CATALYSIS BY METAL COMPLEXES 36

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Olefin Upgrading Catalysis by Nitrogen-based Metal Complexes II

State-of-the-art and Perspectives

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Catalysis by Metal Complexes

Volume 36

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Foreword

Olefin polymerization has remarkably progressed over the last two decades, mainly thanks to the contribution of organometallic chemistry to the design of innovative ligand systems and metal complexes. The irreversible decrease of fossil-resources requires continuous efforts to improve the selectivity and productivity of the industrial processes as well as to reduce the environmental impact, especially in terms of energy and waste. Due to the wealth of possible ligand structures and metal combinations, organometallic-based catalysis can indeed address many of the issues of the sustainable production of polymeric and composite materials.

These two volumes edited by Giambastiani and Campora cover a hot research subject such as that of post-metallocene nitrogen-containing complexes and their use in homogeneous catalysis for the efficient and selective olefin upgrading. These books cover the state-of-the-art of olefin polymerization by catalysts with N-donor ligands as well as hybrid ligands in conjunction with a wide range of metals across the periodic table. Particular attention has been devoted to important, still unresolved issues such as the efficient insertion polymerization of polar monomers. Advantages and limits of the known technologies have been discussed and critically addressed in the light of the most relevant contributions of the many thousand researchers active in the field.

Claudio Bianchini
Director ICCOM-CNR

Preface

Millions of tons of polyolefin-based materials are produced yearly, in most cases under relatively mild conditions mediated by transition-metal catalysts. Through a simple insertion reaction, inexpensive and abundant olefins (such as ethylene and propene) are transformed into polymeric materials for a wide range of applications, including plastics, fibers, and elastomers. The discovery of the Ziegler–Natta catalysts and the seminal works at Phillips Petroleum in the 1950s not only revolutionized polyolefin production, but also paved the way to the development of modern organometallic chemistry. Despite its long history, the polyolefin industry keeps growing steadily and remains technologically driven by the continuous discovery of new catalysts, processes, and applications.

Since Ziegler–Natta's time, important milestones in the field of homogeneous oligomerization/polymerization catalysis were set-up one after the other; from nickel complexes with phosphine donors (SHOP-type catalysts) for the highly selective and efficient production of α-olefins to Group IV metallocene polymerization catalysts and their subsequent industrial exploitation (in the early 1980s) due to the discovery of partially hydrolyzed organoaluminum compounds (MAOs) as co-catalysts/activators. All these scientific successes have shown how discrete "single-site" molecular catalysts could offer unmatched opportunities, compared with heterogeneous systems, towards the tailored synthesis of new polymeric architectures as well as the in-depth understanding of complex reaction mechanisms.

Until a few years ago there have been relatively few reports on late transition metal complexes capable of catalyzing the polymerization of ethylene and α-olefins efficiently. A distinct feature of the latter systems is a high rate of chaintransfer which favors their application as oligomerization catalysts. The discovery of new ligands and activators has been fundamental to fill the gap and make late transition metal catalysts as efficient (and in some cases even more versatile) as metallocene-based systems for the oligomerization and polymerization catalysis.

In 1995, Brookhart and co-workers synthesized a new class of $Ni^{II}$and Pd^{II} complexes stabilized by bulky α-diimine ligands (Schiff bases) which represented a real breakthrough into the development of late transition metal catalysts for the efficient olefin polymerization/oligomerization.

Since then, an almost infinite variety of imine-based ligands or, more generally, nitrogen-containing ligands in combination with either *d*- and *f*- block metals have been explored as efficient and selective oligomerization and polymerization catalysts. The major advantages of this ligand class are represented by the facile control of their stereoelectronic properties, their simple preparation from available and cheap building blocks and their easy handling and storage. All these considerations, together with the capability of most of their metal derivatives to impart high activity and selectivity in olefin upgrading processes, have contributed to make nitrogen-containing catalysts highly desirable for industry and academy.

The aim of these books is to provide an overview on the state-of-the-art and the perspectives in the field of oligomerization/polymerization catalysis mediated by metal complexes (spanning from early to late and lanthanide series) stabilized by ligands containing nitrogen donor groups. Rather than a systematic revision of the major breakthroughs achieved over the last decades, these two volumes offer to the readership the critical point of view of researchers active in specific fields of polymerization catalysis. The amplitude and rigor of each contribution also provide an exhaustive account on the topic: from the synthesis of ligands and related complexes to mechanistic details, the investigation of the catalyst performance and future perspectives. Although the chapters' extension has made the book division into two separate volumes necessary, this partition is merely due to editorial reasons.

Finally, the editors are extremely grateful to all book co-authors for their enthusiasm in participating to this editorial project and for writing up their contribution at their best. A special thank is also due to Sonia Ojo, Claudia Culierat and Ilaria Tassistro from the London Springer office, whose precious assistance in facing technical and logistic details has been essential for the success of the Editors' efforts.

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Chapter 1
Phenoxy–Imine Group 4 Metal Complexes for Olefin (co)Polymerization Including Polar Monomer Copolymerization

Akihiko Iwashita, Haruyuki Makio, and Terunori Fujita

Abstract About 50 years after the discovery of Ziegler–Natta catalysts, phenoxy–imine-based group 4 transition metal complexes (FI catalysts) emerged as the next frontier catalysts for the controlled (co)polymerization of olefinic monomers. FI catalysts are highly versatile catalysts capable of producing a wide range of novel polymer architectures. The inherent electronic and structural features of FI catalysts and the accessibility and variability of the phenoxy–imine ligands offer precise control over olefin polymerization. This chapter deals with the key features of FI catalysts, homopolymerization and copolymerization by FI catalysts, and the value-added olefin-based materials that can be produced with FI catalysts.

1.1 Introduction

With the discovery of the Ziegler–Natta catalyst in the 1950s, the polyolefin industry was launched into a period of unprecedented growth [1]. One reason for this growth lies in the fact that polyolefins are the most versatile of polymers in that they possess superior mechanical and physical properties, excellent chemical inertness, good processability, and easy recyclability. Another reason lies with the development of new catalysts that helped initiate new production processes and new product lineups. As a result, polyolefin resin is the most produced resin today, and polyolefinic materials are ubiquitous in everyday life (Fig. 1.1).

While the majority of commercially available polyolefins are still produced with the heterogeneous, multi-site Ziegler–Natta catalysts (as represented by

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Fig. 1.1 Examples of the application of polyolefinic materials

$MgCl_2$-supported $TiCl_4$ catalysts), single-site metallocene catalysts have become more prevalent in the polyolefin industry. Originally discovered by Kaminsky and coworkers [2], single-site metallocene catalysts offered people a better understanding of reaction mechanisms, introduced new catalyst design possibilities [3–5], and allowed for the production of differentiated materials such as high-performance linear low-density polyethylenes (LLDPEs), isotactic polypropylenes (iPPs), syndiotactic polypropylenes (sPPs), ethylene/1-butene amorphous copolymers, and ethylene/propylene diene elastomers.

