

Study of the Influence of the Reaction Parameters on the Composition of the Metallocene-Catalyzed Ethylene Copolymers Using Temperature Rising Elution Fractionation and ^{13}C Nuclear Magnetic Resonance

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ABSTRACT: Polyethylene copolymers prepared using the metallocene catalyst *rac*-Et[Ind]₂ZrCl₂ were fractionated by preparative Temperature Rising Elution Fractionation (p-TREF) and characterized by ^{13}C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), and gel permeation chromatography (GPC) to study the heterogeneity caused by experimental conditions. Two ethylene–1-hexene copolymers with different 1-hexene content and an ethylene–1-octene copolymer all obtained using low (1.6 bar) ethylene pressure were compared with two ethylene–1-hexene copolymers with different 1-hexene content obtained at high ethylene pressure (7.0 bar). Samples obtained at low ethylene pressure and with low 1-hexene concentration in the reactor presented narrow distributions in composition. Samples prepared with high comonomer concentration in the reactor or with high ethylene pressure showed an heterogeneous composition. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 155–163, 2002; DOI 10.1002/app.10284; DOI 10.1002/app.10284

Key words: ethylene copolymers; Temperature Rising Elution Fractionation; ^{13}C NMR; metallocene catalysts

INTRODUCTION

Studies about metallocene/methylaluminumoxane (MAO) catalytic systems have grown in importance since their discovery in the 1980s.^{1,2} Their significance is specially due to the characteristic of being

single-site catalysts and therefore to the generation of materials of great homogeneity in molecular weight and comonomer distributions. Moreover, recent studies^{3,4} using multiple-step isothermal crystallization treatment and combination of fractionation techniques question this homogeneity.

In previous works,^{5–12} we have studied the synthesis of ethylene- α -olefin copolymers by using different experimental conditions. Differences in differential scanning calorimetry (DSC) thermograms were observed between copolymers ob-

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tained at low (1.6 bar) and high (7.0 bar) ethylene pressure. More than one peak appears for copolymers prepared at higher pressure, suggesting some heterogeneity in these materials.

The study of the heterogeneity, caused by experimental conditions, of ethylene–1-hexene and ethylene–octene copolymers was performed through fractionation by p-TREF (preparative Temperature Rising Elution Fractionation), which is a very powerful technique to enhance the knowledge of molecular heterogeneity in polymers.^{13–16} This technique achieves fractionation on the basis of crystallizability that has been shown to be influenced mainly by comonomer content, degree of tacticity, and monomer sequence length. The elution temperature is only affected by molecular weights lower than 10,000 g/mol, which is below to the range of polymers obtained in this work. The obtained fractions were characterized by ¹³C nuclear magnetic resonance (NMR), DSC, and gel permeation chromatography (GPC).

EXPERIMENTAL

Polymerization

All polymerizations were carried out under an inert atmosphere. Toluene and comonomers (1-hexene and 1-octene) were refluxed over metallic Na and freshly distilled under argon. Polymerization grade ethylene was dried by passing through a 4 Å molecular sieve column. *rac*-Et[Ind]₂ZrCl₂ catalyst was prepared according to the literature.¹⁷ Polymerizations performed at 1.6 bar were carried in a 1 L glass reactor at 60°C for 30 min. The reagents were introduced in the reactor in the following order: toluene, comonomer, MAO, ethene, and the required amount of catalyst solution. Polymerizations performed at 7.0 bar were carried in a stainless-steel reactor at 65°C for 30 min. The reactor was filled with reagents in the following order: toluene, comonomer, MAO, the catalyst, and ethylene (this must be added the last due to the high pressure used). The [Al]/[Zr] ratio was 1750 and the amount of catalyst was kept constant at 6.3×10^{-6} mol/L in all cases. Reactions were stopped by addition of an acidic methanol solution. Polymers were subsequently filtered, washed with methanol, and dried in vacuum.

All experiments were reproduced until the obtainment of three results of catalytic activity differing in less of 20%.

