



Production of bimodal polyethylene on chromium oxide/metalocene binary catalyst: Evaluation of comonomer effects

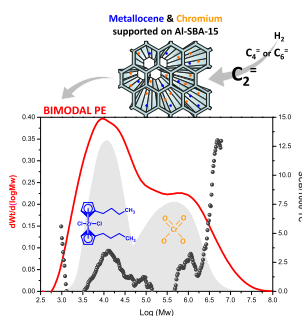
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HIGHLIGHTS

- Ethylene/ α -olefins copolymerizations on chromium-metalocene catalyst are evaluated.
- Chromium contribution increases by using comonomers, leading to wider MWDs.
- Hydrogen can be used for tuning catalytic activity and polyethylene bimodality.
- Comonomer placement across MWD of bimodal polyethylene shows a growing profile.

GRAPHICAL ABSTRACT



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ABSTRACT

A novel option to produce bimodal polyethylene is by using binary catalytic systems, able to generate polyethylene chains with different predominant molecular weights in only one-step polymerization process. In this work, we explore in depth the catalytic behavior of a binary chromium-metalocene catalyst in the co-polymerizations of ethylene with 1-butene or 1-hexene looking for the production of bimodal polyethylene with an adequate comonomer profile across its molecular weight distribution. Likewise, the effect of the hydrogen together with comonomers was also evaluated for controlling polymers properties. Results indicate that the relative contribution of chromium and metalocene sites in the binary catalyst is strongly affected by using comonomers. Specifically, chromium contribution noticeably increases when using 1-hexene or 1-butene due to the positive comonomer effect observed in the individual chromium catalyst. The methodology used for hydrogen supply (continuous or discontinuous addition) plays a key role for tuning catalytic activity and polyethylene bimodality. Finally, comonomer placement across the molecular weight distribution of bimodal polyethylenes shows a growing profile, with a higher SCB concentration in the longest polymer chains than that obtained for a commercial PE100 sample.

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1. Introduction

Bimodal polyolefins came up as a result of the need to meet application requirements, combining the best properties of the low and high molecular weight fractions: processability coming

from the short chains and good mechanical properties coming from the long chains [1]. Nowadays, the bimodal resin most usually employed is the polyethylene classified as PE100 (i.e., pipe must withstand hoop stress of 10 MPa for up to 50 years at 20 °C, ISO 12162) [2]. PE100 provides important advantages over earlier grades because combines the strength and stiffness of high density polyethylene (HDPE) with the high stress crack resistance and processability of unimodal medium density grades [3].

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Bimodal polyethylene can be made by three different ways:

1. Producing the components or fractions separately and then physically melt mixing into a uniform blend. However, these blends usually contain high gel levels, and as a result, miscibility problems can take place [2,4].
2. Using a two stages cascade polymerization process. In the first reactor a low molecular weight ethylene homopolymer is formed (with high hydrogen concentration) and, in the second one, the polymer particles with the still active catalyst polymerize under different conditions (low hydrogen concentration and presence of a comonomer) leading to the high molecular weight fraction [5,6]. This scheme is inherently complex involving higher capital and operation costs than a single reactor technology.
3. Using binary catalytic systems able to produce an in situ blend of polyethylene chains with different predominant molecular weights in only one-step polymerization process. For this single reactor bimodal technology, a greatly advanced catalyst design is required [7–9]. Options are the use of a hybrid catalyst, consisting on two kinds of active sites loaded on the same support, or mixed catalysts, which is a physical mixture of two independent catalysts that are introduced together to the reactor at the beginning of the reaction.

We have previously reported the synthesis of a novel chromium oxide/metallocene binary catalyst for bimodal polyethylene developed by supporting a MAO/metallocene system on a mesostructured chromium catalyst [10,11]. Results indicate that a clear bimodality can be easily obtained in only one-step polymerization process by adjusting catalysts properties and hydrogen concentration during the reaction. However, the effect of the comonomer on this novel binary catalyst has not been yet evaluated. As it is shown in the polymerization literature, comonomer effect is a very interesting subject widely studied for about three decades [12–16]. The short chain branching coming from the incorporation of α -olefins to polyethylene chains leads to lower melting point, crystallinity and density, making resins more flexible and better suited to be processed [17]. Thus, the comonomer content and distribution, which are sensitive towards numerous variables of the polymerization reaction (such as catalyst type and structure, cocatalysts, pressure or temperature), govern the melting behavior of the resin [18,19]. Apart from the commercial interest on copolymers synthesis and properties, the observation of the called “comonomer effect”, consisting in an important change of the ethylene polymerization rate in presence of α -olefins, has been also a subject of great interest for numerous authors [12,14]. This “comonomer effect” differs from one reaction system to another since depends on the catalyst type and α -olefin properties. In this sense, many theories have been reported for Ziegler-Natta, metallocene and Phillips catalysts by using different α -olefins such as linear ones (from C3 to C18), 4-methyl-1-pentene or styrene [12].

