

Research Article

Influence of Organoboron Compounds on Ethylene Polymerization Using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ as Catalyst System

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Organoboron compounds of nonionic and ionic nature, tris(pentafluorophenyl)borane, and N,N-dimethylanilinium tetra(pentafluorophenyl)borate were evaluated to act in conjunction with MAO as activators on ethylene polymerization by using the catalyst Cp_2ZrCl_2 . A decrease on the catalytic activity was observed in both cases in relation with a reference polyethylene which was synthesized in absence of any organoboron compound. An increase on the crystallinity degree and molecular weight, as well as an improvement in thermal and dynamic-mechanical properties, was observed in polyethylenes synthesized in presence of tris(pentafluorophenyl)borane. A low density polyethylene with improved thermal stability was obtained when N,N-dimethylanilinium tetra(pentafluorophenyl)borate was employed as activator.

1. Introduction

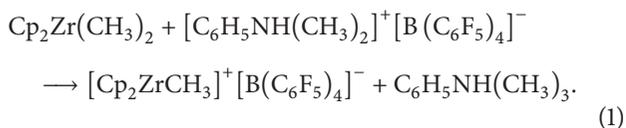
Due to the increasing current demand of polyethylene (PE), since the last decades some strategies have been developed in order to reduce the production costs and the quantity of impurities in the final products, as well as improve the final properties of the obtained polymers. One of these strategies has been the use of organoboron compounds as activators of metallocene catalysts [1–3], since these compounds have proved to have the capacity of producing highly active catalysts systems for ethylene polymerization and in low molar ratios Boron compound (B)/Zirconium catalyst (Zr) (between 0.1–5) in comparison with alkyl-aluminums which commonly require fixed molar ratios alkyl-aluminum/Zr between 1,000 and 15,000 [4–7]. Nonetheless, one disadvantage of these compounds as cocatalysts is their noncapacity of alkylating halide metallocene catalysts such as Cp_2ZrCl_2 , therefore for using these compounds on these kinds of systems, a necessity of being combined with an

alkyl-aluminum such as MAO is required where, besides of alkylating the Zr catalyst, acts as scavenger during the polymerization; however in the literature there is very few information reported about the influence wielded on the final properties of the materials by using a mixture of organoboron compound and MAO, and specifically depending on the ionic nature of the organoboron compound.

As it was previously exposed, organoboron compounds can be classified according to their ionic nature in nonionic or ionic compounds [8–10], where nonionic are constituted by an only species (mainly tris(pentafluorophenyl)borane) [11, 12] which abstracts one of the methyl groups of the catalyst leading to the formation of two ionic species, an “activated” cationic metallocene ($[\text{Cp}_2\text{ZrCH}_3]^+$), which proceed to be coordinated by an ethylene molecule, beginning the polymerization, and an anionic boron compound of general formula $[\text{CH}_3\text{B}(\text{C}_6\text{F}_5)_3]^-$. Nonetheless, even though these kinds of compounds have been referred as “an ideal boron-based Lewis acid” because of their acid strength and stability,

it has been suggested that the catalyst reactivity is mildly decreased by a persistent interaction between the previously abstracted methyl group and the transition metal atom.

On the other hand, ionic compounds are constituted in an ion-pair configuration, where the cationic species (commonly anilinium or carbonium) takes the function of activating the alkylated active sites, while the anionic species (tetra(pentafluorophenyl)borate) prevent the interaction between the abstracted methyl and the Zr center (1), therefore the catalytic activity is better. Consider



This work is focused on the use of one of each kind of organoboron compound, according to their ionic nature, as activators of the halide catalyst Cp_2ZrCl_2 by employing a reduced amount of MAO to act as alkylating agent and scavenger, besides activating in a synergistic way with the organoboron compound at a fixed molar relation of MAO/B = 20, MAO/Zr = 100. Furthermore another material in which no boron compound was employed was synthesized as reference material. A complete characterization of the synthesized PE was carried out in order to elucidate the influence of the B on the ethylene polymerization and the final properties of the obtained polymers.

