

Linear low density polyethylene (LLDPE) from ethylene using $\text{Tp}^{\text{Ms}}\text{NiCl}$ (Tp^{Ms} = hydridotris(3-mesitylpyrazol-1-yl)) and Cp_2ZrCl_2 as a tandem catalyst system

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Abstract

Linear low density polyethylene (LLDPE) with different branching contents were prepared from ethylene, without the addition of α -olefin comonomer, using a combination of catalyst precursors $\{\text{Tp}^{\text{Ms}}\}\text{NiCl}$ (**1**) (Tp^{Ms} = hydridotris(3-mesitylpyrazol-1-yl)) and Cp_2ZrCl_2 (**2**) activated with MAO/TMA (1:1) in toluene at 0 °C and by varying the nickel loading mole fraction (x_{Ni}). The polymerization results showed that the turnover frequencies are strongly dependent on the x_{Ni} varying from 6.6×10^3 to 32.1×10^3 mol $[\text{C}_2\text{H}_4]/\text{mol}[\text{Zr}]$ h. The ^{13}C NMR spectra of the copolymers showed that the branch contents of the polymers increase as the x_{Ni} increase in the medium promoting the production of polymers with a wide range of melting point (T_m).

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1. Introduction

The synthesis of linear low density polyethylene (LLDPE) is a matter of both technical and academic interest [1]. Typically, LLDPE is produced when ethylene is copolymerized with an α -olefin such as 1-butene or 1-hexene utilizing conventional heterogeneous Ziegler-Natta and metallocene catalysts [2]. One of the most important limitations of the current processes for LLDPE production is the cost of the α -olefin used as comonomer. However, an alternative method that has recently received attention consists in the use of a binary system where one catalyst produces 1-alkenes in situ and the another one polymerizes ethylene and incorporates the 1-alkene into the growing chain [3]. This process has the main advantage of requiring only ethylene as a monomer. Early studies in this field developed by Komon and Bazan [4] involves the use of homogeneous binary catalyst system comprising $\{[(\eta^5\text{-C}_5\text{Me}_4)\text{SiMe}_2(\eta^1\text{-NCMe}_3)]\text{TiMe}\}\{\text{MeB}(\text{C}_6\text{F}_5)_3\}/[(\text{C}_6\text{H}_5)_2\text{-PC}_6\text{H}_4\text{C}(\text{OB}(\text{C}_6$

$\text{F}_5)_3\text{O-}\kappa^2\text{-P,O}]\text{Ni}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)$. More recently, Marks and co-workers introduced a novel binary catalyst system comprising $[(\eta^5\text{-3-ethylindenyl})\text{Me}_2\text{Si}(\eta^1\text{-NCMe}_3)]\text{ZrMe}_2$ and $[(\eta^5\text{-C}_5\text{Me}_4)\text{Me}_2\text{Si}(\eta^1\text{-NCMe}_3)]\text{TiMe}_2$ activated by a binuclear activator [5].

In the recent years, we have been interested in the development of the homogeneous binary catalyst systems aiming at produce polymeric materials with interesting properties [6]. Our initial studies have revealed that the turnover frequency (TOF) as well as the properties of the polymer are strongly influenced by the polymerization parameters such as metal mole fraction, solvent, cocatalyst, and temperature of polymerization. Herein, we report the combination of $\text{Tp}^{\text{Ms}}\text{NiCl}$ [Tp^{Ms} = $\text{HB}(\text{3-mesityl-pyrazolyl})_3^-$], which is highly selective ethylene oligomerization catalyst [7], with standard metallocene Cp_2ZrCl_2 , that copolymerizes ethylene with an α -olefin, in order to produce linear polyethylene with short chain branches. The branching content on the copolymer varies with the mole fraction of nickel (x_{Ni})¹ in the catalyst mixture.

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¹ x_{Ni} is defined as the nickel mole fraction calculated from $[\text{Ni}]/([\text{Ni}] + [\text{Zr}])$.

2. Experimental

2.1. Materials

$\text{Tp}^{\text{Ms}}\text{NiCl}$ (**1**) was synthesized following procedures described in the literature [7]. Cp_2ZrCl_2 (**2**) was purchased from Aldrich and used as received. Ethylene, provided by White Martins Company, and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (3 Å) prior to use. Methylaluminoxane (MAO) (Witco, 5.21 wt.% Al, in toluene, average molar mass 900 g mol^{-1}) and trimethyl aluminum (TMA) (Aldrich, solution 10 wt.% in hexane) were used as received. Toluene was refluxed and distilled over sodium diphenylketyl complex prior to use.

