-ray diffraction studies [168]. This monoalkoxide, which exists as a monomer in the solid state, was found less active for the ROP of CL than the homoleptic alkoxide complex **137** and operating in a less controlled manner (broader dispersity values and initiation efficiency limited to 50% with **150**). The same trend of higher activity of **137** *vs.* **150**, although less pronounced, was observed toward LA polymerization under comparable conditions. In contrast to what is generally reported, complex **150** displays higher activity toward LA than CL, in a similar manner to that found with complex **137**. It is however worth mentioning that a lack of reproducibility was noticed, due, according to the authors, to too high sensitivity to impurities.

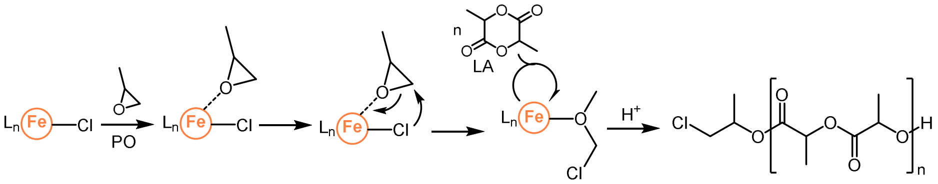
The discrete diketiminate iron(II) monoalkoxide **151**, which was prepared by Gibson and coworkers from the chloro diketiminate precursor [169], adopts a monomeric structure in the solid state [170]. The authors showed that this compound behaves efficiently as initiator toward the ROP of LA and CL. Under mild experimental conditions (room temperature, toluene solution), TOF values reach 282 h^{-1} (1 140 h^{-1} for CL) and the process is well-controlled in term of kinetics. However transesterification was observed at high conversion and M_n values (not corrected, based on PS standards) were higher than theoretically expected for one polymer chain per metal (M_{nexp} = 37.5 kg/mol *vs.* M_{nth} = 13.5 kg/mol), which argues for uncomplete catalyst efficiency. A decade later, Li *et al.* synthesized the less sterically congested diketiminate monoalkoxide Fe(II) complex **152**. The ROP of *rac*-lactide was performed with this complex in toluene solution at 70 °C, which exhibited moderate activity and poor control with respect to molecular weights [171]. Lower activities than the similar iron complex **151** reported by Gibson were noted [170], suggesting that the steric hindrance of the diketiminate iron(II) monoalkoxides has an impact over their polymerization activity. No stereo-selectivity was observed.

With the aim to specifically study the capability of an iron-silylamido bond to operate in the ROP of TMC, Carpentier and coworkers compared the behavior of the β-diketiminate (BDI = $CH(CMeNC_6H_3\text{-}2,6\text{-}^iPr_2)_2$) iron(II) complex **153** with that of homoleptic iron(II) **139** and iron(III) **140** derivatives in bulk at 60 °C, under immortal conditions (*i.e.* in the presence of an excess of BnOH) [172]. Among them, the order of activity was **139** > **140** > **153**. Raising the temperature to 110 °C was highly beneficial to the activity, by a factor of up to 150 for compound **153** (TOF value from 25 h^{-1} at 60 °C to 3 720 h^{-1} at 110 °C), which could additionally enable the conversion of high loadings of monomers (TMC/BnOH/Fe = 50 000/20/1), albeit with modest control over molar masses and dispersity. No clear effect of the oxidation state of the iron metal was noted, as the divalent complex

139 was more active, at both 60 °C and 110 °C, than the trivalent one **140**, while divalent **153** remained the least active at 60 °C. All complexes were found active but far less than their Ca, Mg, Zn and Y congeners.

The first study in which a Salen-iron(III) complex **154** was used as catalyst to polymerize *L*-lactide was published in 2010 [173]. Reactions were performed in bulk at 200 °C with a monomer to catalyst ratio of 2 500. No mention is made of the conversions obtained for a given time, although the authors stated that the polymerization was quantitative. M_n values reach up to 31 kg/mol, along with very narrow dispersities, which speaks in favor of unicity of active species. However, these M_n values are one order of magnitude lower than expected, 360 kg/mol, for 100% conversion and absence of transfer reactions. The resulting PLLA is isotactic, which agrees for absence of any epimerization reactions. The mechanism of the initiation of the polymerization is not discussed.

More recently, the group of Pang achieved the ROP of lactide (*rac*-, *L*- and *meso*- were studied) and CL in bulk with a series of new Salen-iron(III) complexes (**155a-h**) [174]. The initiation was promoted by activating the air-stable (Salen)FeCl precursors with propylene oxide (PO), which also served as solvent. Varying the substituents and ligand backbone made stereo-selective polymerization of *rac*-LA possible, for the first time with an Fe(III) catalyst and little later to the studies of Byers (*vide supra*), to yield either predominantly isotactic (P_m up to 0.78) or heterotactic (P_r up to 0.63) polylactides. The stereo-selectivity was shown to proceed via a chain end control mechanism. The activity of these catalysts, which was related to the flexibility of the bridging moiety as well as to the substitutions on the phenolic rings, was found significantly higher than their Al-based Salen counterparts. Complexes **155a-h** were also found active toward the ROP of CL, under similar conditions as for lactide but at room temperature. Similar structure-reactivity relationships were noted regarding the impact of the phenyl substituents, but the presence of the methyl on the amine bridge severely decreased the activity. The control over molecular weights was average with both types of monomers. The mechanism (**Scheme 9**) was demonstrated to proceed by coordination-insertion into the metal-alkoxide moiety resulting firstly from the insertion of epoxide (as co-initiation reagent) into the Fe-Cl bond.



Scheme 9. Proposed mechanism of iron-catalyzed ROP activated by epoxide [174].

In a study from Kang *et al.*, the dimeric dinuclear iron(III) Schiff-based acac complexes **156^{tBu}** and **156^{H}**, in which the two metals have different coordination environment, were synthesized [175]. These complexes behaved as efficient catalysts for the ROP of lactide (*L*-LA and *rac*-LA) at 130 °C in toluene and in bulk. By comparison, the homoleptic derivative **129** showed lower activity under the same conditions toward *L*-LA. A living character was observed for both complexes **156^{tBu}** and **156^{H}** as initiators, but the M_n values were found generally inferior to the expected ones. Concerning the ROP mechanism, the authors advance cautiously by proposing the formation of cationic species by loss of one acetylacetonate ligand or by splitting into two ionic mononuclear entities.

The benzoic acid functionalized Schiff base iron Fe(III) complex **157** was synthesized and assessed toward ROP of CL in bulk at 125 °C [176]. Poor results in term of activity (TOF = 2.1 h^{-1}) were noticed. The metal-ligand rather than coordinated water was supposed to initiate the ROP process.

A series of new half-Salen iron(III) chloride complexes **158(a-h)** were recently prepared by Shaver, Garden and coworkers. These complexes have been found to be stable with respect to air and moisture [177]. After activation by means of propylene oxide (here not exceeding 50 equivalents of that toxic co-reagent, to be compared to the conditions used by Pang, *vide infra*), they afforded active catalysts for the ROP of *rac*-LA at 120 °C in toluene, with moderate control over molecular weights. The authors noticed a clear variability of initiation with the strength of the Fe-Cl bond in the precursors, due to the nature of the substituents in complexes **158(a-h)**. Optimized ROP conditions (TOF = 45 h^{-1}), were found by performing the reaction at lower temperature (85 °C), short reaction times (2 h rather than 24 h) and preforming the active Fe-alkoxide species by reacting **158h** with excess PO prior to the addition of the monomer. Remarkably, this family of complexes **158a-h** was also used efficiently in styrene and MMA reverse atom-transfer radical polymerization.

