 DOI: 10.1002/masy.201300166

Performance of a Bis(imine)Pyridine Iron Catalyst System in Ethylene/Norbornene Copolymerization with Zinc Diethyl

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Summary: Brookhart catalysts are widely used in ethylene polymerization to produce polymers with high molecular weight and crystallinity degree. In the present work, the performance of a bis(imine)pyridine iron catalyst and methylaluminoxane (MAO) as a catalytic system was evaluated for ethylene/norbornene copolymerization and the influence of adding zinc diethyl (DEZ) in the reaction medium was investigated. The results showed that the system was effective in copolymerization besides the low incorporation of norbornene in polymer chain, as indicated by multimodal profiles in DSC and high crystalline degree.

Keywords: ethylene/norbornene copolymer; iron catalyst; zinc diethyl

Introduction

Polymers based on cyclic olefin copolymers (COC) are very attractive materials due to their high heat and chemical resistance and transparency. The chain microstructure of these polymers consists of rings with high tension, which are synthesized by addition of cyclic olefins in polymerization reactions, exhibiting unique properties comparatively different from those based on acyclic olefins. The materials are generally insoluble and have high melting temperatures ($T_m > 400\,^{\circ}C$). The glass transition temperature (T_g) and decomposition temperature have close values. However, polycyclic-olefins are difficult to process, in this way lowering the commercial interest in these materials.[1]

To improve the processing of the polycyclic-olefins, the introduction of α-olefins in the polymer chain by coordination polymerization has been reported as an efficient method, whereas the introduction of a comonomer can decrease the material's stiffness.[1,2] Therefore, copolymers of ethylene/norbornene (E/NB) have attracted much attention due to their exceptional properties, such as high transparency, excellent optical properties and high refractive index.[3]

These properties can be controlled by varying the comonomer content in the copolymer composition, as well as the monomer sequence distribution and norbornene (NB) stereoregularity in the copolymer chain. In turn, these parameters are directly dependent on the catalyst structure, since the ligand can facilitate or hinder the norbornene insertion in the growing chain.[4,5] Furthermore, in the industrial field, ethylene-norbornene copolymers are considered the newest promising thermoplastics.[6]

The new complex of titanium (IV) $[(OC(Ph)HC(Ph)O)TiCl(\mu\text{-}OCH(Ph)C(Ph)\text{-}(n\text{-}Bu)O)]_2$ activated by methylaluminoxane (MAO) was found to be effective in the synthesis of random ethylene/norbornene copolymers with high molecular weight and able to incorporate the comonomer in the range from 17 to 52%. ^{13}C-NMR analyses showed that the copolymers contain alternating units of norbornene and isolated dyad and triad sequences.[4] Many authors have concluded there is a direct relationship between the amount of NB

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incorporated in the polymer chain and the glass transition temperature. Ethylene/norbornene copolymers were also polymerized using constrained geometry catalysts (GCG) and Al_iBu_3 or $Ph_3CB(C_6F_5)_4$ as cocatalysts. The catalytic activity was strongly influenced by the reaction temperature, i.e., at 30 °C the lowest activity reported was 3.66 kg/mol.h and at 70 °C the highest activity was 8.90 Kg/mol.h.[6] Besides this, the same influence of polymerization temperature has been observed in other works in the literature dealing with ethylene-norbornene polymerization, like using a half-metallocene Ti complex cocatalyzed by modified methylaluminoxane (MMAO),[7] or using the catalytic system bis(α-alkoxyimine)titanium/MAO,[8] as well as for systems using metallocenes with C_2 or C_s symmetry.[9]

Studies investigating the influence of catalyst ligands in the E/NB copolymer microstructure showed that the catalytic system $_i$Pr[($_3$-*i*Pr-Cp)Ind] $ZrCl_2$/MAO generated copolymers whose chains contained sequences of norbornene with the maximum length equal to two norbornene units, but a slight increase in the number of NB units in sequence was achieved by the replacement of the *i*Pr group in the catalyst structure.[10]

The behavior of E/NB copolymerizations using the metallocene catalysts rac-Et[Ind]$_2ZrCl_2$ (Cat. A) and Cp_2ZrCl_2 (Cat. B) with MAO as cocatalyst was previously investigated.[11] The concentration of comonomer was varied in the polymerizations to assess the characteristics of the catalytic system. The results showed that Cat. A was more active than Cat. B, independently of the amount of norbornene used in the polymerization. However, for both systems the catalytic activity was higher at lower comonomer concentration.