Following the development of metallocene catalysts, a lot of research has been undertaken to develop novel molecular catalysts based on non-cyclopentadienyl-based ligands, in other words, new post-metallocene catalysts based on both early and late transition metals [6–12]. One of the earliest examples were the bis(phenoxy–imine) group 4 metal complexes (now known as FI catalysts) that were discovered [13–15] based on the "ligand oriented catalyst design concept", a concept that is founded on the belief that the flexible electronic nature of a ligand is a key requirement for achieving high activity [16]. And due to their extremely high activity, unique selectivity, and remarkable versatility, it is not an exaggeration to say that FI catalysts represent one of the most successful post-metallocene catalysts to date.

In this chapter, unique olefin polymerization with FI catalysts and the polymerization mechanisms involved will also be discussed, and the resulting value-added polyolefin materials will be introduced.

1.2 Key Features of FI Catalysts

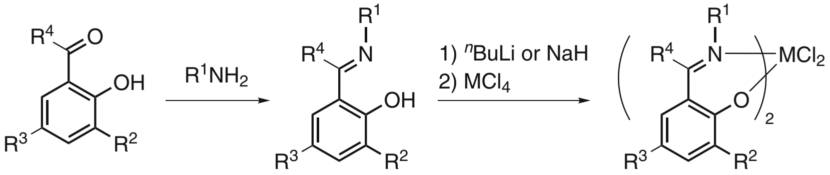
1.2.1 General Synthetic Schemes of FI Complexes

As shown in Scheme 1.1, a phenoxy–imine group 4 metal complex is generally synthesized by reacting MCl_4 ($M = Ti, Zr, Hf$) with a lithium or sodium salt of a phenoxy–imine ligand precursor which is derived from the Schiff-base condensation reaction of an *ortho*-hydroxy aromatic aldehyde or ketone and a primary amine. The initial phenol and amine derivatives with various substituents are easily synthesized and some of them are commercially available. This ease of synthesis allows FI catalysts to possess a wide range of catalyst design possibilities. Thus, catalyst efficiency and resulting polymer properties can be tuned by efficiently and systematically examining diverse ligands, which have sterically and electronically varied substituents, including O, S, N, P and halogen-based functional groups at strategic positions. Substituents R^1 to R^4 are defined according to Scheme 1.1 throughout this chapter.

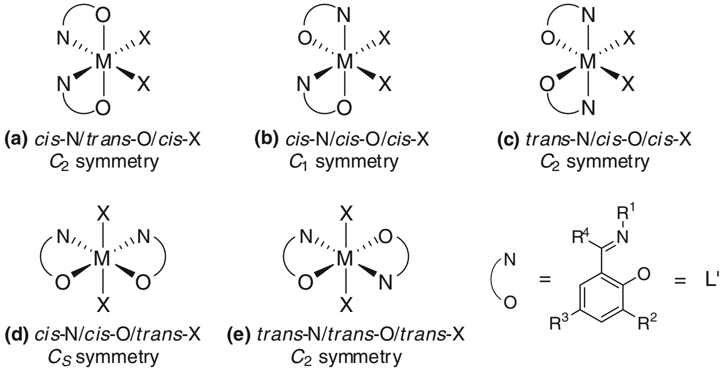
1.2.2 Structural Features

In contrast to group 4 metallocenes that have a tetrahedral framework, bis(phenoxy–imine) group 4 complexes adopt an octahedral geometry around the metal furnished with two imine nitrogens, two phenolic oxygens, and two non-spectator ligands (X). Figure 1.2 depicts the theoretically possible five structural isomers arising from the coordination modes of FI ligands in an octahedral configuration.

Crystallographically determined structures of phenoxy–imine group 4 metal complexes (catalyst precursors) have revealed that in the solid state the complexes



Scheme 1.1 General synthetic scheme of phenoxy–imine group 4 metal complexes



(a) *cis*-N/*trans*-O/*cis*-X C_2 symmetry

(b) *cis*-N/*cis*-O/*cis*-X C_1 symmetry

(c) *trans*-N/*cis*-O/*cis*-X C_2 symmetry

(d) *cis*-N/*cis*-O/*trans*-X C_S symmetry

(e) *trans*-N/*trans*-O/*trans*-X C_2 symmetry

Fig. 1.2 Possible structural isomers for the FI catalyst most often exist as isomer (a) in a *cis*-N/*trans*-O/*cis*-X arrangement and thus possess C_2 symmetry [17, 18]. The crystal structures of prototypical complexes **1** and **2** are shown in Fig. 1.3. Because of the steric repulsions of the substituents on the imine nitrogen (R^1) of the FI ligands, two nitrogens and two oxygens cannot exist on a plane including the metal center unlike isomers (d) and (e), and this inevitably results in one of those *cis*-X geometries (isomers (a)–(c)), among which isomer (a) is most commonly found. It is important to note that the *cis*-X geometry, which is similarly observed in metallocenes or any other high-performance olefin polymerization catalyst, is considered to be essential for the efficient olefin insertion reaction [3–5, 19–21]. When schematically looking at the ordinary C_2 symmetric phenoxy–imine complexes (isomer (a)), the imine nitrogens are located at the backside of the X–M–X moiety, whereas phenoxy-oxygens are situated above and below the X–M–X moiety. Therefore, the R^1 substituents on the imine nitrogen and the R^2 substituents ortho to the phenoxy–oxygen are located at specific positions near the X ligands. Since the X–M–X moiety becomes an olefin polymerization site upon activation, these R^1 and R^2 substituents located in close proximity to the X ligands heavily influence the polymerization behavior of the FI catalysts in specific ways relative to each substituent (Fig. 1.4).

NMR studies of FI catalysts in solution sometimes exhibit a minor isomer with C_1 symmetry (the two FI ligands are chemically non-equivalent, most likely a *cis*-N/*cis*-O/*cis*-X isomer in Fig. 1.2) in addition to the major C_2 symmetric isomer [22–27]. These isomers are often fluxional and interchangeable with each other on

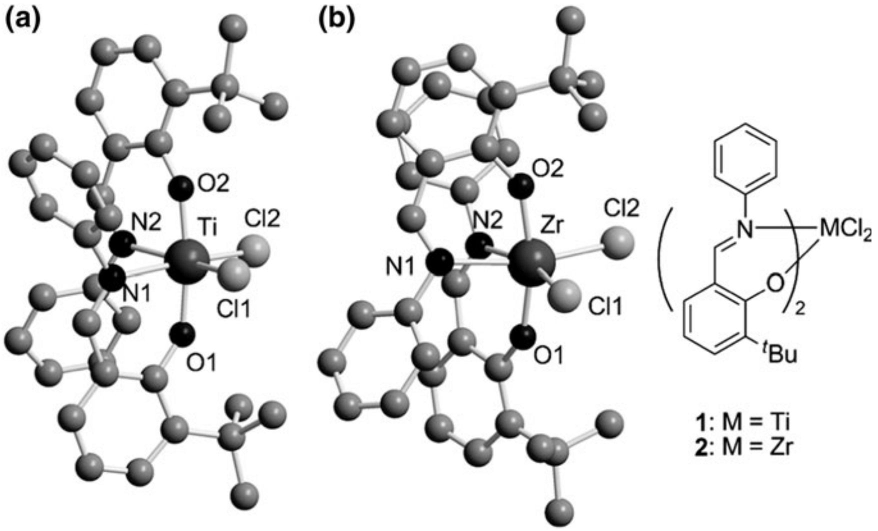


Fig. 1.3 Molecular structures of Ti– and Zr–FI complexes **1** and **2**. All hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): **a** Ti–O1 1.852(4), Ti–N1 2.236(4), Ti–Cl1 2.305(2), O1–Ti–O2 171.6(2), N1–Ti–N2 76.4(2), Cl1–Ti–Cl2 103.10(8); **b** Zr–O1 1.985(2), Zr–N1 2.355(2), Zr–Cl1 2.4234(9), O1–Zr–O2 165.5(1), N1–Zr–N2 74.0(1), Cl1–Zr–Cl2 100.38(5)