The iron(III) phenoxyimine complex **159** was synthesized and its crystalline structure was determined [178]. This complex was assessed as initiator for the ROP of *L*-LA under bulk conditions at temperatures between 120 – 180 °C. Rather poor activity was obtained under these conditions and the low M_n values and broad dispersities observed suggest uncontrolled transfer reactions. A coordination-insertion mechanism was proposed by the authors.

Peng, Roesky and coworkers could isolate a multimetallic iron(II)-lithium "ate" complex **160** from ionic metathesis between the lithium salt of *N*-methyl-β-ketimine, $FeCl_2$, $LiN(SiMe_3)_2$ and water. This compound was used as a single component initiator for the ROP of CL [179]. At room temperature in toluene solution, moderate activity (TOF up to 174 h^{-1}) but low M_n were noticed, which were explained by transesterification reactions. A cationic mechanism leading to cyclic oligomers was postulated.

The group of Shen was interested in the preparation of functionalized *N*-heterocyclic iron complexes bearing a phenolate or an enolate moiety. The NHC-phenolate iron(II) complex **161** was prepared by ionic metathesis of $FeBr_2$ with the corresponding imidazolium-phenol protio reagent [180]. X-ray structure determination showed that this complex was monomeric, the metal being surrounded by two bidentate ligands as a distorted tetrahedron, with the two Fe-O bonds *trans* to each other. Upon the ROP of CL, **161** was found fairly efficient (TOF = 25 h^{-1}) to convert the monomer into polycaprolactone, through a coordination-insertion mechanism as established by the authors. Decrease of the M_n values with conversion along with dispersity broadening indicated the occurrence of uncontrolled transesterification during the polymerization process. No specific role of the NHC moiety was noted. Regarding the bis enolate *N*-heterocyclic carbene Fe(II) complexes, $L^1{}_2Fe$ (**162^{OMe}**) and $L^2{}_2Fe$ (**162^F**) $\{4\text{-R-}C_6H_4CH[C(NCHCHN^iPr)]O\}_2Fe$ (R = OCH_3, L^1; R = F, L^2) were prepared in a similar way as NHC-phenolate **161** by ionic metathesis between $FeBr_2$ and two equivalents of anionic ligand *in situ* generated by double deprotonation of the protio precursor [181]. Both complexes, which display a monomeric structure in the solid state, were shown moderately efficient toward the ROP of ε-caprolactone in toluene solution at 80 °C (TOF = 45 h^{-1}), the methoxy derivative **162^{OMe}** being more active that the fluorinated one **162^F**. As same as with **161**, poor control over the ROP process was observed, which was attributed to transesterification. No specific role of the NHC moiety was either noted.

Table 8
Selected polymerization data for the ROP of cyclic esters with iron-based complexes.

Complex (ox. state)	monomer	[M]/[Fe]	Initiator/CTA ([I]/[Fe])	T (^{0}C)	Time (h)	Conv (%)	TOF (h^{-1})	M_n (kg/mol)	Đ	Solvent	Ref.
122 (III)	*L*-LA	1000	-	150	96	80	8.0	-	-	bulk	134
123 (III)	CL	200	^{i}PrOH (5)	25	2	94	94	8.9	1.30	bulk	136
123 (III)	CL	200	^{i}PrOH (5)	25	72	80	2.2	5.8	1.46	bulk	136
125 (III)	CL	200	^{i}PrOH (5)	25	48 min	84	210	5.1	1.63	bulk	136
123(H_2O) (III)	CL	200	-	27	27 min	100	444	36.1	2.22	bulk	137
123(H_2O) (III)	CL	200	-	27	1	100	200	31.2	1.27	toluene	137
123(H_2O) (III)	CL	200	BnOH (5)	27	17 min	100	706	67.3	1.26	bulk	137
123(H_2O) (III)	CL	200	BnOH (5)	27	30 min	100	400	18.2	1.25	toluene	137
122(H_2O) (II)	CL	200	-	27	24	100	8.3	48.5	2.15	bulk	137
122(H_2O) (II)	CL	200	BnOH (5)	27	14	100	14.3	82.1	1.43	bulk	137
123(H_2O) (III)	VL	200	-	27	0.96 min	100	12 500	74.3	2.07	bulk	137
123(H_2O) (III)	VL	200	-	27	9.6 min	100	1250	82.2	1.19	toluene	137
123(H_2O) (III)	VL	200	BnOH (5)	27	0.78 min	100	15 385	61.7	1.78	bulk	137
123(H_2O) (III)	VL	200	BnOH (5)	27	6 min	100	2 000	54.5	1.18	toluene	137
122(H_2O) (II)	VL	200	-	27	2.33	100	85.8	82.7	2.06	bulk	137
122(H_2O) (II)	VL	200	BnOH (5)	27	1.67	100	120	144.4	1.37	bulk	137
123(H_2O) (III)	BL	200	-	27	0.24 min	100	50 000	24.2	1.95	bulk	137
123(H_2O) (III)	BL	200	-	27	6 min	100	2 000	29.7	1.21	toluene	137
123(H_2O) (III)	BL	200	BnOH (5)	27	0.18 min	100	66 667	44.9	1.25	bulk	137
123(H_2O) (III)	BL	200	BnOH (5)	27	3 min	100	4 000	19.2	1.20	toluene	137
126^{H} (II)	*L*-LA	1 000	-	150	96	85	8.8	-	-	bulk	134
126^{Me} (II)	*L*-LA	1 000	-	150	96	84	8.7	-	-	bulk	134
126^{Ph} (II)	*L*-LA	1 000	-	150	96	80	8.3	-	-	bulk	134
127^{Me} (II)	*L*-LA	2 000	-	210	2	96	960	> 50	-	bulk	133
128^{Et} (III)	Gly	833	-	150	48	92	16	> 40	-	bulk	138
129 (III)	Gly	833	-	100	96	91	7.9	> 40	-	bulk	138
123 (III)	Gly	833	-	100	96	80	6.9	> 40	-	bulk	138
128^{Et} (III)	*L*-LA /Gly	833	-	150	144	96	5.6	77 M_v	-	bulk	138
129 (III)	*L*-LA /Gly	833	-	100	144	95	5.5	65 M_v	-	bulk	138
123 (III)	*L*-LA /Gly	833	-	100	144	71	4.1	40 M_v	-	bulk	138
126^{Me} (II)	*L*-LA /Gly	833	-	100	144	60	3.5	15 M_v	-	bulk	138
130a (III)	CL	100	BnOH (5)	110	24	98	20.4	14.1	1.23	toluene	139

