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A Quantitative Evaluation of Chemical Composition Distribution in Linear Low-Density Polyethylenes by Differential Scanning Calorimetry

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The chemical composition distribution (CCD) of 1-butene comonomer in linear low-density polyethylene (LLDPE) has been studied by means of thermal analysis. After an appropriate thermal treatment of the polymers using thermal fractionated crystallization, the melting endotherms were subdivided into zones with fixed temperature ranges. The distribution of the endotherms in the different zones permitted the calculation of a composition index that gave a quantitative estimate of the CCD based on a calibration curve. Three LLDPEs and their fractions, having a significantly different CCD, have been tested using this method. A comparison with another thermal method is also discussed.

KEY WORDS Differential scanning calorimetry, linear low density analysis, chemical comonomer distribution, thermal fractionated crystallization.

INTRODUCTION

Physical and mechanical properties of polyethylene can be modified by the copolymerization of ethylene with 1-olefins such as 1-butene, 1-pentene, and so on, [1] to obtain linear low-density polyethylene (LLDPE). It should be emphasized that by changing the chemical composition distribution (CCD) with the same 1-olefin type and content, the physical-mechanical behavior of the copolymer can be significantly changed [2]. Therefore for a detailed characterization of LLDPEs it is very important to obtain information concerning the CCD. Many techniques can be applied to study the CCD; the simplest one is IR analysis of 1-olefin content as a function of the absolute density, melting point, and soluble fraction of the polymer [3]. This information, however, is limited because the results only represent the average comonomer distribution. More detailed information can be obtained by the coupling of thermal rising elution fractionation (TREF) and IR or NMR analysis on the fraction [4, 5]. With this method, the polymer fractions are sepa-

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rated according to different ethylene sequence length between the insertion of two 1-olefins and consequently to different comonomer content [5]. The most complete picture of the copolymer is obtained by the analysis of 1-olefin on cross-fractionated samples. In this way the polymer is divided both on molecular mass and chemical composition [6]. All these procedures, however, are time consuming, limiting the number of samples which can be analyzed. Thus a faster evaluation of CCD is requested, especially for routine analysis.

TREF curves of LLDPE samples are similar in shape to their DSC heating tracings that are recorded after slow cooling [7–10]. The explanation of this similarity is that both techniques give an image of the crystallite size distribution in the sample.

In our recent work, [11] we proposed an application of DSC analysis to obtain a semiquantitative evaluation of CCD in 1-butene modified polyethylene. We obtained a fractionation by crystallite size, performing sets of isothermal crystallization steps from the melt. We found that, if the subsequent endotherm is divided into the same number of zones as the number of crystallization steps, the relative area of each zone, with respect to that of the whole endotherm, is proportional to the amount of crystallites with a particular size. The distribution of the partial areas gave a qualitative crystallite size distribution. It was, in turn, related to the 1-olefin distribution considering each crystallite size as consisting of macromolecules having a particular ethylene monomer sequence length. The method was applied to polymers from different catalytic systems and the results were compared with those from TREF analysis. The two set of data were nicely correlated.

As the previous work was focused only on obtaining a qualitative evaluation of the CCD, here we wish to obtain a quantitative estimate. By applying “average calculations” on the partial areas of the DSC curves after the thermal fractionated crystallization (TFC) treatment, we define an index capable of representing the chemical composition distribution of the copolymer.

EXPERIMENTAL

Materials

The polymers were synthesized in a laboratory scale by using different types of catalytic systems to obtain polymers with different molecular characteristics. Sample 1 is an LLDPE, with a narrow CCD, obtained by the copolymerization of ethylene and 1-butene by using an homogeneous zirconocene-based system. Samples 2 and 3 were synthesized by using two different heterogeneous MgCl_2 -supported titanium-based catalysts. The main characteristics of the polymers are reported in Table I.