2. Materials and Methods

2.1. Reactants and Manipulations. All manipulations were carried out under inert atmosphere using a dual vacuum-argon line and standard Schlenk techniques or in a glove box. Toluene was twice distilled from sodium and benzophenone under argon atmosphere before use. Bis(cyclopentadienyl)zirconium (IV) dichloride (Cp_2ZrCl_2 , 98%) and methylaluminoxane (MAO, 10 wt-% in toluene) were purchased from Aldrich and were used as received. Tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$, 95%) and N,N-dimethylanilinium tetra(pentafluorophenyl)borate ($[\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{H}]^+ [\text{B}(\text{C}_6\text{F}_5)_4]^-$, 98%) were supplied by Strem Chemicals and they were used as received as well. Polymer-grade ethylene was purchased from Praxair and it was purified by passing it through 3-4 Å activated molecular sieves.

2.2. Ethylene Polymerization. All polymerizations were performed in a 1L stainless steel Parr reactor through the following procedure: several vacuum-argon cycles at 80°C were carried out in order to purify the reactor. Then it was cooled to room temperature and filled with 150 mL of distilled toluene under argon atmosphere. The reactor stirring system was set at 100 rpm and it was heated to 50°C. The catalyst system was fed into the reactor as follows: (i) solution comprising MAO + B, prepared in toluene at 5 wt-% by stirring during two hours under inert atmosphere; (ii) catalyst solution at 3.7 wt-% in toluene prepared under inert atmosphere. The molar ratios MAO/Zr and B/Zr were 100 and 5, respectively. The polymerization started by adding

the monomer at a continuous flow. All experiments were performed at an ethylene pressure of 1 bar during 1 hour.

The polymerization reaction was terminated by the closure of the ethylene feeding and finally by adding an acidified (10% of hydrochloric acid) methanol solution. The obtained polymer was filtered off, washed with methanol, and vacuum-dried.

2.3. Characterization. Density was measured as described in the ASTM D4052-11 standard test method for density. Molecular weight distributions (MWD) were determined by size exclusion chromatography (SEC) using an Alliance chromatograph (GPC V-2000) equipped with two on-line detectors: a differential viscometer and a differential refractometer. The calibration was executed under polystyrene standards using 1,2,4-trichlorobenzene as eluent; measurements were performed at a flow rate of 1 mL/min at 140°C. Differential scanning calorimeter (DSC) thermograms were obtained by means of a TA instrument DSC 2920 at a heating rate of 10°C/min under inert atmosphere. Each sample was heated twice in order to eliminate the thermal history. Thermogravimetric analyses (TGA) were performed using a TA-Q500 apparatus, in which the samples were heated to 10°C/min under nitrogen atmosphere and at a flow rate of 50 mL/min. Thermograms were recorded from 30 to 600°C. Wide-angle X-ray diffraction (WAXD) measurements were carried out in a Siemens D5000 diffractometer with a Ni-filtered $\text{CuK}\alpha$ radiation generator (wave length of 1.5406 Å). Patterns were recorded from 5 to 35° (in 2θ) with 5 sec per step. Transmission electron microscopy (TEM) analyses were performed on a TITAN 80–300 kV. Samples were prepared employing a cryogenic ultramicrotome Leica Ultracut at –125°C and a cut rate of 2 mm/min. The sample slices were stained using ruthenium tetroxide (RuO_4) steam to contrast amorphous and crystalline phases. Dynamic mechanical analyses (DMA) were measured in a TA Instrument, in flexural mode at a frequency of 0.1 Hz, and a temperature range from –103 to 103°C. During the measurement, the heating rate was 5°C/min and the amplitude was 0.5 mm. The sample test specimens were prepared in a LMM Laboratory Mixing Molder from Dynisco Instruments at 180°C and 60 rpm.

3. Results and Discussion

The effect of B on the final product properties was determined by evaluating two different compounds, one of each kind of ionic nature, and using as reference material a synthesized PE in which only MAO was used as activator at a fixed molar ratio of MAO/Zr = 100 and B/Zr = 5. Table 1 shows the catalytic activity, density, and molecular weight (Mw) of the synthesized PE.