2.2. Polymerization procedures

All polymerization reactions were performed in a double-walled glass reactor (120 ml) equipped with magnetic stirring, thermocouple temperature control, and a continuous ethylene feed (1.1 atm). Under an argon atmosphere the proper amounts of toluene and MAO/TMA solution were introduced sequentially, and then the system was saturated with ethylene. After complete saturation with ethylene at atmospheric pressure and thermal equilibration of the system, the polymerization reactions were started by adding solutions of **1** and/or **2** to the reactor. The total volume of the reaction mixtures was 60 ml for all polymerizations. The polymerizations are quenched with acetone, filtered and the polymer washed with acidic ethanol, then water and ethanol, and dried in a vacuum oven at 40°C for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of the productivities to $\pm 8\%$.

2.3. Polymer characterization

Melting temperatures were determined by means of differential scanning calorimetry (DSC) with a thermal analysis instruments DSC-2010 using a heating rate of $10^\circ\text{C}/\text{min}$ after twice previous heating to 190°C and cooling to 40°C at $10^\circ\text{C}/\text{min}$. The molecular weight (M_w) was evaluated by gel permeation chromatography (GPC) with the waters 150CV system equipped with three columns Styragel HT3, HT4, and HT6 (10^3 , 10^4 , and 10^6 Å, respectively) and a refractive index detector. Analyses were undertaken using 1,2,4-trichlorobenzene as solvent (with 0.5 g/l of Irganox 10/10 as antioxidant) at 140°C and the M_w were calculated using a universal calibration curve built with polystyrene standards (American Polymer Standard Corporation) and checked with polyethylene and polypropylene known samples. The ethyl and butyl branch content in the LLDPE samples were determined by NMR spectroscopy. The ^{13}C NMR spectra were obtained with a Varian Inova 300 spectrometer operating at 75 MHz and at 90°C , with a 71.7° flip angle, an acquisition time of 1.5 s and delay

of 4.0 s. Samples solutions of the polymer were prepared in *o*-dichlorobenzene and benzene- d_6 (20 vol.%) in a 5 mm NMR tube.

3. Results and discussion

The ethylene polymerization (or oligomerization) reactions were carried out using $\text{Tp}^{\text{Ms}}\text{NiCl}$ (**1**) and Cp_2ZrCl_2 (**2**) (Plate 1) in toluene at 0°C using a mixture of MAO/TMA (1:1) as cocatalyst. Table 1 shows the results of polymerization runs by varying the nickel loading mole fraction (x_{Ni}). Previously studies have demonstrated that **1** shows high selectivity in 1-butene (dimers: 86%; 1-butene: 78%) with turnover frequency of $5.4 \times 10^3 \text{ h}^{-1}$ for ethylene oligomerization reactions performed in toluene at 0°C in the presence of a mixture of MAO/TMA (1:1). Under identical polymerization conditions **2** showed turnover frequency of $7.9 \times 10^3 \text{ mol}[\text{C}_2\text{H}_4]/\text{mol}[\text{Zr}] \text{ h}$, and produced linear high density polyethylene.

In order to produce branched polyethylene, we carried out the polymerization of ethylene using the combination of **1** and **2** under identical polymerization conditions studied for the systems employing the catalysts separately. Table 1 shows the data concerning to the performance of this catalytic system. Polymerization runs carried out varying x_{Ni} showed that the turnover frequencies are strongly dependent on this parameter, varying from 6.6×10^3 to $32.1 \times 10^3 \text{ mol}[\text{C}_2\text{H}_4]/\text{mol}[\text{Zr}] \text{ h}$. Scheme 1 shows a plausible tandem catalytic mechanism using a combination of **1** and **2**. The mechanism is composed by two complementary catalytic cycles characterized by ethylene dimerization, and the copolymerization process. In the first cycle, we assumed that the active species is a neutral $\text{Tp}^{\text{Ms}}\text{NiH}$ complex that promotes the production of 1-butene via β -hydrogen elimination in a similar way described by the nickel oligomerization catalysts [8]. Once the 1-alkene has been generated the copolymerization reaction takes place by insertion of 1-butene into the growing polyethylene chain (P) at the $\text{Cp}_2\text{Zr(P)}^+$ catalytic specie.