Complex (ox. state)	monomer	[M]/[Fe]	Initiator/CTA ([I]/[Fe])	T (^{0}C)	Time (h)	Conv (%)	TOF (h^{-1})	M_n (kg/mol)	*Đ*	Solvent	Ref.
129 (III)	*L*-LA	100	-	130	1	63	63	10.0	1.10	toluene	141
129 (III)	*rac*-LA	225	BnOH (3)	130	15 min	76	684	9.2	1.23	bulk	142
131 (III)	*rac* -LA	225	OH (3) ^{c}	130	10 min	66	891	8.1	1.16	bulk	142
131 (III)	CL	225	OH (3) ^{c}	110	4	56	14	5.9	1.38	bulk	144
128^{Et} (III)	*rac* -LA	1 000	-	130	48	94	19.6	61.4	1.61	bulk	146
128^{Et} (III)	*L*-LA	1 000	-	130	48	98	20.4	106.3	1.54	bulk	146
128^{Pr} (III)	*rac* -LA	1 000	-	130	48	94	19.6	50.8	1.68	bulk	146
128^{iPr} (III)	*L*-LA	1 000	-	130	48	97	20.2	90.3	1.63	bulk	146
128^{iPr} (III)	*rac*-LA	1 000	-	130	48	91	18.9	29.6	1.73	bulk	146
128^{iPr} (III)	*L*-LA	1 000	-	130	48	96	20	54.3	1.74	bulk	146
128^{Bu} (III)	*rac*-LA	1 000	-	130	48	96	20	18.6	1.92	bulk	146
128^{Bu} (III)	*L*-LA	1 000	-	130	48	96	20	30.3	1.89	bulk	146
132 (II)	CL	100	HEBiB	110	24	100	4.2	21.7	1.22	toluene	147
132 (II)	CL	100	HEBiB/BnOH (1)	110	24	99	4.1	10.1	1.39	toluene	147
127^{Me} (II)	*L*-LA	200	-	170	10	51	10.2	12.5	5.25	bulk	145
127^{iPr} (II)	*L* -LA	200	-	190	7	80	22.9	45.0	1.97	bulk	145
127^{CF3} (II)	*L* -LA	200	-	170	10	51	10.2	12.5	5.25	bulk	145
133 (II)	*rac*-LA	200	-	25	1	81	162	25.4	1.33	DCM	148
133 (II)	*rac*-LA	220	EtOH (1)	25	2	98	108	16.8	1.72	DCM	148
133 (II)	*rac*-LA	380	EtOH (2)	25	3	98	124	20.8	1.67	DCM	148
133 (II)	*rac*-LA	380	EtOH (3)	25	3	99	29	13.9	2.07	DCM	148
133 (II)	*rac*-LA	370	-	60	0.5	97	718	27.7	1.87	toluene	148
134 (II)	*rac*-LA	210	-	25	1	83	174	25.2	1.89	DCM	148
135 (III)	*rac*-LA	450	-	70	21min	97	1 250	32.0	1.17	toluene	149
136 (III)	*rac*-LA	450	-	70	35 min	98	756	34.0	1.60	toluene	149
137 (III) ^{a}	*rac*-LA	1 000	-	70	37 min	94	1 524	54.4	1.25	toluene	150
137 (III) ^{a}	CL	200	-	25	26 min	100	462	20.9	1.20	toluene	150
138 (III)	CL	300	BnOH (1)	25	40	83	6.2	1.54	1.7	toluene	151
129 (III)	TMC	400	-	110	6	97	64.7	49.4	1.6	bulk	140b
129 (III)	DMC	400	-	130	30	95	12.7	53.9	1.6	bulk	140b
129 (III)	TMC	500	BnOH (3)	110	3	96	160	18.5	1.63	bulk	140a
129 (III)	TMC	2 000	BnOH (20)	110	2	85	850	12.2	1.56	bulk	140a
139 (II)	TMC	2 000	BnOH (20)	60	1.5	75	1 000	9.1	1.59	bulk	152
139 (II)	TMC	2 000	BnOH (20)	110	20 min	97	5 820	13.3	1.64	bulk	152
140 (II)	TMC	2 000	BnOH (20)	60	15	64	85	7.8	1.25	bulk	152

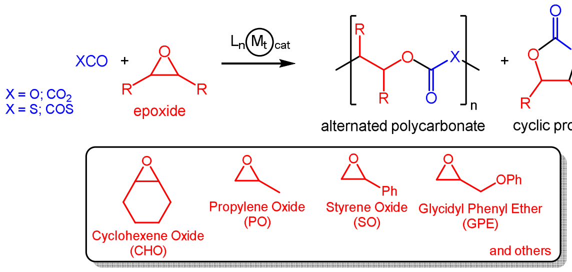
Complex (ox. state)	monomer	[M]/[Fe]	Initiator/CTA ([I]/[Fe])	T (^{0}C)	Time (h)	Conv (%)	TOF (h^{-1})	M_n (kg/mol)	Đ	Solvent	Ref.	
140 (II)	TMC	2 000	BnOH (20)	110	3	66	440	9.7	1.47	bulk	152	
$\mathbf{2^{Me}(OR_a)}$ (II)	*rac*-LA	50	-	RT	3	93	15.5	6.8	1.16	DCM	153	
$\mathbf{2^{Me}(TMS)}$ (II)	*rac*-LA	50	4-MeO-C_6H_4OH (2)	RT	3	88	14.7	6.2	1.18	DCM	153	
$\mathbf{2^{Me}(TMS)}$ (II)	*rac*-LA	50	NpOH (2)	RT	2	96	24	4.1	1.27	DCM	153	
$\mathbf{2^{Me}(OR_a)}$ (II)	*rac*-LA	50	-	RT	20 min	94	141	16.1	1.15	CB	154	
$\mathbf{2^{Me}(OR_b)}$ (II)	*rac*-LA	500	-	RT	10 min	94	2 820	94.8	1.37	toluene	154	
$\mathbf{2^{Me}(TMS)}$ (II)	*rac*-LA	50	Ph_3SiOH (2)	RT	9	-	-	42.9	1.31	THF	159	$P_r = 0.66$
5(TMS) (II)	*rac*-LA	50	$MePh_2SiOH$ (2)	RT	9	-	-	15.7	1.38	THF	159	$P_r = 0.75$
5(TMS) (II)	*meso*-LA	50	Et_3SiOH (2)	RT	3	-	-	11.5	1.62	THF	159	$P_r = 0.92$
141 (II)	*rac*-LA	50	Ph_3SiOH (2)	RT	9	-	-	43.1	1.40	THF	159	$P_r = 0.85$
$\mathbf{2^{Me}(OR_a)'}$ (I)	*rac*-LA	100	-	RT	20 min	86	258	25.7	1.16	CB	154	
$\mathbf{2^{Me}(OR_b)'}$ (I)	*rac*-LA	50	-	RT	10 min	91	273	9.6	1.12	toluene	154	
$\mathbf{2^{Me}(OR_a)'}$ (I)	CL	50	-	RT	24	80	1.7	30.6	2.22	toluene	154	
$\mathbf{2^{Me}(OR_b)'}$ (I)	CL	2 000	-	RT	10 min	99	11 880	390.0	1.21	toluene	154	
$\mathbf{2^{Me}(OR_b)'}$ (I)	BBL	50	-	RT	1.5	50	16.7	1.5	1.07	toluene	154	
$\mathbf{2^{Me}(OR_b)'}$ (I)	VL	500	-	RT	10 min	83	2 490	47.8	1.16	toluene	154	
$\mathbf{2^{Me}(OR_b)'}$ (I)	TMC	50	-	RT	10 min	100	300	5.5	6.6	toluene	154	
142 (0)	*L*-LA	50	-	90	17	96	2.8	319.1	1.72	benzene	161	
142 (0)	*L*-LA	50	4-MeO-C_6H_4OH (2)	90	17	95	2.8	6.7	1.55	benzene	161	
143 (II)	*rac*-LA	50	-	RT	3	90	15	39.4	1.26	DME	162	
143 (II)	*rac*-LA	5 000	-	RT	3	85	1 417	368	1.19	DME	162	
144 (III)	CL	300	^{i}PrOH (2)	100	24	90	14.6	11.3	1.18	toluene	163	
145(Cl) (II)	*rac*-LA	500	-	150	30	61	10.2	0.9-3.2	-	bulk	164	
145(TFA) (II)	*rac*-LA	500	-	150	30	87	14.5	2.7	1.9	bulk	164	
$\mathbf{145^{Me}(TFA)}$ (II)	*rac*-LA	500	-	150	30	28	4.7	0.7-4.0	-	bulk	164	
146a (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	25	30	94	376	8.7	1.66	toluene	165	
146a (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	40	30	85	340	9.9	1.53	toluene	165	
146b (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	25	30	92	368	6.1	2.07	toluene	165	
146c (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	25	30	90	360	11	1.44	toluene	165	
146d (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	25	30	74	296	11.1	1.62	toluene	165	
146e (II)	CL	200	$LiCH_2SiMe_3$ (2)/$C_{14}H_{30}O$ (5)	25	30	81	324	10.0	1.54	toluene	165	
147 (III)	*L*-LA	500	-	120	48	25	2.6	-	-	bulk	166	
147 (III)	*rac*-LA	500	-	120	48	30	3.1	-	-	bulk	166	
148 (III)	*L*-LA	500	-	180	48	61	6.4	-	-	bulk	166	
149 (III)	*L*-LA	500	-	180	24	58	12.1	-	-	bulk	166	

