



Mononuclear complexes with heterocyclic ligands as ethylene polymerization catalysts for single-reactor bimodal polyethylene technology



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ARTICLE INFO

Article history:

Received 30 May 2015

Received in revised form 9 July 2015

Accepted 17 July 2015

Available online 26 July 2015

Keywords:

Complexes with heterocyclic ligands

Ethylene polymerization

Mononuclear complexes

Bimodal resins

Single-reactor technology

ABSTRACT

27 complexes of titanium, zirconium and vanadium with 1,2-bis(benzimidazolyl)benzene, 1,2-bis(benzimidazolyl)ethane and 1,1-bis(benzimidazolyl)methane ligands have been synthesized and characterized. After activation with methylalumoxane (MAO) these complexes proved as good catalysts for ethylene polymerization in spite of the hetero atoms in the ligands and the oxophilicity of the metals. Nearly all produced polyethylenes showed bimodal or multimodal molecular weight distributions indicating more than one active site of the catalysts in the various polymerization steps. Obviously, after activation with MAO, a mononuclear catalyst molecule can interact differently with the cocatalyst. This is an easy and elegant approach to single-reactor bimodal/multimodal polyethylene technology. The polymerization activity of the catalyst system 1,2-bis(benzimidazolyl) benzene zirconium tetrachloride (**29**/MAO) was investigated at different polymerization temperatures and structure–property–relationships were studied. The effect of the polymerization temperature on both molecular weights and polydispersities of the polymers produced with catalyst **29**/MAO was investigated at 20, 40, and 60 °C. The molecular weights M_w were $1.3 \cdot 10^6$, $1.2 \cdot 10^6$ and $9.7 \cdot 10^5$ g/mol and the polydispersity indices PDI 693, 248 and 223 respectively.

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1. Introduction

Mononuclear complexes as catalysts for olefin polymerization in homogeneous solution have many advantages because every molecule can act as a catalyst and hence provide high activity [1–3]. In most cases, the molecular weights of the produced resins have narrow molecular weight distributions due to the fact that only one active site is generated in the activation process of the catalyst precursor. This can be disadvantageous when processing polyolefins, and solutions are needed to overcome this problem. So far, special support materials and methods, the mixture of different catalysts, the application of dinuclear or multinuclear catalysts and the use of two or more reactors were applied [4–13]. However, the best solution is the design of catalysts that can solve all these problems in one step and in one reactor. In this contribution we report the synthesis and characterization of complexes with heterocyclic ligands that are perfect candidates for this challenge. 1,2-Bis-benzimidazoles and 2,6-bis(benzimidazolyl) pyridine are well known ligand precursors for transition metal complexes [14–24]. So far, for ethylene polymerization, 1,2-bis(benzimidazolyl) benzene copper [25], titanium, zirconium and

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vanadium complexes were reported [26–28] that can be activated with methylalumoxane (MAO) and then be applied successfully for catalytic ethylene polymerization. The vanadium complexes of bis(benzimidazole) amine tridentate ligands [N,N,N], are active ethylene polymerization catalysts after activation with alkylaluminum compounds [29] and 2,6-bis(2-benzimidazolyl) pyridine zirconium dichloride/MAO polymerizes methylacrylate [30]. Herein we report the first titanium, zirconium and vanadium complexes of 1,2-bis(benzimidazolyl)benzene, 1,2-bis(benzimidazolyl)ethane and 1,1-bis(benzimidazolyl)methane and their applications in catalytic ethylene polymerization after activation with MAO.

2. Results and discussion

2.1. General synthesis of the ligand precursors

The condensation reaction of a dicarboxylic acid or an acid anhydride in preheated polyphosphoric acid is a well established procedure for the preparation of the imidazole based ligand precursors [31,32] in high yields (Scheme 1) (see Table 1).

2.2. Synthesis of coordination compounds

2.2.1. Synthesis of titanium and zirconium complexes

The complexes **10–36** were synthesized according to Scheme 2. The titanium and zirconium complexes were prepared by ligand displacement reactions. The reaction of the tetrahydrofuran adducts of zirconium and titanium tetrachloride with the corresponding ligand precursor in methylene chloride results in an immediate color change and the complexes could be isolated in very high yields (80–95%). The complexes were characterized by NMR, mass spectrometry and elemental analysis.

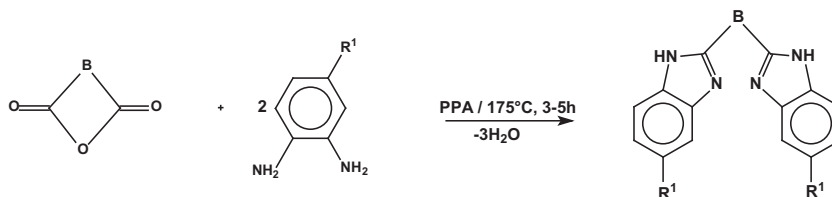
2.2.2. Synthesis of vanadium complexes

The vanadium complexes were synthesized by dissolving vanadium trichloride in diethyl ether followed by the addition of the ligand precursor with constant stirring overnight. The product yields ranged from 60% to 78%.

2.3. Characterization

2.3.1. ¹H and ¹³C NMR spectroscopy

The ligand precursors **1–9** and their titanium and zirconium complexes were characterized by ¹H and ¹³C NMR spectroscopy. The vanadium complexes, due to their paramagnetism, were characterized by mass spectrometry. The ¹H NMR



Compound No.	Bridging unit (B)	R ¹
1	CH ₂	H
2	CH ₂	CH ₃
3	CH ₂	Cl
4	CH ₂ CH ₂	H
5	CH ₂ CH ₂	CH ₃
6	CH ₂ CH ₂	Cl
7	1,2-C ₆ H ₄	H
8	1,2-C ₆ H ₄	CH ₃
9	1,2-C ₆ H ₄	Cl

Scheme 1. Synthesis of the ligand precursors **1–9**.

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