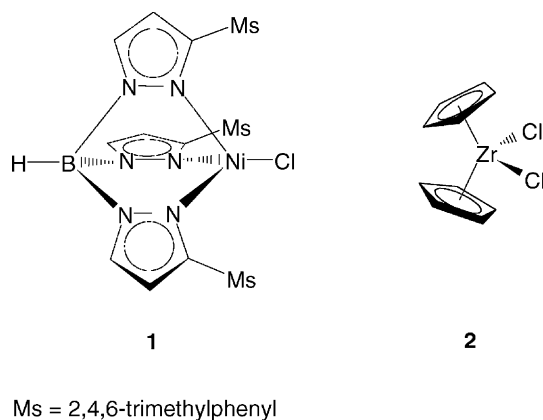


Plate 1.

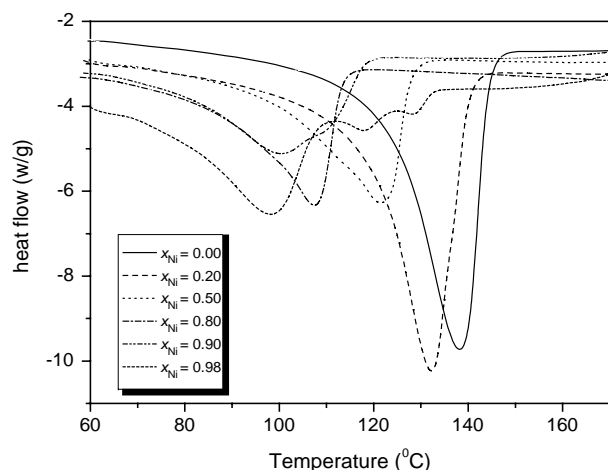


Fig. 1. DSC curves of the polymers varying x_{Ni} . Polymerization reactions performed at 0 °C, $[Al]/[M] = 200$, and using a mixture MAO/TMA (1:1) as activator.

1-butene and 1-hexene incorporation increases as displayed in Fig. 2. It is well-known that due to short chain branches, copolymers have a lower melting point than the ethylene homopolymer [9]. When the amount of short chain branches increases, the melting point decreases due to the decrease of CH_2 crystallizable segments. Crystallization of such a polymer is determined to a major extent, if not completely, by the comonomer distribution along and among the chains.

The ^{13}C NMR spectra of the copolymers (Fig. 3) show the presence of branches due to the 1-butene and 1-hexene incorporation in the polymer chain [4a,10]. In these samples, it was observed one peak at 30.0 ppm, which is characteristic for the linear chain $(CH_2)_n$, and peaks at 11.1, 26.5, 30.5, 33.8, and 39.4 ppm, attributed to the presence of ethyl branches, besides the incidence of much smaller signals corresponding to the butyl branches. The simplicity of polymer structure allows for the percentage of ethyl and butyl

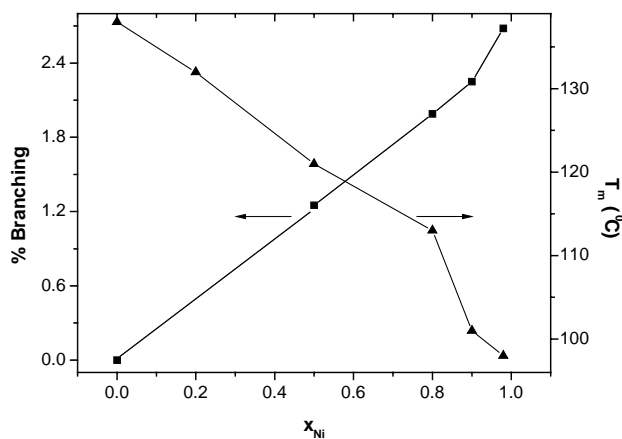


Fig. 2. Melting point and branching content as a function of x_{Ni} of the copolymers. Polymerization reactions performed at 0 °C, $[Al]/[M] = 200$, and using a mixture MAO/TMA (1:1) as activator.

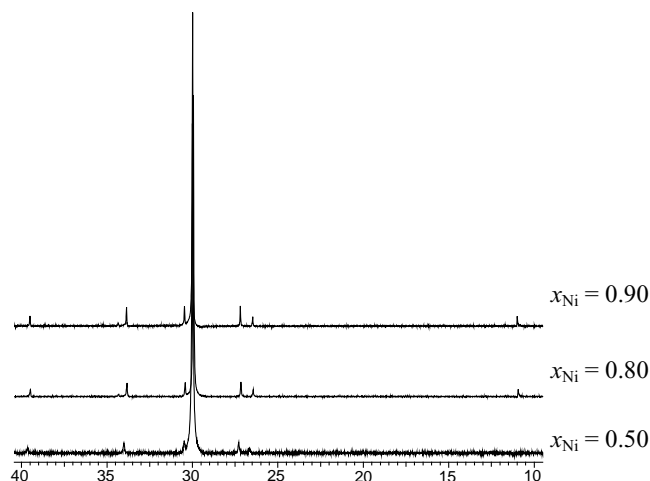


Fig. 3. ^{13}C $\{^1H\}$ NMR spectra of copolymers obtained varying x_{Ni} .

branches in the polymer to be determined and as shown in Fig. 2, the percent of 1-butene/1-hexene in the polymer correlates well against the x_{Ni} . For instance, the number of branches per thousand backbone carbon atoms increases from 12.5 to 26.8 as the nickel mole fraction increases from 0.50 to 0.98.