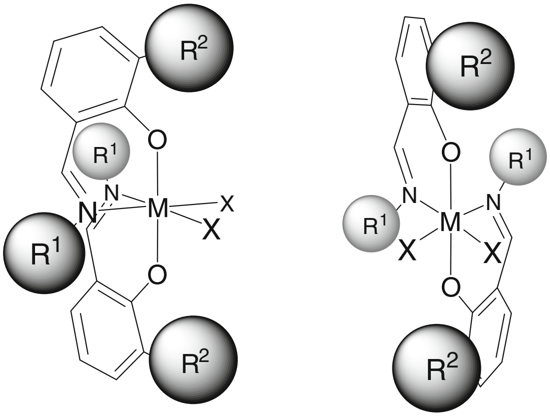


Fig. 1.4 Schematic image of a C_2 symmetric FI catalyst

an NMR time scale [18, 23, 28]. Some of the unique polymerization characteristics of FI catalysts may stem from this structurally dynamic behavior between these possible isomers. For example, for the C_2 symmetric FI catalysts, fluxional isomerization between two enantiomers (Λ/Δ racemization) was proposed by calculations for a syndioselective propylene polymerization with Ti–FI catalysts (see Sect. 1.3.2.1) [29], and has been suggested by low temperature VT-NMR experiments for a cationic monobenzyl Hf–FI catalyst [30] and other related complexes [31]. Thus, the fluxionality of FI catalysts will be an important feature in understanding their polymerization characteristics, and it is believed that the fluxional isomerization probably takes place via M–N bond dissociation due to the labile nature of the imine-N donors.

The labile and dynamic nature of the phenoxy–imine ligands, (especially of the imine-N donors) was also supported by DFT calculations, which demonstrated that the bond distances of the Zr metal center and the imine-N's of a methyl cationic FI catalyst derived from complex **2** were lengthened significantly (0.02–0.1 Å) by the coordination of an ethylene molecule, while the Zr–O bond lengths remained virtually unchanged [32].

1.2.3 Electronic Features

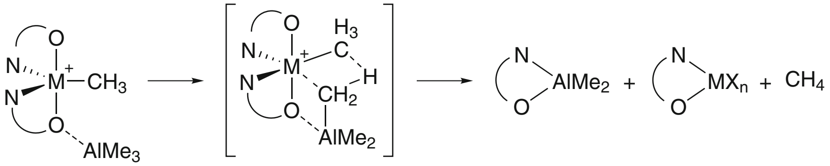
Another distinctive feature of FI catalysts vis-à-vis metallocene catalysts is their heteroatom ligation when compared to the sp^2-hybridized carbon-based cyclopentadienyl (Cp) anion of metallocene compounds. The Mulliken charge at the metal center calculated by DFT methods for three cationic monomethyl titanium species clearly shows the trend between these two types of catalyst. The cationic properties of the metal center increase in the following order: $(C_5H_5)_2TiMe^+$ (1.417 au) < $Me_2Si(C_5Me_4)(^tBu{-}N)TiMe^+$ (1.599 au) < $(Ph{-}N{=}CH{-}C_6H_3{-}2{-}O{-}3{-}^tBu)_2TiMe^+$ (1.741 au), implying that the presence of the heteroatom-coordinating FI ligands makes the complex more electrophilic [33]. In general, one of the reasons for the high activity of the FI catalysts is believed to be this high electrophilicity. In addition, heteroatom ligation renders the M–L bonding properties of the FI catalysts more ionic or polarized relative to that of metallocenes, which may cause the stronger affinity to inorganic surfaces and the higher tolerance to polar functionalities of the FI catalysts (vide infra).

1.2.4 Activation Methods and Active Species

Similar to metallocene catalysts, upon appropriate activation, neutral FI complexes (L'_2MX_2, L': a generic form of an FI ligand) are transformed into coordinatively unsaturated, highly electrophilic monoalkyl cationic complexes, (L'_2M^+–R) (R: alkyl group), which mediate olefin polymerizations via a coordination-insertion mechanism. The monoalkyl cationic species of some Ti–FI catalysts (and related complexes [31, 34]) were actually observed by NMR upon activation of L'_2TiCl_2 with MAO [24, 35], L'_2TiMe_2 [36] or $L'_2Hf(benzyl)_2$ [30] with $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$, and L'_2ZrCl_2 with $AlMe_3/Ph_3CB(C_6F_5)_4$ [35, 37]. Since these cationic species of FI catalysts exhibited only one set of ligand signals, the species still possess C_2 symmetric structures in solution at room temperature within an NMR time scale.

Activation of metallocene ($Cp'MX_2$, Cp': a generic form of a cyclopentadienyl ligand) by triisobutylaluminum ($^iBu_3Al$) and $Ph_3CB(C_6F_5)_4$ generated a cationic alkyl species, and thus this activation method is considered to be chemically equivalent to the activation with MAO. However, when FI catalysts are activated by $^iBu_3Al$ and $Ph_3CB(C_6F_5)_4$, the imine moiety is reduced to an amine by $^iBu_3Al$ (or contaminant $^iBu_2AlH$) accompanied by isobutene formation, (FI catalysts and $^iBu_3Al$ are mixed for 10 min before polymerization) [32, 38, 39], resulting in phenoxy–amine complexes. The reduced species exhibited a number of interesting polymerization characteristics owing to their unusual N donors, $^iBu_2Al$–N, which will be bulkier and weaker as a coordinating donor than the imine-N′s (See Sects. 1.3.1.2, 1.3.2.2, and 1.3.3).

Meanwhile, it was demonstrated that $AlMe_3$ included in MAO can cause deactivation of FI catalysts [24, 35]. The deactivation is probably initiated by an attack of $AlMe_3$ on a phenoxy-O group. Subsequent C–H bond activation in $AlMe_3$ by a cationic L'_2M^+–Me species yields an Al–FI complex ($L'AlMe_2$)



Scheme 1.2 A deactivation path of FI catalysts caused by $AlMe_3$

together with a methane molecule and a paramagnetic group 4 metal compound (Scheme 1.2). As another deactivation pathway, the formation of dinuclear μ-complexes [40, 41] or heterodinuclear complexes with alkyl aluminums [37] have also been proposed.

