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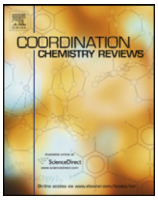

Review

Development of new polymerization catalysts with manganese(II) complexes

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Dedicated to Professor Edward I. Solomon
on the occasion of his 65th birthday.

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ABSTRACT

Many transition metal catalysts including both early and late transition metal ions have been investigated for olefin polymerization and copolymerization reactions. Less attention has been paid to group 7 metal catalysts. Yet, manganese(II)-based catalysts are expected to have features distinct from early and late transition metal catalysts. In this context, the present review summarizes our recent results and strategy about ethylene polymerization and ethylene copolymerization with 1-hexene with manganese(II)-based catalysts.

Abbreviations: PE, polyethylene; PP, polypropylene; Cp, cyclopentadienyl ion; MAO, methylaluminoxane; acac, acetylacetonato; salen, 1,2-cyclohexanediamino-*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene); LFSE, ligand field stabilization energy; Tpb, hydrotris(pyrazolyl)borate; Tpm, tris(pyrazolyl)methane; Tp^{R3,R5}, the 5-substitutent follows the 3-substituent as a subscript in both Tpb and Tpm; MMAO, modified methylaluminoxane; GPC, gel permeation chromatography; Mes, mesityl; Cum, cumyl; TIBA, triisobutylaluminum; TB, triphenylcarbenium tetrakis(pentafluorophenyl)borate; Ad, adamantyl; pzH, pyrazole; MeCN, acetonitrile; bipy, bipyridine; ESR, electron spin resonance; SCB, short chain branch; ESI-MS, electrospray ionization mass spectrometry.

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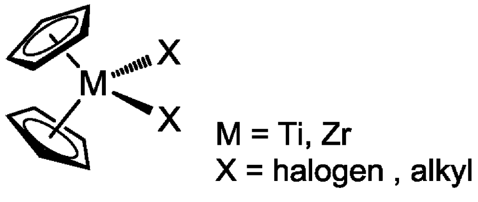
1. Introduction

Precise polymerization with the effective carbon–carbon bond formation in a higher yield is a key issue from the viewpoint of a resource saving and energy saving society. Polyolefins such as polyethylenes (PEs), polypropylenes (PPs), and ethylene/α-olefins copolymers are significant commercial synthetic polymers in our everyday life [1–3] with worldwide consumption exceeding 100 million tons in 2005 [4].

The discovery of heterogeneous Ziegler–Natta catalysts, which contain a binary mixture of $TiCl_4$ and organoaluminum compounds AlR_3 (R = alkyl, aryl and hydride), in the 1950s enabled us to produce high-density PEs and isotactic PPs [5,6]. In 1963, Ziegler and Natta were awarded the Nobel Prize in Chemistry "*for their discoveries in the field of the chemistry and technology of high polymers*" [7–10]. In 1980, Kaminsky and co-workers reported an efficient activator for homogeneous group 4 metallocene catalysts, which contain metal complexes with two cyclopentadienyl (Cp) or substituted Cp groups, with a partially hydrolyzed $AlMe_3$ reagent such as methylaluminoxane (MAO) [11]. By using these highly active homogeneous catalysts, it is possible to obtain linear low-density PE by so-called "single-site" catalysts with narrow molecular weight distributions ($M_w/M_n \approx 2$) [12]. These catalysts also performed well in producing isotactic PPs, syndiotactic PPs, ethylene/1-butene amorphous copolymers, and ethylene/propylene/diene elastomers, etc. To date, group 4 metallocenes (Scheme 1) and the related catalysts such as the half-sandwich amide or constrained geometry catalysts have been at the forefront of these developments [13].

In 1995, Brookhart and co-workers discovered the high catalytic activity of Ni(II) and Pd(II) complexes with a bulky diimine ligand for olefin polymerization and ethylene copolymerization with acrylate [14]. This report opened the door to a new category, so-called "post-metallocene catalysts", to expand the use of the transition metal complex catalysts [15] based on Sc and Y (group 3) [16]; vanadium, tantalum, and niobium (group 5) [17]; chromium (group 6) [18]; iron and ruthenium (group 8) [19]; cobalt and rhodium (group 9) [20]; nickel and palladium (group 10) [14,21]; copper (group 11) [22]; zinc (group 12) [23]; aluminum (group 13) [24]; lanthanides [25]; as well as group 4 metals [26].