Polymer Characterization

The p-TREF was used to obtain fractions of narrow short chain branching distribution for further analysis. A 2 g polymer sample was dissolved in 200 mL of *o*-dichlorobenzene (ODCB) at 140°C during 1 h (an antioxidant, such as 2,6-di-*tert*-butyl-4-methylphenol (BHT), was added to the solution to prevent oxidative degradation) and transferred to a steel column (100 × 20 mm ID) packed with inert material (silica) through which ODCB could be pumped. The crystallization step was carried out at a rate of 2°C/h down to 25°C. The temperature was then increased discontinuously at a rate of 20°C/h in steps of 5 up to 140°C. For each fraction, 300 mL of solvent were pumped through the column, at 10 mL/min after allowing 20 min for equilibrium at the elution temperature. Each fraction was precipitated with excess of methanol, filtered, and dried at 80°C during 6 h and weighted.

The ¹³C NMR spectra were obtained at 90 or 120°C depending on the fraction solubility. The equipment used was a Varian Inova 300 operating at 75 MHz. Sample solutions of the polymer were prepared in ODCB and benzene-*d*₆ (20% v/v) in 5 mm sample tubes. The deuterated solvent was used to provide the internal lock signal. The chemical shifts were referenced internally to the sequence $-(CH_2)_n-$, which was taken as 30.00 ppm from Me₄Si. Spectra were taken with a 74° flip angle, an acquisition time of 1.5 s and a delay of 4.0 s. Under these conditions the spectra are 90% quantitative if only carbon atoms that have relaxation times (*T*₁) of 2.0 s or less are taken into account.¹⁸

The triad distributions and compositions of the copolymers were evaluated from the ¹³C NMR spectra following Randall's methodology,¹⁹ using only the backbone carbon integrals that have *T*₁ ≤ 2 s.

The molecular weight of the copolymers was determined by gel permeation chromatography in a Waters 150 CV-plus System, equipped with an optic differential refractometer, 150 C model. A set of three columns, Styragel HT type (HT3, HT4, HT6), was used. The analysis was performed in 1,2,4-trichlorobenzene (TCB) (high performance liquid chromatography grade with 0.05 % BHT) at 140°C and 1.0 mL/min. The columns were calibrated with narrow molar mass distribution standards of polystyrene and polyethylene.

DSC measurements were performed on a Polymer Laboratories DSC instrument under N₂ at

Table I Characteristics of the Unfractionated Polyethylene Copolymers

Sample	Ethylene Pressure	Comonomer	C ^a (¹³ C-NMR)	T _m	X _c ^b (DSC)	M _w	M _w /M _n
G110	1.6	1-Hexene	3.7	106.4	26	21,700	3.0
G69	1.6	1-Octene	3.3	107.5	25	77,650	2.2
G117	1.6	1-Hexene	13.3	102.0	4	85,900	2.5
PSL22	7.0	1-Hexene	5.6	117.5	25	23,500	4.1
PSL19	7.0	1-Hexene	10.7	102.5	5	45,900	3.4
				81.6			
				133.2			
				113.6			
				87.0			

^a Comonomer incorporated.

^b Percent crystallinity.

mosphere. The samples were heated from 40 to 150°C and cooled down to 40°C at a heating/cooling rate of 10°C/min to determine the melting temperature values T_m and the heat of fusion (ΔH_f) were taken from the second heating curve. The degree of crystallinity was calculated from ΔH_f , using the equation $X_c = \Delta H_f \times 100/64.5^{20}$ (ΔH in cal/g).

RESULTS AND DISCUSSION

Five samples of copolymers were studied. Table I shows the characteristics of unfractionated materials.

Samples G110, G117, PSL22, and PSL19 are ethylene–1-hexene copolymers. The first two were obtained at 1.6 bar and the last two at 7.0 bar. To

compare the effect of different comonomers, a sample of ethylene–1-octene copolymer (G69) was also studied. Samples G110 and G69 have very similar comonomer contents (3.7 and 3.3 mol %), which agree with their very similar melting temperatures (106.4 and 107.4°C) and crystallinities (26 and 25%).

