

Influence of diethyl zinc on ethylene-norbornene copolymerization

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ABSTRACT

E thylene-norbornene copolymers were synthesized with a homogeneous catalyst system based on bis(imino) pyridine iron with the addition of diethyl zinc (DEZ) as alkyd transfer agent to promote immortal copolymerization. The addition of DEZ did not influence the catalytic activity in copolymerization with 7.5 mmol of norbornene (NB), but in the reactions with 70 mmol, the comonomer promoted an increase of activity. We observed by thermal analysis that the norbornene inserted in the chains promoted an increase in thermal stability of the synthesized material with higher amounts of comonomer, since the temperature of initial degradation was much higher for these copolymers compared to polyethylene. In addition, for the copolymers with 7.5 mmol of norbornene, the DEZ served as alkyd transfer agent, as shown by the gel permeation chromatography analysis, leading to a decrease in both molar mass and polydispersity. The UV-Vis spectra showed that the diethyl zinc did not change the catalytically active center, but only acted as an alkyd transfer agent. **Polyolefins J (2018) 5: 71-84**

Keywords: Homogeneous catalyst; bis(imino)pyridine iron complex; ethylene-norbornene copolymerization; alkyd transfer agent.

INTRODUCTION

Norbornene (bicyclo[2.2.1.]hept-2-ene) can be polymerized by three different mechanisms. Each route produces polymers with different microstructure and properties [1, 2]. Ring-opening metathesis polymerization (ROMP) is often used for norbornene polymerization, having been widely studied in recent years, as indicated by the large number of publications. Despite this fact, its application still faces many challenges [2-4]. The ROMP technique generates an unsaturated polymer backbone, increasing solubility in a variety of organic solvents [4], and employs catalysts of tungsten, molybdenum and rhenium complexes. The cationic and the radical norbornene polymerization result in a low molar mass oligomeric material [1]. Vinyl-addition polymerization promotes only the opening the double bond of the π -component, leading to a polymer with a saturated backbone and a bicyclic structure [1, 4].

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In recent years there has been great interest in cyclic olefin copolymers (COCs) due to their favorable properties, such as thermal stability and high moisture barriers, which enables their application as engineering materials to make products like lenses, vials, monitors, medical devices and microelectronic or microfluidic components. Thus, ethylene-norbornene copolymers (P(E-co-NB)) are the cyclic olefin copolymers that have attracted the greatest interest, since vinyladdition polymerization is the most efficient synthesis method in a single-step catalytic reaction [5, 6].

These materials are amorphous and the glass transition temperature (T_g) can reach levels higher than 200 °C, depending on the content of norbornene incorporated in the polymer chain. The T_g of copolymers increases with increasing norbornene content [7]. Besides that, the other mentioned properties can be precisely controlled, not only by the norbornene incorporation but also by the sequence distribution and stereoregularity of norbornene units in the copolymer backbone. All these factors depend on the structure of the catalyst employed as the ligand structure and the metal center [8, 9].

When homogeneous single-site Ziegler-Natta catalyst was discovered, this enabled control over the polymer microstructure and the design of polymers with new architectures [10]. Therefore, the microstructure of ethylene-norbornene copolymers can be tailored by different metallocene catalysts, such as zirconium [11-15] and titanium complexes [16-19] as well as by constrained geometry catalysts (CGC) [10, 15, 20].

Another method to copolymerize ethylene with α -olefin is the so-called living addition polymerization. The "living" catalyst site allows the consecutive enchainment of monomer units without termination. Thus, it is possible to promote high-yield polymers with blocks of one monomer and blocks of monomer-comonomer [16, 21]. Besides that, living polymerization produces polymers with perfectly controlled molecular weight (MW), composition, architecture, and also syntheses of monodisperse and terminally functionalized polymers [16, 22]. These materials can exhibit unique properties not achievable with random copolymers [23]. Most of these systems are titanium-based catalysts with fluorenyl [9], bis(phenoxy-phosphine) [16], bis(pyrrolideimine) [22], fluorinated enolate-imine [23] or salicylaldiminate [24] ligands, as well as alkylidene molybdenum or tungsten complexes [21, 25].