As described above, FI catalysts have distinctive features derived from a pair of non-symmetric phenoxy–imine ligands, which inevitably results in; (a) enormous structural diversity stemming from ligand accessibility and amenability to modification; (b) isomers arising from ligand coordination arrangements in an octahedral framework, among which *cis*-X configurations are favored; and (c) potential fluxionality among these isomers. The phenoxy–imine ligands also make FI catalysts highly electrophilic, chemically absorbable (possible chemisorption on a solid surface), and functional-group tolerant, presumably due to the heteroatoms that are present and their M–L bonding characteristics. Additionally, the high reactivity of the imine moieties allows in situ ligand modification by the choice of activation methods. The following sections reveal the basic polymerization behavior of FI catalysts and how they are able to upgrade olefins.

1.3 Homopolymerization by FI Catalysts

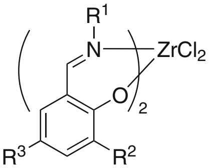
1.3.1 Ethylene Polymerization and Oligomerization

1.3.1.1 Exploration of High Activity

The catalytic activity of polymerization is generally measured by weight of polymers per a specific catalyst (metal) amount, time, and sometimes monomer concentration and stated in, for example, g-polymer/(mmol-M h) or g-polymer/(mmol-M h atm). Activity is one of the most important performance parameters of any catalyst. The group 4 metallocene catalysts were once known as the most active catalysts among olefin polymerization catalysts (10^1–10^2 kg-polymer/(mmol-M h)), until FI catalysts eclipsed them with an activity of the order of 10^3 kg-polymer/(mmol-M h) [15]. Even the prototypical zirconium FI catalyst **2** showed a strikingly high ethylene polymerization activity of 519 kg-polymer/(mmol-M h), which is one of the highest activities among known olefin polymerization catalysts including metallocenes.

Taking advantage of the straightforward synthesis and modular property of phenoxy–imine ligands (Sect. 1.2), systematic studies on catalyst efficiency have been carried out by introducing substituents with different steric and electronic properties [32, 42–44]. As summarized in Table 1.1, a keen relationship between the ethylene polymerization activity and the steric bulkiness of the R^2 substituents can be observed for a series of Zr–FI catalysts **2**–**11**. When a particularly bulky tertiary R^2 group, CPh_2Me, is introduced, the activity of complex **11** reaches an unprecedented level, 6552 kg-polymer/(mmol-M h). This activity corresponds to a

Table 1.1 Effects of the substituents of the Zr–FI complexes on ethylene polymerization activity



Entry	Complex	R^1	R^2	R^3	Activity [kg-polymer/(mmol-M h)]
1	**3**	Ph	Me	H	0.4
2	**4**	Ph	^{i}Pr	H	0.9
3	**2**	Ph	^{t}Bu	H	519
4	**5**	Ph	^{t}Bu	Me	331
5	**6**	Ph	1-adamantyl	Me	714
6	**7**	Ph	cumyl	Me	2096
7	**8**	Cy	^{t}Bu	Me	82
8	**9**	Cy	1-adamantyl	Me	434
9	**10**	Cy	cumyl	Me	4315
10	**11**	Cy	CPh_2Me	H	6552
11[a]	**12**	Cy	cumyl	OMe	7224

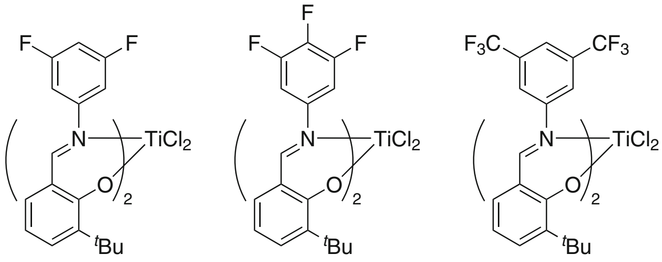
Polymerization conditions toluene 250 mL, MAO 1.25 mmol, Al/Zr = 250–625,000, ethylene 0.1 MPa, 25 °C, 5 or 10 min

[a] Polymerization conditions: *n*-heptane 500 mL, complex 0.005 μmol, MAO 1.25 mmol, ethylene pressure 0.9 MPa, 75 °C, 15 min

TOF of 64,900 s^{-1} atm^{-1}, standing as one of the most efficient catalysts not only for olefin polymerization but also for any catalytic reaction. The complexes having methyl at para to the phenolic oxygen (R^3 substituents) consistently show slightly lower activity than the unsubstituted complexes (R^3 = H) (complex **5** vs. **2**), although the reason is not clear.

The introduction of an electron-donating methoxy group at the R^3 position (para to the phenoxy-O′s) was found to increase the thermal stability of the FI catalysts, making them available for polymerizations in an industrially practical higher temperature range (e.g., **12**: 7224 kg-polymer/(mmol-M h), 75 °C, 0.9 MPa ethylene pressure) [45].

With regard to Ti–FI catalysts, the activity enhancement by bulky R^2 substituents is rather modest, but the catalytic efficiency of Ti–FI catalysts can be electronically increased by electron-withdrawing R^1 substituents (Chart 1.1). The activity increase from 3.58 kg-polymer/(mmol-M h) for prototypical Ti–FI catalyst **1** to 34.8 kg-polymer/(mmol-M h) for **13** (R^1 = 3,5-$F_2C_6H_3$) has been demonstrated. Likewise, activity values of 43.3 kg-polymer/(mmol-M h) for **14** (R^1 = 3,4,5-$F_3C_6H_2$) and 40.3 kg-PE/mmol-M h for **15** (R^1 = 3,5-$(CF_3)_2C_6H_3$) are the typical examples [46, 47].



13 **14** **15**

Chart 1.1 Structures of complexes **13–15**

1.3.1.2 Control of Molecular Weight

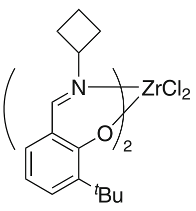
The controllability of the molecular weight of polymers is one of the most important requirements for a catalyst vis-à-vis the end uses of polyolefin materials. Profound understanding of chain transfer reactions is necessary to gain the controllability, which may also result in gaining a control of the chain-end structures. FI catalysts permit an exceptionally wide range of molecular weight from 10^3 to 10^6 as a result of varying catalyst structures or changing activation methods (vide infra). As will be seen in Sect. 1.3.1.3, controllability of chain transfer reactions of FI catalysts can lead to living polymerizations with practically no chain-terminating processes taking place.

With regard to the molecular weight control with FI catalysts, activation methods and the size of the R^1 substituents are important. As discussed above, activation of FI catalysts with $^i\mathrm{Bu}_3\mathrm{Al}$ and $\mathrm{Ph}_3\mathrm{CB(C}_6\mathrm{F}_5)_4$ causes formation of phenoxy–amine complexes, which consistently shows lower activities but furnishes higher molecular weight polymers than the phenoxy–imine complexes irrespective of the Ti or Zr complexes.

When R^1 substituents were varied in a series pertaining to Zr–FI catalysts as shown in Table 1.2, the molecular weights of polyethylenes (PEs) show a clear dependence on the size of the R^1, that is, $M_w = 2000$ g/mol with **16** (R^1 = cyclobutyl), $M_w = 3600$ g/mol with **17** (R^1 = cyclopentyl), $M_w = 14{,}000$ g/mol with **18** (R^1 = cyclohexyl), and $M_w = 290{,}000$ g/mol with **19** (R^1 = 2-methylcyclohexyl) [44, 48]. The terminating chain-end structures were revealed to be almost exclusively a vinyl group for the low molecular weight PEs (>90 mol%), suggesting that the main chain transfer reaction of these FI catalysts is a β-hydrogen elimination.

