Influence of diethylzinc on ethylene polymerization using iron catalyst homogeneous and supported on clay

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ABSTRACT

Diethylzinc (DEZ) was introduced in ethylene polymerizations using iron based catalyst system both homogeneous and also supported on clay. The aim was to evaluate the influence of this compound on catalytic activity as well as on crystalline structure and thermal properties of polyethylene. The results showed that using the homogeneous system, the compound DEZ slightly decreased the catalytic activity while increased melting temperature of the synthesized polyethylene as observed by DSC analysis. Besides, X-ray diffraction technique showed that the crystallographic peaks of polyethylene were shifted to higher angles probably due to the dilatation of the orthorhombic unit cell by chain branching. In the polymerizations employing the iron catalyst supported on clay, the addition of DEZ also promoted an increase of the melting temperature of the polyethylene, and a slight increase in the degree of crystallinity was also observed.

1. Introduction

The discovery of new catalysts is the key to the development of new polymeric materials, and to promote improvement in the performance of the various grades existing polyolefin [1]. Although olefin polymerization has been dominated by catalysts which metal is in the beginning of the transition series (early transition metals: Zr, V, Cr, Ti), those at the end of the transitions series (late transition metals: Fe, Co, Pd, Ni) have attracted an abrupt interest in recent decades [2].

Since non-metallocene catalysts based on α-diimine with Ni, Fe and Pd were founded, the scientific world has intensively studied these systems due to their ability to synthesize various types of branched polymers, their higher thermal stability, tolerance to polar functional groups and capacity of polymerizing cyclic monomer such as norbornene [3]. Moreover, these catalytic complexes based on metals like iron and cobalt synthesized homogeneously linear polyethylene with high activities [4–6]. The use of iron catalyst in acetylene oligomerization and polymerization leads to a highly active catalyst using diethylzinc (DEZ) as a chain transfer agent [6]. Using a series of bis(imino)pyridyl complexes of cobalt and iron it was observed that the iron catalyst produces polyethylene with higher molecular weight than its cobalt analogues. Furthermore, the influence of the stereo bulkiness around the metal center, the metal type and also the polymerization conditions on yield and molecular weight of polyethylene were studied. The results showed that this effect is the key to retarding chain transfer to obtain high molecular weight polyethylene [7–9].

Recently, it has been observed that using coordination catalysts with transition metals of both the beginning and the end of the series, under certain reaction conditions, the growing polymer chain is transferred to aluminum (from alkyl compound used as activator or cocatalyst) during polymerization, and this process is the chain transfer on aluminum. If the transfer of growing polymer chain to aluminum is the only chain transfer mechanism in polymerization and the exchange of the growing chain between the transition metal (catalyst) and aluminum is extremely fast and reversible, it appears that the polymer chain grows on aluminum compound, which is not true [10].

A living polymerization is a method of polymer synthesis that results in products with narrow molecular weight distribution, which in turn allows a more accurate control of the polymer microstructure. The number of polymer molecules produced equals the number of molecules of initiator and even after all the monomer has been consumed, if added more monomer, the chain continues to grow, indicating that the active center is still "alive". In the case of coordination polymerization, this process is not economically attractive. Moreover, the addition of an aprotic compound such as

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DEZ, does not promote the "death" of the polymer chain while still allowing the continued propagation. Furthermore, the number of polymer molecules produced is much larger than the initiator, since the zinc participates in alkyd exchange reactions forming polymers with the same characteristics of those by living polymerization, but with higher catalytic activities. This type of process is called immortal polymerization [11]. What happens is the rapid and reversible exchange of dormant chain connected to the metal site (zinc) with the growing chain attached to the active center. The chain that was dormant, now attached to the metal active center, passes to propagate yielding a polymer with narrow molecular weight distribution [12].

Nanocomposites consisting of hybrid materials are particles of inorganic nature dispersed in a polymeric matrix, and these particles have at least one dimension in the nanometer range [13]. In recent years, there has been considerable interest in the type polymer/layered-silicate (clay) nanocomposite by having improved properties when compared to pure polymers or conventional composites [14]. Due to its structure, the clays may be used as nanofillers to exhibit high rigidity and dimensional stability [15].

In the present work, we report the synthesis of polyethylene by immortal polymerization using a catalyst based on iron supported on clay to assess the influence of DEZ on catalytic activity, and on thermal properties and crystalline degree of the obtained materials.

2. Experimental

All substances sensitive to moisture and oxygen were handled under an inert atmosphere of nitrogen using the Schlenk technique. The catalyst bis (imino) pyridine iron was synthesized according to the literature [8] and evaluated in homogeneous polymerization of ethylene with the addition of DEZ at different concentrations. Subsequently the iron catalyst was impregnated on treated clay [16] and evaluated in ethylene polymerizations.