There are two kinds of chain transfer reactions, β -H elimination and chain transfer to aluminum. The former prevails in olefin polymerization with metallocene/ methylaluminoxane (MAO) catalyst. Only a few publications have appeared about the occurrence of chain transfer to aluminum in a predominant step, since this type of chain transfer is described as a minor chain termination process using this kind of catalyst system [26]. Assuming that chain transfer to aluminum consists of a single transfer mechanism, and the exchange of the growing polymer chains between the metal catalyst and the aluminum center is very fast and reversible, the polymer chains seems to grow on the aluminum centers [27]. The dormant chain might become bound to the metal active site in the next moment and then begins to propagate, resulting in a polymer with a narrow molecular weight distribution [28]. An attractive manifestation of this type of chaingrowth reaction is a Poisson distribution of the main alkyl group products, as opposed to the Schulz-Flory distribution of olefinic products that arises when β-H transfer accompanies propagation [27].

Recent research has shown the possibility of using diethyl zinc (DEZ) as reversible chain transfer agent. The alkyl-metal compound is stable to decomposition under the polymerization conditions. What happens is the rapid and reversible exchange between the dormant chains bonded to the metal zinc with the growing chain linked to the active center [28]. In other words, there is no chain transfer reaction and the active center is still "alive", like in living polymerization. This mechanism is called immortal polymerization [29]. The great advantage of living polymerization is that the number of polymer molecules with narrow molar mass distribution is much greater than the number of initiator molecules, thus the activity of the catalyst using immortal polymerization is much greater than that using the living polymerization systems [30, 31, 33-35]. In the literature there are few papers dealing with iron catalyst and diethyl zinc. Britovsek et al. [27] reported the first highly active chain growth process on zinc, catalyzed by bis(imino)pyridine iron complex in ethylene polymerization to regenerate DEZ, where a polymer with narrow distribution (MWD = 1.1) was obtained. The same researchers in another study [36] showed the use of other alkyl metal compounds with the same iron catalytic system. The results indicated that in the system composed of catalyst/MAO/tributyl

gallium (ratio 2/200/4000 μ mol) with ethylene polymerization at room temperature and using 520 GaBu₃ equivalents the polydispersion (M_w/M_n) was 1.2 and the molar mass (M_w) was 500. With 500 GaBu₃ equivalents, the M_w/M_n was 12.7 and M_w was 150,000. On the other hand, without the alkyl metal compound, polydispersion was 19.1 and M_w was 199,000. In turn, with 500 Et₂Zn equivalents of instead of GaBu₃, M_w/ M_n was 1.1 and M_w was 800 employing a Cat/MAO/ Et₂Zn ratio of 2/200/3500 µmol.

In the present work, our goal was to investigate a novel copolymerization system comprised of ethylene and norbornene monomers catalyzed by bis(imine) piridine iron, cocatalyzed by MAO, with diethyl zinc as chain transfer agent. In the literature, this catalyst system has never been used for ethylene-norbornene copolymerization in the presence of DEZ.

EXPERIMENTAL

General experimental details

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 [37] and was evaluated in ethylenenorbornene copolymerization with the addition of diethyl zinc at different concentrations.

Copolymerization

Ethylene-norbornene copolymerization reactions 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 was 0.135 M) and the reaction temperature was 80°C. Norbornene was distilled under metallic sodium and was dissolved in toluene to a certain concentration. Two different amounts of norbornene were used in the reactions: 7.5 mmol and 70 mmol.

Characterization

The catalytic complex was characterized by hydrogen and carbon nuclear magnetic resonance spectroscopies (¹H and ¹³C-NMR), energy dispersive X-ray spectroscopy (EDX), and mid-infrared (FTIR) absorption spectroscopy. The obtained copolymers (CENBs) were characterized by differential scanning calorimetry (DSC) to determine thermal properties and degree of crystallinity (X_c). Equation (1) was used: (ΔH_m^a : melting enthalpy of sample and ΔH_m^{100} : melting enthalpy of 100% crystalline polyethylene = 293 KJ/mol).

$$X_c = \frac{\Delta H_m^a}{\Delta H_m^{100}} \times 100 \tag{1}$$

CENBs were also analyzed in terms of X-ray diffraction patterns to study the material's degree crystallinity, using Equation (2), where: A_c : crystalline peak area and A_a : amorphous halo.