Some articles[12,13] report the effect of comonomer on the reaction kinetics, finding the same behavior, which is related to the ease of diffusion of the comonomer. When the diffusion rate is greater than the rate of polymerization, this facilitates the insertion of the comonomer in the growing chain. This is called the comonomer effect.

Homoleptic allyl complexes of divalent metals such as $Cr(CH_2SiMe_3)_4$/MAO were found to be highly active for ethylene/norbornene copolymerizations and to yield copolymers with high molecular weight. For this system, the catalyst activity increased sharply with the increase in norbornene concentration. The copolymers showed block structure, and norbornene was incorporated at least as dinorbornene units, even at incorporation levels as low as 10 mol%. At higher norbornene concentrations, NNN sequences prevailed.[14]

Stereoregular, alternating ethylene/norbornene copolymers were synthesized with high comonomer conversion and high catalyst activity using the C_1-symmetric mono cyclopentadienyl complex. This high-performance polyolefin has high melt temperatures and excellent clarity, making it a potential candidate for engineering applications.[15]

Recent research into diethyl zinc compounds has shown that these compounds act as chain transfer agents. The alkyl-metal compound is stable to decomposition under the polymerization conditions and the polymer chain is eventually transferred back to a central propagating transition metal. Thus, the polymerization becomes similar to living polymerizations, with some of their advantages, and is called immortal polymerization.[16] In coordination polymerization, the addition of a metal alkyl compound, for example zinc diethyl (DEZ), under certain reaction conditions can cause the polymer chain to end. What happens is rapid and reversible exchange of the dormant chain connected to Zn with the growing chain attached to the active center. The polymer chain that was dormant now is connected to the metal of the active center and starts to propagate, yielding a polymer with a narrow molecular weight distribution.[17]

Moreover, the great advantage in relation to living polymerization is that the number of polymer molecules with narrow molar mass distribution is greater than the number of molecules of the initiator, so the activity of the immortal polymerization system is much stronger than that of living polymerization

systems.[18–23] Another article reported the use of bis(imino)pyridine iron catalyst activated by MAO and the addition of zinc diethyl as reversible chain transfer agent, showing that the polymers produced had narrow molecular weight distribution.[17]

In polymerization of ethylene using the catalyst bis(imino)pyridine iron activated with MAO, Britovsek and coworkers[24] reported that the addition of the $ZnEt_2$ compound promoted a decrease of polydispersity, although it is characteristic of the catalyst used to produce polyethylene with broad molar mass distribution. Moreover, $ZnEt_2$ tended to increase polymer molar mass and all Zn-ethyl bonds were converted into Zn-polyethylene, a result characteristic of immortal polymerization.

In the present work, ethylene/norbornene copolymer was synthesized by bis(imine) pyridine based catalyst and the use of zinc diethyl as chain transfer agent was evaluated. The influence of this compound on the parameters catalytic activity, thermal properties and norbornene chain incorporation was observed, and also the results were compared with those of ethylene homopolymerization under the same reaction conditions.

Experimental Part

All substances sensitive to moisture and oxygen were handled under an inert atmosphere of nitrogen using the Schlenk technique. The catalyst 2,6-diisopropyl bis(imine)pyridine iron (II) was synthesized according to the literature[25] and it was evaluated in ethylene homopolymerization and also ethylene/norbornene copolymerization with the addition of diethyl zinc (DEZ) at different concentrations.

