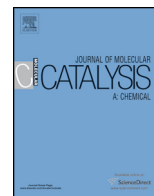




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Combinations of 2,6-bis(imino)pyridine iron with zirconocenes in ethylene polymerization: A cyclic and differential pulse voltammetry study

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ABSTRACT

In the present study, binary systems based on 2,6-bis(imino)pyridine iron and zirconocene complexes were evaluated in the polymerization of ethylene using different catalyst molar ratios and methylaluminoxane as the cocatalyst. The catalyst activity and polydispersity were evaluated, supported by electrochemical data of isolated and binary systems. The results indicated that in binary systems, each complex solely forms an active species. The combination effect was shown to be dependent on the nature of the complexes and on the ratio between them. For an equal molar ratio, a synergistic effect occurs on the catalyst activity. A redox reaction between the complexes was detected, which led to a decrease in the concentration of active species for the other ratios. In addition, it was found that such combined systems can produce polyethylene with a broad polydispersity with bimodal patterns and higher crystallinity than isolated systems.

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1. Introduction

Polyethylenes are widely employed materials in several segments of modern society. Using some active catalyst systems and polymerization processes, these polymers can be produced by catalytic polymerization using coordination compounds with high catalytic activity, which may produce high density polymers. In this system, the growth step occurs from a single active site (metal center) [1,2].

Among such single-site catalyst systems, metallocene compounds are active in this reaction and are already established in a few industrial plants, and they can provide, in addition to the features already mentioned, control over the polymer microstructure [3]. In the coordination sphere around the metal center in zirconocenes there is a bond between the aromatic ring and Zr(IV), an weak bond between carbon (aromatic ring) and zirconium makes such compounds kinetically more active [4]. Other compounds, known as non-metallocene or post-metallocene, have

shown promising results [5]. Among them, the complex of iron(II) coordinated to the ligand 2,6-bis(imino)pyridine (Felpy) is less toxic, more stable under oxidizing and reducing atmospheres and is easier to obtain than metallocene catalysts [6–12]. Paulino and Schuchardt [6,7] reported high catalytic activity for the Felpy complex with Al/Fe molar ratios of 1000 and 2000.

Both compound classes have in common versatility in modulating the stereo-electronic features of the structure through various substituents in the rings and bridges between the rings, which allows the polymerization conditions and the characteristics of the resulting polyethylenes to be adjusted [13,14]. The active species in the polymerization is a cationic complex stabilized by methylaluminoxane (MAO), a compound that acts as the cocatalyst [15].

Among the polyethylene properties of interest, the molar mass and polydispersity can be considered to be the most important because they affect the mechanical properties and the processability of the resin. Monodisperse polymers tend to be very viscous, and thus, a certain degree of dispersion is desirable [16]. Among the strategies adopted for this purpose [16,17], the following can be highlighted: (i) anchoring catalytic systems on solid matrices—leads to the formation of surface active sites with different reactivities, which influences the degree of polymer-

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ization and consequently the chain size; (ii) use of dual-site catalysts—combination of different compounds in a single catalyst system. The challenge is to combine compounds with similar activities but with different preferred chain transfer reactions to produce different chain sizes.

The objective of this study was to evaluate the effect of binary combinations of metallocene and non-metallocene catalysts in the polymerization of ethylene using cyclic voltammetry (CV) and differential pulse voltammetry (DPV).

2. Experimental

2.1. Materials and methods

2.1.1. Reagents

All the chemicals were manipulated in inert atmosphere using Schlenk techniques. MAO (Witco, 10.0 wt.% toluene solution, average molar mass of 900 g mol^{-1}) and the metallocenes [$\text{ZrCl}_2(\text{Cp})_2$, [$\text{ZrCl}_2(i\text{-BuCp})_2$], [$\text{ZrCl}_2(n\text{-BuCp})_2$] and [$\text{ZrCl}_2\text{Me}_2\text{Si}(\text{Ind})_2$] were purchased from Boulder or Aldrich and were purified by recrystallization from stock solutions. Ethylene and argon (White Martins) were passed through a 13 \AA molecular sieve prior to use. Toluene was purified by refluxing with sodium, followed by distillation under nitrogen immediately prior to use. Acetonitrile (MeCN) was refluxed for 6 h followed by distillation, and it was stored over a molecular sieve. Tetrabutylammonium tetrafluoroborate (TBTF), which was obtained from Merck or Fluka, was purified through successive extractions with ethyl acetate at 78°C . The crystals were collected by filtration and were vacuum dried. The reagents 2,6-diacetylpyridine, 2,6-dimethylaniline, formic acid and anhydrous iron chloride were purchased from Aldrich.