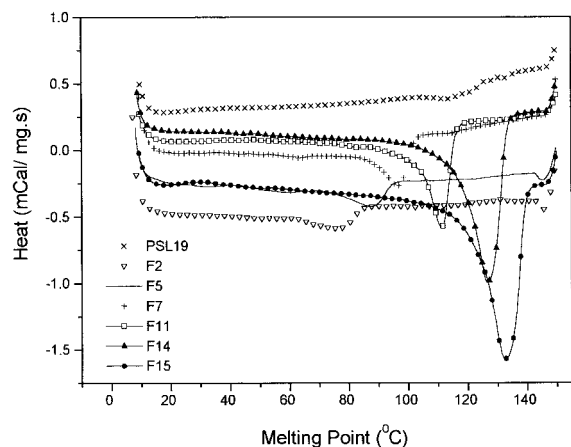


Figure 1 DSC thermograms of sample PSL19 and its fractions.

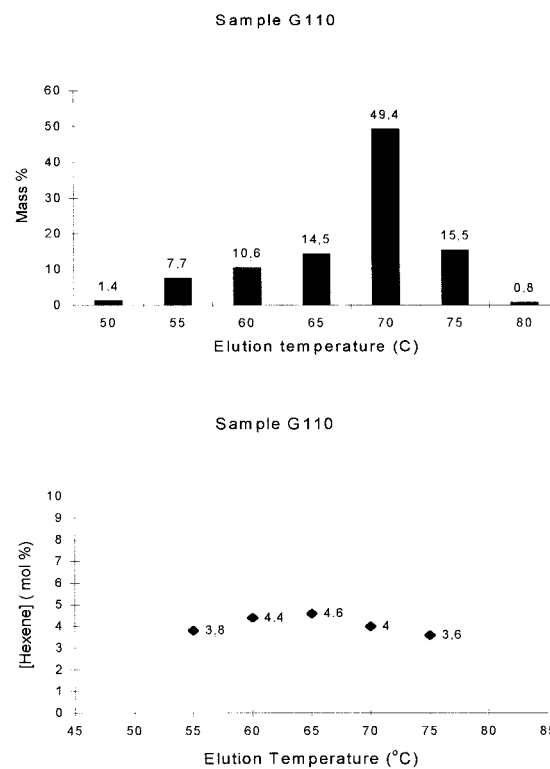


Figure 2 The p-TREF mass and comonomer content distribution of an ethylene–1-hexene copolymer prepared using *rac*-Et[Ind]₂ZrCl₂, [H] = 0.26M in the reactor and an ethylene pressure of 1.6 bar.

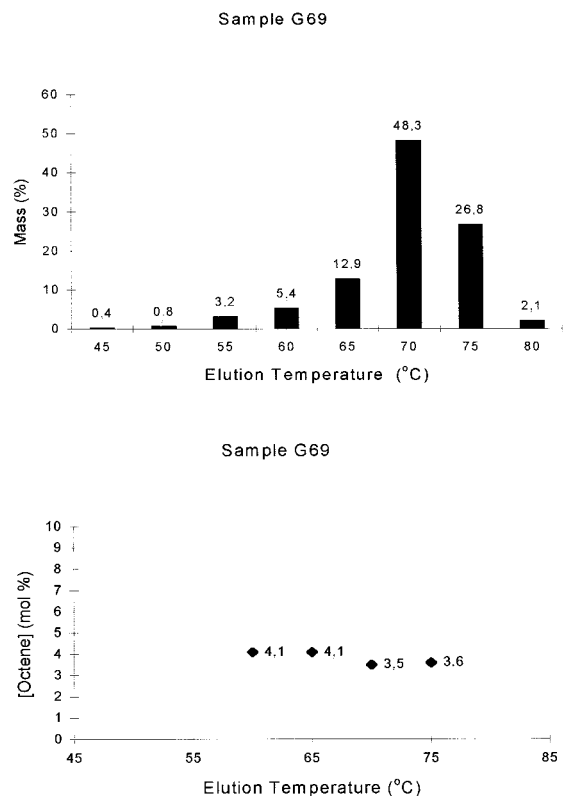


Figure 3 The p-TREF mass and comonomer content distribution of a ethylene-1-octene copolymer prepared using *rac*-Et[Ind]₂ZrCl₂, [H] = 0.21M in the reactor and an ethylene pressure of 1.6 bar.

