Roberto Martins, Leticia Quinello, Giuliana Souza and Maria Marques

POLYMERIZATION OF ETHYLENE WITH CATALYST MIXTURE IN THE PRESENCE OF CHAIN SHUTTLING AGENT

Instituto de Macromoleculas Eloisa Mano
IMA (UFRJ) Cidade Universitaria. Av. Horacio Macedo,
2.030. Centro de Tecnologia. Predio do Bloco J. Rio de Janeiro. RJ. Brasil
fmarques@ima.ufrj.br

Abstract. Mixture of two catalysts in one reactor for ethylene/α-olefin copolymerization in the solution process can result in the combination of microstructures related to both catalysts in the polymer framework. Thus, novel polymer configuration is synthesized, which is characterized by containing sequences of monomers produced with each catalyst in the same polymer chain. Adding a reversible transfer agent (CSA) to the binary system enables the production of new block copolymers with enhanced properties. Late transition metal catalysts, such as α-diimine nickel catalyst when activated with methylaluminoxane (MAO) show high activity towards olefin polymerization and produces highly branched homopolymers. On the other hand, C_2 symmetry metallocene catalysts produce linear polyethylenes. This paper describes the synthesis of ethylene homopolymer with amorphous and crystalline blocks using a binary mixture containing a nickel catalyst with α-diimine ligand, which produces ф highly branched polyethylene (soft PE) and a metallocene (*rac*-ethylene bis(H_4-indenyl)$ZrCl_2$) that converts ethylene into polyethylene with high activities and melting temperatures (hard PE). The influence of polymerization temperature and CSA concentration were investigated. The polymeric materials were characterized by density, thermal properties, X-ray diffractometry and dynamic-mechanical properties.

Keywords: ethylene polymerization, single-site catalyst, catalysts mixture, chain shuttling.

1. Introduction

Polyolefins are in general commodity type polymers with a wide range of applications [1-4]. It occupies a prominent position in the world market compared to other polymers due to its specific characteristics as: non-toxicity, chemical inertness, good physical and mechanical properties, low production cost and easy availability of raw materials [5, 6]. It can be found commercially with an incredible variety of properties and applications ranging from ultra-hard (harder and less dense than steel), to high-performance materials such as thermoplastic elastomers [7].

The term elastomer is applied to macromolecular materials that have low modulus and a wide range of elasticity at room temperature [8]. The mechanical properties of elastomers are improved by crosslinking, leading to covalent bonds between the polymer chains. The main commercial elastomers such as vulcanized rubber materials are thermosets, which lead to processing and recycling problems [9]. However, block copolymers, which have rigid and elastomeric domains, also provide elastomeric properties. An example of such polymer is poly(styrene-*b*-butadiene-*b*-styrene), SBS. In this material the hard domains (polystyrene) act as physical cross links, while the segments of butadiene sequences form the elastomer phase, providing high chain mobility [7]. The crosslinking *via* vulcanization process is irreversible. However, in materials such as SBS, the intermolecular bonds that form the hard domains can be reversibly broken by heat. Therefore, these copolymers can be melted and solidified again, showing properties of thermoplastic elastomer. The commercially important elastomers have a block structure with ф high melting temperature or high glass transition temperature, which are the rigid blocks, combined with flexible segments. The former blocks comprise the hard domains that serve as a reinforcement and as cross-links, which are connected with the flexible blocks.

Another example of this advance is the development in the area of catalysts produced by Dow Chem. with the first patent in 2006 [10-14]. This new

technology allows the production of new multiblock copolymers, using two catalysts with different capacities for the incorporation of comonomers, and adding a chain transfer agent that has the function to promote the exchange between the growing chains linked to each catalyst in a continuous reactor [15, 16].

The transfer agent (chain shuttling agent, CSA) refers to a compound or mixture of compounds that allows the transfer of chain fragments from different catalysts during polymerization (Scheme 1). The most suitable compound is diethyl zinc, which has been used as CSA [17-20].

$K_{ex} < K_p$ chain transfer; $K_{ex} >>> K_p$ chain growth [17-20]
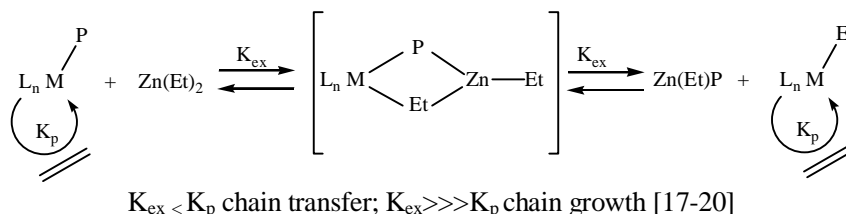
Scheme 1

The synthesized multiblock copolymer consists of blocks of crystalline ethylene/α-olefin (low commoner content and high of T_m) alternating with amorphous blocks (high comonomer content and low T_m) [21, 22].

The present paper describes the synthesis of ethylene homopolymer consisting of blocks with amorphous and crystalline chain segments derived from a binary catalyst mixture comprising a nickel catalyst with α-diimine ligand able to converting ethylene in a highly branched polyethylene (flexible PE) and a metallocene catalyst, the *rac*-ethylene bis(H_4-indenyl) $ZrCl_2$, which produces polyethylene with a high linearity and melting temperatures (hard PE). Besides the evaluation of the influence of polymerization temperature (333, 353 and 373 K), the concentration of Et_2Zn as a chain transfer agent was also varied.