In summary, we have developed a novel homogeneous binary catalyst system able to produce linear low density polyethylene using only ethylene as feedstock. The turnover frequencies as well as the polymer properties are dependent on x_{Ni} . Higher activities were reached using high nickel mole fraction. The melting points of the copolymers and the branching contents show a linear correlation with respect to x_{Ni} . Further investigations into the reactivity of this catalytic system will be the subject of a future report.

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References

- [1] (a) A.K. Kulshrestha, S. Talapatra, in: C. Vasile (Ed.), Handbook of Polyolefins, Marcel Dekker, New York, 2000, pp. 1–70; (b) D.E. James, in: H.F. Marks, N.M. Bikales, C.G. Overberger, G. Menges (Eds.), Encyclopedia of Polymer Science and Engineering, Wiley-Interscience, vol. 6, New York, 1985, pp. 429–454.
- [2] (a) A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587; (b) O. Olabisi, M. Atiqullah, W. Kaminsky, Rev. Macromol. Chem. Phys. C37 (1997) 519; (c) K. Soga, T. Shiono, Prog. Polym. Sci. 22 (1997) 1503; (d) B.A. Krentsel, Y.V. Kissin, V.I. Kleiner, L.L. Stotskaya, Polymers and Copolymers of Higher α -Olefins, Hanser/Gardner Publications Inc., Cincinnati, 1997, p. 243; (e) R. Quijada, G.B. Galland, R.S. Mauler, Macromol. Chem. Phys. 197 (1996) 3091;

- (f) P. Lehmus, O. Härkki, R. Leino, H.J.G. Luttikhedde, K.H. Näsmän, J.V. Seppälä, *Macromol. Chem. Phys.* 199 (1998) 1965;
- (g) J. Koivumäki, G. Fink, J.V. Seppälä, *Macromolecules* 27 (1994) 6254.
- [3] (a) Z.J.A. Komon, G.C. Bazan, *Macromol. Rapid Commun.* 22 (2001) 467;
- (b) R.F. de Souza, O.L. Casagrande Jr., *Macromol. Rapid Commun.* 22 (2001) 1293;
- (c) O. Sperber, W. Kaminsky, *Macromolecules* 36 (2003) 9014;
- (d) K. Musikabhumma, T.P. Spaniol, J. Okuda, *J. Polym. Sci. Part A: Polym. Chem.* 41 (2003) 528.
- [4] (a) Z.J.A. Komon, X. Bu, G.C. Bazan, *J. Am. Chem. Soc.* 122 (2000) 1830;
- (b) Z.J.A. Komon, X. Bu, G.C. Bazan, *J. Am. Chem. Soc.* 122 (2000) 12379.
- [5] G.P. Abramo, L. Li, T.J. Marks, *J. Am. Chem. Soc.* 124 (2002) 13966.
- [6] (a) F.A. Kunrath, R.F. de Souza, O.L. Casagrande Jr., *Macromol. Rapid. Commun.* 121 (2000) 277;
- (b) F.F. Mota, R.F. de Souza, R.S. Mauler, O.L. Casagrande Jr., *Macromol. Chem Phys.* 202 (2001) 1016;
- (c) F.A. Kunrath, R.S. Mauler, R.F. de Souza, O.L. Casagrande Jr., *Macromol. Chem Phys.* 203 (2002) 2058;
- (d) F.F. Mota, R.F. de Souza, R.S. Mauler, O.L. Casagrande Jr., *Polymer* 44 (2003) 4127.
- [7] F.A. Kunrath, R.F. de Souza, R.S. Mauler, O.L. Casagrande, *Organometallics* 22 (2003) 4739.
- [8] G. W. Parshall, S. D. Ittel, *Homogeneous Catalysis*, second ed., Wiley-Interscience, New York, 1992, p. 68.
- [9] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 143;
- H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1143.
- [10] G.B. Galland, R.F. de Souza, R.S. Mauler, F.F. Nunes, *Macromolecules* 32 (1999) 1620.