$$\%X_c = \frac{A_c}{A_a + A_c} \times 100 \tag{2}$$

The catalytic activity was calculated using Equation (3), 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); t: time of polymerization (hours).

$$Activity = \frac{yield}{mol_{Fe} \cdot [E]t}$$
(3)

The norbornene incorporation in the polymer chain was calculated by integrating the signals from the carbon nuclear magnetic resonance (13 C-NMR) using Equation (4), where: IC₇ (33- 36.7 ppm), IC₄-C₁ (37- 44 ppm), IC₂-C₃ (44.5-56 ppm), IE (29.9 ppm).

$$\% NB = \frac{1/3[2IC_7 + IC_1 - C_4 + IC_2 - C_3]}{IE} \times 100$$
(4)

Molar masses (M_n and M_w) and polydispersion index (PDI) of the copolymers were measured by gel permeation chromatography (GPC) at 150°C using 1,2,4-trichloro-benzene (TCB) as solvent and at a 1.0 mL/min flow rate. The analysis was performed in duplicate and the average was calculated.

RESULTS AND DISCUSSION

Catalytic activity

The copolymerization was performed in duplicate. Polymers were synthesized under the same general reaction conditions, varying both the DEZ concentration $(0.05 \times 10^{-3} - 2.00 \times 10^{-3} \text{ M})$ and the NB content (7.5 mmol and 70 mmol). Table 1 shows the results of homopolymerization of NB, E-NB copolymerization and the polymers' properties. Although the catalytic activity for NB homopolymerization was extremely low, for the copolymerization without DEZ it was high. The synthesis of PNB was carried out at room temperature for 24 h. The concentration of the catalyst was the same as that in the other copolymerizations (amount of Fe = 0.05 mmol), as well as the other conditions, without addition of DEZ.

Moreover, it could be observed that DEZ did not influence the catalytic activity in E-NB copolymerizations (CENB 1.0–CENB 5.0) employing the comonomer content of 7.5 mmol, once all runs presented the same catalytic activity and CENB 1.0 was produced in the absence of DEZ. For the sample CENB 4.0, obtained at polymerization temperature of 30 °C, the yield was three times higher than that in the other copolymerizations conducted at 80 °C. This fact was expected for this iron catalytic system, since according to the literature [38], the catalytic activity increases at low polymerization temperatures, reaches a maximum at around 30°C and decreases at higher polymerization temperatures.

In the reactions (CENB 6.0 - CENB 11.0) with 70 mmol of NB, the increase of DEZ concentration promoted an increase in catalytic activity. This is the

opposite of what was observed in a previous work using the same catalyst system and DEZ in ethylene homopolymerizations [39]. Comparing the reactions using 7.5 mmol of NB and those using 70 mmol of NB, it could be observed that the copolymerization with lower norbornene amount produced a higher yield. According to Kaivalchatchawal and coworkers [40], the catalytic activity rises with the increase of comonomer feed concentration due of the improvement of monomer diffusion to the catalyst center on account of the reduced crystallinity of the polymer structure when introducing a small amount of comonomer.

Moreover, another factor can be that the inserted comonomer promoted the separation between the cationically active species and anionic cocatalyst, providing more space for monomer insertion, which improved the polymer yield. However, in this work we did not observe this effect. Probably the inserted norbornene hampers the diffusion and the coordination of the comonomer with the active center.

However, this fact depends on the catalytic system employed. According to Vanegas and coworkers [41], the increase of NB content in reaction medium promoted the decrease of catalytic activity, as we observed. The addition of bicyclic comonomer promoted an intense stereo impediment, which greatly reduced the subsequent insertion speed of the monomer and/or comonomer, and consequently led to lower activity of the catalysts. The literature [42-