Solution Fractionated Crystallization

A 0.1 wt % solution of polymer in *o*-xylene stabilized with 0.05 wt % of 2,6-*t*-butyl *p*-cresol (BHT) was put into a 1.5 L glass reactor and stirred until a complete solution was obtained. Successively, the temperature was slowly decreased to 55°C

TABLE I

Molecular characterization of the LLDPE samples

Sample	$[\eta]^a$ (dL/g)	$M_w \cdot 10^{-3}^b$ (g/mol)	M_w/M_n^b	1-butene ^c (mol %)	density ^d (g/mL)	XSRT ^e (wt %)	T_m^f (°C)	ΔH^f (J/g)
1	2.04	55.5	2.0	3.1	0.9172	0.3	108	100
2	1.93	117.5	11.2	5.1	0.9273	9.0	122	130
3	1.52	103.9	4.3	3.9	0.9201	11.8	121	120

^a Intrinsic viscosity measured in tetrahydronaphthalene at 135°C.^b Measured by SEC in *o*-dichlorobenzene at 135°C.^c From ¹³C-NMR analysis.^d By density gradient column following the standard method ASTM D-1505.^e Weight % of polymer soluble in xylene at 25°C after the complete dissolution at 110°C.^f By DSC standard method, see experimental section.

and kept at this temperature for 1 h. After one additional hour without stirring, the undissolved polymer was left to precipitate, then filtered, and finally the collected solution was coagulated with excess methanol. After adding 1 L of fresh solvent and 0.01 wt % of BHT, the undissolved polymer was redissolved and crystallized at the new crystallization temperature (70°, 80°, 90°, and 110°C) following the procedure previously described.

Standard DSC Analysis

Calorimetric measurements were performed by using a differential scanning calorimeter Perkin Elmer DSC-7. The instrument was calibrated with indium and tin standards. Weighted samples (10 mg) were sealed into aluminum pans, heated to 180°C, and kept at that temperature for a sufficient time (4 min) to allow complete melting of all the crystallites; in this way any influence of the previous thermal history was removed. Successively, after slow cooling at 1°C/min to 0°C, the samples were heated to 180°C at a rate of 10°C/min.

Thermal Fractionated Crystallization (TFC)

In order to fractionate the polymer in terms of lamella size, the melted sample (180°C), was cooled at a nominal rate of 200°C/min to the fixed crystallization temperatures (T_C) of $T_{C_1} = 120^\circ\text{C}$, $T_{C_2} = 110^\circ\text{C}$, $T_{C_3} = 100^\circ\text{C}$, $T_{C_4} = 90^\circ\text{C}$, $T_{C_5} = 80^\circ\text{C}$, $T_{C_6} = 65^\circ\text{C}$, $T_{C_7} = 50^\circ\text{C}$, $T_{C_8} = 30^\circ\text{C}$ (Figure 1a). The isothermal crystallization time (60 min) was chosen to obtain complete crystallization of the polymer fractions at a fixed temperature. Finally, the sample was heated at 10°C/min to 180°C and the corresponding DSC curve was recorded. The melting curve was characterized by a number of peaks as the isothermal crystallization temperatures. Each curve of the endotherm of fusion was divided into nine parts according to the chosen crystallization steps, as shown in Figure 1b. By using the calculating program of the Perkin-Elmer DSC-7, it was possible to calculate the value of the partial areas of the melting endotherms.

Calibration Curve

A calibration curve, T_m vs. short-chain branching (SCB) expressed as the amount of $\text{CH}_3/100\text{C}$ atoms, was obtained by analyzing polymer fractions having narrow