2. Experimental

2.1. Materials

All reagents were manipulated under inert atmosphere of nitrogen using the Schlenk technique. Ethylene and nitrogen were purified by sequential passage through columns containing 4A molecular sieves and a copper catalyst to remove oxygen, carbon dioxide, and moisture. Toluene was refluxed over metallic sodium/ benzophenone and was distilled under nitrogen atmosphere prior to use. Methylaluminoxane (MAO) (10 wt % solution in toluene, obtained from Chemtura, Germany), diethyl zinc was obtained from Akzo Nobel, Brazil, and used as received. The commercial catalyst *rac*-ethylene bis(H_4-indenyl)$ZrCl_2$ obtained by Witco TA 028 was used without further purification.

The ligand *N*-(2,6 diisopropylphenyl) imino] acenaphthene and the catalyst (*i*Pr_2Ph)$_2$bis(imino) acenafteno·$NiBr_2$ were prepared according to published procedures in the literature [23]. All other chemicals were commercial materials and were used as received.

2.2. Synthesis of Ligand and Complex

2.2.1. [N-(2,6-Diisopropylphenyl)imino] acenaphthene

2,6-Diisopropylaniline (4.2 ml, 22 mmol) was added to a solution of acenaphthenequinone (2 g, 11 mmol) in 25 ml of ethanol. After the addition of a few drops of glacial acetic acid, the solution was refluxed during 4 h. It was then cooled to room temperature and the solid filtered to give a yellow product that was washed with cold ethanol and air dried. Yield 4.7 g (85.5 %). IR (cm^{-1}): 1673 e 1653 ($v_{C=N}$) e NMR {^{1}H} (δ ppm): 0.98 (d, 12H); 1,24 (d, 12H); 3.03 (m, 4H); 6.64 (d, 2H); 7.36 (dd, 2H); 7.88 (d, 2H). ^{13}C-NMR (δ ppm) (CDCl$_3$,^{1}H gated decoupled): 161.1 (C=N), 148.0 (Ar-C_{ip}), 141.2, 135.5 (Ar-C_p), 131.6, 130.0, 129.2, 128.3, 124.6, 123.9, 123.5 (Ar-C_m), 29.1(N=C-Me), 23.2 (CHMe_2), 23.1(*C*HMe$_2$)

2.2.2. [*N*-(2,6-Diisopropylphenyl)imino] acenaphthene-NiBr$_2$

NiBr$_2$(DME) (0.3g, 0.96 mmol) and *N*-(2,6 diisopropylphenyl)imino]acenaphthene (0.5g, 1 mmol) were added in 15 ml of CH$_2$Cl$_2$, producing a red brown solution and a yellow solid. The mixture was stirred at room temperature for 16 h, producing a brown solution. Then the solvent was evaporated yielding brown oil. After addition of 15 ml of cyclohexane a brown precipitate was obtained, filtrated and dried *in vacuo*. Yield: 0.6 g (83 %). IV (CsI, cm^{-1}): 1649, 1620 ($_{C=N}$), 279,258 ($_{Ni-Br}$) Anal. Calc. for C$_{36}$H$_{40}$N$_2$Cl$_2$Ni: C, 68.6; H, 6.35; N, 4.45. Found: C, 69.8; H, 7.8; N, 4.26

2.3. Polymerization

Ethylene polymerization was carried out in a jacketed Büchi glass reactor of 1000 ml capacity, equipped with mechanical stirring and thermostatic bath for temperature control. Reactions were carried out under the following conditions: 100 ml of distilled toluene, ethylene [C$_2$H$_4$] = 0.135 M, catalyst (metal) concentration

[Me] = $2 \cdot 10^{-4}$ M; cocatalyst methylaluminoxane (MAO) (Al/Me = 200), 1 h. Three temperatures (333, 353 and 373 K) and different concentrations of CSA (chain-shuttling agent) ([Et$_2$Zn]/[C$_2$H$_4$]) were evaluated.

The catalyst activity (catalyst efficiency) was calculated in tons of polymer produced per mol of transition metal, mol of ethylene, hour (t/molMe·molE·h), where: molMe = number of moles of a catalyst (Me = Zr or Ni) in the reaction; molE = number of moles of ethylene in the reaction. The reaction time was 30 min. The concentration of ethylene dissolved in the reaction medium was calculated using the state equation, considering the values of critical temperature, critical pressure and compressibility factor (*w*). The number of moles of ethylene in 100 ml of toluene is 0.135 M at 200, 260 and 300 kPa for 333, 353 and 373 K, respectively [24].

2.4. Characterization

Polymers were characterized by density measurements using the pycnometer method; differential scanning calorimetry (DSC) was used to determine the thermal properties and degree of crystallinity; X-ray diffraction analyses were performed to obtain the materials crystallinity; dynamic mechanical analysis (DMA) was also employed to evaluate the storage (*E'*) and loss (*E''*) moduli of the polymers produced, as well as the damping factor (tan delta) and glass transition temperature (*Tg*). For the characterization of the synthesized ligand and catalyst complex, ^{1}H- and ^{13}C-NMR spectra were measured in a Varian Inova-300 MHz, IR-spectra were obtained in Nicolet equipment, model Magna-IR 760. Elemental analysis was performed on Perkin-Elmer 2400 Series II CHN/O Analyzer.

3. Results and Discussion

3.1. Catalytic Activity

The results of ethylene polymerizations are listed in Tables 1 and 2. Scheme 2 illustrates the molecular structures of the catalysts involved.