Sample	NB (mmol)	DEZ mmol	Yield (g)	a*	X _c ^(a) (%)	X _c ^(b) (%)	T _m (°C)	т _. (°С)	NB ^(c) (%)
PE 4	-	-	6.10	18.0	70	86	127	108	-
PNB*	7.5	0	0.01	n.d	n.d	n.d	n.d	n.d	n.d
CENB 1.0		0	5.00	14.8	64	86	111/119/122	111	1.6
CENB 3.0		5.0	5.10	15.1	41	75	106/117	108	1.12
CENB 4.0***		12.5	17.50	50.1	62	81	130	117	0.70
CENB 4.1		12.5	5.00	14.8	51	79	104/115	107	1.03
CENB 5.0		20.0	5.00	14.8	49	78	109/118/122	110	0.83
CENB 6.0	70	0	0.02	0.06	-	n.d	-	-	-
CENB 7.0		5.0	0.02	0.06	-	n.d	-	-	-
CENB 8.0		12.5	0.178	0.527	79	72	132	120	n.d
CENB 9.0		20.0	0.167	0.494	85	67	132	120	n.d
CENB 10.0****		5.0	0.320	0.948	40	72	130	119	n.d
CENB 11.0*****		5.0	6.00	18.0	78	79	112/125	115	n.d

Polymerization conditions: P ethylene = 2.6 bar; Solvent: 100 mL toluene; cocatalyst MAO; t = 30 min; reaction temperature = 80 °C; Al/Fe= 200; [Fe]= 0.05 mmol; *a: Catalytic activity: Kg/molFe.molE.h; nd: not determined; (a): degree of crystallinity obtained by DSC; (b): degree of crystallinity obtained by X-ray; (c): norbornene incorporation in the polymer chain determined by 13 C-NMR.

PNB*: homopolymerization of norbornene after reaction for 24 h; CENB 4.0***: change of reaction temperature to 30 °C; CENB 10.0****: same reaction conditions as other copolymerizations but norbornene was added after 15 min of ethylene polymerization, total reaction time was 30 min; CENB 11.0****: same reaction conditions as CENB 10.0*** but total reaction time was 1 h.



44] reports the same behavior, besides the decrease in polymer molar mass. When norbornene is inserted in the polymer chain, due to the bulkiness of this monomer, the next insertion occurs predominantly with ethylene.

Nevertheless, a catalyst can be effective in the copolymerization of ethylene with norbornene, showing good catalytic activity, and the homopolymerization of NB can exhibit low yield. Titanium bis (β-dicetaminate) complex showed moderate activity for homo and copolymerization of ethylene with norbornene, but low activities for the homopolymerization of NB [44]. Some authors state that the homopolymerization of NB is complicated due to the bulk stereo hindrance to the insertion of the cycloolefin, which hampers the entry of the next cyclic monomer. However, in copolymerizations, the sequential input of ethylene monomer promotes the spacer effect. Thus, the distance from the active center after the last NB insertion in the chain molecule increases, facilitating the incorporation of a new NB molecule.

Comparing polymerizations with 70 mmol NB, DSC thermograms of samples CENB 6.0 and CENB 7.0 did not show melting endotherm, while the CENB 8.0 and CENB 9.0 presented high melting temperatures. Probably in these copolymers DEZ promoted the formation of long sequences of ethylene, increasing polymer T_m due to the bulkiness of NB.

Crystalline structure

All the copolymers were analyzed by X-ray diffraction to ascertain their crystalline structure and crystalline degree (%X). According to Figure 1, the diffractogram profiles are characteristic of polyethylene, with reflections at $2\theta = 21.3^{\circ}$ and 23.7° , corresponding to the crystalline structure of polyethylene with the crystallographic planes (110) and (200) of the orthorhombic unit cell. It can also be observed that the X_c , calculated by Equation (1), decreased with the increase of DEZ concentration (as shown in Table 1). Probably the DEZ compound assisted the norbornene incorporation in the polymer chain, which interrupted the structural organization of the chain, decreasing the crystalline degree. This occurred with the sample CENB 3.0, where the norbornene incorporation was the highest (1.2%) and X_c was the lowest. The X-ray profile shows a slight decrease in the intensity and width of crystallographic peaks, which corroborates what was mentioned above. In other words, the incorporation of a large amount of norbornene in the copolymer chain decreased the crystalline degree.

Thus, the profile of the sample CENB 1.2 presents higher and narrower diffraction peaks and therefore, the highest X_c .

As for the polynorbornene (PNB 1.0), the XRD pattern in Figure 1 shows two intense reflections at 2 θ of 6.9° and 27.9° and a large amorphous halo between $2\theta = 15^{\circ}$ and 40° and another at low 2 θ , around 2° to 5°. In this figure, the diffractogram of polynorbornene (PNB 1.0) is also presented, where two amorphous halos around $2\theta = 10^{\circ}$ and 20° were found.