3.1. Catalytic Activity. It is noticeable how the addition of B either of ionic or nonionic nature significantly decreased the catalytic activity, in the way that by incorporating tris(pentafluorophenyl)borane (B1) into the reaction system (PE-2) the catalytic activity diminished in 42.36% and in 72.79% by adding N,N-dimethylanilinium

TABLE I: Catalytic activity, density, and molecular weight results.

Sample	Organoboron compound (B)	Nature	Catalytic activity (Kg _{PE} /mol _{Zr})	Density (g/cm ³)	Mw (Kg/mol)	PDI
PE-1	None (reference)	—	123.25	0.970	83.95	2.7
PE-2	B(C ₆ F ₅) ₃ (B1)	Nonionic	67.34	0.974	116.18	4.3
PE-3	[C ₆ H ₅ N(CH ₃) ₂ H] ⁺ [B(C ₆ F ₅) ₄] ⁻ (B2)	Ionic	33.31	0.925	207.76	5.2

Zr = 0.1283 mmol, molar ratio MAO/Zr = 100, B/Zr = 5, toluene = 1.41 mol, polymerization temperature = 50°C, and pressure = 1 bar.

tetra(pentafluorophenyl)borate (B2) (PE-3); this behavior is attributed to reactions that could have taken place during the aging time between MAO and B giving BR₃ and AlR_{3-x}(C₆F₅)_x which subsequently would react with the catalyst species leading to unstable species of the kind Cp₂ZrMe(μ-Me)Al(C₆F₅)₃ which rapidly decomposes to Cp₂ZrMe(C₆F₅), as it has been previously reported in the literature [12, 13].

3.2. Molecular Weight Distribution. It is well known that the molecular weight (Mw) and MWD depend fundamentally on chain transfer reactions which are responsible of deactivating the catalyst active sites, predominating the chain transfer reaction to aluminum, as well as β-elimination and transference to monomer. The influence wielded by the employed B on the Mw and polydispersity index (PDI) is presented in Table 1.

As it can be appreciated that the Mw increased by adding both of B; from 83.95 Kg/mol (PE-1) to 116.18 Kg/mol in the case of B1 (PE-2), and to 207.76 Kg/mol in the case of B2 (PE-3); however, this behavior was expected because of the reduced concentration of active sites which lead to the formation of less polymer chains but of higher Mw.

As it can be observed in Figure 1, a multimodal behavior was exhibited by all PE samples which suggest the presence of more than one family of active centers during the polymerization [14], supporting the assumption that the different kinetic behavior of the existing catalyst sites controls the polymerization kinetics. For this reason, in order to get an approximate notion of this behavior, the obtained MWD were deconvoluted using informatics software. However, it is important to note that while the information acquired is useful, there is no guarantee that is exactly the number of families of active sites. Nevertheless, this technique is interesting to understand how the different families of active sites are carrying out the polymerization with or without B in the reaction medium.

It can be appreciated that MWD of PE-1 (in which only MAO was used as activator) presents two families of active centers, one of them is associated with MAO and another one is related to the presence of trimethylaluminum (TMA), which is the reagent utilized in the synthesis of MAO, and which remains present in about 30% of the total content of MAO solution [15, 16]. Supported by the deconvoluted graphs, it is suggested that TMA can act as activator of

the catalyst; nonetheless, it acts in a lesser extent than MAO.

By adding both of B into the polymerization system, the presence of a third family of active centers was observed (see Figures 3(b) and 3(c)) attributed to the active centers which were activated by B; however they were presented in a lesser extent (10.97 and 6.78%, for PE-2 and PE-3, resp.).

3.3. Density. The density of a material reflects its branching degree, malleability, and hardness; therefore it is determinant in the type of application in which can be submitted. Table 1 shows the influence wielded on the density of materials by adding B into the catalyst system.