Further studies have shown that the molecular weights were apparently independent of the monomer concentration, while the activities increased linearly at higher monomer concentration, showing that both propagation and β-H transfer are first order in monomer concentration. Therefore, the chain transfer involved in these polymerizations is the β-H transfer to a coordinating ethylene.

Table 1.2 Effects of the R^1 substituents of the phenoxy–imine Zr complexes on ethylene polymerization behavior



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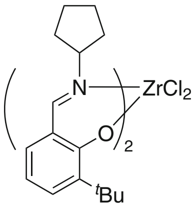

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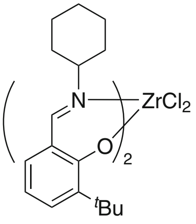

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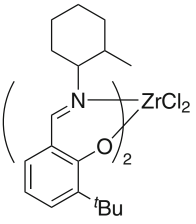

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Entry	Complex	Activity [kg-polymer/(mmol-M h)]	M_w[a] (g/mol)	M_w/M_n[a]	Vinyl terminated chain end[b] (mol%)
1	**16**	31.6	2000	2.0	91
2	**17**	67.2	3600	2.1	95
3	**18**	87.7	14,000	1.7	96
4	**19**	93.0	290,000	4.9	71

Polymerization conditions toluene 250 mL, complex 0.5 μmol, dried MAO 0.625 mmol, ethylene feed 100 L/h, 25 °C, 5 min

[a] Determined by GPC (PE calibration)

[b] Determined by ^{1}H NMR

This bimolecular *β*-H transfer reaction is known to proceed via a six-centered transition state, which is sterically more encumbered than the compact four-centered transition state for the propagation (ethylene insertion) reaction or the unimolecular *β*-hydrogen transfer to a metal. Within a framework of isomer (a), *cis*-N/*trans*-O/*cis*-X in Fig. 1.2, it is quite possible that the R^1 substituents on the imine nitrogens have a non-bonding interaction with the X ligands (see Fig. 1.4). This was confirmed by the X-ray structures of Zr–FI catalysts, which demonstrated that the Cl–Zr–Cl bond angles were narrowed as R^1 substituents became larger (R^1 = cyclobutyl (**16**: 100.64(3)°), cyclohexyl (**18**: 99.8(2)°), 2-methylcyclohexyl (**19**: 98.00(6)°)) [48]. The narrower bond angles observed for the bulkier R^1 groups probably destabilize the six-centered transition state of the chain transfer more than the four-centered transition state of the propagation, and the higher rate of the propagation relative to the chain transfer results in higher molecular weight polymers. DFT calculations have confirmed this scenario, as well as the extremely unstable nature of the Zr hydrides, which means that *β*-H transfer to a metal is disfavored. These vinyl-terminated polymers can be used as a distinctive precursor for the chain-end functionalized polymers (see Sect. 1.3.1.6).

The relationship between the R^1 and the polymer molecular weight holds true for a series of Zr–FI complexes bearing *N*-aryl groups. The molecular weights of PE increase dependently upon the *ortho*-substituent in the order of H < Me < ^{i}Pr at the expense of activity, which decreases in the same order. However, even though the large R^1 substituents virtually shut down the bimolecular *β*-hydrogen transfer path, a chain transfer with main group metal alkyls via transmetallation seems to be still available [42]. Upon activation with MAO or MAO/trimethylaluminum, a Zr–FI complex that has bulky 2-isopropyl phenyl groups as R^1 substituents afforded Al-terminated PEs (M_w = 10–720 kg/mol, M_w/M_n = 2.0–2.6), demonstrating that the chain transfer to alkylaluminums predominantly takes place [49]. The exclusive formation of the Al-terminated PE was confirmed by the ^{13}C NMR study of the PE obtained with deuterolytic quenching. The Al-terminated PEs are expected to serve as useful intermediates for functionalized polyolefins.

FI catalysts can also produce ultra-high-molecular-weight PE (UHMWPE). UHMWPE in general refers to PE that possesses the molecular weights higher than 1.5 million. UHMWPE possesses excellent tribological property, abrasion resistance, impact resistance, and chemical resistance, and has a number of material applications.

As described above, Zr–FI catalysts bearing bulky R^1 substituents can produce PEs with a high molecular weight of over 10^6 g/mol. When Zr–FI catalyst **2** was activated with ^{i}Bu$_3$Al/Ph$_3$CB(C$_6$F$_5$)$_4$, the molecular weight of the obtained polymer reached 5×10^6 g/mol under atmospheric ethylene at 50 °C [32]. The UHMWPE can be produced with supported FI catalysts in an industrially practical manner, which will be discussed in Sect. 1.3.1.5.

Molecular weight distribution is another important parameter particularly relevant to processability as well as properties (strength and modulus) of the polymers. Single-site catalysts like metallocene and post-metallocene catalysts usually afford the most probable molecular weight distributions of around $M_w/M_n = 2$, contrary to conventional heterogeneous Ziegler–Natta catalysts, which are multi-site catalysts consisting of complex mixtures of multiple components and produce polymers with broader molecular weight distributions (M_w/M_n 4–10).

As discussed in Sect. 1.2.2, FI catalysts potentially possess five isomers stemming from the coordination modes of ligands in the octahedral geometry, among which isomer (a), *cis*-N/*trans*-O/*cis*-X, is the most thermodynamically stable in most cases. However, ^{15}N NMR of Zr–FI catalyst **20** having ^{15}N enriched imine functions (–C=^{15}N–Ph) unexpectedly revealed that **20** existed almost exclusively as a C_1 symmetric isomer in solution (isomer (b)), and that the two chemically non-equivalent imine-N′s rapidly interchanged with each other above room temperature [23]. Interestingly, **20** activated with MAO produced PEs with temperature-dependent trimodal molecular weight distributions, which appeared to be formed with three chemically-distinctive active species (Fig. 1.5). Due to the fluxionality of FI catalysts, each isomer can generate multiple single-site active species, which may be the reason for this well-defined multimodality of **20**/MAO.

1.3.1.3 Monodisperse Polymers

An extreme end of the spectrum with regard to control of chain transfer and chain termination reactions is a living polymerization that has no chain transfer or chain termination reactions by definition. Living polymerizations are a tool to regulate the molecular weight and the molecular weight distribution of polymers, and sometimes the means to produce block copolymers, and chain-end functionalized polymers. Living olefin polymerizations via a coordination-insertion mechanism have been achieved in the past but with significant limitations in terms of polymerization conditions, polymerization activity, applicable monomers, and the achievable molecular weight of living polymers. In 2000, scientists at Mitsui Chemicals discovered unprecedented living olefin polymerizations with Ti–FI catalysts that exhibit robust livingness even at temperatures much higher than room temperature [50–54]. The living Ti–FI catalysts possess at least one *ortho*-fluorine in the aryl groups on the imine nitrogens (R^1 substituent). As shown in Table 1.3, the molecular weight distributions (M_w/M_n) are extremely narrow for complexes **21**, **22**, **23**, and **24** that have the *ortho*-Fs, whereas the other complexes **14**, **13**, and **25** without the *ortho*-Fs show ordinary M_w/M_n values of around 2.