The X-ray diffractograms of the copolymers synthesized with 70 mmol of norbornene are presented in Figure 2.

The behavior was different from that of the copolymers at low NB content (Figure 1). The samples without and with small amount of DEZ (samples CENB 6.0 and CENB 7.0, respectively) showed an amorphous diffractogram profile, while in the reactions with higher amounts of DEZ, the polymers showed an increase in crystallinity, because of incorporation of long sequences of ethylene units in the polymer chain.

Molar mass and polydispersion

GPC analysis was performed to determine the polydispersion index (PDI) and molar mass of the synthesized polymers. According to Table 2, for samples obtained at reaction temperature of 80 °C, the DEZ decreased the molar mass and decreased PDI, narrowing the molar mass distribution. This is consistent with a process of chain transfer to zinc taking place. An increase in DEZ concentration is expected to accelerate the chain transfer process and leads to a greater abundance of shorter chain length products [36, 41]. The narrow molar mass distribution is reminiscent of a living polymerization system, in contrast to the broad molecular weight distribution typically observed with bis(imino)pyridine iron catalyst [27, 37].

The GPC curves of samples CENB 1.0 and CENB 4.0 had similar response, with bimodal molar mass distribution. In the first of these samples (without DEZ), this behavior was due the characteristic of this iron catalyst system. According to Small and coworkers [45], for iron catalyst in particular, increasing the amount of activator leads to broadened



polydispersion and bimodal profile. This behavior is consistent with the proposal that chain transfer to aluminum is a viable route for formation of low molecular mass fractions early in the polymerization reaction. Moreover, using large amounts of activator or short reaction times polymers with low molecular mass can be synthesized predominantly. In this work, the Al/Fe ratio was 500 and the reaction time was 30 min, agreeing with the results mentioned above and explaining these results.



 2θ (degree)

Figure 1. X-ray diffractograms of ethylene-norbornene copolymers with 7.5 mmol of norbornene and polynorbornene (PNB 1.0).

In Figure 3 (a), although DEZ was added in the synthesis of sample CENB 4.0, the PDI was broadened and bimodal, since DEZ only works as transfer agent to prevent undesired polymer precipitation at higher temperatures [29]. Therefore, chain transfer involving zinc probably did not occur in this condition, once the polymerization was performed at 30°C.

On the other hand, in Figure 3 (b) it can be observed that the GPC curves are monomodal, the molar mass distribution is narrower and the M_w decreases. This was expected, since DEZ acts as chain transfer in polymerizations at 80°C.

The DEZ behavior for the copolymers synthesized with 70 mmol of NB was very different compared to



2θ (degree)





Table 2. GPC analysis of copolymers with 7.5 mmol and 70 mmol of norbornene.

Sample	NB (mmol)	[DEZ] ×10⁻³ M	M _n ×10 ⁻³	M _w ×10⁻³	PDI
CENB 1.0		-	1.7	3.5	23
CENB 3.0		5.0	1.5	2.4	1.6
CENB 4.0***	7.5	12.5	4.0	7.6	19
CENB 4.1		12.5	1.4	2.3	1.6
CENB 5.0		20.0	1.5	2.7	1.7
CENB 8.0		12.5	158	13	11,7
CENB 9.0	70	20.0	168	16	10.5
CENB 10.0		5.0	37	4.0	9.2

CENB 4.0***: change the reaction temperature= 30°C, CENB 10.0****: same reaction conditions as other copolymers, but ethylene was added after 15 min of reaction time,

the first series of copolymers, as shown in Table 2. The addition of about tenfold more NB substantially reduced the polymerization rate, indicating that the chain transfer reactions occur much more frequently by reducing the molar mass of the polymers and increasing PDI.

However, the molar mass of these materials is much higher than that of the first series of copolymers. Ruchatz [45] and Wendt and Fink [46] observed that increasing molar mass is an indication of greater incorporation of norbornene in the polymer chain. Nevertheless, CENB 8.0 and CENB 9.0 had high T_m (close to that of PE), indicating low incorporation of NB. Interestingly, the CENB 10.0 copolymer (obtained by adding NB after 15 min of reaction) showed the lowest M_n and M_w values of the three polymers synthesized for 30 min, and narrower MWD, as observed in Figure 3 (c).