Taking into account the density values presented in Table 1, it can be appreciated that in the synthesized PE in which B1 was added into the reaction system (PE-2), as well as the reference polymer (PE-1), values of 0.974 and 0.970 were obtained, respectively; thus, the materials correspond to high density polyethylenes as expected by using this kind of catalysts; however, by employing B2 a density value of 0.925 was obtained which indicates that a low density polyethylene was produced.

3.4. Crystallinity Degree. The crystallinity degree of a PE sample can be determined by a variety of methods, each of which measures a different property that is then related to the level of crystallinity via a particular set of assumptions. Ideally, more than one method of determination should be used. In this work the determination of crystallinity was measured according to density, heat fusion, and X-ray scattering. Determination of crystallinity degree from density rests on two simple assumptions: (i) PE samples consist in a two-phase morphology and (ii) the density of each phase is uniform within the sample and consistent from one sample to another. According to this, the crystallinity degree of a sample can be readily determined by its density, if densities of the crystalline and disordered regions are known, just as (2) shows:

$$X_D = \frac{1/\rho - 1/\rho\alpha}{1/\rho c - 1/\rho\alpha} \times 100, \quad (2)$$

where ρ is the material density, $\rho\alpha$ is the density of a PE completely amorphous (0.853 g/cm³), and ρc is the density of a PE completely crystalline (1.0 g/cm³) [17].