Fig. 1 shows the relationship between temperature and catalytic efficiency. It is observed that the activities of Cat1 and Cat2 at 333 K were equal, while the efficiency of the catalyst mixture was slightly lower. At the temperature of 353 K, the efficiency of Cat1 was lower compared to Cat2, which activity increased by a factor of about 6 times, however there was a significant decrease in the activity of the catalyst mixture. Moreover, at 373 K the efficiency of the Cat1 was even lower compared with other temperatures, while Cat2 maintained high activity and the binary mixture remained practically unchanged compared to the result to 353 K. It can be concluded that Cat1 decreases its activity with increasing temperature, while Cat2 is more thermally stable and has a higher activity at elevated temperatures.

Cat1   Cat2
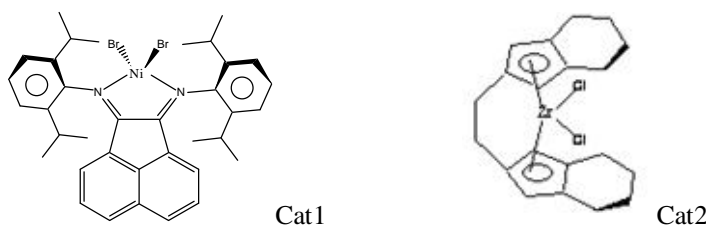
Scheme 2

Table 1

Characteristics of polymerization and catalyst efficiency

Entry (a) (b) (c)	Description	Catalyst	[Et$_2$Zn]/[C$_2$H$_4$] (10^3)	Catalytic activity*		
				Temperature, K		
				333 (a)	353 (b)	373 (c)
1	soft PE	Cat1		43	33	11
2	hard PE	Cat2	0	43	210	214
3	blend	Cat1+Cat2		29	23	22
4	[1] CSA		2	56	37	28
5	[2] CSA		4	40	35	22
6	[3] CSA	Cat1 + Cat2 + Et$_2$Zn	6	142	118	68
7	[4] CSA		8	168	132	102
8	[5] CSA		10	107	59	53

*t/molMe·molE·h

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Table 2

Polyethylene physical properties

Polymer		Density, g/cm^3	T_m, K	T_c, K	T_m-T_c, ^{o}	ΔH_m[a], j·g^{-1}	ΔH_m[b], j·g^{-1}	X_c[c], %	$X_{c\Delta H}$[d], %	X_c[e] WAXD, %
T, K	code									
333	1 a	0.8702	-	-	-	-	-	-	-	-
	2 a	0.9351	404	394	10	220	162	59	55	53
	3 a	0.8856	403	390	13	51	30	23	10	27
	4 a	0.9162	-	-	-	-	-	-	-	-
	5 a	0.8716	400	378	22	9	6	13	2	15
	6 a	0.8677	400	384	16	7	4	-	1.5	-
	7 a	0.9013	404	387	17	147	114	36	39	53
	8 a	0.8641	403	385	18	10	6	-	2	-
353	1 b	0.8594	-	-	-	-	-	-	-	-
	2 b	0.9334	406	396	10	224	155	57	52	49
	3 b	0.9085	405	391	14	179	149	41	50	45
	4 b	0.8594	402	353	50	10	0.5	-	0.02	-
	5 b	0.8893	403	385	18	34	24	26	8	26
	6 b	0.9229	405	389	16	172	155	51	57	63
	7 b	0.9169	405	390	15	188	168	47	55	67
	8 b	0.8893	403	384	19	44	20	27	7	22
373	1 c	0.8710	-	-	-	-	-	-	-	-
	2 c	0.9364	403	393	10	225	218	60	74	85
	3 c	0.9150	404	392	12	156	141	45	50	49
	4 c	0.8573	401	386	15	26	29	18	10	19
	5 c	0.9238	405	390	15	145	143	51	49	50
	6 c	0.8918	404	388	16	91	87	28	30	37
	7 c	0.9320	403	387	16	188	177	57	60	75
	8 c	0.9013	401	381	20	20	4	-	1.5	-

Notes: [a]first heating; [b]second heating; [c]crystallinity from density; [d]crystallinity from heat of melting; [e]crystallinity from WAXD

However, interestingly the catalytic mixture has not the expected behavior, but their activity was similar to that of Cat1. Therefore, the performance of the catalyst mixture was different from that of the isolated systems, showing that there was interference between catalytic systems in the polymerization of ethylene in the presence of MAO.

The influence of CSA concentration in the polymerization using mixture of Cat1 and Cat2 at 333, 353 and 373 K was investigated. Fig. 2 shows the relationship of the used CSA concentrations and the efficiencies obtained in the catalytic polymerization of ethylene. Initially it was observed that the activities of the catalysts in the three reaction temperatures responded similarly to the presence of chain transfer agent (CSA). At 333 K and in all concentrations of CSA the binary catalyst efficiency showed a higher value than that at increased temperatures. In fact, for the catalyst mixture, the increase in polymerization temperature led to the decreased activity. On the other hand, it was observed that there was a significant increase in yield with increasing concentration of CSA in the reaction medium. The major activities can be observed in the molar ratios of $[Et_2Zn]/[C_2H_4]$ = $6 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$. Above this

concentration of $ZnEt_2$ there was a decrease in activity at the three evaluated polymerization temperatures.