Complex (ox. state)	monomer	[M]/[Fe]	Initiator/CTA ([I]/[Fe])	T (^{0}C)	Time (h)	Conv (%)	TOF (h^{-1})	M_n (kg/mol)	Đ	Solvent	Ref.	
150 (III) [a]	*rac*-LA	1 000	-	70	77 min	88	686	39.5	1.88	toluene	168	
150 (III) [a]	CL	200	-	25	4.25	100	47	23.1	1.82	toluene	168	
151 (II)	*rac*-LA	100	-	25	20 min	94	282	37.5	1.12	toluene	170	
151 (II)	CL				5 min	95	1 140	86.2	1.38	toluene	170	
152 (II)	*rac*-LA	500	-	70	24	78	16.2	18 (M_v)	-	toluene	171	
153 (II)	TMC	2 000	BnOH (20)	60	4	<5	25	-	-	bulk	172	
153 (II)	TMC	2 000	BnOH (20)	110	0.5	93	3 720	11.7	1.66	bulk	172	
154 (III)	*L*-LA	2 500	-	200	1	-	-	25.0	1.12	bulk	173	
155a (III)	*rac*-LA	100	PO	60	24	90	3.8	19.4	1.58	PO	174	$P_m = 0.78$
155b (III)	*rac*-LA	100	PO	60	24	91	3.8	18.1	1.46	PO	174	$P_m = 0.77$
155c (III)	*rac*-LA	100	PO	60	4	91	22.8	24.5	1.54	PO	174	$P_m = 0.68$
155g (III)	*rac*-LA	100	PO	100	5.1	94	18.4	3.3	3.46	PO	174	$P_r = 0.63$
155c (III)	CL	100	PO	25	15	95	6.3	25.6	1.47	PO	174	
155h (III)	CL	100	PO	60	1.6	96	60	15.2	2.07	PO	174	
156^{tBu} (III)	*L*-LA	100	-	130	1	47	47	2.8	1.23	toluene	175	
156^{tBu} (III)	*rac*-LA	100	-	130	2	66	33	6.6	1.19	toluene	175	
156^{tBu} (III)	*L*-LA	100	-	130	1	15	15	2.1	1.10	bulk	175	
156^{H} (III)	*L*-LA	100	-	130	1	97	97	7.3	1.40	toluene	175	
156^{H} (III)	*rac*-LA	100	-	130	0.5	78	156	4.5	1.19	toluene	175	
156^{H} (III)	*L*-LA	100	-	130	2	92	46	5.1	1.27	bulk	175	
157 (III)	CL	61	-	125	24	82	2.1	8.5	1.55	bulk	176	
158c (III)	*L*-LA	100	PO (50)	120	2	89	44.5	5.5	1.1	toluene	177	
158f (III)	*L*-LA	100	PO (50)	120	2	91	45.5	42.2	1.5	toluene	177	
158h (III)	*L*-LA	100	PO (excess)[d]	85	2	89	44.5	17.2	1.5	toluene	177	
159 (III)	*L*-LA	500	-	120	24	20	4.1	3.3	1.40	bulk	178	
159 (III)	*L*-LA	500	-	150	24	40	8.3	4.6	1.80	bulk	178	
160 (II)	CL	100	-	25	1.7	98	57.7	8.0	1.28	toluene	179	
160 (II)	CL	300	-	25	1	58	174	5.5	1.06	toluene	179	
161 (II)	CL	300	-	80	12	100	25	40.0	3.1	toluene	180	
162^{OMe} (II)	CL	300	-	80	5	75	45	43	3.2	toluene	181	
162^{F} (II)	CL	300	-	80	5	53	32	43	2.3	toluene	181	

M_n values are corrected (x 0.58 for PLA) when available. Np = neopentyl. PO propylene oxide. (HEBiB = $OH(CH_2)_2O(CO)CMe_2Br$). [a] Lack of reproducibility due to high sensitivity to impurities (cf Table). [c] Alcohol comprised in the catalyst 122. [d] Preformation of the Fe-alkoxide prior to the addition of the monomer. LA = Lactide, CL = ε-Caprolactone, VL = δ-Valerolactone, BBL = β-Butyrolactone, GBL = γ-butyrolactone, TMC = Trimethylene carbonate, DMC = 2,2dimethyltrimethylene carbonate, EC = ethylene carbonate, CHO = cyclohexene oxide, CB = chlorobenzene, THF = tetrahydrofuran, DCM = dichloromethane, DMF = dimethylformamide, DME = dimethoxyethane

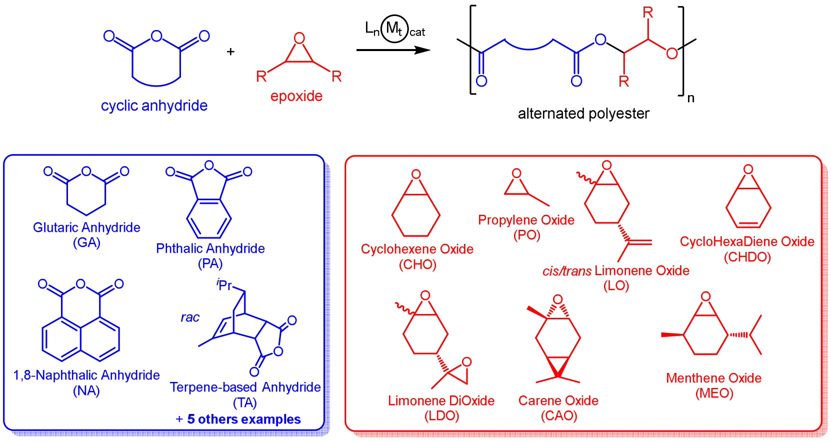
5. Iron-catalyzed the copolymerization of CO_2/epoxides and cyclic anhydrides/epoxides.

The metal-catalyzed reaction of epoxides and CO_2 is an important process that benefits from the use of an inexpensive and abundant raw material that can not only be incorporated into valuable chemicals, but can also reduce the human carbon footprint. Several metal complexes based on Zn, Co, Cr, Al and others have been described in the literature to effectively catalyze the coupling reaction of epoxides and CO_2 for the formation of cyclic carbonates and/or the production of polycarbonates from the alternating copolymerization of both molecules (**Scheme 10**), the selectivity of the reaction being dependent on the reaction conditions and the catalytic system [182]. As mentioned previously, the alternating copolymerization of CO_2 with epoxides in presence of metal coordination complexes has been thoroughly depicted in a very recent review of Kozak *et al.*, where most of the iron-based catalysts used so far for this transformation have been mentioned [19].



Scheme 10. Metal-catalyzed reaction of epoxides/CO_2; formation of polycarbonates and cyclic carbonates.