One rationale for the robust livingness brought by the *ortho*-F was proposed based on DFT calculations on the cationic species bearing an *n*-propyl group as a model of a propagating alkyl group [43, 52, 55–57]. In the calculated structure of the propagating model, one of the *ortho*-F(s) was observed in proximity to the β-hydrogen atoms ($\sim$2.3 Å) of the growing chain (Van der Waals radii of H and F are 1.20 and 1.47 Å, respectively) and weak attractive and electrostatic interactions between the *ortho*-F and β-H were expected (the electrostatic energy $\sim$30 kJ/mol), which can stabilize the chain-transfer-prone β-agostic state of the cationic polymeryl-titanium and avert unwanted β-H transfer reactions. Such hypothetical C–F···H–C interactions were experimentally observed by Chan and coworkers for some phenoxy–pyridine Zr complexes (for example, **26**) bearing a cyclometallated aryl group by NMR spectroscopy and X-ray and neutron crystallography (Fig. 1.6) [58–62]. Furthermore, Mecking and co-workers revealed that a structurally related Ti enolatoimine complex bearing an *ortho*-F *N*-aryl group was an excellent ethylene living polymerization catalyst, whereas the

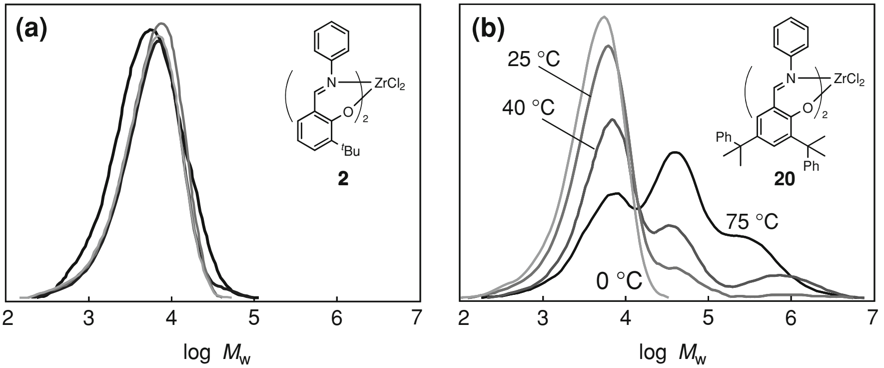


Fig. 1.5 GPC elution curves for the PEs formed by polymerization at 0–75 °C with FI catalysts **a 2** and **b 20** with MAO

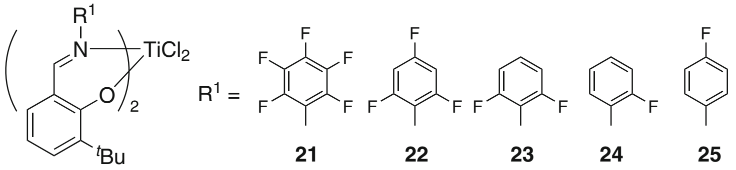
corresponding complexes having *ortho*-methyl substituted or non-substituted *N*-aryl groups were not [63, 64].

Even though the *ortho*-F effects must be further clarified experimentally, the proposed concept may lead to the prospect of a new catalyst design strategy to manipulate olefin polymerizations together with conventional steric/repulsive interactions [51, 56, 57].

1.3.1.4 Selective Ethylene Trimerization

Oligomerization of ethylene to produce linear α-olefins (LAOs) is of great interest because LAOs are widely used as polyethylene comonomers, detergent alcohols, oil-field chemicals, and lubricant additives. The oligomerization catalysts employed in industry produce a range of LAOs following a Schulz–Flory distribution. In order

Table 1.3 Effects of the R^1 substituents of the phenoxy–imine Ti complexes on ethylene polymerization behavior



Entry	Complex	Activity [kg-polymer/(mmol-M h)]	M_n[a] (kg/mol)	M_w/M_n[a]
1	**21**	18.12	424	1.13
2	**22**	2.43	145	1.25
3	**23**	0.828	64	1.05
4	**24**	0.127	13	1.06
5	**14**	44.6	98	1.99
6	**13**	32.0	129	1.78
7	**25**	5.31	128	2.18

Polymerization conditions toluene 250 mL, MAO 1.25 mmol, complex 0.4–5.0 μmol, ethylene 0.1 MPa, 100 L/h, 1–5 min, 50 °C

[a] Determined by GPC (PE calibration)

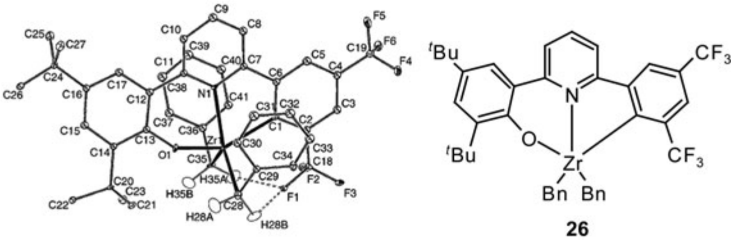


Fig. 1.6 Molecular structure of **26** from the neutron diffraction study (50% probability ellipsoids) showing selected hydrogen atoms. Reprinted with permission from [59]. Copyright 2006 Wiley–VCH Verlag GmbH & Co. KGaA

to meet the fluctuating market demands among LAOs and to reduce the fractions of unprofitable LAOs, investigation on the selective oligomerization catalysis to yield the desired LAOs has been intense, particularly on ethylene trimerization to produce 1-hexene. Most of the catalysts studied are Cr-based, although there are a few examples of Ti-, V-, or Ta-based catalysts.

Recently, scientists at Mitsui Chemicals developed tridentate phenoxy–imine ligated titanium complexes, which served, upon activation with MAO, as selective ethylene trimerization catalysts with extremely high activities [65]. The tridentate ligands possessed the 2′-alkoxybiphenyl-2-yl groups as the R^1 substituent (complexes **27**, **28**, and **29**) and the tridentate ligands wrapped around the Ti center in a facial fashion (Fig. 1.7). The oligomerization results are summarized in Table 1.4. Complex **29** exhibited exceptionally high activities and selectivity, in which branched decenes (cotrimerization products of 1-hexene and two molecules of ethylene) and a small amount of PE were the only side products. The activities were two orders of magnitude higher than commercial Cr-based catalysts (Phillips catalyst) under comparable conditions.

A metallacyclic propagation mechanism was proposed for the selective formation of 1-hexene as shown in Scheme 1.3, consisting of the oxidative addition of two ethylene molecules to form a metallacyclopentane species, insertion of another ethylene to form a metallacycloheptane intermediate, and subsequent *β*-hydride elimination (and subsequent reductive elimination or 3,7-H transfer). The pendant OMe donor was considered to stabilize the Ti(II) species as seen in similar cyclopentadienyl-arene titanium complexes. However, the reaction demonstrated second order dependence on ethylene pressure, indicating that formation of the metallacyclopentane intermediate can be the rate-determining step (RDS). This result contrasts with the cyclopentadienyl-arene titanium complexes which showed apparent first order dependence on [ethylene] and therefore ethylene insertion to the metallacyclopentane species is considered to be the RDS [66].

