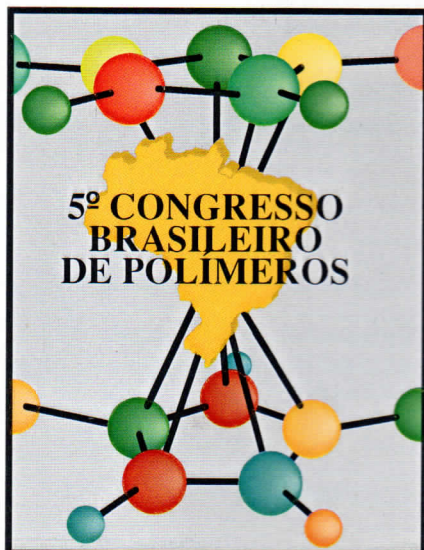


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**TREF AND CRYSTAF ANALYSES OF AN ETHYLENE-1-BUTENE COPOLYMER SYNTHESIZED WITH A HETEROGENEOUS ZIEGLER-NATTA CATALYST**

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Abstract

The distributions of molecular weight (MWD) and chemical composition (CCD) of a linear low-density polyethylene (LLDPE) resin synthesized with a Ziegler-Natta (ZN) catalyst and its fractions were analysed with preparative temperature rising elution fractionation (P-TREF), crystallization analysis fractionation (CRYSTAF), high-temperature gel permeation chromatography (GPC). Differential scanning calorimetry (DSC), ^{13}C nuclear magnetic resonance (^{13}C -NMR), Fourier transform infrared (FT-IR) and gradient density column were used to obtain the structural properties of the samples. These results were used to correlate the multiplicity of active species on the catalyst to the chemical and molecular weight distributions. It will be shown that these fractionation techniques can be powerful tools to understand the behaviour of ZN- type catalysts and the structural properties of the produced resins.

KEY WORDS : TREF, CRYSTAF, FRACTIONATION, CCD, LLDPE, MWD**INTRODUCTION**

It is well known that multiple-site-type heterogeneous Ziegler-Natta catalysts produce polyolefins with broad MWD and CCD. Each site type is characterized by a different set of polymerization kinetic constants, producing polymer chains of different molecular weight and chemical composition averages [1]. The polymer produced with these catalysts is a mixture, at the molecular level, of several chains differing in comonomer content and chain length. Average structural properties are not enough to completely describe catalyst behaviour during polymerization and uniquely determine the final properties of these resins. Therefore, fractionation techniques have been developed to separate polymer fractions according to molecular weight and chemical composition, generating a very detailed microstructural information [2-5]. This investigation combines state-of-the-art characterization techniques to correlate polymer microstructure to the types of active sites present on a heterogeneous Ziegler-Natta catalyst used to copolymerize ethylene and 1-butene.

EXPERIMENTAL**Polymerization**

$\text{TiCl}_3(\text{AA})/\text{MgCl}_2/\text{THF}/\text{SiO}_2/\text{DEAC}(\text{Al}/\text{THF}=0.32)/\text{TnHAL}(\text{Al}/\text{THF}=0.15)$ was used as the catalytic system to produce ethylene-1-butene (EB-01) in a hexane-slurry semi-batch reactor. The polymerization was carried out at

90°C during 1h at an ethylene pressure of 11 bar. Initial monomer/comonomer molar ratio was 0.40 for ethylene-1-butene copolymerizations. TEA (Al/Ti=60) was used during the polymerization.

Polymer Characterization

Gel Permeation Chromatography (GPC)

Molecular weight distributions for the whole resin and its fractions were determined on a Waters 150C gel permeation chromatograph (DV-RI detection) at 140°C in trichlorobenzene (TCB) (HPLC grade with 0,05% BHT) at a flow rate of 1,0 ml/min. Dissolution was carried out at a concentration of 0,1 w/V % at 170°C during 2h or until complete dissolution. Calculation was made according to standards techniques (universal calibration curve using narrow polystyrene standards).

Fourier Transform Infrared Spectroscopy (FT-IR)

Short chain branch contents (CH_3 /1000C) of the whole samples and fractions were determined with a FT-IR spectrometer Nicolet 710 using the absorption at 1378cm^{-1} , related to the symmetric stretch of the methyl group. A calibration curve built with NMR standards was used to quantify the results.