Similar to the alternating copolymerization of epoxides/CO_2, the preparation of aliphatic or semi-aromatic polyesters from the metal-catalyzed copolymerization of epoxides with cyclic anhydrides (**Scheme 11**) is currently attracting increasing interest, mainly due to the wide range of applications of the resulting biodegradable polymers as well as the ready availability of a variety of cyclic anhydride monomers. The group of Williams [183] and Coates [184] have reviewed this area of research in 2015 and 2016, respectively; the readers are redirected to these two excellent articles for more information regarding the performances of various homogeneous metal-based catalysts and the structures/properties relationships of the obtained copolymers.



Scheme 11. Metal-catalyzed reaction of epoxides/cyclic anhydride; formation of polyesters.

In this section, we will only describe and focus on single-site iron-based catalysts that have been used so far for the alternating copolymerization of CO_2/epoxides (data in **Table 9**) and cyclic anhydrides/epoxides (data in **Table 10**); the iron-based complexes are illustrated in **Fig. 15**, most of them being of formal oxidation state +III [apart from complexes **159**, **160** and **161(Cl)**]. On the other hand, reports of discrete iron-based catalysts for the selective homopolymerization of epoxides have been little studied because it has been mainly involved in copolymerization with other comonomers [185]; this topic will not be discussed here.

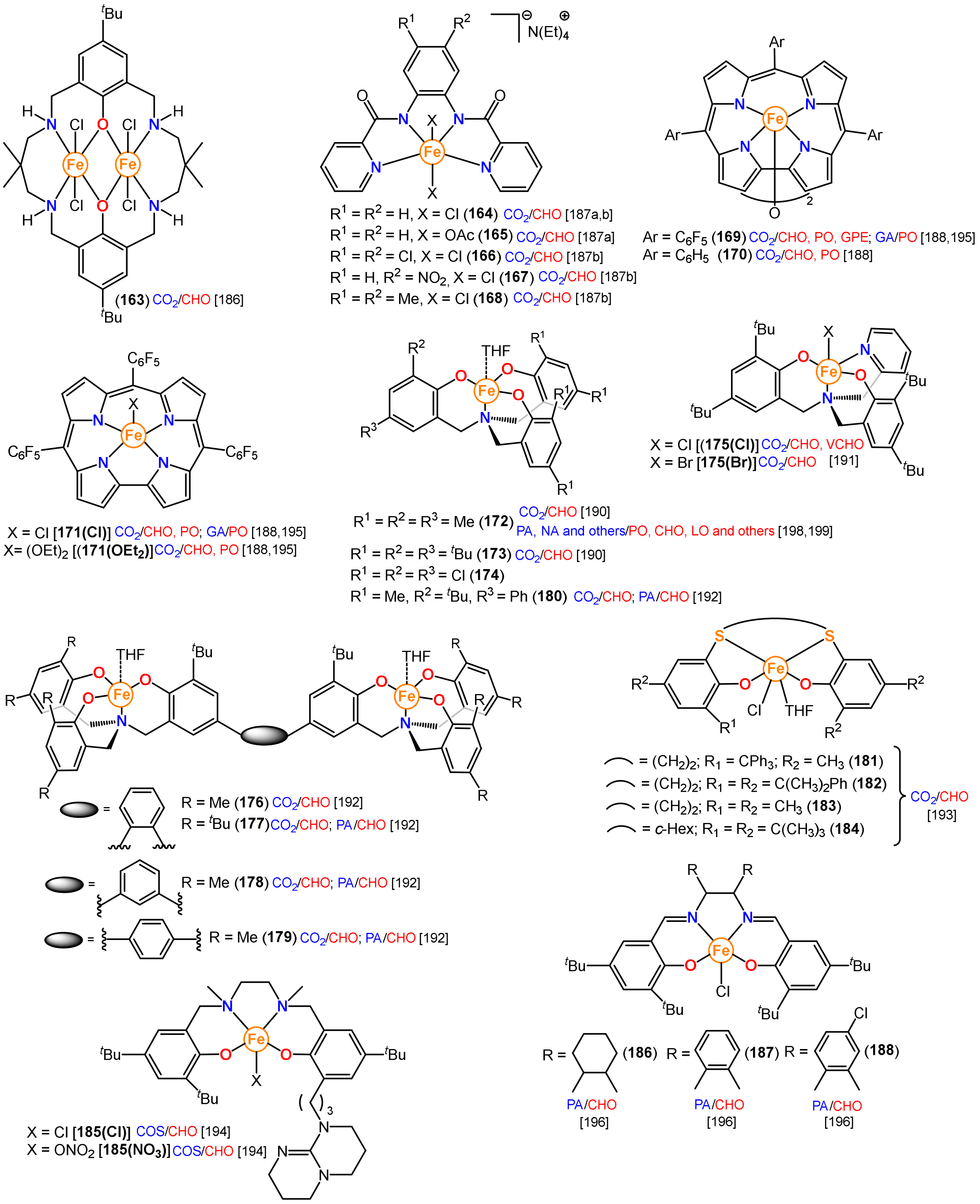


Fig. 15. Iron-based complexes for the copolymerization of epoxides/CO_2 or cyclic anhydrides.

5.1. Iron-catalyzed the alternating copolymerization of CO_2/epoxides.

In 2011, Williams and coworkers described the copolymerization of CO_2 with cyclohexene oxide (CHO) using the di-iron complex (**163**) bearing a “reduced Robson type” macrocyclic ligand [186]. This catalyst has been found to provide poly(cyclohexene carbonate) in good yield (TOF = 107 h^{-1}), with carbonate linkages up to 99% at 80 °C under 10 atm of CO_2. However, the copolymerization of CO_2 with propylene (PO) or styrene oxide (SO) using **163** yielded exclusively cyclic carbonate products.

Subsequently, the copolymerization of CHO with CO_2 at 80 °C have been successfully achieved by Zevaco and coworkers with complexes **164 – 168**, producing exclusively poly(cyclohexene carbonate) under 49.3 atm. of CO_2, whereas a certain amount of cyclic carbonate was found when 34.5 atm. of CO_2 was used with complexes **164** and **165** [187].

Later on, the group of Nozaki has investigated the copolymerization of CO_2 and PO in presence of the iron-based complexes **169 – 171** supported by different trianionic tetradentate corrole ligands [188]. Under 19.7 atm. of CO_2 at 60 °C, complex **169** was not capable of producing either the copolymer or the cyclic carbonate. However, the presence of an additional amount of bis(triphenylphosphino)iminium chloride [PPN]Cl (0.5 equiv./Fe) enabled the selective formation of poly(propylene carbonate) with high catalytic activity (TOF = 1 004 h^{-1}), which is a first for an iron-based catalyst. It has previously been reported that several ammonium salt cocatalysts, such as [PPN]Cl, increase the productivity of a series of metal halide catalysts in various polymerization systems [189]. Similar results for the copolymerization of PO with CO_2 were found with the iron-based complexes **170**, **171(Cl)** and **171(OEt$_2$)**. Furthermore, complexes **169 – 171** were able to copolymerize CHO and CO_2 and complex **169** was shown to exhibit moderate activity for the copolymerization of glycidyl phenyl ether (GPE) with CO_2.