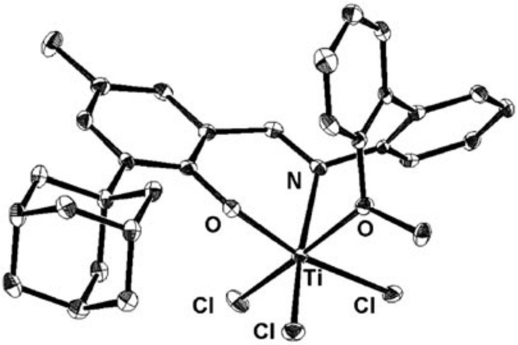
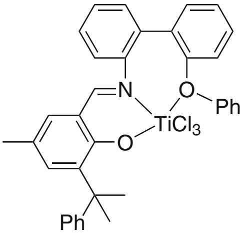


Fig. 1.7 Molecular structure of complex **29**. Reprinted with permission from [65]. Copyright 2010 American Chemical Society

Table 1.4 Catalytic ethylene conversion with the tridentate phenoxy–imine Ti complexes



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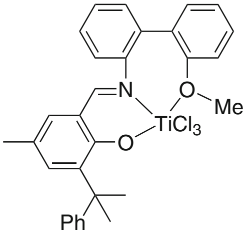

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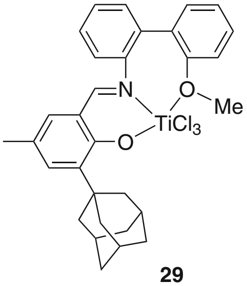

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Entry	Complex	C_2H_4 pressure (MPa)	Activity [kg-hexene/(mmol-M h)]	Selectivity (wt%)		
				C_6	C_{10}	PE
1	**27**	0.8	0.19	76.6	0	23.4
2	**28**	0.8	5.7	86.2	12.2	1.6
3	**29**	0.8	7.4	91.4	6.4	2.1
4[a]	**29**	5.0	315	92.3	7.3	0.4

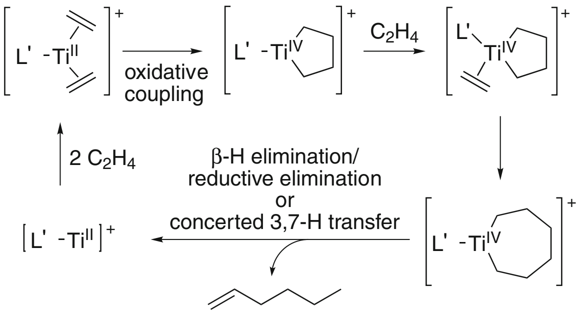
Conditions cyclohexane 30 mL, complex 0.5 μmol, MAO 5.0 mmol, 30 °C, 1 h
[a] Cyclohexane 150 mL

1.3.1.5 Ultra-Fine Non-Coherent Polyethylene Particles

$MgCl_2$ is widely used in industry as a support for Ziegler–Natta catalysts. It was demonstrated that the introduction of $MgCl_2$ increased the number of active sites and that unexpectedly and significantly it also enhanced the rate of olefin insertion reactions by about two orders of magnitude on average relative to classical Ziegler–Natta catalysts.

Inspired by the active roles that $MgCl_2$ plays in olefin polymerization, $MgCl_2$ was examined in the polymerization catalyzed by FI catalysts. As discussed in Sect. 1.2, FI catalysts have more ionic and polarized metal–ligand bonds compared to metallocene catalysts, and probably due to this feature, FI catalysts are more strongly adsorbed on Lewis acidic surfaces of inorganic compounds and generate an active supported catalytic system in combination with, for example, $MgCl_2$, hetero-poly compounds, and clays [17, 67–75].

Scheme 1.3 A plausible mechanism for the selective ethylene trimerization catalyzed by the tridentate Ti–FI catalysts



$MgCl_2$ catalyst supports can be prepared from adducts of $MgCl_2$ and alcohol (e.g., 2-ethyl-1-hexanol), which are dissolved in *n*-decane. Upon addition of R'_3Al, the $MgCl_2$ supports are precipitated out via dealcoholysis as a mixture of $MgCl_2/R'_nAl(OR)_{3-n}$. The ethylene polymerization activities of Ti–FI catalysts supported on the $MgCl_2/R'_nAl(OR)_{3-n}$ (R′: ^{i}Bu, Et) were very high and roughly comparable with those activated with MAO. With Zr–FI catalysts, ethylene polymerization activity reached 1820 kg-polymer/(mmol-M h) at 0.9 MPa ethylene pressure without using conventional MAO or boron-based activators, demonstrating that the $MgCl_2/R'_nAl(OR)_{3-n}$ serves as a highly efficient activator in a similar way to the classical Ziegler catalysts.

In addition, these FI catalysts supported on the $MgCl_2/R'_nAl(OR)_{3-n}$ keep the single-site polymerization characteristics and afford polymers with good morphology, demonstrating simultaneously the advantages of homogeneous and heterogeneous catalysts (high-performance heterogeneous single-site catalysts).

Under carefully controlled conditions, $MgCl_2/R'_nAl(OR)_{3-n}$ catalyst supports can be prepared into nearly perfectly spherical particles free from agglomerations having a wide range of controllable particle sizes (1–15 μm) and narrow size distributions. On the other hand, FI catalysts can produce UHMWPE by introducing bulky R^1 substituents as discussed in Sect. 1.3.1.2. By combining these two technologies, Zr–FI complexes bearing sterically demanding R^1 (= 2-methylcyclohexyl) with $MgCl_2/^iBu_nAl(OR)_{3-n}$ gave UHMWPE particulates (M_v 2–5 × 10^6 g/mol) at an extremely high activity of 750–1800 kg-polymer/(mmol-M h) under industrially applicable conditions (50 °C, 0.9 MPa ethylene pressure) [67–69]. Because the morphology of catalysts is replicated to that of the obtained polymers, the obtained UHMWPE particulates possess noncoherent and uniform spherical shapes. The obtained polymer shows a very high bulk density of up to 0.50 g/mL with variable diameters (Fig. 1.8).

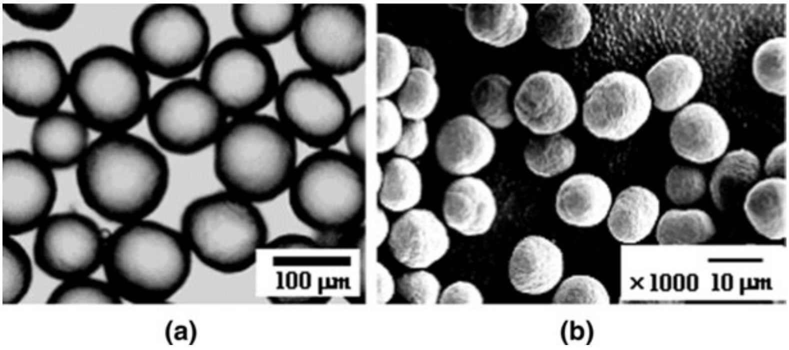


Fig. 1.8 **a** Photograph and **b** SEM images of the ultra-fine non-coherent PE particles formed with $MgCl_2$-supported Zr–FI catalyst. Average particle size: **a** 120 μm, **b** 10 μm. Reprinted with permission from [33]. Copyright 2009 American Chemical Society

These UHMWPE particulates are expected to have a wide array of applications such as sintered sheets and filters, light diffusion films, high-performance resin modifiers, and cosmetics.