Synthesis of Iron Catalyst

The ligand was synthesized by reacting 1 equivalent of 2,6-diacetylpyridine with 2 equivalents of 2,6-diisopropylaniline in ethanol and allowing the mixture to reflux for 40 hours. 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 yield was 1.5 g of catalyst.

Homo and Copolymerizations

Ethylene polymerization and ethylene/norbornene copolymerizations were carried out in duplicate (error of 13% in yield) in a Büchi 280 Glassuster BEP reactor with a 1000-mL beaker, coupled to a mechanical stirrer (maintained at 650 rpm during polymerization time). The total pressure of ethylene was 2.6 bar (ethylene concentration of 0.135 M) and the reaction temperature was 80 °C. Norbornene was distilled under metallic sodium and it was dissolved in toluene to a certain concentration. For each copolymerization the same amount (7.5 mmol) of norbornene was used.

Characterization

The catalytic complex was characterized by hydrogen and carbon nuclear magnetic resonance spectroscopy (^{1}H- and ^{13}C-NMR) and mid (FTIR) absorption spectroscopy. The polyethylene (PE) and copolymers (CENB) obtained were characterized by differential scanning calorimetry (DSC) to determine thermal properties and degree of crystallinity (X_c). Equation (A) was used: (ΔH_m^a: melting enthalpy of sample and ΔH_m^{100}: melting enthalpy of 100% crystalline polyethylene 293 KJ/mol).[26]

$$X_C = \frac{\Delta Hma}{\Delta Hm100} \times 100 \quad \text{(A)}$$

PE and CENB were also analyzed in terms of X-ray diffraction patterns to study the crystallinity of the material and crystallinity degree, using Equation (B), where: A_c: crystalline peak area and A_a: amorphous halo area.[27]

$$X_C = \frac{A_a}{A_a + A_c} \times 100 \quad \text{(B)}$$

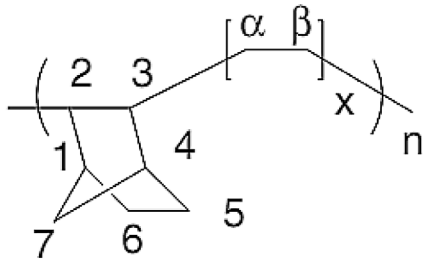
The catalytic activity was calculated using Equation (C), where Yield: Amount of obtained polymer in kg; mol Fe: amount of catalyst in mol; [E]: molar concentration of ethylene in the reaction medium (0.135 M),

and t: polymerization time (hour).

$$A.C = \frac{\text{Yield}}{mol\,Fe.[E].h} \quad \text{(C)}$$

The norbornene incorporation in the polymer chain was calculated by integrating the signals from the carbon nuclear magnetic resonance (^{13}C-NMR) using Equation (D) where: IC_7 (33 to 36.7 ppm), IC_4-C_1 (37–44 ppm), IC_2-C_3 (44.5 to 56 ppm), and IE (29.9 ppm).[9] The signals are marked in the structure below.

$$\%NB = \frac{100(\text{IC2,3} + \text{IC1,4})}{2(\text{IC5,6} + \text{IE})} \quad \text{(D)}$$



P(E–co–N)

Polydispersity of the copolymers was measured by gel permeation chromatography (GPC) at 150 °C using TCB as solvent and 1.0 mL/min flow rate.

Results and Discussion

Synthesis of 2,6-Diisopropyl Bis(Imine) Pyridine Iron (II)

Infrared absorption spectrometry (FTIR) analysis of the synthesized iron catalyst (structure in Figure 1) showed the characteristic band of the C=N group at 1645 cm^{-1}, indicating the formation of the bis(imino)pyridine ligand.

The synthesized diimine ($iPr_2Ph)_2$PDI has a complex structure with three aromatic rings, two C=N bonds and four isopropyl groups, producing a spectrum with several vibrations of the carbonic backbone.[28]

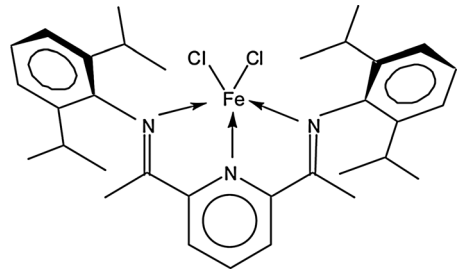


Figure 1.
Catalyst structure of the iron catalyst synthesized.