The study of the activity in binary systems in the presence of non-metal alkyl compound has not been fully understood. Tynys *et al.* [25] and Chien *et al.* [26] observed the increased activity in a mixture of catalysts in the presence of trimethylaluminum (TMA) and triisobuthylaluminum (TIBA), respectively. While Bastos *et al.* [27] reported a decrease in catalytic activity in binary systems also using TIBA. The increased activity could mean that reversible chain transfer is occurring. A catalyst could act continuously consuming the product of chain termination on the other catalyst, leading to the increased activity. This mechanism explains the results observed in the binary catalyst system of the present study. On the other hand, the reason for the decrease in catalytic efficiency with the excess $ZnEt_2$ was proposed by Bruaseth and Rytter [28].

According to those authors, the product of polymer chain termination by chain transfer with the metal alkyl compound can remain coordinated with the active catalyst, resulting in decreased activity at high CSA concentrations.
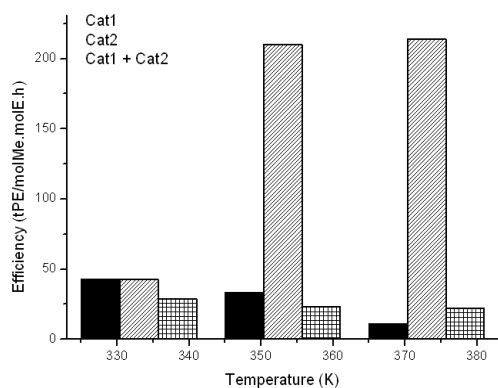
**Fig. 1.** Relationship between catalytic efficiency and temperature
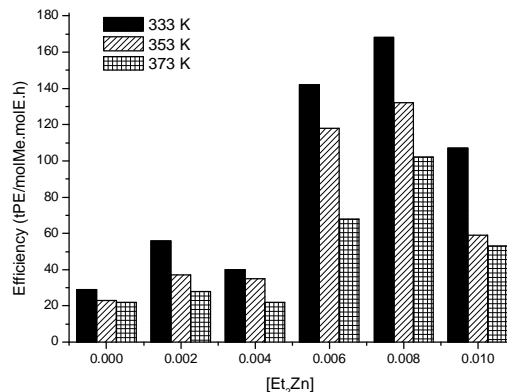
Fig. 2. Relationship between catalytic efficiency and [Et$_2$Zn]/[C$_2$H$_4$]

3.2. Crystalline Structure

The WAXD profiles for the polymers synthesized at 333, 353 and 373 K are shown in Fig. 3 (a, b and c, respectively). This shows the XRD patterns of the polymers synthesized with the two catalysts acting isolated with and without the transfer agent ZnEt$_2$. For most samples, the peaks at 2θ of 21.5° and 23.9° were designated as (110) and (200) to equivalent structures of the crystallographic planes of the orthorhombic unit cell of polyethylene.

While the Cat1 produces amorphous polymer in all reaction temperatures, as shown in the XRD patterns 1a, 1b and 1c, where the amorphous PE halos appear, Cat 2 produces crystalline PE (patterns 2a, 2b and 2c). Since the binary catalyst without CSA produces less crystalline PE, indicated by the broadening of the crystalline peak, it is possible that this polymer consists of a mixture of polyethylenes synthesized by both catalytic systems. The mixture of crystalline and amorphous PE decreased the overall crystallinity of the PE obtained.

a)

b)

c)
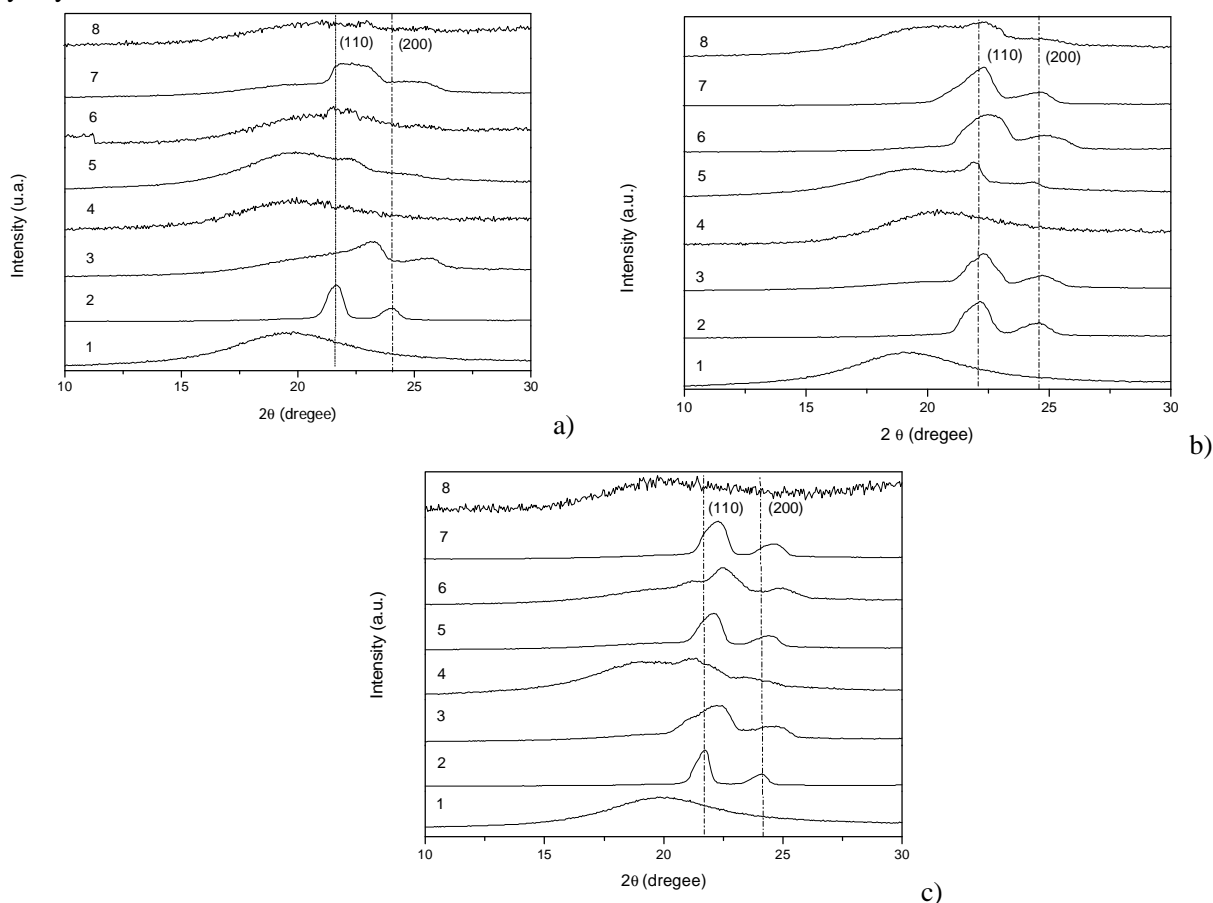
Fig. 3. Diffractograms of polyethylenes synthesized at: 333 K (a), 353 K (b) and 373 K (c)