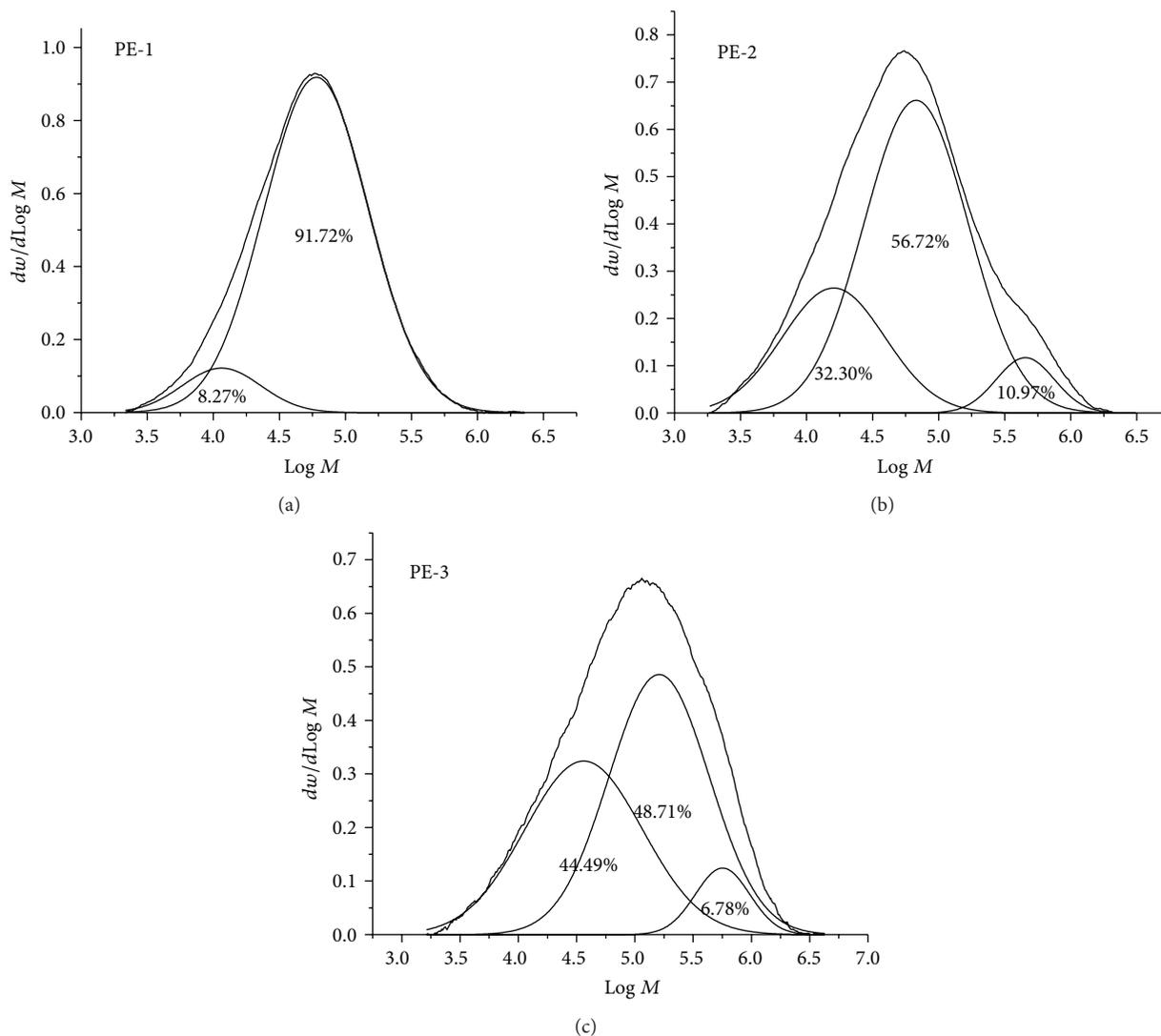


FIGURE 1: Deconvoluted MWD of, PE-1, PE-2, and PE-3.

On the other hand for determining the crystallinity degree according to the heat fusion it was calculated by means of the ratio between the melting enthalpy (the area between the measured curve and the baseline in the region of the peak) and the melting enthalpy of a completely crystalline PE (69 cal/g) [17].

Moreover, measurement of crystallinity degree by means of X-ray diffraction is based in the fact that X-ray scattering occurs from both the crystalline and the noncrystalline material illuminated with X-rays, being the difference between the two types of scattering the ordering of the material; thus by deconvoluting the amorphous from crystalline scattering it is possible to determine the ratio of intensity from the crystalline peaks (at an angular orientation (2θ) of 21.5° and 24.0°) corresponding to the crystallographic planes of $\{110\}$ and $\{200\}$, respectively, in the orthorhombic structure [18, 19] to the sum of the crystalline and amorphous intensities (3) and in this way to obtain a reliable value of crystallinity degree

of the material. The deconvoluted spectra of synthesized PE are presented in Figure 2. Consider

$$X_D = \frac{I_{\text{crystalline}}}{I_{\text{crystalline}} + I_{\text{amorphous}}} * 100. \quad (3)$$

The crystallinity of the obtained PE is shown in Table 2. It is appreciated that the results obtained by each technique differ from each other; however the obtained value by density is the most accurate according to the reported in literature [20]. By adding B1 into the reaction system, the crystallinity increased in 2.08% (taking as reference the value obtained by density) in comparison with PE-1, while by incorporating the B2 (PE-3), the crystallinity degree decreased in 29.73%. This behavior is suggested to be induced by the presence of chain branches as well a higher Mw that inhibit the movement of the polymer chains preventing their ordering, thus causing a disordered lamellar structure arrangement of these materials

TABLE 2: Crystallinity degree.

Sample	Organoboron compound	Crystallinity degree		
		By density (%)	By DSC (%)	By X-ray (%)
PE-1	None (reference)	82.62	69.95	68.11
PE-2	B1	84.70	71.02	68.72
PE-3	B2	52.89	58.49	51.49