1.3.1.6 End Functionalization of Polyethylenes

The addition of functionality to polyolefins that are otherwise non-polar can greatly enhance the range of attainable properties (e.g., adhesion, wettability, dyeability, printability, and compatibility). The functionalized polyolefins can also be used as versatile precursors when preparing hybrid polyolefins with non-polyolefinic materials possessing complementary functionalities. In the latter context, chain-end functionalized (telechelic) polymers serve as a building block for the hybrid polymers possessing well-defined architectures such as (multi-) block, graft and polymer networks. In this section, chain-end functionalized polyolefins prepared by FI-based catalysts are discussed.

We have already discussed in Sect. 1.3.1.2 that Zr–FI catalysts having relatively small R^1 groups afforded vinyl-terminated PE, which can be chemically modified according to various methods.

The chain-end vinyl groups can be efficiently converted into epoxy groups by treatment of the vinyl-terminated PE (M_w 2000 g/mol, M_w/M_n 2.4, vinyl functionality 95%, T_m 122 °C) with hydrogen peroxide (30% water solution) in toluene at 90 °C in the presence of Na_2WO_4 as an oxidation catalyst and methyl-tri-*n*-octylammonium hydrogen sulfate as a phase transfer catalyst [76]. In fact, epoxy-terminated PE (M_w 2000 g/mol, M_w/M_n 1.8, epoxy functionality 96%, T_m 121 °C) was obtained in almost quantitative yield. The epoxy-terminated PEs were highly reactive and could be transformed into a diol-terminated PE by the in situ hydrolysis using aqueous 2-propanol or a triol-terminated PE via a reaction with diethanolamine [44, 48, 77]. The obtained diol- or triol-terminated PEs can serve as precursors for well defined hybrid materials of PE and polyethylene glycol (PEG) having AB^2 and AB^3 type block structures (Scheme 1.4) [76, 77]. These hybrid materials formed stable nano-scale dispersion in water (up to 40 wt% of the hybrid materials) without adding any surface-active agents. The transmission electron microscopy (TEM) revealed that the AB^3 hybrid (PE, M_n 1100 g/mol; PEG, average M_n 400 × 3 g/mol, T_m 120 °C) formed a semi-transparent dispersion, consisting of nanoparticles (~18 nm on average) with a narrow size distribution. The nanoparticles appeared to have very lipophilic PE cores with hydrophilic shells of PEG because they can encapsulate large organic molecules such as 2,7,12,17-tetra-*tert*-butyl-5,10,15,20-tetraazaporphyrinato copper (II) (a water-insoluble dye) or 8-anilino-1-naphthalene sulfonic acid (a probe showing no fluorescence in a hydrophilic environment) as shown in Fig. 1.9.

As the second example of chemical modification of the vinyl chain-end PE, the Alder-ene reaction with maleic anhydride can give succinic anhydride-terminated PE. The reaction of the vinyl terminated PE (M_w 1400 g/mol, M_w/M_n 2.0, vinyl group 95%, T_m 116 °C) with maleic anhydride was carried out in the presence of

2,6-di-*tert*-butyl-4-methylphenol as a radical quencher at 195 °C for 16 h, which furnished the corresponding succinic anhydride-terminated PE (sa-t-PE: M_w 1700 g/mol, M_w/M_n 1.7, succinic anhydride functionality 102%, T_m 117 °C) (Fig. 1.10) [78].

The sa-t-PE exhibited higher thermal stability than its parent vinyl-terminated PE although the PE having epoxy-, diol-, triol-, and diamino-functionalities introduced above displayed no such improvement regarding thermal stability. The sa-t-PE also exhibited higher melt viscosity. The sa-t-PE possesses a high potential as a dispersant of hydrophilic materials (e.g., pigment) and as a modifier for polar polymers, in particular, engineering plastics.

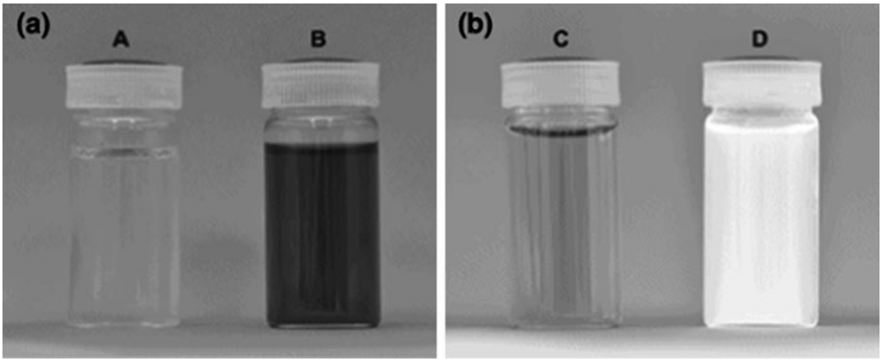


Fig. 1.9 **a** 2,7,12,17-tetra-*tert*-butyl-5,10,15,20-tetraazaporphyrinato copper (II) (0.07 mmol) or **b** 8-anilino-1-naphthalene sulfonic acid (0.01 mmol) with water (10 mL) in the absence (A, C) or in the presence of AB^3 nanoparticles (0.2 wt%; B, D)

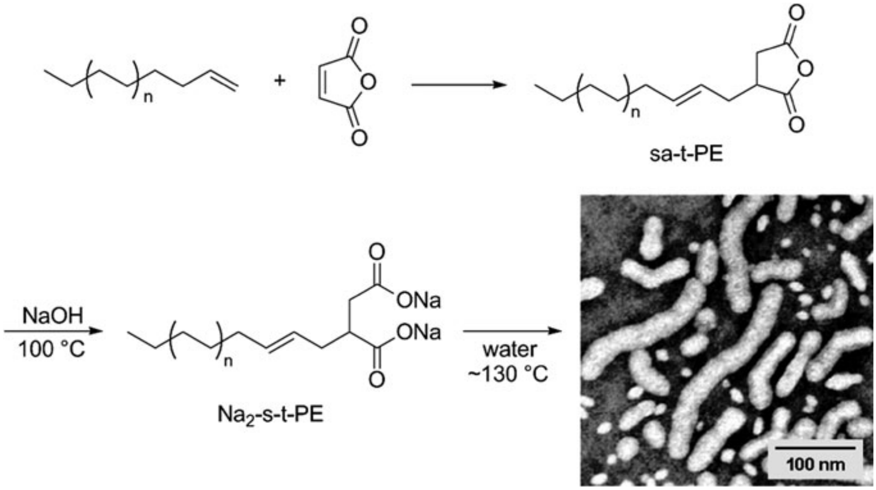


Fig. 1.10 Synthetic scheme and TEM image of a Na_2-s-t-PE water dispersion. Reprinted with permission from [78]. Copyright 2009 American Chemical Society