Sample G117 has a surprising high melting temperature (102.0°C) for an incorporation of 13.3 mol % of 1-hexene.

Samples PSL22 and PSL19 are different in comonomer content (5.6 and 10.7 mol %) and have a slight larger molecular weight distribution (4.1 and 3.4) than the others. DSC thermograms of PSL22 and PSL19 present several peaks as already described in a previous paper¹² and as shown in Figure 1 for sample PSL 19 and its fractions.

All the samples were fractionated by p-TREF and the fractions containing enough material were analyzed by ¹³C NMR, DSC, and GPC.

TREF mass and comonomer content distributions are shown in Figures 2–6. TREF mass distribution of samples G110 and G69 (Figs. 2 and 3) are very similar in spite of being copolymers with different comonomers. Both of them present a fraction at an elution temperature of 70°C, which represents about 50% of the sample. Ninety percent of these samples mass is eluted between 60 and 75°C, which show a very narrow distribution.

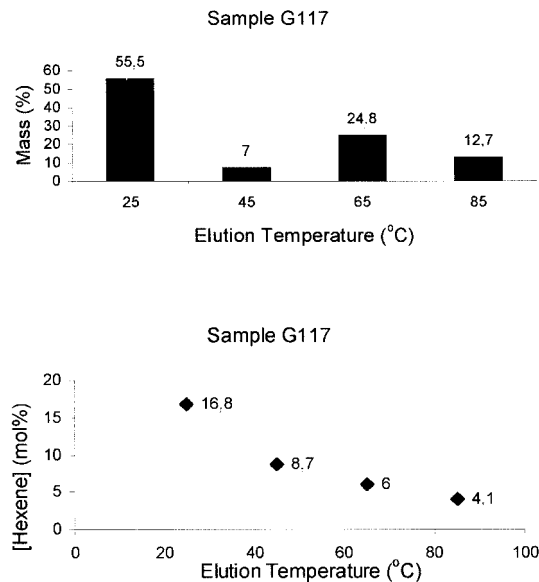


Figure 4 The p-TREF mass and comonomer content distribution of a ethylene-1-hexene copolymer prepared using *rac*-Et[Ind]₂ZrCl₂, [H] = 0.50M in the reactor and an ethylene pressure of 1.6 bar.

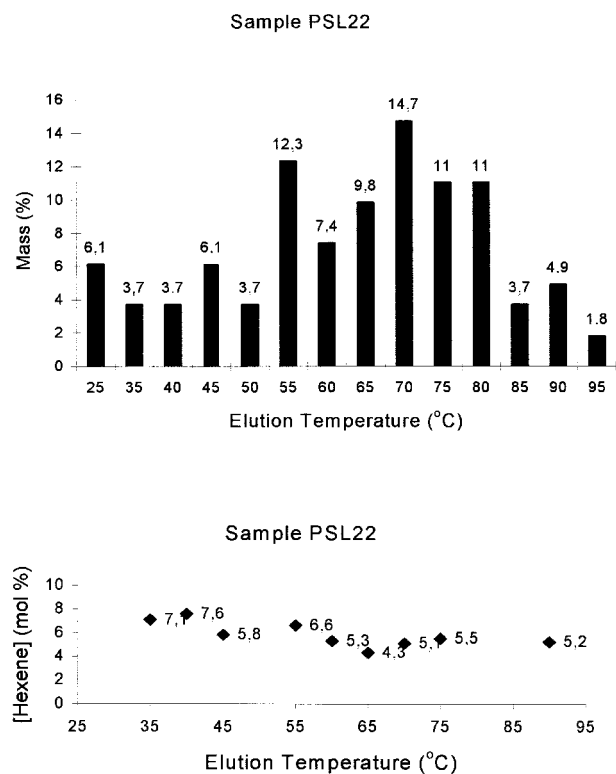


Figure 5 The p-TREF mass and comonomer content distribution of a ethylene-1-hexene copolymer prepared using *rac*-Et[Ind]₂ZrCl₂, [H] = 0.19M in the reactor and an ethylene pressure of 7.0 bar.