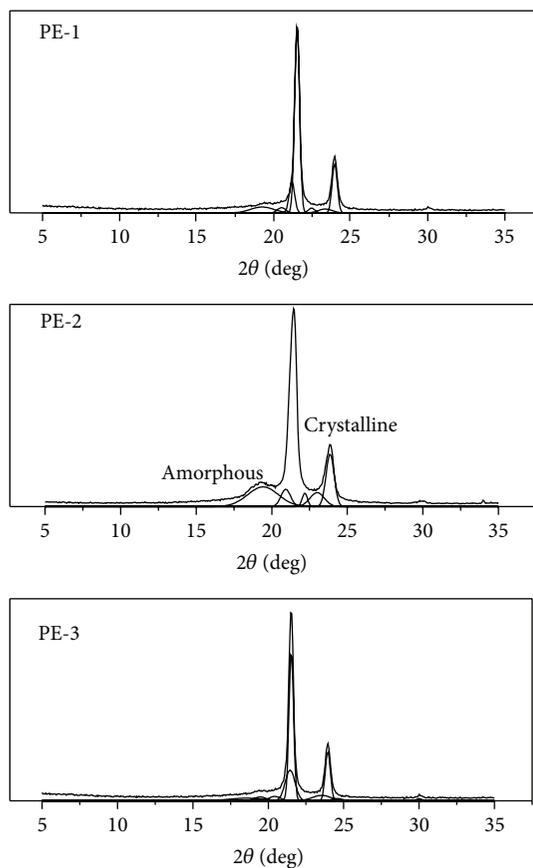


FIGURE 2: Deconvoluted diffractograms of the synthesized PEs.

and a lower crystallinity degree. Nevertheless, in order to corroborate these lamellar arrangements, TEM analyses were carried out (Figures 3), where it can be observed that the lamellar structure of the reference polymer (PE-1), as well as PE-2 (using B1), is mostly ordered; while by using B2 the lamellar structure is more dispersed.

3.5. Thermal Analyses. DSC thermograms of the synthesized PE are shown in Figure 4. An increase in the melt temperature was noticed by the addition of B1 and B2, which is attributed to the increment in Mw that led to an increase of the tension between the lamellas and therefore a higher thermal energy was required to melt the crystalline structure of materials.

Through TGA analysis (Figure 5), the influence wielded by the B on the thermal stability was determined. It can

TABLE 3: TGA results.

Sample	Organoboron compound	Temperature of 5% weight loss (°C)	Temperature of 10% weight loss (°C)
PE-1	None (reference)	341.04	389.75
PE-2	B1	393.19	420.71
PE-3	B2	380.94	419.90

be noticed that in all the cases a slightly weight loss was presented at low temperatures (<275°C), which can be attributed to an oligomeric degradation. Later, a more significant weight loss was exhibited corresponding to the breakdown of polymer chains bonds, either in the main polymer chains or in branches. However, by employing B, the temperature decomposition range was shifted to highest temperatures (from 300 to 400°C, approximately), thus in order to have a better appreciation of this improvement in the thermal stability, Table 3 shows the temperatures in which the 5 and 10% of weight loss were presented. It can be noticed a significant difference between the reference material (PE-1) and the PE in which B1 was added; for instance, PE-1 lost 10% of weight at 389.75°C, while at a very similar temperature the PE synthesized with B1 only presented a 5% loss weight, as well as PE-3 which presented a similar behavior. In other words, the addition of B improves the thermal stability of PE, due to the higher molecular weight obtained in their polymer chains.

3.6. Dynamic-Mechanical Analysis. DMA analyses were only performed to PE-1 and PE-2, since these materials presented significant differences on their catalytic activity, morphology, and thermal stability. Storage and loss modulus as a function of the temperature is presented, respectively, in Figure 6. Two main transitions corresponding to different movements in the molecular structure were detected. One of these transitions, which took place at around -100°C (γ transition) is originated by the rotational motion of 4 to 6 methylene groups at the polymer chains in the amorphous phase of PE, in addition to the reorientation of chain ends within the crystalline and amorphous phases [21]. The another identified transition (α transition) was presented at temperatures near 50°C and corresponds to a premelting transition that is originated by the movement of the chains inside the crystals.

