

Structural Evaluation of Copolymers of Ethylene and 1-Octadecene by Using the Temperature Rising Elution Fractionation Technique

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ABSTRACT: Three samples of ethylene-octadecene copolymers having different quantitative composition were analyzed structurally and in terms of their thermal behavior. The samples were fractionated by temperature rising elution fractionation, presenting different chemical composition distributions (CCD) that are essentially the result of the proportion of incorporated octadecene. The CCD profiles were relatively wide for samples generated by metallocene catalysts. The analyses of the fractions showed that the melting and crystallization temperatures decrease with increasing comonomer incorporation, but this relation is affected by the average molecular weight of the chains. The melting thermograms of those fractions having higher proportions of octadecene may be divided into two characteristic regions: the first one, at a higher temperature, originates from the melting of the least modified chains, which crystallize more perfectly. The second one is formed by the melting of chains having a high degree of comonomer incorporation, which melt in a diffuse manner over a wide range of temperatures. It is probable that the morphology of the crystals formed in this region does not follow the folded chain model, and are better represented by a model involving the alignment of chain segments (bundling). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 221–227, 2001

Key words: copolymers; ethylene-1-octadecene; temperature rising elution fractionation; chemical composition distribution; fractionation

INTRODUCTION

The copolymerization of ethene with α -olefins such as 1-butene, 1-hexene, and 1-octene with

both Ziegler–Natta catalysts as well as with metallocene catalysts is widely described in the literature and is covered by various industrial patents. However, at present, copolymerization using heavier olefins such as 1-octadecene and metallocene catalysts may be considered exploratory. In a recent work it has been synthesized and characterized ethene-1-octadecene copolymers with a metallocene catalyst.¹ In principle,

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homogeneous catalysis would give rise to resins having narrow molecular weight distributions and equivalent composition in intra- and intermolecular terms.

It is particularly interesting to evaluate the effect of the incorporation of relatively long chains to the main chain on the morphology and thermal properties of these copolymers.

EXPERIMENTAL

Three samples of ethylene-octadecene copolymers, prepared at the Universidad de Chile in Santiago, originally designated as ANE-011, ANE-022, and ANE-051, were evaluated in this study. The samples were characterized by Fourier transform infrared (FTIR), differential scanning calorimetry (DSC) and gas permeation chromatography (GPC). Samples ANE-011 and ANE-051 were studied by analytical temperature rising elution fractionation (TREF) to evaluate their chemical composition distribution (CCD). Sample ANE-051 was analyzed by preparative TREF to study in detail the CCD of the fractions produced. Some selected fractions were analyzed by ^{13}C -NMR and by GPC.

TREF is a technique used for evaluating the CCD of polyolefins, because it separates polymer fractions according to crystallizability, or in other words, according to lamellar thickness developed during the solution crystallization step.^{2,3} The lamellar thickness is correlated to the crystallizable average sequence length of each polymer fraction and, for linear low density polyethylene resins, it is mainly dependent on ethylene average sequence length as a function of comonomer content or branching frequency.^{4,5} In preparative TREF (p-TREF) the fractions of the sample dissolved in *o*-dichlorobenzene crystallize by lowering the temperature at a rate of 2°C/h. In the next stage, the crystallized fractions are eluted according to a temperature gradient, i.e., as the temperature increases, the fractions having a higher crystalline content are eluted. The fractions eluted at predetermined temperatures are collected and analyzed separately. Analytical TREF (a-TREF) basically differs from p-TREF by its higher response rate and because it does not allow fractions to be collected for further analyses.

The ^{13}C -NMR spectra were obtained at 85–90°C. The equipment used was a Varian Inova 300 operating at 75 MHz. Sample solutions of the polymer were prepared in *o*-dichlorobenzene and benzene- d_6 (20% v/v) in a 5 mm sample tube.

Spectra were taken with a 74°C flip angle, an acquisition time of 1.5 s and a delay of 4.0 s. T_{br} , $S_{\beta\delta}$, and C_{15} carbon integrals were used to calculate the proportion of C18 carbons and $S_{\delta\delta}$ the proportion of ethylene carbons.