With reaction time of 1 h, the produced sample (CENB 11.0) had much lower T_m than CENB 10.0 and higher crystallinity degree. The catalytic activity was much higher than that with reaction time of 30 min, which indicates that alkyd transfer reactions occurred, leading to increased reaction yield.

Norbornene incorporation in polymer chain

To determine the norbornene incorporation, ¹³C-NMR analysis was performed and Equation (4) was used to calculate its content. The literature indicates that the ¹³C-NMR spectra of ethylene-norbornene copolymers are complex, because these copolymers include different monomer sequences, varying lengths of NB microblocks [17], meso or racemic connections of the norbornene units, and pentad sensitivity [47].

Figure 4 shows the ¹³C-NRM spectrum of CENB



0.005

0.004

Figure 3. GPC analysis of ethylene-norbornene copolymers.

3.0. The spectra of the other copolymers have almost the same profile. The NB incorporation in the polymer chain changed from 0.7-1.6 mol%, as reported in Table 1. According to Hasan et al. [47], the ¹³C-NMR spectra of copolymers are strongly dependent on the catalytic complexes used. The spectrum of sample CENB 1.1 shows peaks at 29.9 ppm, corresponding to



Figure 4. ¹³C-NMR spectra of ethylene-norbornene copolymer.

successive ethylene (E) sequences, and at 30.54 ppm, related to the isolated E+ NB (carbons C5/C6 of NB unit).

Thermal properties

Figure 5 shows the DSC thermograms of the first set of copolymers, obtained with 7.5 mmol of NB. All the copolymers showed broad melting endotherms with multimodal profiles, with the exception of CENB 4.0 (polymerization performed at 30°C), where the profile was monomodal. This profile suggests that the sample consists essentially of PE (with very low comonomer content). Since the copolymers obtained at 80°C contained higher levels of NB, this markedly modified the size distribution of the polymer crystals by extending the calorimetric curve. Thus, it is possible that the polymer chain contains different sizes of ethylene sequences, with the longest length



Figure 5. DSC thermogram of ethylene-norbornene copolymer with 7.5 mmol of NB.

corresponding to the highest melting temperatures.

Note that increasing DEZ concentration narrowed the endotherm curve, reducing the peak with higher T_m , although it decreased the incorporated NB content. This suggests that these conditions allow more frequent alkyd transfer reactions between the active centers of the catalyst, which leads to the formation of structures with lower ethylene sequences in the chain.

The addition of DEZ promotes the exchange among the alkyd chains, producing randomly distributed segments with long sequences of ethylene units and ethylene-NB statistically distributed segments. Therefore, these segments may be of different lengths and have different compositions, which cause broadening of the DSC curve. These parameters vary with the amount of DEZ added to the reaction medium. The higher the concentration of the compound, the more frequent the alkyd exchanges are, producing smaller segment sizes and narrowing the DSC curve [48].

However, for the copolymers synthesized using 70 mmol of NB (Figure 6), the thermogram profiles were very different from the curves shown in Figure 5, with well-defined thin peaks and high crystalline melting temperatures. Apparently, there was low incorporation of NB in the polymer chain. However, for CENB 11.0 (norbornene was added 15 min after the start of ethylene polymerization and total reaction time was 1 h), there was only a slight decrease in T_m (approximately 5°C) and an endotherm shoulder appeared at 112°C. According to the literature [41], as explained above, the crystals that melt at lower temperature consist of molecules that are likely to have



Figure 6. DSC thermogram of ethylene-norbornene copolymer with 70 mmol of NB.

errors in the polymer chain when norbornene units are incorporated, which breaks the regularity of ethylene sequences, lowering the melting temperature.

What probably happened in copolymer CENB 11.0 was that in the first 15 min of reaction, there was synthesis of long polyethylene chains, which after transfer were linked to the zinc in DEZ. These chains form crystals which melt at 125°C. When norbornene was added to the polymerization medium, there was reversible alkyd transfer. These chains continued to propagate and insertion of NB in the macromolecule possibly occurred, forming multiblocks with long ethylene sequences (synthesized in the first 15 min of reaction) and smaller sequences of ethylene with NB units inserted. These blocks with stereo errors promoted the decrease of T_m .