In relation to the free ligand, the iron complex presents few changes in the vibration spectrum in the medium IR frequency range, except for the appearance of the band at 1578 cm^{-1}, corresponding to a red shift of ν(C=N) by *ca.* 60–70 cm^{-1}, which suggests the coordination of the imine nitrogen to the iron atoms,[29] as shown in Figure 2.

In the proton nuclear magnetic resonance spectrum, the chemical shifts observed were: H^1-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, C H Me_2), 2.27 (s, 6H, N=C-Me), 1.18 (d, 24H, CH Me_2); ^{13}C-NMR (δ ppm) ($CDCl_3$, ^{1}H decoupled): 166.80 (N=C), 155.15 (Co-Py), 146.47 (Ar, Cip), 136.75 (Ar-Co), 135.70 (Ar-Cp), 123.51 (Cp-Py), 122.93 (Cm-Py), 122.10 (Ar-Cm), 28.26 (N=C-Me), 23.15 (C H Me_2), 17.01 (CH Me_2), as presented in Figure 3.

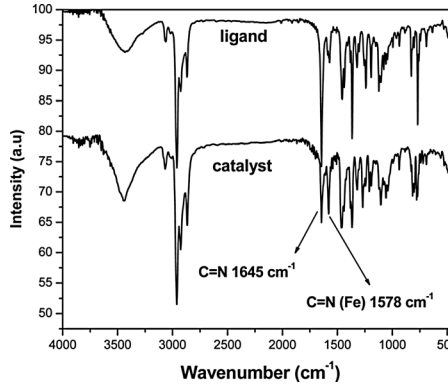


Figure 2.
FTIR spectra of ligand and catalyst based on bis(imine) pyridine.