From the data generated by ^{13}C -NMR for ethylene-octadecene samples of different composition, a calibration curve was made for determining the proportion of octadecene by FTIR. Therefore, a specific method was developed in which the proportion of methyl groups is converted into hexadecyl groups, using the absorptivity coefficient characteristic of these branches.

A Nicolet 710 infrared spectrophotometer (FTIR) was used to obtain transmission spectra of thin films made with the TREF fractions. The integrated absorbance methyl symmetric deformation band at approximately 1378 cm^{-1} was measured, after a subtraction with a ultrahigh molecular weight polyethylene standard, in the same spectral range.

This methodology, which is simpler than solution ^{13}C -NMR analysis, has proved to be very efficient when applied to the determination of short chain branches such as ethyl, butyl, and hexyl ones. Furthermore, since the method is very simple and fast, a large number of samples could be analyzed.

The average molecular weights and molecular weight distributions of the whole samples and their TREF fractions were determined by using a Waters 150C gel permeation chromatograph (DV-RI detection) with a set of mixed-type columns at 140°C. Trichlorobenzene (high performance liquid chromatography grade with 0.05% w/w BHT) was used as the mobile phase at a flow rate of 1.0 mL/min. Dissolution was carried out at a concentration of 0.1 w/v % at 170°C for 2.0 h or until complete dissolution was achieved. The universal calibration curve built with narrow polystyrene standards was used to calculate the data. The use of differential viscometric detection allowed the corrections for the differences in intrinsic viscosity due to the presence of the relatively long side branches.

Crystallinity, melting, and crystallization temperature measurements were made on a TA Instruments model 2910 DSC. Each sample was heated from 30 to 150°C, at a rate of 10°C/min, remaining at the final temperature for 5 min. The sample was then cooled down to –50°C, at a rate of 10°C/min, and reheated up to 150°C at the same rate. The melting temperature values given in this paper refer to the second heating curve. The crystallinity was calculated using as refer-

Table I Structural Characteristics and Thermal Properties^a

Sample	ANE-011	ANE-022	ANE-051
CH ₃ /1000 C	2	11	26
C ₁₈ H ₃₆ (mol%)	1.1	2.4	5.7
<i>T</i> _m (°C)	120	112	14/88
<i>T</i> _c (°C)	108	99	72
Δ <i>H</i> _f (J/g)	149	105	76
<i>M</i> _w (g/mol)	133600	128600	124500
<i>M</i> _n (g/mol)	37200	42800	41000
<i>M</i> _w / <i>M</i> _n	3.6	3.0	3.0
[η] (dL/g)	1.94	1.74	1.28

^a *T*_c and *T*_m: crystallization and melting temperature. Δ*H*: melting enthalpy. *M*_n and *M*_w: number and weight average molecular weight. MWD: molecular weight distribution determined by GPC as the *M*_w/*M*_n ratio. CH₃/1000 C was determined by FTIR and C₁₈H₃₆ (mol %) was determined ¹³C NMR.

ence the value of 286.18 J/g for the enthalpy of fusion of an ideal polyethylene standard having 100% crystallinity.

RESULTS AND DISCUSSION

Evaluation of the Original Samples

Table I shows the sample composition data and thermal properties of the original samples.

One of the consequences of the effect of incorporating relatively long side chains (hexadecyl) in the copolymers may be seen when the relations between the values of *M*_w and intrinsic viscosity

are compared for samples ANE-051 and ANE-011, which have different degrees of octadecene incorporation. The intrinsic viscosity of sample ANE-051 is lower than that of sample ANE-011, yet their *M*_w values are similar. The existence of a high concentration of hexadecyl groups causes a reduction of the hydrodynamic volume of the copolymer molecules in solution. This effect is also seen in the case of low density polyethylene.

The three samples have different degrees of comonomer incorporation. Sample ANE-011 can be considered as a homopolymeric polyethylene. The degree of chain modification generating side groups determines an increasing lowering of the transition temperatures and of the heat of fusion. This is the expected behavior for ethene- α -olefin copolymers.^{6,7} In this respect, the melting thermograms of samples ANE-011 and ANE-022 are typical. In contrast, the thermogram of sample ANE-051 shows an intense heterogeneity. The sample melts over a broad range of temperatures, reflecting a large lamellar thickness distribution. The lack of definition of a main melting temperature indicates a poor crystallite morphology caused by the intense disrupting effect of hexadecyl groups, present in a large amount. In order to have further elements available for the interpretation of this complex crystallization pattern, it was decided to fractionate the sample and analyze the fractions in detail.