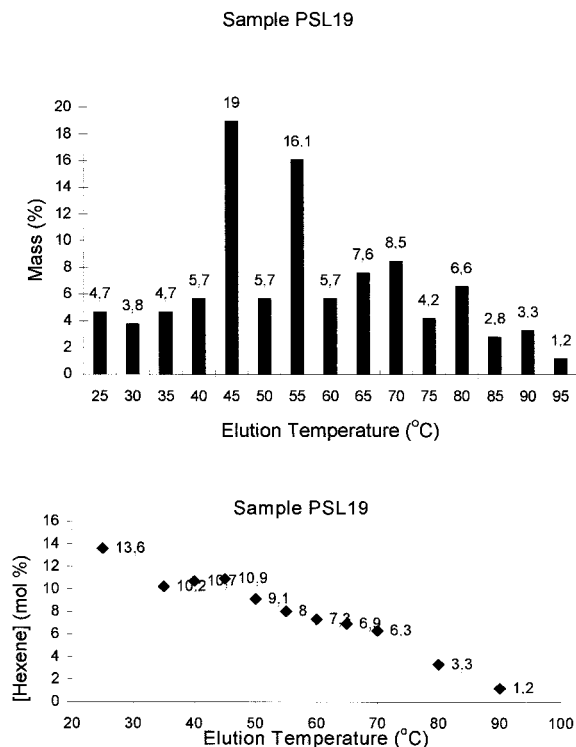


Figure 6 The p-TREF mass and comonomer content distribution of a ethylene-1-hexene copolymer prepared using *rac*-Et[Ind]₂ZrCl₂, [H] = 0.73M in the reactor and an ethylene pressure of 7.0 bar.

Comonomer content in these samples are very close (near 4 mol %) and this value does not vary significantly between fractions showing a very narrow comonomer distribution.

Sample G117 fractions were obtained every 20°C instead of 5°C due to the small amount of the sample available (Fig. 4). In spite of this, a TREF mass distribution slightly larger than the two previous samples can be clearly seen. Anyway, most of this sample (55%) elutes at 25°C

what is due to its high 1-hexene incorporation (16.8 mol %). The most surprisingly fact for this sample is the large comonomer distribution presented, 1-hexene content varies from 4.1 to 16.8 mol %. This distribution is very large for a copolymer obtained with a metallocene catalyst. These results suggest that when low amounts of comonomer (G110 and G69) are used, variations of comonomer in the reactor are not very significant to affect its incorporation. On the other hand, high amounts of comonomer in solution (G117) causes higher incorporations that makes concentration of comonomer in solution to have big variations. At the beginning of the reaction, there would be a high concentration of comonomer in the reactor and at the end this concentration would have lowered and, in consequence, incorporation would lower too. To prove these speculations the α -olefin conversion was calculated and it is shown in Table II. This table shows that for the less incorporated samples (G110 and G69) obtained at low ethylene pressure comonomer, conversion is between 25–30% and for highly incorporate copolymers (G117) and for comonomers obtained at high ethylene pressure (PSL22 and PSL19) conversion is above 50%. The decreasing comonomer concentration during the polymerization reaction would change the reactivity ratios between the two comonomers explaining the heterogeneity of the copolymers.

Figures 5 and 6 show the TREF mass and comonomer distribution of two copolymers obtained at 7.0 bar of ethylene pressure with different comonomer incorporations (5.6 and 10.7 mol %). Both TREF mass distributions are very large. All fractions present less than 19 mass %. Sample PSL22 shows about 60% of its fractions between 55 and 80°C and PSL19 between 45 and 70 °C. This trend is in accord to the higher incorporation

Table II Comonomer Conversion

Sample	Comonomer in Reactor (mol)	Yield of Copolymer (g)	C ^a in Copolymer (mol %)	C ^a in Copolymer (mol)	Comonomer Conversion (%)
G110 ^b	0.08	16.5	3.7	0.02	25.0
G69 ^b	0.065	20.4	3.3	0.02	30.8
G117 ^b	0.31	37.9	13.3	0.14	87.5
PSL22 ^c	0.12	45.0	5.6	0.08	66.7
PSL19 ^c	0.49	86.4	10.7	0.27	55.1

^a C = Comonomer incorporated, 1-hexene for samples G110, G117, PSL22, and PSL19, and 1-octene for sample G69.