Thermal Analysis

Thermal properties of the sample were determined on a DSC TA 2910 dynamic scanning calorimeter using standards procedures.

^{13}C Nuclear Magnetic Resonance (^{13}C -NMR)

Comonomer content of the sample and its fractions were investigated on a Varian 300 spectrometer at 75 MHz. Sample solutions of the polymer were prepared in ortho-dichlorobenzene (ODCB) and benzene- d_6 (20% v/v). The acquisition was carried out with a flip angle of 75° , 1,5 s of acquisition time and 4,0 s of interpulse delay at temperatures varying between 80 and 110°C , taking in account the melting point of the sample.

Density

Density determinations have been obtained by the Gradient Density Column method. A calibration curve was made with certified glass standards.

Temperature Rising Elution Fractionation (TREF)

P-TREF was used to obtain fractions of narrow short chain branching distribution for further analysis by other techniques. Two-gram polymer sample were dissolved in 200ml of ODCB at 140°C during 1h (an antioxidant, such as BHT, was added to the solution to prevent oxidative degradation) and transferred to a steel column (100 x 20mm ID) packed with inert material (silica) through which ODCB could be pumped. The crystallization step was carried out at a rate of $2^\circ\text{C}/\text{h}$ down to 25°C . The temperature was then increased discontinuously at a rate of $20^\circ\text{C}/\text{h}$ in steps of 5°C up to 140°C . Each fraction was precipitated with excess of methanol, filtered, dried at 80°C during 6h and weighted.

Crystallization Analysis Fractionation (CRYSTAF)

This is a recent technique where the crystallization analysis is carried out by determining the polymer concentration in the solution during the crystallization step. The concentration of the polymer solution is determined on-line by a filter-type IR detector adjusted at a frequency of $3.5\ \mu\text{-m}$. [6-7]

After dissolution (160°C for 1h), the crystallization was carried out by decreasing the temperature at $20^\circ\text{C}/\text{h}$ from 160°C down to 100°C and, after 45 min at this temperature, down to 30°C at $12^\circ\text{C}/\text{h}$. The solvent used was TCB HPLC grade stabilized with Irganox 1010 to avoid oxidative degradation.

RESULTS AND DISCUSSION

Original Samples

Table 1 shows the characterization results for the sample studied. Very good agreement has been found between FT-IR and NMR results. The sample presents typical broad MWD arising from ZN polymerization.

P-TREF was used to separate fractions according to crystallinity as shown in the figure 1. Sample EB-01 has a broad crystallinity profile with 14% of the total mass eluted at temperatures above 90°C, which means that the ethylene-1-butene copolymer has fractions with very low or no comonomer incorporation.

Table 1 - Structural properties of sample EB-01

PROPERTY	RESULT
1-butene mol% by FT-IR	3.5
1-butene mol % by ¹³ C-NMR	3.2
Density (g/ml) 23°C	0.927
Mw (g/mol)	131300
Mn (g/mol)	26100
Mz (g/mol)	574900
MWD	5.03
Tm2 (°C)	124
Tc (°C)	110