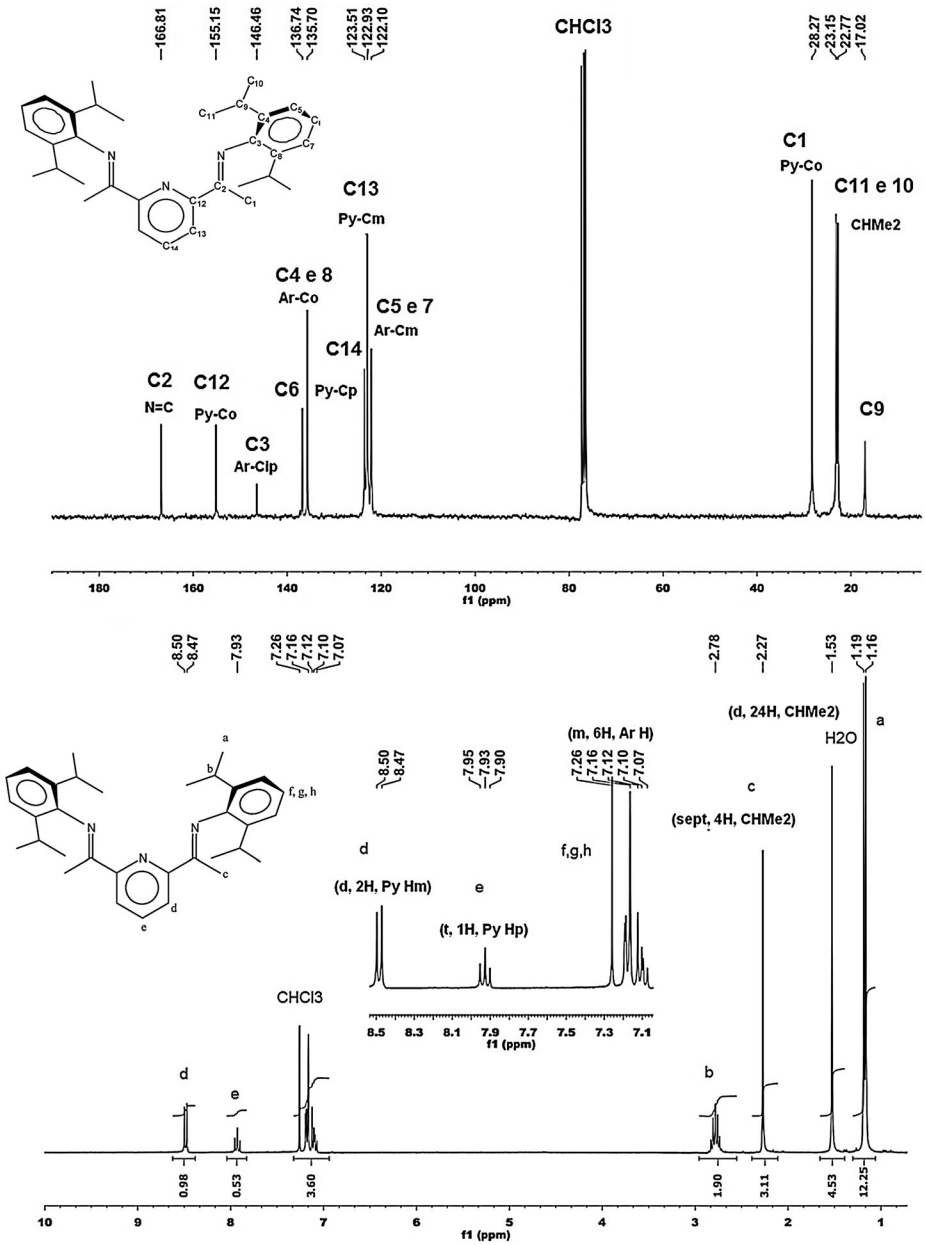


Figure 3.
^{1}H- and ^{13}C-NMR spectra of the ligand bis(imine)pyridine.

Synthesis of Polyethylene and Polyethylene/Norbornene Copolymer

Catalytic Activity

All the homo and copolymerizations were performed in duplicate and the homopolymers (PE) and copolymers (CENB) were synthesized in the same general reaction conditions. In all copolymerizations, the norbornene amount was fixed in the reaction medium at 7.5 mmol in 100 mL of toluene. On the other hand, the

concentration of diethyl zinc (DEZ) varied from 0.05 to 2.00×10^{-3} M in the polymerization. According to Table 1, it can be observed that the introduction of DEZ at lower concentration (0.05×10^{-3} M) increased the catalytic activity for ethylene homopolymerization, but the increase of DEZ concentration promoted a decrease in catalytic activity. This behavior has been observed by other authors in the literature,[17,24] although no explanation has been offered for the fact. Probably there is competition between zinc and iron metals, and the iron complex is the active center of the catalyst, where the polymer chain grows. Paulino and Schuchardt[27] synthesized iron catalyst with *para*-bromoaryl substituent, varying the reaction conditions for ethylene polymerization. Our work presented similar catalytic activities as reported by those authors.

In the copolymerizations, the compound DEZ did not show a strong influence on catalytic activity, as can be observed for all reactions, which presented approximately the same polymer yield. On the other hand, many authors have reported the comonomer effect, making monomer diffusion easier, probably due to crystallinity reduction of the growing polymer when a small amount of comonomer is added, boosting polymer yield.[12,13] However, in the present work this effect was not found. According to Taniike and coworkers,[13] for the comonomer effect to occur it is necessary for the comonomer to have high reactivity towards the catalyst employed, and it should also have small size. Since norbornene is a bulky comonomer and its reactivity ratio is much lower than that of ethylene, the explanation suggests that norbornene did not promote the comonomer effect in the copolymerization.

Catalytic activity decreased when compared with ethylene homopolymerization in the same reaction conditions (sample PE 5). Only for the copolymerization at reaction temperature 30 °C (sample CENB 4.0) the catalytic activity was high. According to Souane *et al.*, [28] the catalytic activity for Brookhart systems is higher for polymerizations at temperatures up to 30 °C and decreases at higher temperatures.