The iron amino-tris(phenolate) (**172 – 174**) complexes have been examined by Taherimehr *et al.* for the reaction of CO_2 with CHO [190]. Under specific conditions, the alternating copolymerization of CO_2 and CHO using complexes **172** and **173** was successfully carried out at 85 °C in the presence of 1 equiv. of [PPN]Cl cocatalyst. On the other hand, the iron-based complex **174** only leads to the homopolymerization of CHO, affording polyether in low yield. It is therefore important to note that the presence of [PPN]Cl cocatalyst was necessary to obtain the required copolymers. Thereafter, the same group studied a similar catalytic system based on two iron pyridylamino-bis(phenolate) complexes (**175**) for the reaction of CO_2 with a variety of epoxides [191]. Again, depending on the reaction conditions, the alternating copolymerization of CHO with CO_2 was, partially or selectively, achieved with complexes **175(Cl)** and **175(Br)**. Interestingly, the copolymerization of 1,2-epoxy-4-vinylcyclohexane (VCHO) and CO_2 has been accomplished with complex **175(Cl)**, yielding mainly poly(vinylcyclohexene carbonate) with a pendant vinyl group that has been further cross-linked by radical reaction with 1,3-propanedithiol in presence of azobisisobutyronitrile (AIBN).

The bimetallic analogs of the iron amino-tris(phenolate) complexes (**176 – 179**) have been evaluated by the group of Jiang for the alternating copolymerization of CHO and CO_2 and have been compared with the related monometallic version (complex **180**) [192]. In presence of 1 equiv. of [PPN]Cl, all these complexes have been shown to exhibit moderate catalytic activity with high selectivity for the formation of poly(cyclohexene carbonate) (>99%), which exhibits exclusively carbonate linkage (> 99%). The bimetallic complex **177** displayed the highest activity, which is quite comparable to the complexes **178**, **179** and the monometallic one (**180**), whereas the less crowded complex **176** showed the lowest activity. Under very low catalytic concentration (40 000 equiv. of CHO/Fe), complex **177** has demonstrated to be more efficient (TOF = 178 h^{-1}) than the monometallic complex **180** (TOF = 67 h^{-1}), "*thereby suggesting the existence of intramolecular cooperativity between the two metal centers*," as stated by the authors.

Very recently, the mononuclear iron-based complexes (**181 – 184**) bearing bis-thioether-diphenolate $[OSSO]^-$ type ligands, in combination with an ammonium salt, have shown to display moderate activity for the alternating copolymerization of CO_2 with CHO, producing exclusively polymers with carbonate linkage up to 99% [193]. In particular, the presence of sterically hindered substituent on the ligand framework (complex **182**) has led to a higher catalytic activity (TOF = 200 h^{-1}) than the related less congested complex **183** (only traces of polymer), under the same experimental conditions. Nevertheless, in all cases, a bimodal distribution of molecular weights was obtained, which is generally ascribed to the presence of traces of water in the reaction medium. The attempts to copolymerize CO_2 with other epoxides resulted in the formation of cyclic carbonate only.

In parallel, the alternating copolymerization of carbonyl sulfide (COS) with epoxides has been investigated by the group of Lu using the iron-based complexes **185(Cl) – 185(NO_3)** supported by a tetradentate salan ligand with a pendant organic base linked on the ligand skeleton [194]. The activity and the selectivity of the copolymerization of PO with COS were found to depend on the nature of the axial Cl ligand [complex **185(Cl)**] being more active but less selective than the NO_3 ligand [complex **185(NO_3)**]. In all cases, the resulting copolymers produced with complexes **185(Cl)** and **185(NO_3)** displayed an entire alternating structure. Additionally, benzyl alcohol has effectively been employed as chain transfer agent for the copolymerization of COS/PO with complex **185(NO_3)** for controlling the molecular weights of the copolymer and the molecular weight distribution. Subsequently, the copolymerization of COS with various epoxides (SO, CHO…) has also been efficiently achieved using complex **185(NO_3)** and, because of the living nature of the catalytic system, a diblock copolymer comprised of poly(propylene moniothiocarbonate) and poly(cyclohexene thiocarbonate) sequences has been successfully prepared by stepwise addition.

Table 9.
Selected polymerization data for the copolymerization of CO_2 and epoxides using iron-based complexes.

Complex	Monomer	Cocat.	T (°C)	Time (h)	TOF (h^{-1})	Conv. (%)[a]	Cyclic carbonate (%)	Polycarbonate (%) [carbonate linkage%]	M_n (kg/mol)	Đ (M_w/M_n)	Ref.
163	CO_2 (10 atm.) CHO	-	80	24	107	25	1	99[99]	17.2	1.03	186
164	CO_2 (34.5 atm.) CHO	-	80	20	5.4	54	14[b]	86[76]	0.76	1.26	187a
165	CO_2 (34.5 atm.) CHO	-	80	20	1.8	18	33[b]	67[83]	1.3	1.10	187a
164	CO_2 (49.3 atm.) CHO	-	80	20	3.1	31	0[b]	100[97]	2.6	1.14	187b
166	CO_2 (49.3 atm.) CHO	-	80	20	2.5	25	0[b]	100[91]	2.0	1.06	187b
167	CO_2 (49.3 atm.) CHO	-	80	20	2.7	27	0[b]	100[100]	2.7	1.15	187b
168	CO_2 (49.3 atm.) CHO	-	80	20	3.3	33	0[b]	100[100]	2.2	1.18	187b
169	CO_2 (19.7 atm.) CHO	[PPN]Cl 0.5 eq./Fe	60	12	30	-	-	-[95]	6.5	1.37	188
170	CO_2 (19.7 atm.) CHO	[PPN]Cl 0.5 eq./Fe	60	12	23	-	-	-[96]	8.7	1.34	188
171(Cl)	CO_2 (19.7 atm.) CHO	[PPN]Cl 0.5 eq./Fe	60	12	50	-	-	-[94]	4.5	1.33	188
171(OEt$_2$)	CO_2 (19.7 atm.) CHO	[PPN]Cl 0.5 eq./Fe	60	12	42	-	-	-[95]	12	1.37	188
169	CO_2 (19.7 atm.) PO	[PPN]Cl 0.5 eq./Fe	60	1	1 004	51	<1	>99[17]	29	1.26	188
170	CO_2 (4.9 atm.) PO	[PPN]Cl 0.5 eq./Fe	60	12	63	19	53	47[60]	11	1.17	188
171(Cl)	CO_2 (19.7 atm.) PO	[PPN]Cl 0.5 eq./Fe	60	1	701	35	<1	>99[18]	30	1.21	188
171(OEt$_2$)	CO_2 (19.7 atm.) PO	[PPN]Cl 0.5 eq./Fe	60	1	1 209	60	<1	>99[19]	39	1.18	188
169	CO_2 (19.7 atm.) GPE	[PPN]Cl 0.5 eq./Fe	60	49	41	99	-	100[11]	13.7	7.01	188
171(OEt$_2$)	CO_2 (19.7 atm.) GPE	[PPN]Cl 0.5 eq./Fe	15	24	26	59	-	100[95]	13.0	1.2	188
172	CO_2 (79 atm.) CHO	[PPN]Cl 1 eq./Fe	85	3	56	187	0	>99[nd]	1.5 6.0	1.25 (86%) 1.05 (14%)	190
173	CO_2 (79 atm.) CHO	[PPN]Cl 1 eq./Fe	85	3	55	183	0	>99[nd]	1.8 6.1	1.18 (86%) 1.06 (14%)	190
175(Cl)	CO_2 (79 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	60	18	60	6.7	18	82[96]	1.4	1.1	191
175(Cl)	CO_2 (79 atm.) CHO	[PPN]Cl 1 eq./Fe	60	18	49	5.4	19	81[>99]	0.7	1.1	191
175(Br)	CO_2 (79 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	60	18	13	1.4	59	41[-]	-	-	191
175(Cl)	CO_2 (79 atm.) VCHO	[Bu_4N]Cl 1 eq./Fe	60	18	48	5.3	2	98[86]	2.0	1.2	191