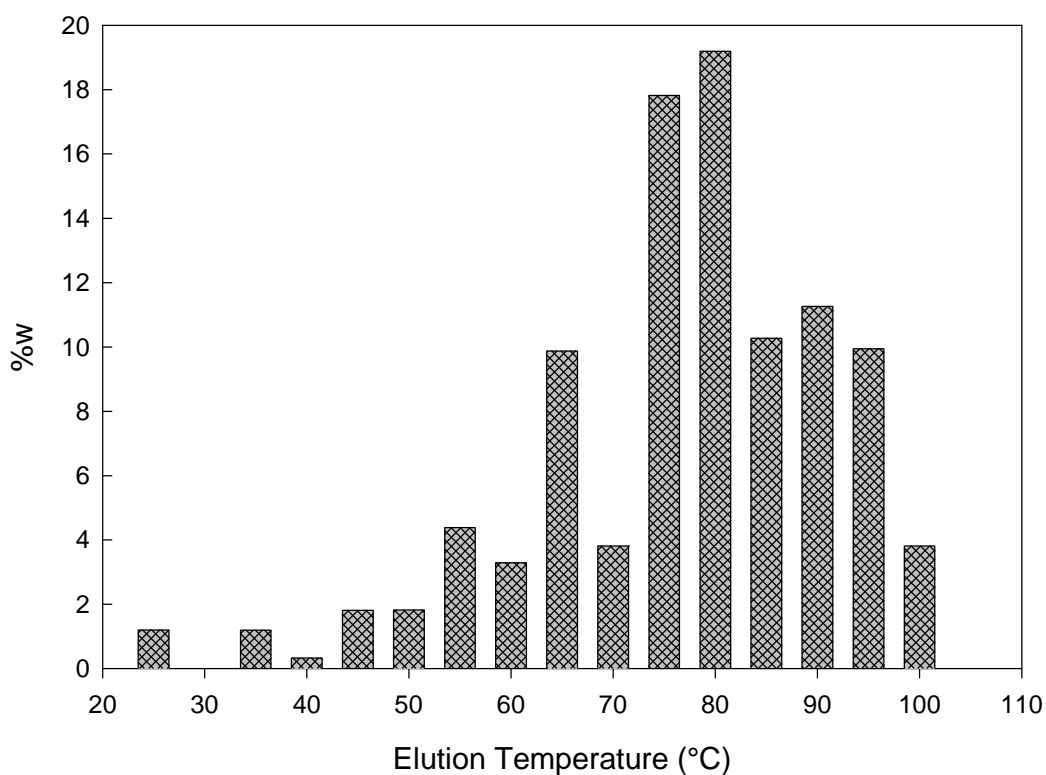


Figure 1 - P-TREF profile of sample EB-01

Crystallization Analysis Fractionation (CRYSTAF) was used to determine the chemical composition distribution for the whole sample. A bimodal distribution (figure 2) was yielded for the resin which presents a sharp peak at high crystallization temperatures. The shape of the CRYSTAF curve is consistent with the P-TREF profile shown in figure 1. As CRYSTAF is measured during crystallization, a shift in the peak temperatures is observed due to supercooling effects. This kind of behaviour has been described elsewhere [6-7]. The area of the rectangular region shown at lower crystallization temperatures of CRYSTAF profiles is proportional to the amount of polymer remaining soluble at that temperature. This is a unique feature of CRYSTAF and provides very important information for the complete understanding of the resins being analyzed.

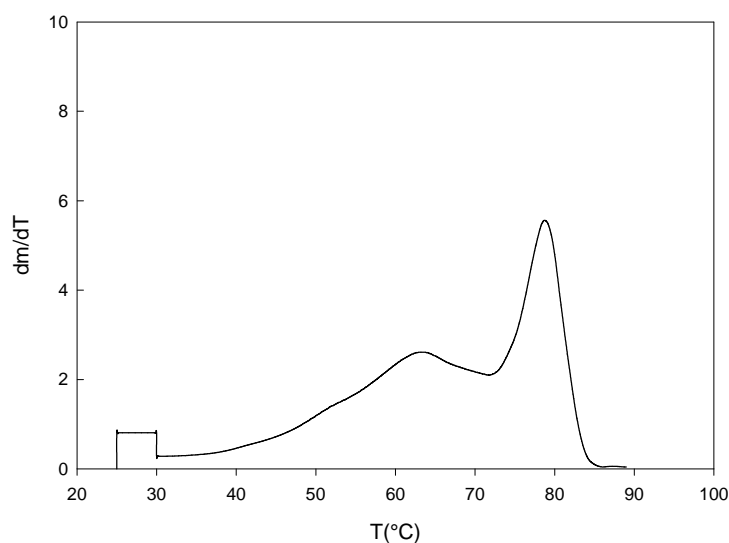


Figure 2 - CRYSTAF profile of sample EB-01

Fractions

Fractions obtained with P-TREF analysis were characterized by GPC, DSC, ¹³C-NMR, FT-IR. The results obtained are shown in the table 2.