Polydispersity Measurements

Figure 4 shows that the profile of GPC curve is monomodal for the copolymer synthesized in the presence of DEZ (CENB 3.0) in comparison with that of the copolymer obtained without the transfer agent (CENB 1.0) under the same reaction conditions, although M_w decreased. This

Table 1.
Comparison between homopolymerization and copolymerization of ethylene-norbornene.

Sample	Al/Fe	T (°C)	[DEZ] 10^3 M	Yield (g)	CA*	X_c[a] (%)	X_c[b] (%)	T_m (°C)	T_c (°C)	NB (%)
PE 4	200	80	0	6.0	16.5	70	73	119/127	108	0
PE 5	200	80	0.05	10.3	30.5	71	67	122/127	114	0
PE 6	200	80	1.25	7.6	22.6	83	68	133	118	0
PE 7	200	80	2.0	6.1	18.1	80	67	135	118	0
PNB 1.0*	200	30	0	0.01	–	–	–	–	–	0
CENB 1.2	200	80	0	5.0	14.8	64	86	111/119/122	111	1.60
CENB 2.0	50	80	0	–	–	–	–	–	–	–
CENB 3.1	200	80	0.05	5.1	15.1	41	75	106/117	108	1.12
CENB 4.0	200	30	1.25	17.5	50.1	62	81	130	117	0.70
CENB 4.1	200	80	1.25	5.0	14.8	51	79	104/115	107	1.03
CENB 5.0	200	80	2.00	5.0	14.8	49	78	109/118/122	110	0.83

Polymerization conditions: P ethylene = 2.6 bar; Solvent: 100 mL toluene, cocatalyst MAO: t = 30 minutes, T: reaction temperature, *CA: Catalytic activity: Kg/mol Fe.[E].h; nd: not determined, X_c[a]: degree of crystallinity obtained by DSC, X_c[b]: degree of crystallinity obtained by XRD, T_m: melting temperature, T_c: crystallization temperature, PNB 1.0*: 24 hours of reaction, without the addition of ethylene in the reaction medium; NB concentration in the reaction = 7.5 mmol, NB: norbornene incorporation in polymer chain determined by ^{13}C-NMR.

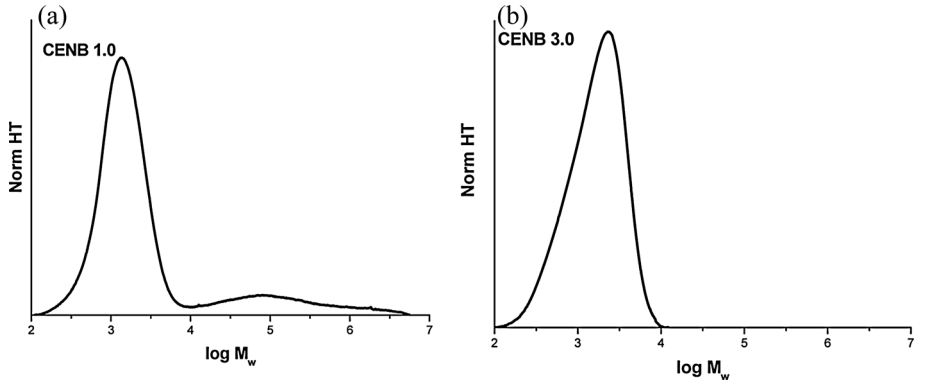


Figure 4.
GPC curves of ethylene/norbornene copolymers. (a) CENB 1.0 ($M_w = 38.5 \times 10^3$; PDI = 23.0) and (b) CENB 3.0 ($M_w = 2.4 \times 10^3$; PDI = 1.6).

is in accordance with what was expected, since the DEZ compound promoted a reversible chain transfer.

