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Review

Polymerized metallocene catalysts and late transition metal catalysts for ethylene polymerization

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Contents

Abstract

This review describes recent advances in the synthesis of novel polymerized metallocene catalysts and late transition metal catalysts for ethylene polymerization. The characteristics of these polymerized catalysts and the resulting polyethylene are discussed here.

Keywords: Metallocene; Polymerized catalysts; Late transition metal catalysts; Ethylene; Polymerization; Polyethylene

1. Introduction

In 1980, Kaminsky and co-workers [1] introduced the use of methylalumoxane (MAO) as a co-catalyst for olefin polymerization; since then metallocene complexes have revolutionized the world of polyolefins [2–4] and they are going to contribute polymers with new properties and applications.

Metallocene-based catalysts are dramatically different from previous generations of catalysts. For example, metallocene catalysts can be tailored to produce polyolefins with special stereoregularities and a high degree of tacticity. Moreover, owing to their homogeneous nature every molecule has an active site and thus metallocene catalysts can be many times more active as Ziegler–Natta and Phillips catalysts and

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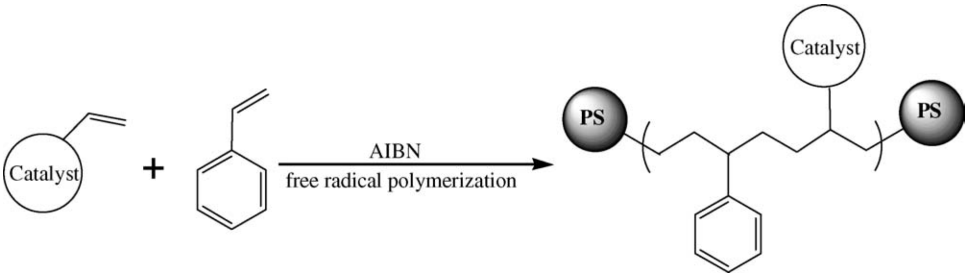

Scheme 1. Synthesis of a polymerized catalyst.

can produce high molecular weight polymers and copolymers, characterized by a narrow molecular weight distribution (≈2) and homogeneous chemical composition.

During the second half of the 1990s, interest grew in developing a new generation of late-transition metal catalysts, due to their lower oxophilicity. A greater functional-group tolerance of late transition metals relative to early transition metals was presumed, which makes them likely targets for the development of catalysts for the co-polymerization of ethylene with polar co-monomers under mild conditions. In 1995, Brookhart reported diimine nickel and Pd catalysts [5], well known for the polymerization of ethylene, α-olefins, and cyclic olefins and the co-polymerization of olefins with a variety of functionalized olefins. In 1998, Brookhart and co-workers [6] and Gibson and co-workers [7] reported highly active ethylene and propylene polymerization catalysts based on iron(II) and cobalt(II) bearing 2,6-bis(imino)pyridine ligands.

Regardless of the virtues these catalysts possess, they would remain mere playthings of the laboratory if they could not be adapted for commercial polymerization processes.

Solution polymerization processes are suitable for the preparation of low-crystallinity polyolefins, such as elastomers, very-low-density ethylene copolymers and amorphous poly-α-olefins. In these cases, the polymer product is soluble in the reaction medium and a solution-soluble catalyst system can be used. Higher-crystallinity resins, such as isotactic polypropylene or high-density polyethylene, are usually prepared in continuous slurry, fluidized-bed gas phase, or bulk monomer processes. Here, the polymer is insoluble in the reaction medium. A morphologically uniform polymer particle is needed to avoid reactor fouling and facilitate smooth operations, and thus a continuous process is possible [8]. So, it is necessary to support homogeneous catalysts for industrial applications.

Inorganic supports, such as silica or alumina [9,10], and also organic supports, such as polystyrene and starch [11,12], have been used to heterogenize soluble polymerization catalysts. These methods have the disadvantage that the catalysts can lose activity [13] because their metal centers (Lewis acids) are not accessible at the surface or they can be blocked by oxygen functions (Lewis bases). As a different heterogenization strategy, Alt et al. [14–17] developed the self-immobilization of metallocene catalysts, which have an olefin or alkyne function that can be used as a co-monomer in the polymerization process. Our group [18–21] introduced the self-immobilization of metallocene to the field of late transition metal catalysts, and Herrmann and co-workers [22] also reported on the self-immobilization of a Fe catalyst for olefin polymerization. Our group [23–26] reported a different approach that can both keep the advantages of homogeneous catalysts and improve the morphology of polymer in order to meet the requirement for industrial application. The idea was to synthesize homogeneous catalysts containing an alkenyl group on the ligand and then co-polymerize the catalysts and styrene with free radical polymerization. The resulting polymers containing catalysts as co-monomers are called polymerized catalysts (Scheme 1).

2. Preparation of precursors of polymerized metallocene catalysts

2.1. Preparation of symmetric metallocene complexes

Synthetic methods to prepare these symmetric metallocene complexes are quite general. Treatment of 2 equiv. of the ligand lithium salt with $ZrCl_4$ or $ZrCl_4·2THF$ in THF affords the symmetric metallocene complexes.

The ligand lithium salt can be synthesized by two methods. One method is to treat the ligand with *n*-BuLi. Chen and Wei [27] reported two synthetic methods for alkenyl substituted cyclopentadiene, the sodium method and the phase transfer method, and the two methods were compared. When the sodium salt of cyclopentadiene reacted with allyl chloride, the yield was small. Using the phase transfer method, the yield was more than 70%. So, four new alkenyl substituted cyclopentadienes were synthesized by the phase transfer method (Scheme 2).

The other synthetic method for the ligand lithium salt is to react fulvene with lithium amide. The method was introduced by Rausch in 1982 [28]. Two ligand salts of alkenyl substituted cyclopentadienes were easily synthesized by this method (Scheme 3).

Using these ligands, the alkenyl substituted symmetrical metallocenes complexes **1–6** were synthesized by the reaction of 2 equiv. of the lithium salts with $ZrCl_4$ or $ZrCl_4·2THF$ in THF (Scheme 4). The solid-state structure