2.1. Synthesis of homogeneous catalyst

The ligand was synthesized by reacting 1 equivalent of 2,6-diacetylpyridine with 2 equivalents of 2,6-diisopropylaniline in ethanol and allowed to reflux for 40 h. Then the ligand solution was complexed with ferrous chloride in butanol to yield a dark blue precipitate. The complex was dried under vacuum and the yielding was 1.5 g of catalyst.

2.2. Treatment of clay

Initially, 30 g of sodium clay (Argel 40, Bentonit Uniao Nordeste, Brazil) was heated at 120 °C for 24 h and cooled under nitrogen; 50 ml of toluene were added until complete dispersion of the clay. Thereupon, 150 mL of MAO (10% solution in toluene, Chemtura, Germany) were added and suspension was stirred for 90 min at room temperature. The solid clay/MAO was then washed with toluene (3 × 20 mL) and dried under nitrogen. XRD analysis was performed on clay/MAO.

2.3. Preparation of iron catalyst supported on clay

0.6 g of clay/MAO was suspended in 15 mL of iron catalyst solution in toluene (0.05 mmol Fe) and stirring for 12 h. After that, it was observed a colorless supernatant indicating the impregnation of catalyst on clay. The catalyst suspension was directly introduced in the polymerization reaction.

2.4. Ethylene polymerizations

Ethylene polymerizations were carried out in duplicate (error up to 13% in yield) in a reactor Büchi 280 Glassuster BEP with a 1000 mL beaker, coupled with mechanical stirrer (maintained at 650 rpm during polymerization). For the homogeneous catalyst system, the total pressure of ethylene was 2.6 bar and the reaction temperature was varied from 70 to 100 °C for 30 min. In the case of the polymerizations with the supported catalyst, the reactions were performed at 80 °C.

2.5. Characterization

The catalytic complex was characterized by magnetic resonance spectroscopy of hydrogen and carbon (^{1}H and ^{13}C-NMR), energy dispersive X-ray spectroscopy (EDX) and absorption spectroscopy in the infrared (Fourier transform infrared spectroscopy [FTIR]) and near infrared (near-FTIR) regions. The obtained polyethylene was characterized by differential scanning calorimetry (DSC) to determine thermal properties and degree of crystallinity (X_c). Eq. (A) was used: (ΔH_m^a: melting enthalpy of sample and ΔH_m^{100}: melting enthalpy of 100% crystalline polyethylene 293 KJ/mol).

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \times 100 \tag{A}$$

Polymers were also evaluated according to their morphological stability. In a DSC the samples were maintained 15 min above melting temperature and then they were cooled at 10 °C/min to room temperature and heated again at the same rate to obtain T_m and X_c after annealing.

PE was also analyzed in terms of X-ray diffraction pattern to study the crystallinity of the material, and the interplanar spacing of the crystal (d) was calculated using the Bragg's law in Eq. (B), where: n is the order of reflection, λ is the wavelength of the incident X-rays (K_α Cu = 0.15418 nm), and θ is the angle of incidence.

$$d = \frac{n\lambda}{2sin\theta} \tag{B}$$

The catalytic activity was calculated using Eq. (C), where Yield: amount of obtained polymer kg; mol Fe: amount of catalyst in mol; mol E: amount of ethylene in the reaction medium (0.135 M), t: time of polymerization (h).

$$C.A. = \frac{Yield}{(mol\,Fe) \times (mol\,E) \times t} \tag{C}$$

Molecular weight (M_n and M_w) and polydispersity index (PDI) of the polymers were measured by gel permeation chromatography (GPC) at 150 °C using TCB as solvent and 1.0 mL/min flow rate. The analysis was done in duplicate and the average was presented.

3. Results and discussion

3.1. Synthesis of catalyst 2,6-diisopropyl bis(imino)pyridyl iron (II)

The analysis of infrared absorption spectrometry (FTIR) of the synthesized iron catalyst showed the characteristic band of the C=N indicating the formation of the molecule ligand bis (imino) pyridine at 1645 cm^{-1}. The IR spectra of the catalyst show a red shift of υ(C=N) by ca. 50–60 cm^{-1} when compared to the free ligand, which suggests the coordination of the imine nitrogen atoms to the iron atom [17], as Fig. 1.

In magnetic resonance spectrum the chemical shifts observed were: {1H} NMR (δ ppm) (CDCl$_3$): 8.49 (d, 2H, Py-Hm), 7.94 (t, 1H, Py-Hp), 7 12 (m, 6H, Ar-H), 2.78 (sept, 4H, CHMe$_2$), 2.27 (s, 6H, N=C-Me), 1.18 (d, 24H, CHMe$_2$); {13C} NMR (δ ppm) (CDCl$_3$, 1H