Crystalline Structure

In the X-ray diffractograms in Figure 5, the peaks at 2θ of 21° and 23° can be observed. They were assigned to the (110) and (200) crystallographic planes of the orthorhombic unit cell of polyethylene.[29] The crystallinity degree (% X_c) did not significantly change in all PE obtained with different amounts of DEZ. However, for the copolymers the X_c value decreased slightly although it was higher than that of the polyethylenes. This fact can be attributed to the presence of norbornene in the copolymer chain. Since norbornene is a cyclic olefin, it conferred more stiffness to the polymer chain, in spite of the low amounts of norbornene incorporation, as determined by ^{13}C-NMR (Table 1). In Figure 5, the diffractograms of the polyethylene profile and the intensity decreased whereas the broad amorphous halo increased with increasing DEZ amount in the polymerization. It is also apparent that the reflections broaden, suggesting a decrease in the crystallite size of the polymer. These observations are consistent with the presence of two crystalline structures.[30]

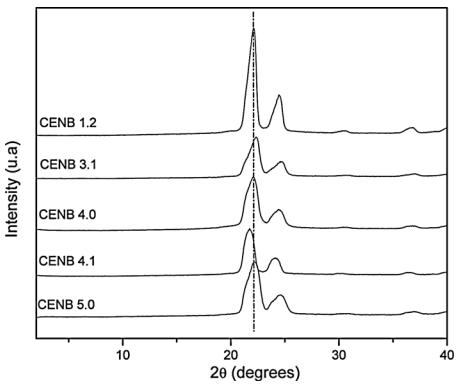


Figure 5.
X-ray diffractograms of the synthesized copolymers.

Thermal Properties

The DSC thermograms (Figure 6) show that all copolymers had more than one crystalline melting temperature (T_m), with shoulders featuring crystals of different shapes and sizes. Besides this, the profile of the copolymers synthesized at 80 °C is quite different than that obtained at 30 °C (sample CENB 4.0). The copolymer synthesized at 30 °C shows a characteristic profile of polyethylene, with well-defined peaks and high crystalline melting temperature.

Therefore, both conditions of high reaction temperatures combined with the presence of DEZ promoted the synthesis of polymers with a broadening of the

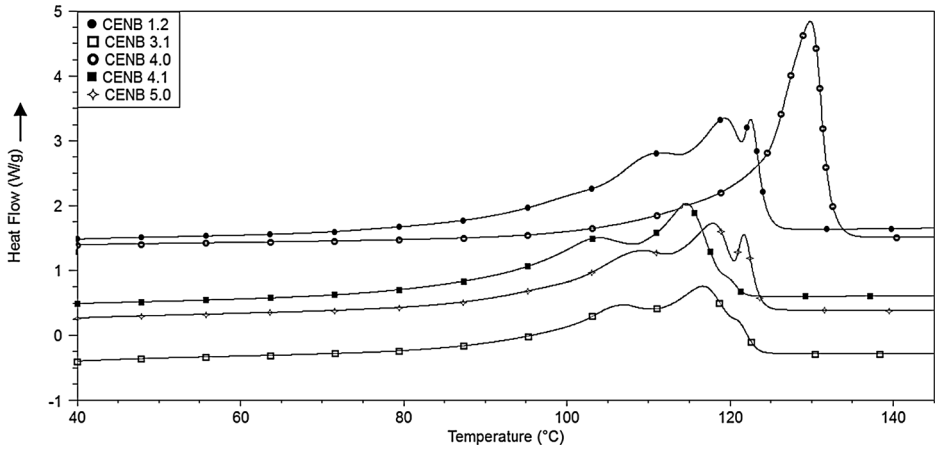


Figure 6.
DSC thermograms of ethylene/norbornene copolymers.

endotherm peak, which can be observed in DSC thermograms with multimodal profiles.[29] This fact may be an indication that a reversible alkyl transfer occurred.

The thermogram profiles of the copolymer and homopolymer (Figure 7) are quite different. Although the incorporation of norbornene in the polymer chain was around 1%, according to the NMR calculations (Figure 8), it is clear that the comonomer influenced the microstructure of the material when compared with the results of homo- and copolymerization.

