Available online at www.sciencedirect.com

ScienceDirect

Catalysis Communications 8 (2007) 2025–2031

CATALYSIS
COMMUNICATIONS

www.elsevier.com/locate/catcom

Ethylene polymerization using an asymmetric dinuclear titanocene catalyst carrying a novel 3-oxa-pentamethylene bridge

Xu Li [a], Xutao Zhao [b], Bochao Zhu [b], Feng Lin [a], Junquan Sun [a,*]

[a] Department of Chemical Engineering, College of Material and Chemical Engineering, Zhejiang University, Hangzhou 310027, China
[b] Lanzhou Petrochemical Research Institute of Petrochina, Lanzhou 730060, China

Received 7 December 2006; received in revised form 13 March 2007; accepted 19 March 2007
Available online 27 March 2007

Abstract

The asymmetric 3-oxa-pentamethylene bridged dinuclear titanocenium complex $(CpTiCl_2)_2(\eta^5\text{-}C_9H_6(CH_2CH_2OCH_2CH_2)\text{-}\eta^5\text{-}C_5H_3CH_3)$ (**1**) has been prepared, characterized by ^{1}H NMR spectroscopy and elemental analysis, and after activation with MAO tested as a homogenous catalyst for the polymerization of ethylene. The results show that the catalytic activity of **1** as well as the molecular weight of the produced polyethylene are higher than those using the alkylidene bridged asymmetric dinuclear metallocenes $(CpTiCl_2)_2(\eta^5\text{-}C_9H_6(CH_2)_n\text{-}\eta^5\text{-}C_5H_4)$, $n = 3$ (**4**), 4 (**5**). The molecular weight distribution of polyethylene produced with **1**/MAO reaches 11.00 and the HT-GPC curve shows a bimodal distribution. The melting point of the polyethylene obtained by **1**/MAO is higher than 135 °C and the ^{13}C NMR spectrum of PE shows only one strong signal at 30 ppm for the methylene units indicating a highly linear and crystalline polymer.

Keywords: Asymmetric dinuclear titanocene catalysts; Ethylene polymerization; Polyethylene

1. Introduction

Polyolefins produced using common metallocene catalysts possess in general a narrow molecular weight distribution (MWD) which causes difficulties in industrial processing. In contrast, polyolefins with high MW and broad MWD, ideal polymers with superior physical properties are easy to process [1,2]. Therefore, it is an attractive research project to produce polyolefins with high MW and broad MWD. Several methods have been reported to control the MW and MWD of polymers such as polymerization in a series of reactors with different polymerization conditions and polymerization in a single reactor with a mixture of individual mononuclear catalysts. However these methods also cause problems, e.g. in miscibility [3] in processing and they increase the capital costs [4].

Polymerization using dinuclear or multinuclear metallocene catalysts seems to be the most effective way to produce broad MWD polyolefins. In recent years, a variety of dinuclear metallocene catalysts has been developed for olefin polymerization due to their potential of tailoring the polymer properties in this direction [5–7]. Muelhaupt [8] first studied olefin polymerization using phenylene-bridged dinuclear zirconocene catalysts and discovered cooperative effects. In 1996, Green [9] reported the synthesis of a series of homo- and hetero-dinuclear metallocene complexes of group four metals and investigated their catalytic activities in the polymerization of ethylene and propylene. The resulting PE shows high melting points (Tm) in the range of 137–140 °C, indicating high linear and crystalline polymers. A systematic polymerization study of dinuclear metallocene catalysts was performed by Noh [10–14] using polysiloxane and polymethylene

---

[*] Corresponding author. Tel.: +86 571 8795 3159; fax: +86 571 8795 1227.
E-mail address: sunjunquan@zju.edu.cn (J. Sun).

1566-7367/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.catcom.2007.03.022

bridged dinuclear zirconocenes. They found that a higher electron density delivered by a longer polymethylene bridge seems to stabilize the active site of the catalysts and accelerates the rate of polymerization. More recently, Alt [15] prepared a series of asymmetric alkylidene bridged dinuclear metallocene complexes of zirconium and hafnium and investigated the polymerization of ethylene using those dinuclear complexes. Their results showed that a broad or bimodal MWD polyethylene. We also reported a variety of symmetric and asymmetric dinuclear metallocenes which were efficient catalysts to produce high molecular weight polymers with broad MWD, not only in methyl methacrylate (MMA), but also in ethylene polymerization [16–22].

In this paper, we report on the synthesis of a novel asymmetric dinuclear metallocene complex with a 3-oxapentamethylene bridge, which is different from the polymethylene and polysiloxane bridge. Primary studies showed that the catalytic system 1/MAO afforded polyethylene with a high MW and a broad bimodal MWD.

2. Experimental

All reactions were carried out under a dry, oxygen-free atmosphere using standard Schlenk techniques with a double manifold vacuum line. Argon gas was purified by passage through a column of molecular sieves (4 Å) and Drierite (8 mesh).

2.1. Materials

Tetrahydrofuran, diethyl ether, hexane and toluene were distilled from sodium-benzophenone ketyl and methylene chloride from calcium hydride prior to use. 2,2′-dichlorodiethyl ether, purchased from Aldrich was used after distilling from calcium hydride. $CpTiCl_3$ was synthesized according to the literature [23]. MAO (10 wt% in toluene, provided by Witco) was used without further purification. Ethylene (Polymer grade) was purified by bubbling through a solution of triethylaluminium in toluene.