Figure 7 shows the weight loss profile by TGA for the copolymers synthesized with 70 mmol of NB. Note that for the copolymers CENB 6.0 and CENB 7.0, obtained without adding DEZ or with low concentration of NB, the curves showed two mass losses, one at low temperature (around 130°C) and another at high temperature (above 400°C). This shows that two distinct polymer fractions were produced with this material. Thus, absence of the DEZ alkyd chain transfer effect causes the formation of different polymer fractions with different thermal resistances. We also observed that the copolymers CENB 8.0, CENB 9.0, CENB 10.0 and CENB 11.0 had a single mass loss range, with thermal resistance higher than that of PE 4 (PE synthesized without DEZ at 80 °C, 0.05 mmol Fe catalyst and Al/Fe=500 molar ratio), and the degradation rate of the copolymers was also much higher, since the curve indicates steep mass drop. Probably the norbornene units inserted in the ethylene sequences promoted the increase of the material's thermal resistance. Rigid molecules tend to increase the degradation onset temperature, as mentioned above.

The samples CENB 10.0 and CENB 11.0 exhibit much higher t_{onset} than PE, indicating that the ethylene sequences produced in the first 15 min of reaction were reinserted in the Zn sites and then transferred to the active sites where NB was added in the chain. The few NB units incorporated in the polymer chains were probably well distributed in long ethylene sequences, leading to an increase in thermal resistance.

In order to check the influence of the addition of MAO and DEZ in the catalyst solution, UV-Vis absorption spectroscopy analysis of the complex solution of pure iron complex and with the addition of MAO and DEZ was carried out. Figure 8 contains the spectrum of the catalyst solution in toluene, showing a broad peak absorbing visible light at a wavelength of 740 nm, corresponding to blue color (characteristic of this catalyst). According to the literature [27], this absorption is due to metal charge transfer to the binder.

After addition of MAO to the catalyst solution, there was a color change to orange-red, along with disappearance of the band at 740 nm in the absorption spectrum, while a new peak appeared at wavelength λ =540 nm (corresponding to red), in addition to decreasing intensity. This change in spectrum profile is related to the appearance of a new species, promoted by the reaction of iron complex with MAO, indicating that all iron was transformed into the activated catalyst



Figure 7. TGA thermograms of ethylene-norbornene copolymer with 70 mmol of NB.





species. Probably the red-orange color acquired by the solution was due to oxidation of Fe^{+2} to Fe^{+3} promoted by the trimethyl aluminum (TMA) contained in the MAO solution [49]. When the catalyst deactivates, the solution presents a greenish color [50].

When DEZ was added to the catalyst solution and MAO, the color of the solution did not change. Moreover, no shift band in the spectrum was observed (the absorption remained at 640 nm), with only a slight increase in its intensity. This suggests that DEZ did not promote changes in the type of active sites of the catalyst.

CONCLUSION

The compound DEZ did not influence the catalytic activity in ethylene-norbornene copolymerizations with 7.5 mmol of NB, but in the reactions with 70 mmol, the comonomer promoted an increase of catalytic activity. The X-ray diffraction profiles of all copolymers synthesized presented characteristics of PE crystallinity, since as shown by ¹³C-NMR analyses, low incorporation (around 1%) of NB in the polyethylene chain occurred. DEZ worked as an alkyd transfer agent, promoting narrowed polydispersion and decreased molecular weight of copolymers with 7.5 mmol. However, in copolymerizations of the second series, with 70 mmol NB in the reaction medium, the behavior of DEZ was opposite that of the samples with 7.5 mmol of norbornene. In the thermal analysis, the copolymers synthesized with 7.5 mmol of NB presented multimodal profiles and the copolymers with 70 mmol of NB exhibited narrow and well-defined peaks with higher crystalline melting and crystallization temperatures, therefore, at this condition NB was not highly incorporated in the chain. The TGA analyses indicated that NB promoted an increase in thermal resistance of the materials. When NB was added 15 min after the ethylene polymerization, the endotherm peak showed bimodal profile, which indicated that alkyd chain transfer of Zn to the active sites occurred and the polymer chain continued to grow. The UV-Vis analysis showed that DEZ did not influence the nature of catalytic active sites.

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