It can be appreciated that by adding B1 the material presented higher values of storage modulus as well as of both

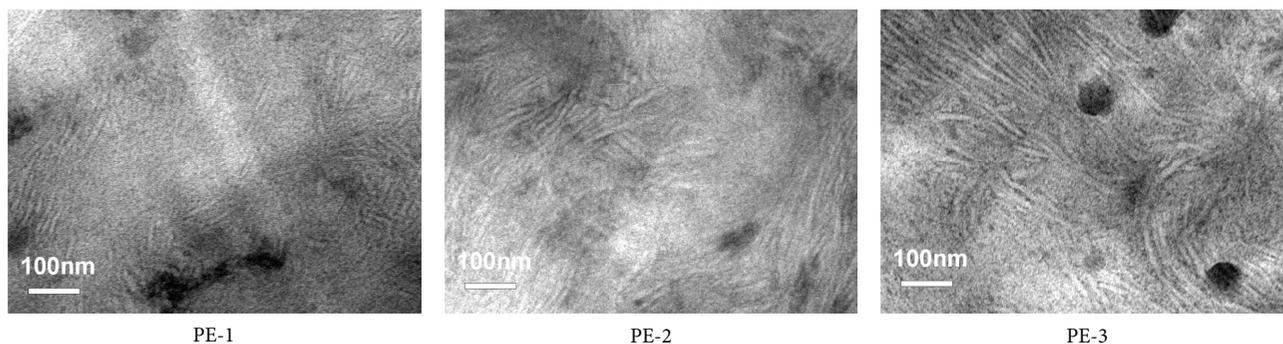


FIGURE 3: TEM images of, PE-1, PE-2, and PE-3.

TABLE 4: DMA results.

Sample	Organoboron compound	Storage modulus (MPa)		Loss modulus (MPa)		Transition temperature (°C)	
		γ transition	α transition	γ transition	α transition	γ transition	α transition
PE-1	None (Reference)	4523	2019	292	200	-110.63	42.72
PE-2	B1	7059	2919	424	225	-107.67	47.97

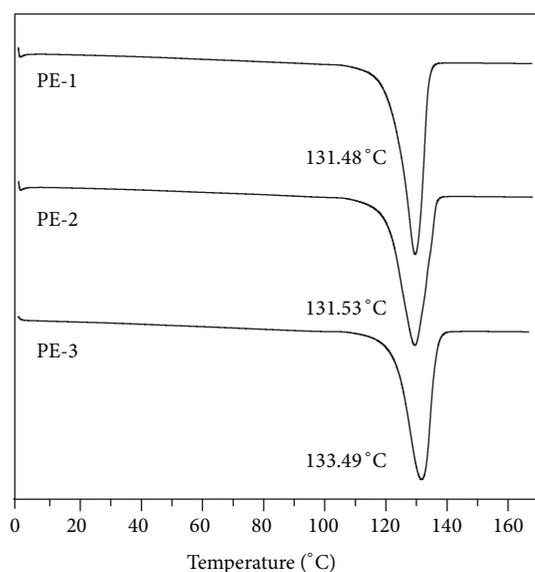


FIGURE 4: DSC thermograms of, PE-1, PE-2, and PE-3.

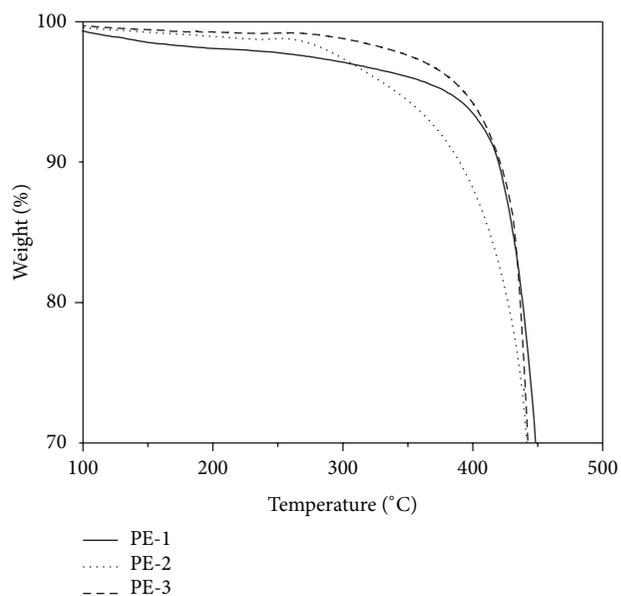


FIGURE 5: TGA Thermograms of PE-1, PE-2, and PE-3.