2.1.2. Synthesis of Ipy ligand

The 2,6-bis-[1-(2,6-dimethylphenylimino)ethyl]pyridine (Ipy) was prepared as previously described [6,18] with slight modifications. 1.00 g (6.13 mmol) of 2,6-diacetylpyridine was dissolved in deaerated methanol (10 mL), and argon was bubbled through the mixture. After dissolution, it was added under stirring to a solution of 1.8 mL (14.7 mmol) of 2,6-dimethylaniline and 5 drops of formic acid. The mixture was heated to 65°C and maintained at this temperature under stirring and bubbling argon for 4 h. Thereafter, the mixture was stirred for 20 h. The resulting yellow solid was then collected by filtration and washed with cold methanol and vacuum dried. The average yield was 80 %.

2.1.3. Synthesis of Felpy complex

The 2,6-bis-[1-(2,6-dimethylphenylimino) ethyl]pyridinedi-chlorideiron(II) (Felpy) was prepared as described in the literature [6] with slight modifications. 0.05 g (0.354 mmol) of anhydrous iron chloride was dissolved in 10 mL of *n*-butanol, and argon was bubbled through the solution. The mixture was stirred at 40°C , and then 144.5 mg (0.394 mmol) of Ipy was added and continuous

argon bubbling was maintained. After 2 h, the mixture was filtered, and the resulting blue power was collected and washed with cold *n*-butanol. The average yield was 68.8 %.

2.1.4. Polymerization reactions

Polymerizations were performed in toluene (150 mL) in a 300 mL Pyrex glass reactor connected to a constant temperature circulator equipped with a mechanical stirrer and inlets for argon and ethylene. For each experiment, a mass of catalytic system corresponding to $10^{-5} \text{ mol L}^{-1}$ of metal center ($M = \text{Fe}$ or Zr) was suspended in 10 mL of toluene and transferred into the reactor under argon. The polymerizations were performed under atmospheric pressure with ethylene at 60°C for 30 min at a molar ratio of $\text{Al}/M = 1000$, using MAO as the cocatalyst. Ethanol acidified by HCl was used to quench the processes, and the reaction products were separated by filtration, washed with distilled water, and finally dried under reduced pressure at 60°C .

2.2. Characterization

2.2.1. Electrochemical measurements

The DPV and CV measurements were performed using a Parc model 273 potentiostat/galvanostat. All experiments were conducted using a conventional three-electrode cell. Glassy carbon was used as the working electrode. An Ag/AgCl electrode was used as the reference electrode, and a platinum wire was used as the auxiliary electrode. The Ag/AgCl electrode was calibrated with ferrocene, which was used as an internal reference. These measurements versus the ferrocene (Fc^+/Fc^0) redox couple ($+0.50 \text{ V}$ in MeCN solutions) were reported versus an Ag/AgCl electrode. Electrochemical data were obtained using 0.1 mol L^{-1} solutions of TBTF in MeCN as the supporting electrolyte. In the DPV or CV, neither anodic nor cathodic peaks were observed in the absence of zirconocene or Felpy in the investigated potential range. All solutions were deaerated by bubbling high purity argon. The cocatalyst solutions were prepared with different molar ratios of $\text{Al}/M = 2.5, 5, 10$ and 30. DPVs were recorded with a scan rate of 100 mV s^{-1} , and CVs were recorded with a scan rate of 200 mV s^{-1} .

2.2.2. Polydispersity measurements

The molar mass distribution of polyethylene was measured at 150°C using a Waters CV Plus high temperature GPC instrument equipped with a viscosimetric detector and three Styragel HT-type columns (HT3, HT4 and HT6) with an exclusion limit of 10^7 for polystyrene. 1,2,4-Trichlorobenzene was used as the solvent at a flow rate of $1 \text{ cm}^3 \text{ min}^{-1}$. The analysis were performed at 140°C . A universal calibration method with narrow polystyrene standards was used.

2.2.3. Calorimetric measurements

DSC measurements were performed to determine the fusion temperature (T_m), crystallization temperature (T_c) and crystallinity

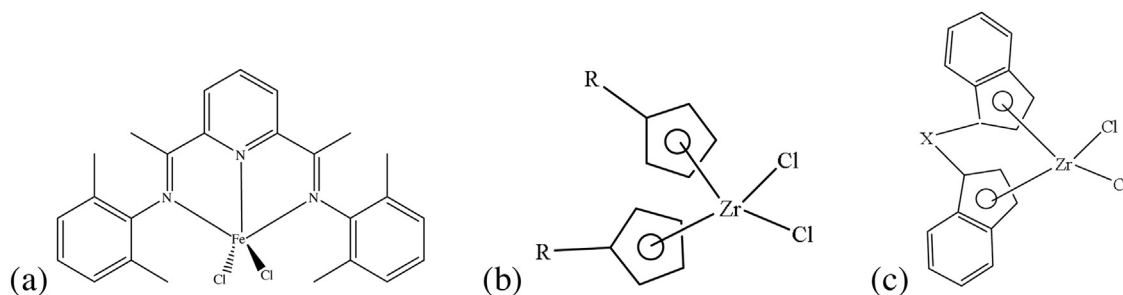


Fig. 1. Molecular structures of complexes: (a) Felpy; (b) and (c) zirconocenes, where “R” can be H, *n*-butyl or *i*-butyl and “X”, the bridge, is dimethylsilane.

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