



Evaluation of catalytic activity in ethylene polymerization and ethylene/10-undecen-1-ol copolymerization of new orthopalladated complexes derived from tridentate ligands [C,N,S]

Fernando Ortega-Jiménez^{a,*}, José G. López-Cortés^b, M. Carmen Ortega-Alfaro^c, J. Guillermo Penierres-Carrillo^a, Raúl Quijada^d, Cecilio Alvarez-Toledano^b

^a Departamento de Ciencias Químicas, Facultad de Estudios Superiores Cuautitlán-UNAM, Campo 1, Avenida 1ro. de Mayo s/n, Cuautitlán Izcalli, C. P. 54740 Estado de México, Mexico

^b Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04360 México, D.F., Mexico

^c Instituto de Ciencias Nucleares, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, C.P. 04360 México, D.F., Mexico

^d Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile y Centro para la Investigación Interdisciplinaria Avanzada en Ciencias de los Materiales (CIMAT), Santiago, Chile

ARTICLE INFO

Article history:

Received 30 September 2011

Received in revised form 1 December 2011

Accepted 3 December 2011

Available online 9 December 2011

Keywords:

Orthopalladated complexes

Ethylene polymerization

Copolymerization

ABSTRACT

This paper describes catalytic applications of new orthopalladated complex/MAO systems in polymerization of ethylene and copolymerization of ethylene/10-undecen-1-ol. Orthopalladated complexes **1–5** were synthesized from tridentate ligands [C, N, S], with a general formula of PdLX, where L=[Ph₂NN=C(CH₃)–C=SRSR] and R=CH₃, –CH₂CH₂– and X=Cl, –C≡CPh, –C≡CSi(CH₃)₃. These catalytic systems show high catalytic activity in ethylene polymerization, especially when the reactions were carried out at a temperature of 80 °C. The polyethylene obtained is linear with narrow molecular weight distributions, indicating that Pd/Al systems behave as single site catalysts. The results obtained in copolymerization of ethylene/10-undecen-1-ol indicate that orthopalladated complex/MAO system produces copolymers with molecular weight distributions unimodal and close to 2, indicating that the Pd/Al systems also act as single site catalysts.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Polyethylene is one of the most common materials used in our daily lives and accounts for 40% of the total volume of world production of plastic materials, due to its easy handling, low production cost, low density and excellently balanced physical properties [1]. There are three kinds of polyethylene which are described by their acronyms HDPE, LDPE and LLDPE [1b]. High Density Polyethylene (HDPE) is a linear semi-crystalline polymer ($T_m \approx 135^\circ\text{C}$). Linear Low Density Polyethylene (LLDPE) is a random copolymer of ethylene and 1-olefins (for example: 1-butene, 1-hexene or 1-octene). These are produced commercially by Phillips catalysts [2], Ziegler [3] and metallocenes [4]. On the other hand, Low Density Polyethylene (LDPE) is a branched homopolymer prepared at high temperatures and high pressures through a process of free radicals [5]. Metallocenes [4a,4b] and other catalysts based on early transition metals [4c] allow an effective method of synthesis of polyethylene and polyolefin. However, the high oxophilicity of

these complexes particularly when polar olefins are used often causes catalyst poisoning.

During the first half of the 1990s, there was great interest in developing a new generation of non-metallocene catalysts, partly to cover the growing demand of organometallic systems based on group 4 metals, and also in order to explore and enhance the synthetic potential of other transition metal in olefin polymerization [6]. Olefin polymerization catalyzed by complexes of late transition metals has been recently investigated [7], and in comparison with complexes of early transition metals, they are more tolerant to functional groups present in either the monomer or in the reaction media [8]. In this regard, Brookhart and co-workers [9a] developed ethylene polymerization using catalysts based on transitional metals such as Pd (II) and Ni (II) and α -diimines as ligands, thereby achieving the efficient polymerization of α -olefins, cyclic olefins, and also the copolymerization of non-polar olefins with functionalized olefins that have high catalytic activities and high molecular weight polymers. The main feature of these catalysts is the presence of bulky and symmetric substituents in the *ortho*-position to the imino nitrogen atom, which effectively block axial coordination and thus delay chain completion [7,9]. Since the publication of this report, the search for other palladium complexes with N-donor ligands, which can also catalyze olefin polymerization reactions,

* Corresponding author. Tel.: +52 5556232024; fax: +52 5556232024.

E-mail address: fdo.ortega@unam.mx (F. Ortega-Jiménez).