^b Toluene = 300 mL.

^c Toluene = 600 mL.

Table III Characteristics of p-TREF Fractions Obtained at 1.6 Bar

Elution Temperature (°C)	Mass (%)	T_m (°C)	X_c (DSC) (%)	M_w (g/mol)	M_w/M_n
Sample E-H G110 P = 1.6 bar					
55	7.7	99.0	26	34100	1.7
60	10.6	101.1	47		
65	14.5	103.0	52	47200	1.6
70	49.4	104.6	48	51500	1.6
75	15.5	108.5	52	48200	1.5
Sample E-O G69 P = 1.6 bar					
55	3.2	100.7	25	23700	2.1
65	12.9	103.4	36	44600	1.5
70	48.3	105.3	25	60700	1.5
75	26.8	108.4	25	54600	1.5
80	2.1	112.5	31	50500	1.5
Sample E-H G117 P = 1.6 bar					
25	55.5	—	—	39400	1.8
45	7.0	89.5	11	51900	2.1
65	24.8	100.3	17	79100	1.8
85	12.7	108.9	18	77300	1.6

of the last one. Comonomer incorporation in PSL22 is between 4 and 7 mol % and in PSL19 from 1.2 to 13.6 mol %. As it was commented for the previous samples obtained at ethylene pressure of 1.6 bar, the highest incorporated sample (PSL19) has the larger comonomer distribution and this behavior seems to be generally independent of the ethylene pressure used. The effect of a higher ethylene pressure is to increase the heterogeneity of copolymer chains.

Table III and Table IV show the characteristics

of TREF fractions obtained at 1.6 bar and 7.0 bar respectively.

Table III shows that G110 melting temperature fractions vary only about 8°C from 100 to 108°C between elution temperatures from 60 to 75°C. This behavior in which melting temperatures and crystallinity increase with the increase of elution temperature is expected as TREF is based in differences of crystallinity. Molecular weight has also a tendency to increase with elution temperature. Sample G69 shows a similar

Table IV Characteristics of TREF Fractions Obtained at 7.0 Bar

Elution Temperature (°C)	Mass (%)	T_m (°C)	X_c (DSC) (%)	M_w (g/mol)	M_w/M_n
Sample E-H PLS22 P = 7.0 bar					
25	6.1			17100	2.3
50	3.7	96.3	27	31000	2.3
70	14.7	106.9	28	67500	2.4
80	11.0			66400	1.9
85	3.7			89500	1.9
95	1.8	130.0	56		
Sample E-H PSL19 P = 7.0 bar					
30	3.8	76.1	8	44000	1.9
45	19.0	87.5	5	55600	1.9
55	16.1	96.6	10	62500	2.7
75	4.2	111.2	28	79000	1.8
90	3.3	126.6	69	80200	2.4
95	1.2	132.7	72	127900	2.4