Complex	Monomer	Cocat.	T (°C)	Time (h)	TOF (h^{-1})	Conv. (%)[a]	Cyclic carbonate (%)	Polycarbonate (%) [carbonate linkage%]	M_n (kg/mol)	Đ (M_w/M_n)	Ref.
175(Cl)	CO_2 (79 atm.) VCHO	[PPN]Cl 1 eq./Fe	60	18	39	4.3	5	95[>99]	0.9	1.2	191
175(Br)	CO_2 (79 atm.) VCHO	[Bu_4N]Cl 1 eq./Fe	60	18	14	1.6	41	59[-]	-	-	191
176	CO_2 (44.4 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	90	3	44	147	1	>99[99]	6.9	1.17	192
177	CO_2 (44.4 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	90	3	78	260	1	>99[99]	16.4	1.18	192
178	CO_2 (44.4 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	90	3	70	233	1	>99[99]	14.0	1.20	192
179	CO_2 (44.4 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	90	3	67	223	1	>99[99]	14.0	1.19	192
180	CO_2 (44.4 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	90	3	63	210	1	>99[99]	14.7	1.21	192
182	CO_2 (9.9 atm.) CHO	[Bu_4N]Br 1 eq./Fe	80	2	205	41	-	>99[99]	32.1 15.8	1.01 1.03	193
182	CO_2 (9.9 atm.) CHO	[Bu_4N]Cl 1 eq./Fe	80	1	340	34	-	>99[99]	23.2 11.0	1.01 1.03	193
181	CO_2 (9.9 atm.) CHO	[Bu_4N]Br 1 eq./Fe	80	2	110	22	-	>99[99]	21.1 10.1	1.01 1.03	193
183	CO_2 (9.9 atm.) CHO	[Bu_4N]Br 1 eq./Fe	80	2	-	trace	-	-	-	-	193
184	CO_2 (9.9 atm.) CHO	[Bu_4N]Br 1 eq./Fe	50	24	15	70	-	>99[98]	24.3 11.2	1.01 1.04	193
185(Cl)	COS/CHO	-	25	1	-	1 040	-	94[>99][c]	33.3	1.15	194
185(NO_3)	COS/CHO	-	25	1	-	700	-	99[>99][c]	22.3	1.14	194
185(NO_3)	COS/CHO	-	50	24	-	83	-	99[>99][c]	65.6	1.18	194
185(NO_3)	COS/CHO + 25 equiv./Fe of BnOH	-	50	24	-	83	-	99[>99][c]	3.0	1.09	194

[a] Conversion of epoxide; [b] % of cyclic carbonate + short chain oligomers; [c] thiocarbonate linkage

5.2. Iron-catalyzed the alternating copolymerization of cyclic anhydrides/epoxides.

With regard to the preparation of polyesters from the reaction of cyclic anhydrides with epoxides (**Scheme 11**), using iron-based systems (**Fig. 15**, **Table 10**), the iron-corrole complexes **169** and **171** have been evaluated for the copolymerization of glutaric anhydride (GA) with an excess of PO in the presence of 1 equiv. of [PPN]OBzF_5 (OBz = pentafluorobenzoate) in bulk at 30 °C [195]. By using 100 equiv. of GA with PO, complexes **169** and **171(Cl)** combined with [PPN]BzF_5 were able to produce the alternated copolymers in good yield, whereas complex **171(OEt_2)** was completely inactive. Besides, this contribution presents one example of the homopolymerization of epoxides using a single-site iron-based catalyst.

The copolymerization of CHO with phthalic anhydride (PA) has been successfully achieved by the group of Merna using the iron-based complexes **186 – 188** supported by a salen-type ligand in presence of either 4-(dimethlyamino)pyridine or [PPN]Cl cocatalysts [196]. However, the presence of the cocatalyst was required for the transformation to proceed with complexes **187** and **188**, whereas complex **186** was able to produce efficiently the desired copolymers even in the absence of a cocatalyst. The obtained copolymers showed only the alternating structure when combined with a cocatalyst, but in the case of complex **186** alone, the ester linkages dropped to 40%. It is worth mentioning that DMAP and [PPN]Cl cocatalysts alone are capable of copolymerizing CHO with PA [197].

The groups of Coates and Kleij have succeeded in preparing a series of renewable aliphatic polyesters by conducting the alternating copolymerization of CHO or PO with various tricyclic anhydride monomers, some of them being fully or partially bio-sourced, using the iron-based complex **172** with [PPN]Cl as cocatalyst [198]. In almost all cases, the copolymerization proceeded with high conversion of the tricyclic anhydride, affording copolymers with a high content of ester linkages. Independently, Kleij and coworkers have studied the alternating copolymerization of renewable terpene oxides [limonene oxide (LO), carene oxide (CAO), limonene dioxide (LDO), cyclohexadiene oxide (CHDO) and menthene oxide (MEO)] with PA or 1,8-naphtalic anhydride (NA) using the same complex **172** with 1 equiv. of [PPN]Cl cocatalyst [199]. The synthesis of a family of semi-aromatic polyesters with high glass transition temperature (T_g) has been successfully obtained with high selectivity for the alternating copolymer, one of them displaying an exceptional T_g of 243 °C.

Finally, the bimetallic iron-based complexes **177** – **179** well as complex **180** have shown to afford perfectly alternated polyesters from the copolymerization of CHO and PA in presence of [PPN]Cl in toluene, however, an increase in the catalytic activity was observed in neat CHO but producing polyesters with lower M_n [192].

Table 10.
Selected polymerization data for the copolymerization of CO_2 and epoxides using iron-based complexes.

Complex	Monomer	Cocat.	T (°C)	Time (h)	Conv. of cyclic anhydride (%)	M_n (kg/mol)	$Đ$ (M_w/M_n)	Ref.
169	PO/GA	$[PPN]BzF_5$ 1 eq./Fe	30	30	99	6.9	1.2	195
171(Cl)	PO/GA	$[PPN]BzF_5$ 1 eq./Fe	30	30	81	8.0	1.2	195
171(OEt$_2$)	PO/GA	$[PPN]BzF_5$ 1 eq./Fe	30	30	-	-	-	195
186	CHO/PA	DMAP 1 eq./Fe	110	5	70	10.0	1.27	196
187	CHO/PA	[PPN]Cl 1 eq./Fe	110	5	73	9.7	1.33	196
188	CHO/PA	[PPN]Cl 1 eq./Fe	110	5	68	10.3	1.24	196
172	PO/TA	[PPN]Cl 0.9 eq./Fe	60	6	>99	17.2	1.10	198
172	CHO/TA	[PPN]Cl 0.9 eq./Fe	60	20	>99	11.6	1.37	198
172	LO/PA	[PPN]Cl 1 eq./Fe	65	24	>99	9.5	1.21	199
172	CHDO/PA	[PPN]Cl 1 eq./Fe	65	48	>99	19.6	1.42	199
172	CAO/PA	[PPN]Cl 1 eq./Fe	95	48	89	3.3	1.52	199
172	MEO/PA	[PPN]Cl 1 eq./Fe	65	24	75	5.1	1.28	199
172	LDO/PA	[PPN]Cl 1 eq./Fe	45	24	52	6.7	2.41	199
172	CHO/NA	[PPN]Cl 1 eq./Fe	95	72	>99	6.9	1.71	199
172	LO/NA	[PPN]Cl 1 eq./Fe	95	72	50	1.6	1.52	199