Table 2 - Characterization analyses of P-TREF fractions

F N ^o	Te (°C)	1-C4 ⁻ mol % ^(a)	1-C4 ⁻ mol % ^(b)	Tm2 (°C)	Tc (°C)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	MWD
1	25								
2	35	12,0		81	86				
3	40	10,1		85	87				
4	45	8,9	8.1	91	86	8190	58500	225400	7.1
5	50	8,2	6.3	97	88				
6	55	7,1		100	88				
7	60	6,2	5.1	103	91	13200	60900	372700	4.6
8	65	5,4	4.5	106	91				
9	70	4,8		109	97				
10	75	3,8		113	100	23200	68200	178600	2.9
11	80	2,9		117	105				
12	85	2,0	2,2	121	108	32200	89800	249500	2.8
13	90	1,2	0,9	126	112	44800	117300	303200	2.6
14	95	0,5		131	116	62300	152400	39680	2.4
15	100	0,4		133	117				

(a) by FT-IR

(b) by ¹³C-NMR

(c) Te is the elution temperature

The elution temperature increases as the comonomer contents of the fractions decrease as expected. Melting temperatures of the fractions follow the same trend. The relation between elution temperature and comonomer content is given in the figure 3 (calibration curve) which shows the efficiency of 1-butene in decreasing copolymer crystallinity. The figure 4 presents the relation between melting temperature (T_m) and elution temperature measured by P-TREF.

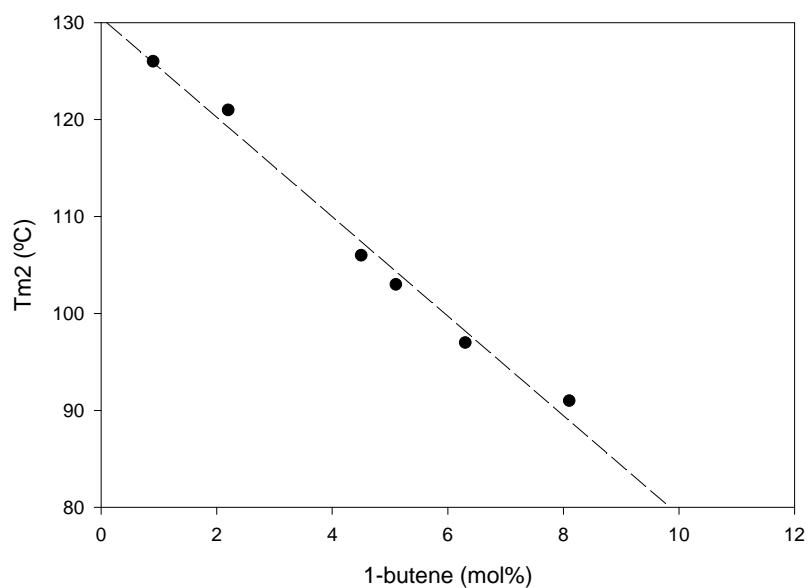


Figure 3 - Relation between Tm2 and comonomer content of P-TREF fractions

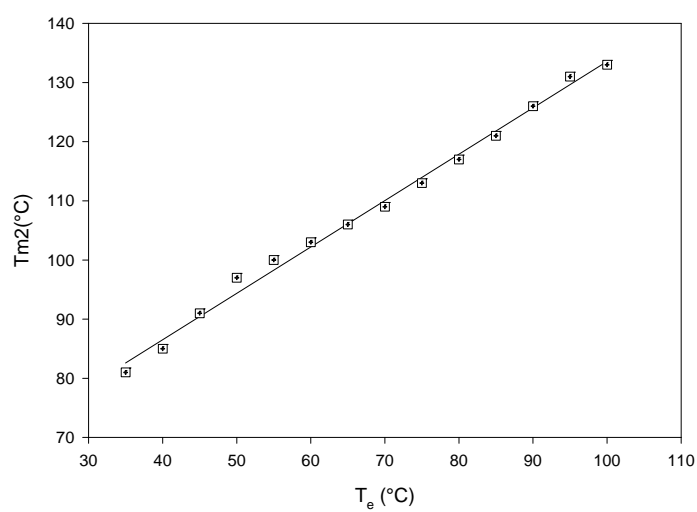


Figure 4 - Relation between Tm2 and the elution temperature of P-TREF fractions

As the elution temperature increases T_m2 also increases. This indicates that the fractionation was carried out according to crystallizability of each fraction or, in other words, according to lamellar thickness developed during the crystallization step [8-9].