On the other hand, the displacement of the reflection peaks corresponding to the crystallinity of the PE mixture obtained with CSA (diffractograms 6b, 6c, 7b and 7c in Fig. 3) may be explained by the increased amount of soft segments in the polymer chain. Thus, the unit cell undergoes an orthorhombic distortion due to the presence of branches in the polymer chain – orthorhombic reflections (110) and (200) remain, but the intensity decreases – while the extension of the halo is due to the reduction of rigid segments, as shown in Fig. 3. However, the distortion was much lower in polyethylene synthesized at 373 K (Fig 3c). The diffraction peaks of the orthorhombic unit cell were dilated for all PE samples produced with catalytic mixture in the presence of CSA. This fact became even more pronounced with the presence of high amount of CSA, which may indicate the presence of soft and hard blocks in the polymer chain. It can be observed that at 333 K the profiles of the PE obtained with the binary catalyst resemble the profile of the polymer synthesized with Cat1, which produces the amorphous polymer, indicating the high activity of this system at this temperature. Already at 373 K the polymers have the profile of sample 2 synthesized with Cat2 which produces crystalline polyethylene, this was due to the fact that Cat1 has the decreased activity at high temperature. The XRD patterns of the polymers obtained at 353 K in the presence of CSA suggests the presence of soft and hard domains in the same polymer chain. The profiles have the most outstanding changes in samples 6 and 7 at $[Zn]/[C_2H_4] = 6 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$. We can estimate the degree of crystallinity of the samples through the areas of crystalline peaks and amorphous halo, using Eq. (1) [29].

$$\% X_c = \frac{A_c}{A_c + A_a} \qquad (1)$$

where: A_c – area on the crystalline peak; A_a – area on the amorphous halo.

The results presented in Table 2 for the degree of crystallinity of the polyethylene obtained showed a good correlation with the other determinations of crystallinity.

Morphological studies have shown that long sequences of ethylene in rigid olefin block copolymers can crystallize in the form of lamellar crystals with few defects and high melting temperatures, featuring the hard segments.

The crystalline phase acts as the reinforcement to train physical nodes, connecting with the elastomeric chains (soft segments) [30]. The trend line gives us the coefficient of determination/correlation (*R*), an indicator ranging from 0 to 1 and reveals the closeness of the estimated values of the trend line in correspondence with the veracity of the data. The reliability of the linear trend is given when the value of *R* is equal or close to 1. Fig. 4 illustrates the relationship between X_c values calculated by DSC and WAXD with the value of $R = 0.9647$.

In general the values of X_c obtained by DSC are lower, which can be explained by different factors. One is that the X-ray scattering is sensitive to organized

structures at the nanometer scale, not only crystal structures.
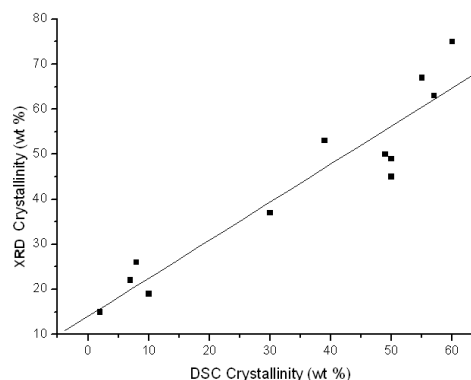