γ and α transitions, which is shown in Table 4, in a wide range of temperatures, which can be attributed to the increase in Mw of the polymer chains.

Finally, it is important to mention that polymers that present relevant loss transitions at temperatures below -50°C tend to exhibit good impact strength. This is because the molecular motion is directly associated with the toughness. For this reason, knowing that the γ transition in PE-2 is higher than in PE-1, it can be predicted that by adding B1 the mechanic performance improves.

4. Conclusions

The addition of organoboron compounds of ionic and non-ionic nature on the ethylene polymerization using $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$ as catalyst system promoted a partial deactivation of the catalyst, causing a reduction on the catalytic activity; however the properties of the obtained polyethylenes were mostly improved. Tris(pentafluorophenyl)borane allowed the synthesis of a material with higher molecular weight and better thermal properties than the corresponding polyethylene obtained in absence of this organoboron

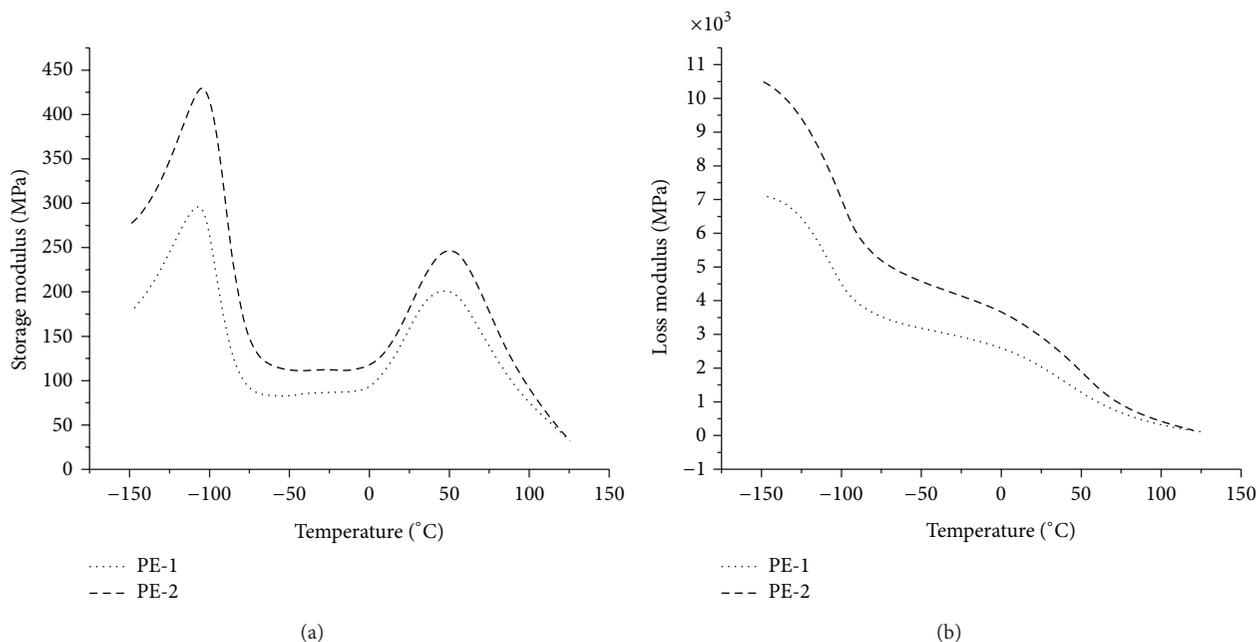


FIGURE 6: Storage and loss modulus as a function of temperature for PE-1 and PE-2.

compound; however the crystallinity degree was not considerably affected. On the other hand, N,N-dimethylanilinium tetra(pentafluorophenyl)borate of ionic nature considerably decreased the catalytic activity in comparison with the reference polyethylene; nonetheless the thermal stability was improved. This organoboron compound produced a low density polyethylene in contrast to the nonionic organoboron compound that produced a high density polyethylene.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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