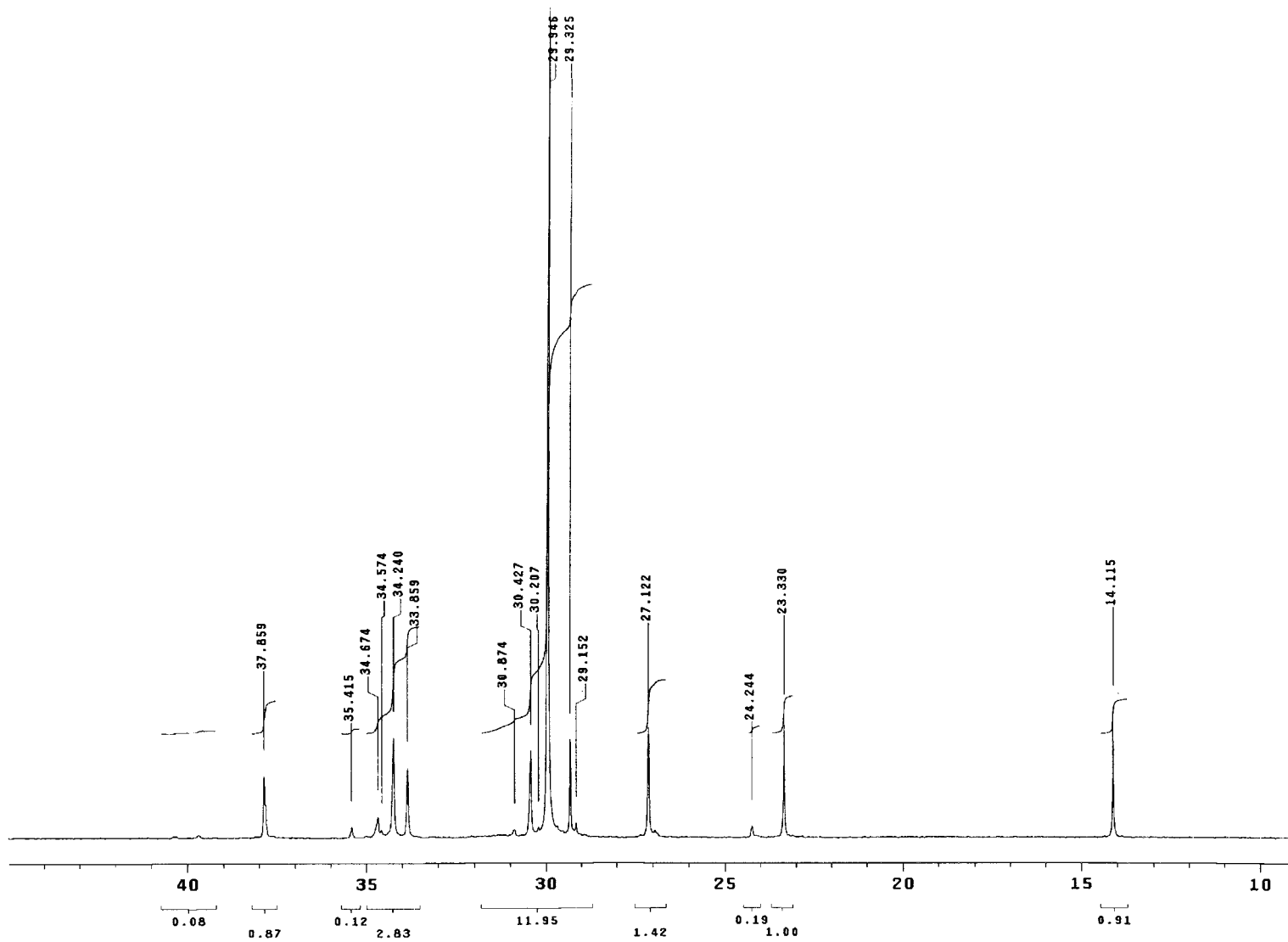


Figure 7 ^{13}C NMR spectrum of sample G117 (unfractionated copolymer).

Table V Copolymer Triads and Ethylene Average Sequence Length Obtained by ^{13}C NMR