**Fig. 4.** Relationship between crystallinity (X_c) measured by XRD and DSC

Another factor is that lamellar crystals of different thicknesses have different melting enthalpies, as a result of different entropies of fusion. Therefore, samples with relatively small crystals have underestimated their crystalline fractions by DSC [31].
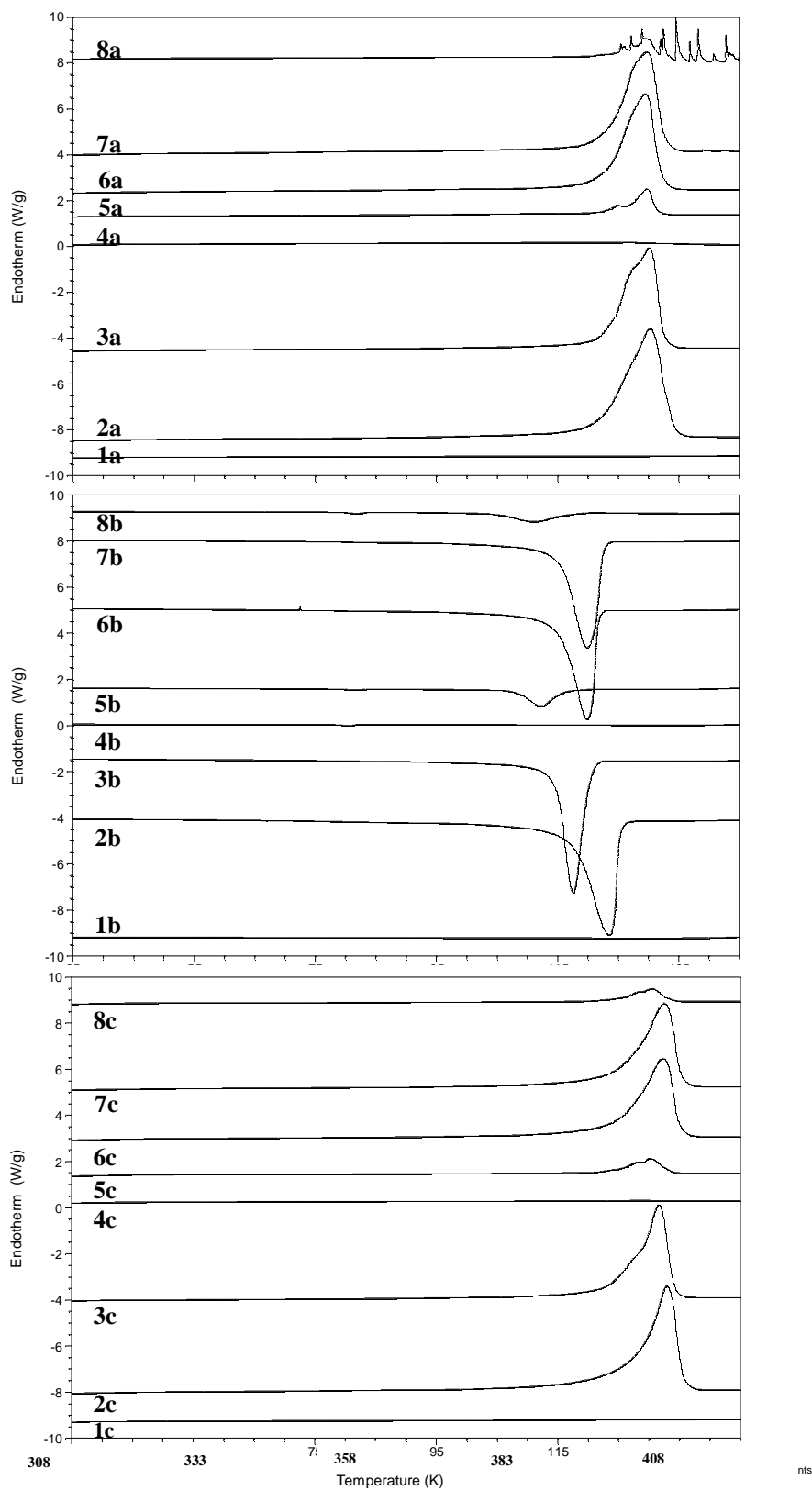
3.3. Thermal Behavior

The thermograms of first heating, cooling and subsequent heating for polymers synthesized at 333, 353 and 373 K are shown in Figs. 5-7, respectively. All polymers synthesized presented high melting (T_m) and crystallization (T_c) temperatures, with exception of the samples synthesized with Cat1, which produces amorphous PE. The results of the melting temperatures (T_m), crystallization (T_c) and melting enthalpies (ΔH_m) for the first and second heating are shown in Table 2. The values of T_m showed slight variation in the PE synthesized with the addition of transfer agent, which can be observed in the DSC thermograms by the peak shift to lower temperatures, justifying the reduction of rigid sequences. The main effect caused by the composition of flexible and rigid segments in the chain was shown by the decrease of the transition enthalpies (ΔH_m). According to Wang *et al.* [21], the increased values of the melting enthalpies (ΔH_m) observed from the first heating, means an increase in the amount of crystallizable blocks.

The polymers synthesized with Cat1, samples 1, 2 and 3 have the following values of T_m: 404, 406 and 403 K, respectively. The samples obtained by the binary catalytic without CSA revealed the values of T_m: 403, 405 and 404 K, showing that there was no influence on the T_m of polymers.