All the three samples have molecular weight distributions relatively high for metallocene samples.

Figure 1 shows the superposition of the melt-

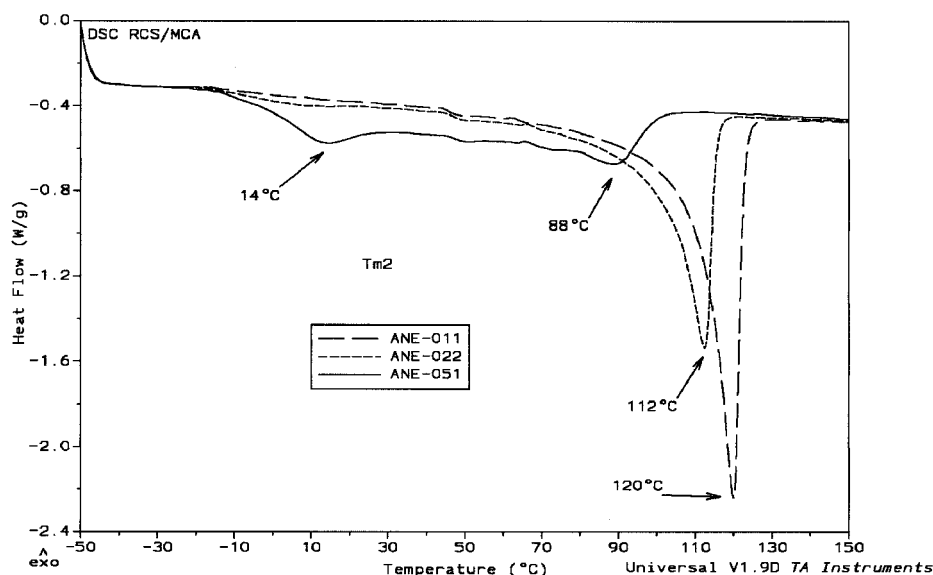


Figure 1 Superposition of the melting thermograms of the original samples.

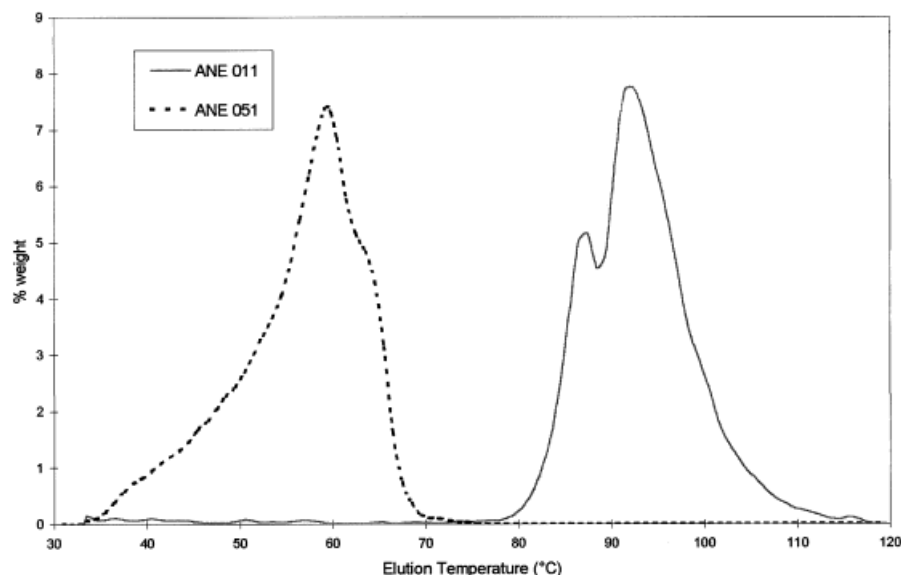


Figure 2 Chemical composition distribution profiles generated by a-TREF.

ing thermograms of the three ethylene-octadecene samples having increasing comonomer proportions.