Elution Temperature ($^{\circ}\text{C}$)	[H] mol %	[HHH] mol %	[EHH] mol %	[EHE] mol %	[EEE] mol %	[HEH] mol %	[HEE] mol %	n_E
G110								
55	3.8	0	0	3.8	88.5	0	7.7	25
60	4.4	0	0	4.4	86.7	0	8.9	22
65	4.6	0	0	4.6	86.2	0	9.2	21
70	4.0	0	0	4.0	88.1	0	8.0	24
75	3.6	0	0	3.6	89.3	0	7.2	25
G117								
25	16.8	2.8	2.1	11.9	56.2	3.1	23.9	6
45	8.7	0	0.7	8.0	75.2	0	16.1	11
65	6.0	0	0.2	5.7	81.7	0.9	11.5	15
85	4.1	0	0	4.1	87.6	0	8.3	23
PSL22								
35	7.1	0	0	7.1	77.5	1.3	14.1	12
40	7.6	0	0.4	7.2	77.3	0.8	14.3	12
45	5.8	0	0	5.8	80.6	2.1	11.5	14
55	6.6	0	0	6.6	80.3	0	13.1	14
60	5.3	0	0	5.3	84.2	0	10.5	18
65	4.3	0	0	4.3	87.2	0	8.6	22
70	5.1	0	0	5.1	84.6	0	10.3	24
75	5.5	0	0	5.5	83.5	0	11.0	17
90	5.2	0	0	5.2	84.4	0	10.4	18
PSL19								
25	13.6	0	2.1	11.5	60.5	2.9	23.0	6
35	10.2	0	0	10.2	69.4	0	20.4	9
40	10.7	0	0	10.7	67.8	0	21.4	8
45	10.9	0	2.1	8.8	68.8	2.7	17.6	8
50	9.1	0	1.2	7.9	75.1	0	15.8	11
55	8.0	0	0	8.0	75.9	0	16.1	11
60	7.3	0	0	7.3	78.0	0	14.7	13
65	6.9	0	0	6.9	79.4	0	13.7	14
70	6.3	0	0	6.3	83.5	0	10.2	17
80	3.3	0	0	3.3	89.8	0	6.7	27
90	1.2	0	0	1.2	97.1	0	1.7	106
G69								
60	4.1	0	0	4.1	87.6	0	8.3	23
65	4.1	0	0	4.1	87.8	0	8.1	24
70	3.5	0	0	3.5	89.5	0	7.0	28
75	3.6	0	0	3.6	89.1	0	7.3	26
G69								
60	4.1	0	0	4.1	87.6	0	8.3	23
65	4.1	0	0	4.1	87.8	0	8.1	24
70	3.5	0	0	3.5	89.5	0	7.0	28
75	3.6	0	0	3.6	89.1	0	7.3	26

behavior. Sample G117 has a larger variation of melting temperature between fractions. The main fraction eluted at 25°C is completely amorphous and melting temperature variations between the other fractions are of about 20°C . The unusual high melting point (102.0°C) detected for the unfractionated sample is explained by the fact that the main fraction corresponding to the most incorporated one is completely amorphous and melting

point correspond only to the less incorporated crystalline fractions.

Table IV shows melting temperatures, crystallinity, and molecular weights of PSL22 and PSL19 samples. Variation in melting temperature and crystallinity are according to the comonomer incorporation. As TREF is based on fractionation by crystallinity, the higher eluted temperatures give fractions with less comonomer

incorporated, with higher crystallinity and melting temperatures. Molecular weights increase with eluted temperatures.

Copolymer compositions, triad sequences, and ethylene number average sequence length (n_E) have been obtained from ^{13}C NMR spectra. The ^{13}C NMR spectrum of sample G117 is shown in Figure 7.

Table V shows copolymers triad sequences. In the case of samples G110 and G69 of low comonomer incorporation, 1-hexene and 1-octene units are isolated between ethylene sequences. Ethylene number average sequence length (n_E), presented in the last column of this table, remains almost constant showing a very uniform distribution. For all these analysis it can be concluded that these two samples are highly homogeneous which is expected for copolymers obtained with metallocenes.

In the case of samples G117, PSL22, and PSL19, as they are more incorporated in the comonomer, there is some amount of triads [HEH] and [EHH] in some fractions. This behavior corresponds to a random distribution of comonomers as it is expected for copolymers obtained with metallocene catalysts. However, the ethylene number average sequence length varies significantly for these fractions, confirming the heterogeneity of the comonomer distribution.

CONCLUSIONS

Inhomogeneity in copolymers obtained with metallocenes as the *rac*-Et[Ind]₂ZrCl₂ can be attributed to experimental conditions. The use of liquid comonomers such as 1-hexene and 1-octene, added to the reactor at the beginning of the reaction is the most common way of copolymerization in research works, however this way of addition can produce a large comonomer distribution for high concentrations of comonomers. This heterogeneity is expected for high conversions as comonomer concentration varies during the reaction, but this work showed that the comonomer distribution can be surprisingly high. To have an homogeneous copolymer, all monomers should be added in a continuous way, especially for high comonomer conversions. The use of high ethylene pressures enhances the polymerization rate increasing reaction productivity with the consequences of poor control in reaction temperature and diffusion problems due to a high polymer concentration in the reactor. All these facts conduce to a more heterogeneous copolymer with consequences on its properties.

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