However, less attention has been paid to group 7 metal catalysts. Manganese(II)-based catalysts would be expected to have unique features different from early and late transition metal catalysts. Ban et al. reported that manganese(II)-based complexes, such as $[Mn^{III}(acac)_3]$ (acac denotes acetylacetonato), $[Mn^{II}(Cp)_2]$, and $[Mn^{III}(salen)(Cl)]$ (H_2salen denotes *N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-cyclohexanediamine)), could catalyze ethylene polymerization when MAO was used as an activator [27]. However, the search for new catalysts based on manganese(II) and/or manganese(III) ions is far from over. Driven by industry's desire to obtain much greater control over the properties of the resultant polymers and to extend the family of products to new monomer combinations, new highly active and selective catalyst families that tolerate a variety of functional groups are needed. In this review, we highlight recent advances in our research for new catalysts [28–30], focusing primarily on manganese(II)-based catalysts ligated by N3 type ligands (Fig. 1).



Scheme 1.

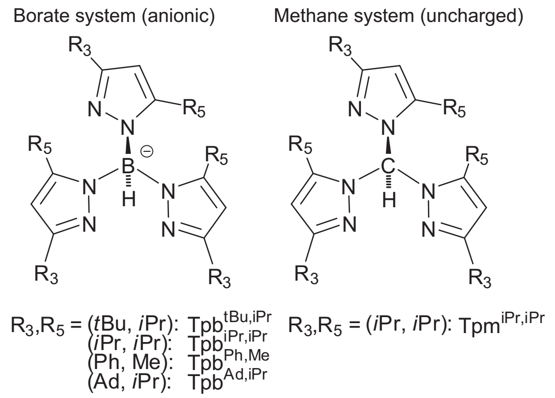


Fig. 1. N3 type ligands for manganese(II)-based catalysts discussed in this review.

2. Manganese ion for polymerization reaction

2.1. Manganese ion

Manganese is an element of relatively high abundance in the earth's crust (0.085%) where it is found mainly in the form of oxides, hydrous oxides, and carbonates [31]. The element can adopt a wide variety of formal oxidation states but it is most often found in the Mn^{II} to Mn^{VII} levels. Manganese acts as a strong Lewis acid in its II, III, and IV oxidation states. It thus prefers hard Lewis bases as ligand donors. This criterion may be satisfied by hydroxide or oxide ligands as well as alkoxides, phenoxides, and caroboxylates. On the other hand, nitrogen and sulfur donor atoms which are softer Lewis bases can also function as ligands to manganese ions. The donor capacity of the ligands to manganese directly affects the electropositivity of the metal center. Therefore, the redox potential and the subsequent ability of the ion to act as an oxidant or a reductant are strongly dependent on the nature of the ligands. Mn(IV) is a strong oxidant and a poor reductant. In part, this accounts for the relative rarity of known stable Mn(IV) species. The Mn(III) ion in most environments is of intermediate potential and can act both as an oxidant or a reductant. These characteristics are largely a result of the d^4 electronic configuration. For Mn(II) (d^5), the loss of the ligand field stabilization energy (LFSE) accounts for its poor reducing ability. In addition, Mn(II) is also a poor oxidant because the addition of a sixth d electron causes a loss in exchange energy and requires the expenditure of pairing energy when Mn(II) has an octahedral geometry and takes a high-spin state. Therefore, the precise type of ligands can change the potential of the metal over a wide range within a given formal oxidation state. In this way the metal's environment interacts strongly to either augment or moderate the above inherent redox tendencies.

Another mode of communication between the metal ion and its environment is the differential preferences of different oxidation state metals to various coordination number and geometry. The charge, the size, and the number of d electrons on the manganese all have direct effects on its preferred coordination number and geometry. Manganese II, III, IV are found in general to employ five or six ligands in their first coordination sphere giving rise to either octahedral or square pyramidal derived geometries. In addition, Mn(II) is also found in tetrahedral geometry. The complexes thus formed are almost invariably high-spin state (except in cases possessing very strong ligand field sets). In environments having these coordination geometries, a simple ligand field model demonstrates that Mn(II), Mn(III), and Mn(IV) have very different specific coordination preferences.

High-spin Mn(II) has five unpaired d electrons, one occupying each of the d orbitals, giving rise to zero LFSE in all geometries. Since