2.2. Measurements

^1H NMR spectra were recorded on a Bruker Avance DMX500 spectrometer at ambient temperature; chemical shifts were referenced with respect to tetramethylsilane. Elemental analyses were conducted using a Perkin–Elmer 240 elemental analyzer. The molecular weight of polyethylenes was measured in decahydronaphthalene at 135 °C by a modified Ubbelohde-type viscometer according to $[\eta] = 6.67 \times 10^{-4}\ M\eta^{0.67}$ (ml/g). The molecular weight distributions of some polymers were determined in *ortho*-dichlorobenzene as solvent by gel-permeation chromatography (GPC, Waters 150, 135 °C) using polystyrene as a standard. The melting temperatures (T_m) of the polymers were measured by a differential scanning calorimeter (Perkin–Elmer DSC-7).

2.3. Synthesis

2.3.1. Preparation of $C_9H_7(CH_2CH_2OCH_2CH_2)C_5H_4CH_3$ (L2)

A solution of $CH_3C_5H_4Na$ (10.0 ml, 1.00 mol/l) in THF (50.0 ml) was cooled to 0 °C and treated dropwise for 30 min with a solution of $C_9H_7(CH_2CH_2OCH_2CH_2)Cl$. (**L1**) (2.22 g, 10.0 mmol) prepared form C_9H_7Li and $Cl(CH_2CH_2OCH_2CH_2)Cl$ in THF according to the literature [15]. The resulting solution was warmed to room temperature and stirred for 6 h. Volatiles were removed in vacuo and the yellowish paste was extracted with pentane. The filtrate was concentrated in vacuo to obtain the products as light yellow oil (1.06 g, 40% yield). GC-MS *m/z* (%): 266 (M^+, 35%), 143 (M^+–$OCH_2CH_2C_9H_7$, 60%), 128 (M^+-$CH_3O(CH_2)_2C_9H_7$, 100%). ^1H NMR ($CDCl_3$, 20 °C, δ ppm): 7.17–7.45 (m, 4 H, C_9H_7), 6.20–6.26 (m, 2H, C_5H_4), 6.02–6.06 (m, 1H, allylic indene-H), 3.80–3.54 (m, 4H, $OCH_2 \times 2$), 3.31 (*d*, $J = 7.2$, 2H, alkyl indene-H), 2.82–2.87 (m, 4H, $CH_2 \times 2$), 2.59–2.82 (m, 2H, C_5H_4), 1.90–2.03 (m, 3H, CH_3).

2.3.2. Preparation of $(CpTiCl_2)_2(\eta^5$-C_9H_6-$(CH_2CH_2OCH_2CH_2)$-$\eta^5C_5H_3CH_3)$ (1)

A solution of $C_5H_5TiCl_3$ (2.2 g, 10.0 mmol) in toluene (30.0 ml) was cooled to 0 °C and treated drop wise over 30 min with a solution of $Li_2[C_9H_6\,(CH_2CH_2OCH_2CH_2)$-$C_5H_3CH_3]$ (1.4 g, 5.0 mmol), prepared from *n*-BuLi and $C_9H_7(CH_2CH_2OCH_2CH_2)C_5H_4CH_3$ (**L2**) in toluene (20.0 ml). The resulting solution was warmed up to room temperature and stirred for 24 h. Volatiles were removed in vacuo and the resulting residue was extracted with CH_2Cl_2. Recrystallization in toluene resulted in a reddish brown solid of **1** (1.9 g, 60.0 % yield). $C_{29}H_{30}OCl_4Ti_2$ elemental analysis (%), Calc: C 55.10%; H 4.78%. Found: C 54.96%; H 4.77%. ^1H NMR ($CDCl_3$, 20 °C, δ ppm): 7.31–7.69 (m, 4H, C_9H_6), 6.58–6.66 (m, 2H, C_9H_6), 6.47 (s, 5H, $1/2 \times C_5H_5$), 6.44 (s, 2.5H, $1/2 \times C_5H_5$), 6.20–6.22 (m, 1H, C_5H_3), 6.19 (s, 2.5H, $1/2 \times C_5H_5$), 6.18 (s, 2.5H, $1/2 \times C_5H_5$), 6.12–6.16 (m, 2H, C_5H_3), 3.70–3.76 (*q*, $J = 7.0$ Hz, 2H, OCH_2), 3.55–3.58 (*t*, $J = 7.0$ Hz, 2H, OCH_2), 3.32–3.38 (m, 1H, $C_9H_6CH_2$), 3.21–3.28 (m, 1H, $C_9H_6CH_2$), 2.75–2.78 (*t*, $J = 7.0$ Hz, 2H, $C_5H_3CH_2$), 2.12–2.17 (m, 3H, CH_3). IR (KBr, cm^{-1}): 3105, 2960, 2866, 1632, 1482, 1439, 1360, 1261, 1108, 1026, 823, 745, 453.

2.3.3. Preparation of the mononuclear complexes $IndTiCpCl_2$ (2) and $MeCpTiCpCl_2$ (3)

The syntheses of complexes **2** and **3** were performed according to the literature [24,25].

$IndTiCpCl_2$ (**2**): ^1H NMR ($CDCl_3$, 20 °C, δ ppm): 7.68–7.71 (m, 2H, C_9H_7), 7.37–7.40 (m, 2H, C_9H_7), 6.89–6.91 (*t*, $J = 3.3$, 1H, C_9H_7), 6.68–6.69 (*d*, $J = 3.3$, 2H, C_9H_7), 6.23 (s, 5H, C_5H_5).

$MeCpTiCpCl_2$ (**3**): ^1H NMR ($CDCl_3$, 20 °C, δ ppm): 6.55 (s, 5H, C_5H_5), 6.40–6.42 (*t*, $J = 2.7$, 2H, C_5H_4), 6.31–6.33 (*t*, $J = 2.7$, 2H, C_5H_4), 2.35 (s, 3H, CH_3).