On the other hand, the presence of CSA at different concentrations revealed that the synthesized polyethylene at 333 K resulted in T_m 3 degrees lower as compared to the polymers synthesized 353 and 373 K. With increasing content of the flexible blocks, the melting peak of the rigid blocks slightly shifts, as shown in Figs. 5-7.
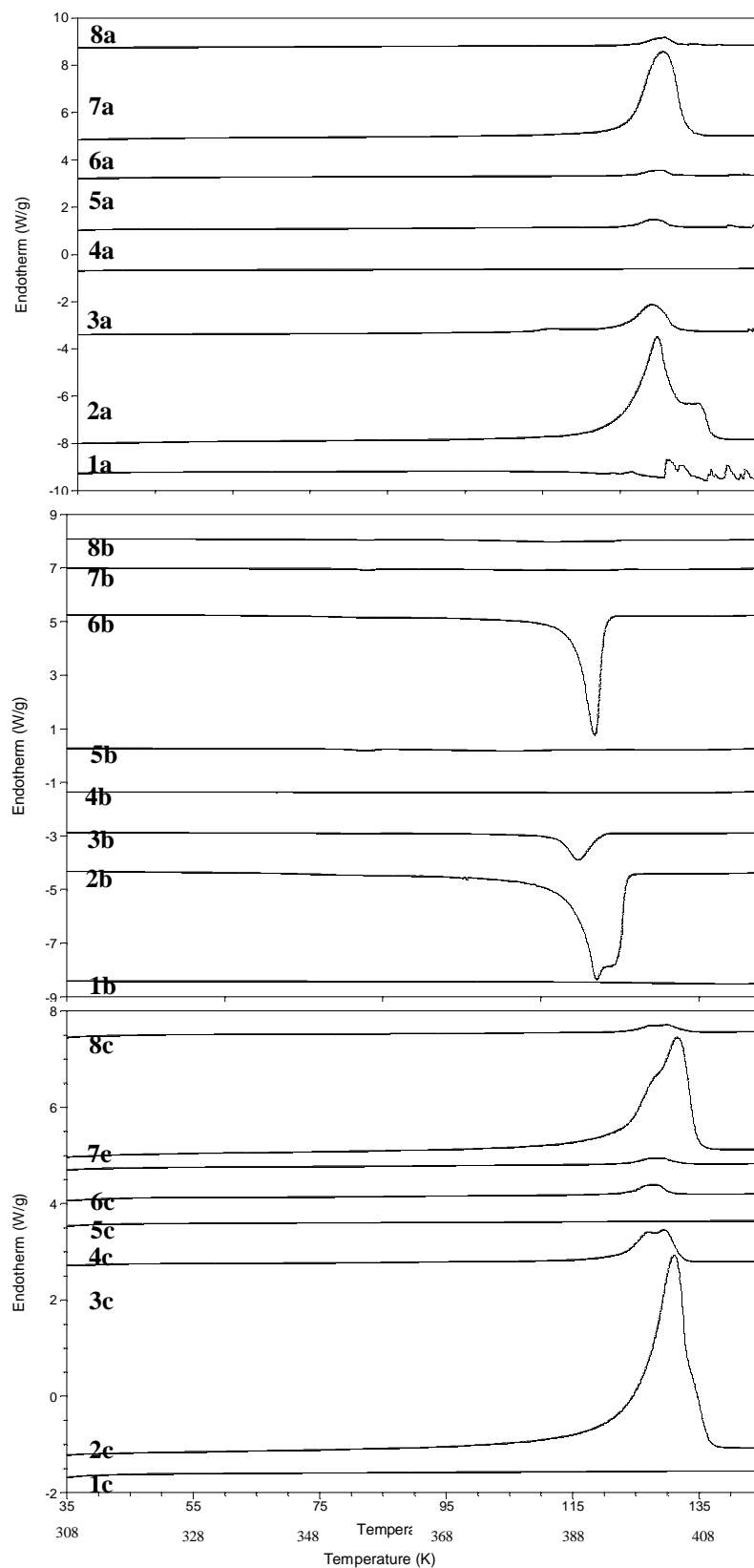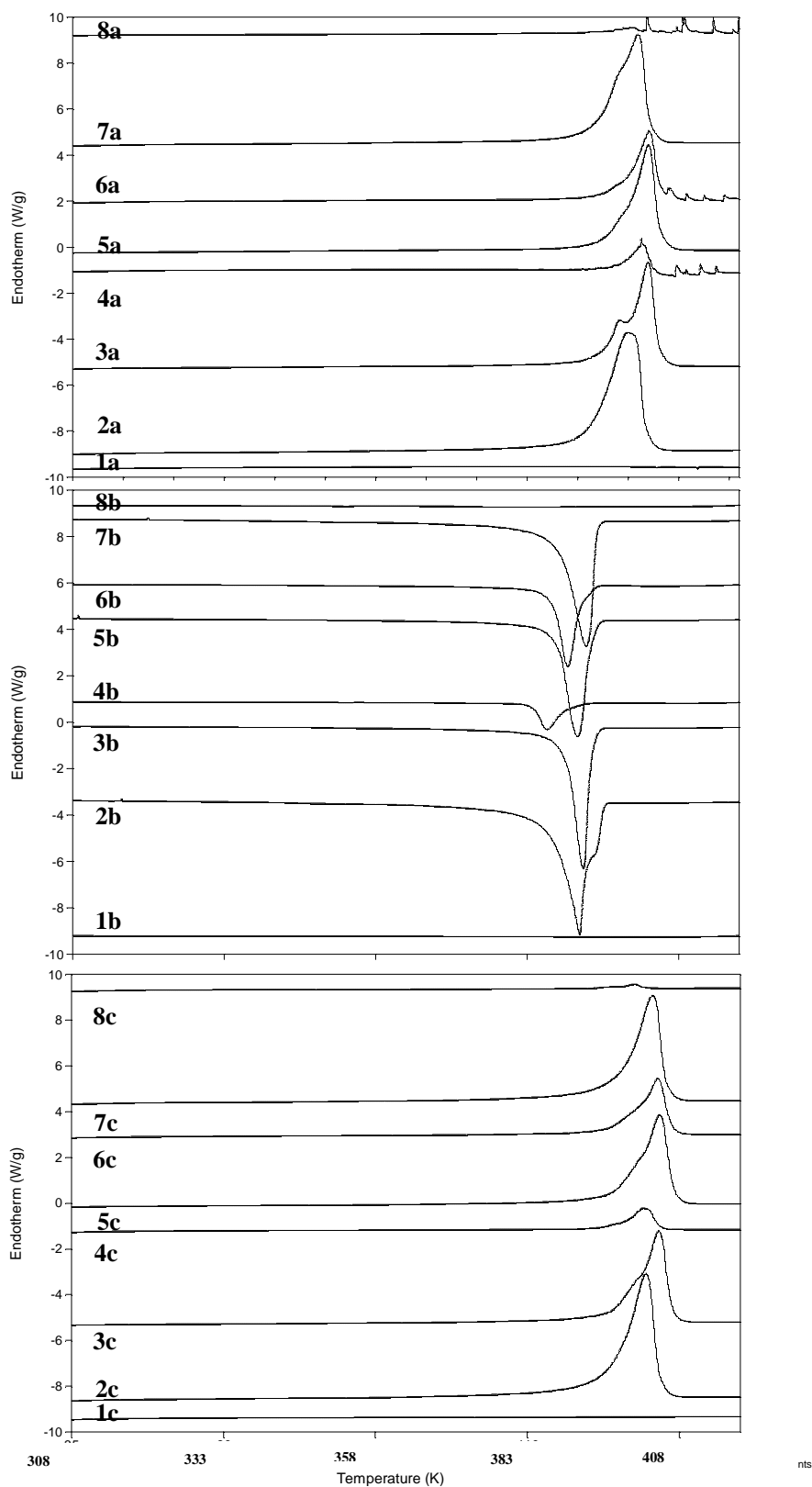
Fig. 5. Thermal behavior of polymers produces at 333 K: first heating thermograms (a); cooling thermograms (b) and second heating thermograms (c). The heating/cooling rate was 10 deg min^{-1}