Fractionation of the Original Resins and Analysis of the Fractions

Figure 2 shows the superposition of the chemical composition distribution profiles of samples ANE-011 and ANE-051 generated by a-TREF.

The less modified sample ANE-011 has its CCD displaced toward higher elution temperatures, showing some heterogeneity expressed by the presence of two maxima, which is not characteristic of metallocene resins. On the other hand, sample ANE-051, which has a higher comonomer content, shows a CCD that covers a relatively wide range of lower temperatures. Although the net temperature ranges of the CCD of samples ANE-011 and ANE-051 are similar, the maximum of the latter corresponds to a lower temperature, as a consequence of the higher degree of chain branches. That effect is confirmed by the DSC endotherm of sample ANE-051, which shows a large crystalline distribution and low crystalline content.

The heterogeneity found in the case of sample ANE-051 is not comparable to that of resins obtained with Ziegler–Natta catalytic systems.⁸ Figure 2 shows that sample ANE-051 has practically no fractions with extremely low proportions of octadecene incorporation, or homopolymeric fractions, i.e., that there was insertion of comono-

mer in almost the totality of the chains, though in variable proportions.

Figure 3 shows a CCD diagram of resin ANE-051 obtained by p-TREF. This diagram can be considered in agreement with the one obtained by a-TREF, taking in account the less quantitative nature of the p-TREF measurements compared to a-TREF. The distribution shows that there is a blend of polymer chains with different degrees of comonomer incorporation, with a predominance of those having octadecene concentrations of about 5.5 mole %.

The fractions obtained from the p-TREF were analyzed in terms of their composition and thermal properties. The results are shown in Table II.

Table II shows that even though there is a trend to lower transition temperatures and crystallinity with increasing proportions of comonomer, that behavior is irregular. The crystallization and melting thermograms of the fractions presented in Figure 4 show some heterogeneity in composition for samples produced by metallocene catalysts.⁸ The thermograms of the fractions having higher comonomer contents can be divided into two regions: one determined by the main melting peak, and another one, including a diffuse endotherm, covering a wide temperature range. The crystallization exotherms follow the same pattern. That melting behavior may point to a second crystallization model determined by the presence of relatively long branches. This characteristic is more pronounced in fraction 1, in which

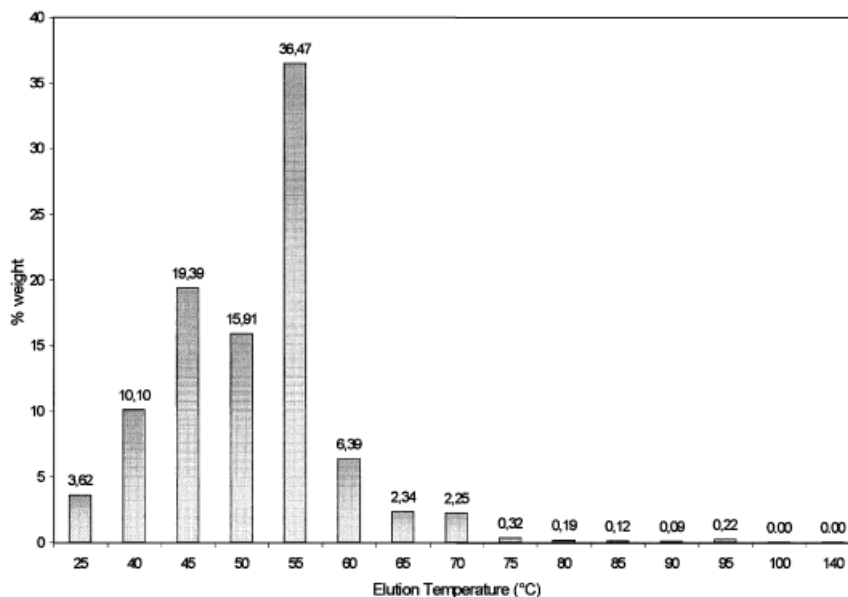


Figure 3 CCD profile of sample ANE-051 obtained by p-TREF.

the proportion of octadecene is higher. That trend had already been observed in the analysis of fractions of copolymers of ethylene with other smaller α -olefins, but present in higher concentrations. It is possible that beyond a certain concentration of branches, crystallization does no longer follow the pattern of lamellae formation (chain folding), and is better represented by a model involving the alignment of chain segments (bundling).⁹ That critical concentration appears to be lower in the case of larger branches such as hexadecyl groups. In this possible crystal structure there would be a greater distribution of crystals having different degrees of perfection that would melt over a wide temperature range.