The CCD of the P-TREF fractions were analysed by CRYSTAF. The fractions with low comonomer content crystallize first followed by the fractions with increasing amount of comonomer incorporation. A linear correlation between the solution crystallization temperature and comonomer content was found, which can be considered a calibration curve for CRYSTAF. Figure 5 shows these results. As the crystallization temperatures increases (comonomer content decreases), the chemical composition distribution becomes narrower and the MWD tends to a statistical value of 2 or, in other words, the CCD becomes to be defined by just one active site type.

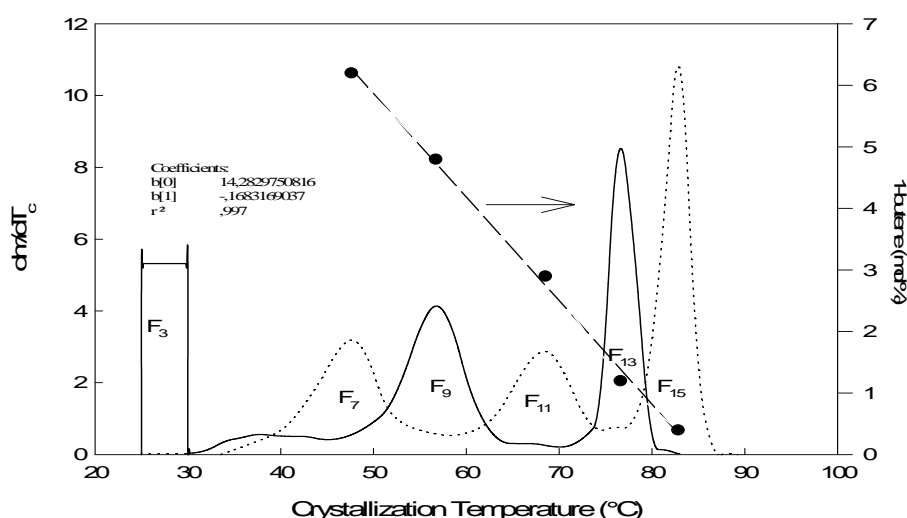


Figure 5 - Relation between solution crystallization temperatures in CRYSTAF analysis and comonomer content of some P-TREF fractions

Obs: Fraction numbers are indicated in each distribution

CONCLUDING REMARKS

A detailed characterization of a poly(ethylene-co-1-butene) sample made with a heterogeneous Ziegler-Natta catalyst was carried out using several analytical and preparative techniques. It was found that fractionation was carried out according to crystallizability of each fraction or, in other words, according to lamellar thickness developed during the crystallization step.

Fractions with higher comonomer content present a broad MWD e CCD . This fact may be related to the to the overlapping of CCD distributions from different site types during the fractionation analysis. Fractions with lower comonomer content present narrow MWD and CCD which means that these distributions may be defined by just one active site type.

A linear curve has been obtained for CRYSTAF analysis which correlates the comonomer content to the solution crystallization temperature.

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REFERENCES

1. J.B.P. Soares and A. E. Hamielec, in *Experimental Methods in Polymer Characterization*, R. A. Pethrick, Ed., John Willey and Sons, 1998, in print
2. F.M. Mirabella and E. Ford, *J. Polym. Sci. Part B: Polym. Phys.*, **25**, 777-790, (1987)
3. S. A. Koroglanian and I.R. Harrison, *Polym. Eng. Sci.*, **36**, 731-736, (1996)
4. J.B.P. Soares and A. E Hamielec, *Polymer*, **36**, (1995)
5. S. Nakano and Y. Goto, *J. Appl. Polym. Sci.*, **26**, 4217-4231, (1981)
6. B. Monrabal, *J. Appl. Polym. Sci.*, **52**, 491-499, (1994)
7. B. Monrabal, *Macromol. Symp.*, **110**, 81-86, (1996)
8. L. Mandelkern, *Prog. Polym. Sci.*, V.2, p.165-200, 1970
9. J. F. Jackson, L. Mandelkern, *Macromolecules*, **1**, 546-554, (1968)