Fig. 6. Thermal behavior of polymers produces at 353 K: first heating thermograms (a); cooling thermograms (b) and second heating thermograms (c). The heating/cooling rate was 10 deg min^{-1}

Fig. 7. Thermal behavior of polymers produces at 373 K: first heating thermograms (a); cooling thermograms (b) and second heating thermograms (c). The heating/cooling rate was 10 deg min^{-1}

Small changes in T_c parallel to the decrease in T_m results in subcooling (T_m-T_c), which in this case were about 15 to 20 degrees for all polymers synthesized, except for the sample 4b, that showed an unexpected behavior with a difference of 50 degrees, revealing a higher concentration of flexible blocks. With this obtained data it can be observed that the polymer block has two contributions of both structures, from the amorphous phase (flexible block) and hard crystalline block.

4. Conclusions

The characterization of solid-state structure and properties of block polymers of ethylene synthesized in this work showed that they relate to the concept of thermoplastic elastomer in which crystallizable blocks serve as physical cross-links connecting amorphous blocks. In the dynamic mechanical properties the CSA promoted decrease in the hard segments in the chains of the copolymers obtained by catalytic mixtures, however, high concentrations of CSA was the increase of the material modulus.

In addition, we observed that the efficiency of the Cat1 decreased at high temperature polymerization and this produced amorphous PE. The addition of Et_2Zn increased efficiency for the binary mixture from the ratio $[Zn]/[Et] = 6 \cdot 10^{-3}$ and $8 \cdot 10^{-3}$ M, as had been previously reported [33], this mixture showed the formation of the PE block – the hard and soft one. Increasing the temperature of polymerization, as well as [Zn] produced PE with higher T_m and X_c which reveals the low thermal resistance of Cat1 which produces the soft segment.

Acknowledgments

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ПОЛІМЕРИЗАЦІЯ ЕТИЛЕНУ З КАТАЛІТИЧНОЮ СУМІШШЮ В ПРИСУТНОСТІ ЛАНЦЮГОВОГО ШАТЛ-АГЕНТУ

Анотація. Показано можливість поєднання мікроструктур каталізаторів в каркасі полімеру внаслідок змішування двох каталізаторів в реакторі, де відбувається кополімеризація етилен/α-олефінів. Синтезовано нові полімерні конфігурації, які характеризуються послідовністю мономерів, отриманих з кожним із каталізаторів в одному полімерному ланцюзі. Додавання реагента зворотнього переходу (РЗП) до бінарної системи дає можливість одержати нові блок-кополімери з покращеними властивостями. Каталізатори на основі перехідних металів, такі як α-діімін-нікелевий каталізатор, активізований метилалюмооксаном, виявляють високу активність по відношенню до полімеризації олефінів і дають можливість отримувати високорозгалужені гомополімери. C_2-симетричні металоценові каталізатори використовують для виробництва лінійного поліетилену. Приведено методику синтезу гомополімеру етилену з аморфними і кристалічними блоками з використанням бінарної суміші нікелевого каталізатора з α-діімін лігандом для одержання високорозгалуженого поліетилену (м'який ПЕ) і металоцену (рац-етилен-біс(H_4-інден) $ZrCl_2$), який перетворює етилен в поліетилен з високою активністю і температурою плавлення (жорсткий ПЕ). Досліджено вплив температури полімеризації і концентрації РЗП. Визначено характеристики одержаних полімерів.

Ключові слова: полімеризація етилену, каталізатор, суміш каталізаторів, ланцюговий шатл-агент.