Furthermore, in Table II it is seen that the heats of fusion of the fractions determined by

DSC, which may be related to crystallinity, oscillate. It is necessary to take into account that the crystallization mechanism occurring during the fractionation by TREF, crystallization in solution, is different from the one that occurs during crystallization by cooling from the molten state, as in the case of DSC. In the latter, the influence of molecular weight on the viscosity of the medium, and therefore on the mobility of the chains, must be considered. Thus, the crystallinity determined by DSC for the fraction may not be equivalent to that produced during the slow process of crystallization from solution by TREF, which is responsible for the separation of the resin into various fractions.

Table III shows average molecular weight data for some of the fractions of resin ANE-051. It is

Table II Characteristics of the Fractions from Sample ANE-051^a

Sample	T_e (°C)	CH ₃ /1000 C	C ₁₈ (mol%)	T_m (°C)	T_c (°C)	ΔH_f (J/g)
Fraction 1	25	39	7.8	24/48	17/62	95
Fraction 2	40	30	5.9	83	66	111
Fraction 3	45	29	5.8	87	67	103
Fraction 4	50	28	5.5	89	70	105
Fraction 5	55	28	5.5	92	75	106
Fraction 6	60	27	5.4	94	78	103
Fraction 7	65	26	5.2	103	88	101

^a T_e = elution temperature; T_m = melting temperature; T_c = crystallization temperature. CH₃/1000 C and C₁₈H₃₆ (mol %) were determined by FTIR using a calibration curve obtained by ¹³C NMR.