177	CHO/PA	[PPN]Cl 1 eq./Fe	100	3	99	22.5	1.23	192
178	CHO/PA	[PPN]Cl 1 eq./Fe	100	3	90	18.7	1.29	192
179	CHO/PA	[PPN]Cl 1 eq./Fe	100	3	77	10.6	1.33	192
Complex	Monomer	Cocat.	T (°C)	Time (h)	Conv. of cyclic anhydride (%)	M_n (kg/mol)	$Đ$ (M_w/M_n)	Ref.
180	CHO/PA	[PPN]Cl 1 eq./Fe	100	3	99	20.7	1.24	192
177	CHO(neat)/PA	[PPN]Cl 1 eq./Fe	100	0.67	99	13.9	1.24	192
178	CHO(neat)/PA	[PPN]Cl 1 eq./Fe	100	0.67	99	13.6	1.24	192
179	CHO(neat)/PA	[PPN]Cl 1 eq./Fe	100	0.67	99	13.8	1.24	192
180	CHO(neat)/PA	[PPN]Cl 1 eq./Fe	100	0.67	99	16.5	1.22	192

6. Conclusions and outlook

As can be seen in this literature survey, the field of well-defined iron-catalyzed coordination-insertion polymerization has given rise to considerable applications in a wide range of monomers including ethylene, α-olefins, cyclic olefins, α,ω-dienes, 1,3-dienes, polar vinyl monomers, polar cyclic esters (or carbonates) and CO_2 (or anhydrides)/epoxides. This clearly demonstrates the flourish and versatile nature of this area of research.

Throughout this review, we often encounter a recurrent catalytic structure based on the bis(imino)pyridyl skeleton, which has been extensively used for the coordination-insertion polymerization of both polar and non-polar monomers. Thanks to the discovery by the Gibson and Brookhart groups of an extremely active system for the polymerization of ethylene, based on the iron-BIP/MAO catalytic system, this finding has attracted a lot of interest and motivation for many research groups to exploit its potential. One can advance that this is mainly related to the modularity of the BIP ligand skeleton, which can be easily adjusted in term of electronic and steric properties according to the type of chemistry envisioned. In parallel, the ability of the BIP ligand to act, in some cases, as electron-reservoir (redox non-innocent ligand [200]) has enabled the development of novel synthesis methodologies in "*iron-catalyzed reactions in organic chemistry*" [13,105].

Following the pioneering work of Gibson and Brookhart, many advances have been made in the field of iron-catalyzed ethylene polymerization [24,25], in particular by the group of Sun which has developed thermally stable systems by improving the rigidity of the catalysts as well as introducing highly hindered *N*-aryl moieties on the BIP ligand [201,24i]. However, this approach may not be directly transposed to the polymerization of more sterically hindered olefins because of the steric repulsion between the incoming monomer and the coordination sphere of the active species (see section 3.1 and 3.2); this might be one reason why less attention has been paid to other families of olefins.

Surprisingly, to our knowledge, only one example of coordination-insertion of styrene has been achieved with an iron-based catalyst [66], this area of research can be highlighted here for future developments in stereo-selective iron-based polymerization processes.

Since the review of Olivier-Bourbigou and coworkers in 2015 [25c], the field of iron-catalyzed 1,3-dienes polymerization has progressed steadily (section 3). Overall, these catalysts are still moderately active compared to the industrial systems based on other transition metals (*e.g.* Ti, Co, Ni) or rare earths (*e.g.* Nd) and the stereo-/regio-selectivity remains an issue that needs to be further improved for iron-based systems. From this point of view, much remains to be done for understanding the structure-properties relationships of iron-catalyzed 1,3-dienes polymerization. This is particularly evidenced by the works described in section 3.1, where the same iron-based complexes gave rise to significantly different results depending on the activation mode of the pre-catalysts (complexes **65** and **69**), the experimental conditions and the nature of the cocatalysts. Nevertheless, some trends can be cautiously drawn from this survey. All truly active iron catalytic systems for the polymerization of 1,3-dienes are supported by nitrogen-based bidentate or tridentate ligands. Overall, it appears that i) the iron-based complexes bearing bidentate ligands are apparently more active than the related pre-catalysts supported by tridentate ligands and ii) the complexes supported by tridentate ligands display a preferential *trans*-1,4 selectivity, due to the preferential *single*-η^2 coordination mode of monomers. Moreover, in the case of iron complexes bearing *N*-alkyl iminopyridyl ligands, the combination of borate co-reagent with alkyl-aluminum or MAO cocatalysts may be beneficial for the formation of *trans*-1,4 units, whereas in the absence of borate, there is a tendency to favor *cis*-1,4 selectivity. In contrast, no obvious pattern regarding the activation mode of the iron complexes supported by *N*-aryl iminopyridyl ligand can be identified: as such i) the use of the dual alkyl aluminum/borate or MAO alone as cocatalysts leads to a slight selectivity for *cis*-1,4 content, while ii) the combination of MAO/borate cocatalysts exhibits a high *trans*-1,4 stereo-selectivity with complexes bearing fluorinated *N*-aryl iminopyridyl ligands. Advances in the area of butadiene polymerization seem to be emerging with respect to the thermal stability of the catalytic system, with the formation of highly regular syndiotactic 1,2-polybutadiene resulting from the combination of an iron precursor with phosphorous additives (section 3.3). On the other hand, the implementation of CCTP processes using an iron-based catalytic system, which has been well developed for ethylene and one example of CCG for acetylene, remains to date a challenge in the field of 1,3-dienes polymerization.

With respect to the ROP of cyclic esters, the best iron catalysts in terms of activity reach a good level of performance, which is approaching that of the most active metal-based complexes [129]. To the extent that the complex is well-defined and bears an alkoxy(aryloxy) group, which may also results from *in situ* reaction of a pre-catalyst with an alcohol/phenol, the reaction can proceed under mild experimental conditions (in solution and at low temperature). This strategy affords a process that can display good activity and control over the molecular weights, even being competitive with efficient catalytic systems based on other metals conventionally used in ROP.

As it also results from the ROP section, a number of neutral and ionic bulky ligands allow the preparation and isolation of iron complexes with several oxidation state (from 0 to +III herein), which makes it possible to highlight the impact of the oxidation state on ROP. To summarize on that point, the best performances were obtained with the lowest oxidation states, even if it is prudent not to deduce a general rule from it. Moreover, the recently proposed [202] concept of redox triggering of a polymerization with complexes based on group 3 and 4, with on-off switch control, could be successfully applied in the field of iron-based ROP of cyclic esters, through the elaboration of well-defined iron(II)/iron(III) couples of catalysts. Regarding the ROP mechanism, with iron salts, it is accepted as of AMM type. In absence of alcohol as co-reagent, protic impurities were suspected to account for the initiation reaction. However, a CM pathway was alternatively proposed when the catalytic species contains an alkoxide moiety, which can also alternatively be formed *in situ*. Noteworthy, higher reactivity towards LA than CL was noticed for a number of iron catalysts. This is quite unusual when compared to other metal complexes where the homopolymerization of CL is much faster than LA for a given complex. This allows us to see opportunities for the controlled statistical copolymerization of LA and CL, one of the major challenges to improve the mechanical and physical properties of biodegradable polymers [160]. Finally, one aspect that is still to improve is the control of the stereo-selectivity with iron, which has just emerged very recently with the work described by the group of Byers, to be able to withstand comparison with the performances of the best catalysts in this area [203,129,155].

In summary, the field of iron-catalyzed coordination-insertion polymerization has been widely investigated in recent years and, despite significant advances from an academic point of view, the industrial application of such systems based on this abundant and low toxic metal is still limited. To our knowledge, there is to date one example of iron-based catalyst that has been successfully applied on a 500 tons pilot plant for the preparation of short chain α-olefins [24d]. The search for efficient iron-based catalysts for industrial applications therefore remains a major challenge.

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