The aim of this work is to deeply study the comonomer effect on a binary catalytic system consisting in $(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}$ species supported on a mesostructured Cr-Al-SBA-15 Phillips catalyst. This dual system has proven its capacity for the production of bimodal polyethylene with very promising properties (for instance, for pipe manufacture [10,11]), so that, the comonomer incorporation could provide novel and highly competitive polyethylene resins. Different concentrations of 1-butene and 1-hexene were used in polymerization reactions in order to evaluate their influence on the catalytic activity and polymer properties. Both Cr-Al-SBA-15 and $(n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}/\text{Al-SBA-15}$ catalysts were also tested separately for studying individual and combined comonomer effect. Finally, the effect of the hydrogen together with comonomer was also evaluated for controlling bimodal molecular weight distribution.

2. Experimental section

2.1. Synthesis of catalysts and polymerization reactions

Individual chromium (Cr-Al-SBA-15) and metallocene $((n\text{BuCp})_2\text{ZrCl}_2/\text{MAO}/\text{Al-SBA-15})$ catalysts as well as binary catalytic system were prepared and characterized according to works previously published [10,11,20,21]. Ethylene polymerizations were performed at 70 °C in a 2.0-L stirred stainless-steel reactor filled with of 1.0-L n-heptane (99%, Scharlab) as diluent, and triisobutylaluminum (TIBA, 1 M in hexane, Aldrich) as scavenger. Ethylene (99.99%, Air Liquide) was deoxygenated and dried through columns containing R-3/15 BASF catalyst, alumina and 3 Å molecular sieves. The flow rate needed to keep a constant pressure of 12 bars during the polymerization was measured with a mass-flow indicator (Bronkhorst Hi-Tec). Comonomer amount in the reactor was varied from 0 to 20 ml by adding 1-butene or 1-hexene at the beginning of the polymerization. Volume of 1-butene was measured by introducing it in a calibrated flask at room temperature and 5 bar (in liquid phase). Comonomer was moved from the flask to the reactor by propelling it with nitrogen. Volume of 1-hexene was measured and introduced into the reactor at by using a calibrated syringe. In experiments carried out by using hydrogen as chain transfer agent, two methods were tested for hydrogen addition:

Discontinuous method: hydrogen volume (1 NI) was added at the beginning of the reaction.

Continuous method: hydrogen volume (1 NI) was uniformly fed during the reaction time (60 min) leading to an average molar ratio $\text{H}_2/\text{Ethylene}$ around 0.015 for all the reactions.

After 60 min, the polymerization was stopped by depressurization and polyethylene (PE) was recovered, filtered and dried for 12 h at 70 °C. Polymerization activities (g PE/gCAT·h) were calculated dividing the weight of dry PE produced by the weight of catalyst used in the reaction (50 mg).

2.2. Polymers characterization methods

Polymerization products were characterized by using different analytical techniques in order to determine their main properties: average molecular weight and molecular weight distribution, melting point and crystallinity, melt index, density, comonomer content and comonomer content distribution. In this section we describe briefly characterization setup and conditions.

- Molecular weight distributions (MWDs) of were determined with a Waters ALLIANCE GPCV 2000 gel permeation chromatographer (GPC) located in the Polymer Technology Laboratory (LATEP) of Universidad Rey Juan Carlos. This apparatus is equipped with a refractometer, a viscosimeter and three Styragel HT type columns (HT3, HT4 and HT6) with exclusion limits of 1×10^7 for polystyrene. 1,2,4-trichlorobenzene was used as solvent, at a flow rate of 1 cm³/min. The analyses were performed at 145 °C. The columns were calibrated with narrow molar mass distribution polystyrene and with linear low density polyethylenes standards.
- Polymer melting points (T_m) and crystallinities were determined in a METTLER TOLEDO DSC822 differential scanning calorimeter (DSC), using a heating rate of 10 °C min⁻¹ in the temperature range 23–160 °C. The heating cycle was performed twice, but only the results of the second scan were reported, because the former could be influenced by the mechanical and thermal history of the samples. Crystallinity (α) was

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