Conclusion

The iron catalyst was effective for ethylene/norbornene copolymerization in the presence of DEZ. The DEZ did not influence the catalytic activity, but the addition of this compound decreased the norbornene incorporation in the polymer chain, probably because the bulky of comonomer hindered the insertion at the catalyst's activity site. Besides this, the crystallinity degree decreased slightly, which agrees with the low incorporation of NB.

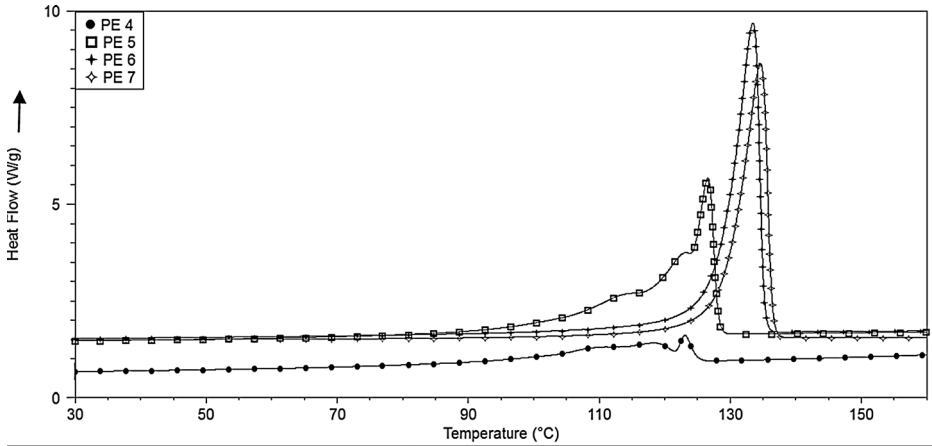


Figure 7.
DSC thermograms of the obtained polyethylenes.

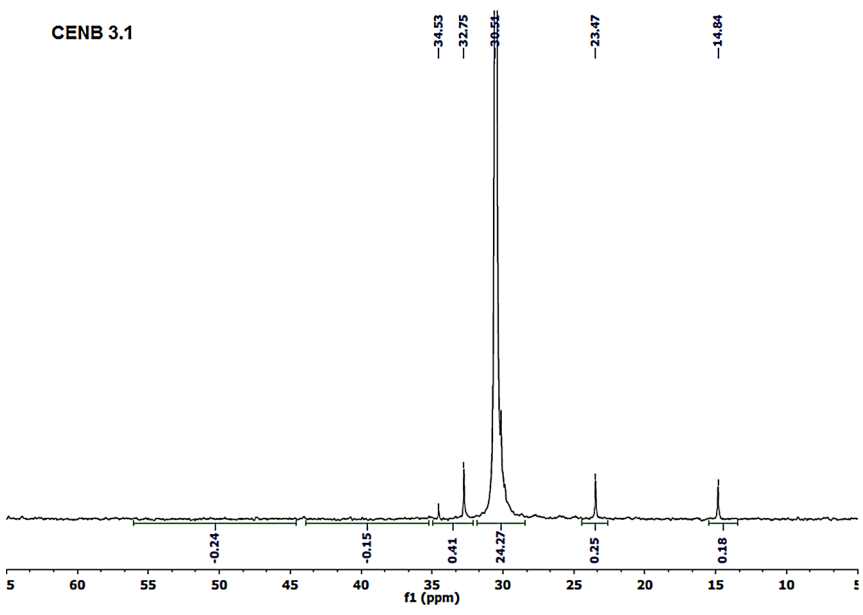


Figure 8.
^{13}C-NMR spectrum of E/NB copolymer, sample CENB 3.1.

We also observed that the thermogram profiles of the copolymers are multimodal, suggesting that the DEZ changed the crystalline structure of PE, promoting the formation of crystals with different shapes and sizes. Moreover, despite the low norbornene incorporation in the polymer chain, it influenced the material's microstructure.

Acknowledgements: This work was financially supported by CNPq and CAPES (Brazil).

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