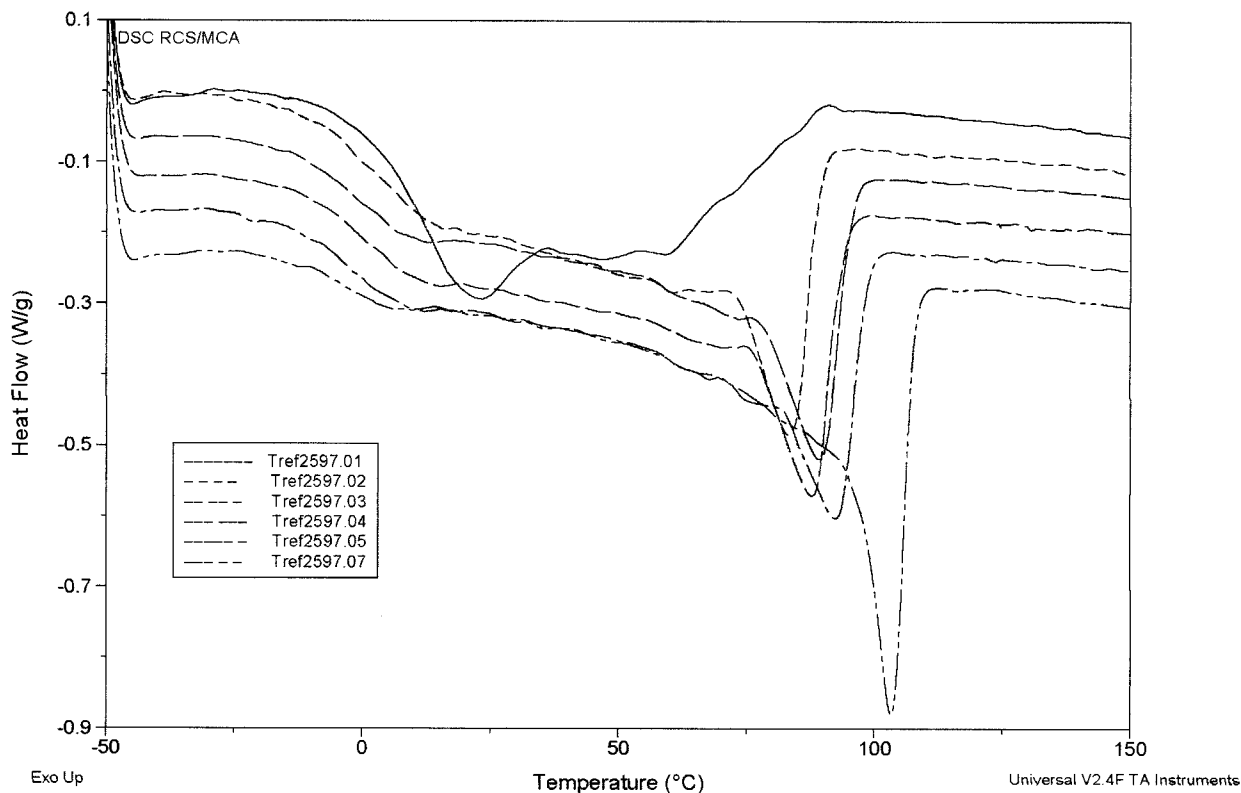


Figure 4 Superposition of the melting thermograms of p-TREF fractions of sample ANE-051.

seen that the chains that are more highly modified by octadecene are those of lower molecular weight. This is probably due to the greater occurrence of chain transfer to comonomer.¹⁰ Even if there are variations in the average dimensions of the chains, the average molecular weight distribution is approximately constant, which is characteristic of metallocene resins.

On the other hand, the data in Table III show that the melting temperature of the fractions decreases with an increasing proportion of branching of the chains. In the case of the ethene-octadecene copolymers, this is due to a disturbance of the crystalline morphology, with the exclusion of the hexa-

decyl branching of the lamellae, and a consequent reduction of the latter's thickness. Meanwhile, the intensity of the decreasing is affected by the molecular weight of the molecular chains. The crystallization of the longer chains is more difficult than that of the smaller chains due to the existence of a greater degree of entanglement and to their lower mobility, as a function of the increasing viscosity of the medium, as the melt is cooled under typical DSC conditions¹¹ (cooling from the molten state). Therefore, the thermal behavior is determined essentially by the chemical composition of the chains, i.e., by the degree of comonomer incorporation and secondarily by the molecular weight.

Table III Average Molecular Weights of Fractions of Sample ANE-051^a

Sample	C ₁₈ H ₃₆ (mol %)	<i>T_m</i> (°C)	<i>M_w</i> (g/mol)	<i>M_n</i> (g/mol)	<i>M_w/M_n</i>
Fraction 2	5.9	83	57200	32300	1.8
Fraction 4	5.5	89	133400	73100	1.8
Fraction 5	5.5	92	133800	79200	1.7
Fraction 6	5.4	94	143500	79700	1.8

^a *M_w*: weight-average molecular mass; *M_n*: number-average molecular mass.

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REFERENCES

1. Quijada, R.; Narvaez, A.; Rojas, R.; Rabagliati, F. M.; Galland, G. B.; Mauler, R. S.; Benavente, R.; Perez, E.; Pereña, J. M.; Bello, A. *Macromol Chem Phys* 1999, 200, 1306.
2. Soares, J. B. P.; Hamielec, A. E. *Polymer* 1995, 36, 1639.
3. Wild, L.; Ryle, *Adv Polym Sci* 1990, 98, 1.
4. Mandelkern, L. *Prog Polym Sci* 1970, 2, 165.
5. Jackson, J. F.; Mandelkern, L. *Macromolecules* 1968, 1, 554.
6. Wilfong, D. L. *J Polym Sci Part B Polym Phys* 1990, 28, 861.
7. Defoor, F.; Groeninckx, G.; Van der Heijden, P.; Shouterden, H. Reynaers, *Macromolecules* 1993, 26, 2575.
8. Mingozzi, I.; Nascetti, S. *J Polym Anal Charact* 1996, 3, 59.
9. Hwang, Y.; Chum, S. R.; Guerra, R.; Sehanobish, K. ANTEC'94 1994, 3414.
10. Quijada, R.; Dupont, J.; Miranda, M. S. L.; Scipioni, R. B.; Galland, G. B. *Macromol Chem Phys* 1995, 196, 3991.
11. Alamo, R. G.; Viers, B. D.; Mandelkern, L. *Macromolecules* 1992, 24, 6382.