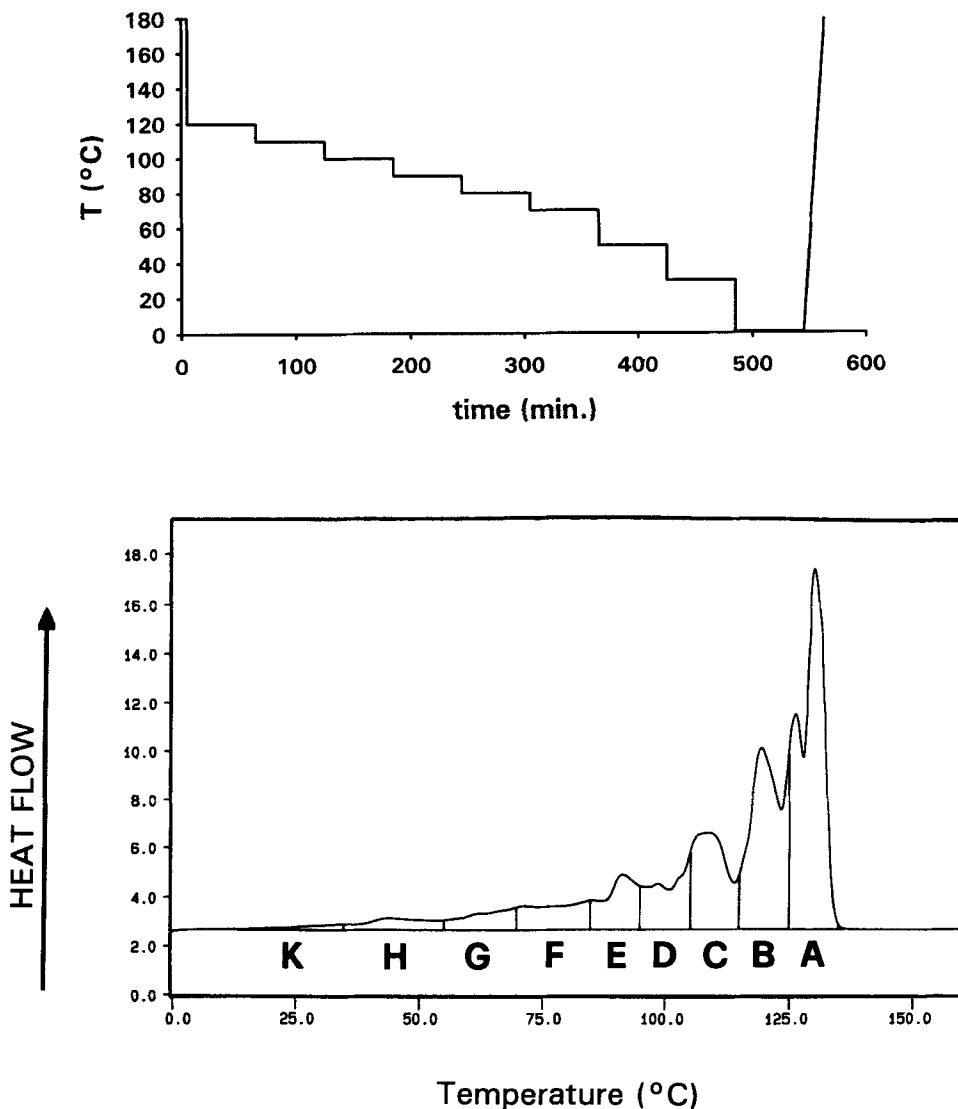


FIGURE 1 Thermal fractionated crystallization (TFC). a) Temperature profile of TFC treatment. b) Melting endotherm of a LLDPE after TFC treatment.

CCD and MMD. The samples were obtained by preparative TREF as already reported [11]. The peak temperature of standard DSC thermograms were chosen as melting temperature of the samples. The SCB, in all the sample, was determined by ^{13}C NMR analysis.

RESULTS AND DISCUSSION

The thermal fractionated crystallization (TFC) is based on several steps of isothermal crystallization of the polymer by decreasing the temperature from the melt.

This process favors the separation of the crystalline material in groups of lamellae having different thickness depending on the amount and distribution of the 1-olefin units in the macromolecular chains. In fact, according to the exclusion model, [12] which describes the formation of the crystallite from copolymer chains consisting of units that can crystallize and units that cannot, the thickening of the polyethylene lamellae can be hindered by the presence of an 1-olefin unit at the chain folding. The fold period will thus depend on the frequency of noncrystallizing units along the copolymer chains.

The melting endotherm, after TFC treatment, consists of the same number of peaks as the isothermal crystallization steps. The shape and position depend on the chosen isothermal crystallization temperatures. The phenomenon is explained by considering that during the crystallization there is a fraction of the polymer which does not crystallize at the T_C because of thermal and kinetic effects [13] and is segregated between the crystalline lamellae. This fraction will then crystallize at lower T_C . The final result, after the complete cycle, will be a distribution of lamellae having different sizes in the spherulites. The area of the thermogram is proportional to the total amount of the crystalline part of the polymer, and the partial area between two fixed temperatures is proportional to the amount of crystalline material constituted of lamellae of a specific size.

The melting curves after TFC treatment of the samples 1-3 are shown in Figures 2a-c. Sample 1, obtained from homogeneous catalyst, melts over a narrower range respect to samples 2 and 3 synthesized from heterogeneous catalyst systems. As previously demonstrated, a specific melting range of each thermogram can be related to a range of crystallite thickness [8,11] which is influenced by the frequency of 1-olefin insertion. We could substitute the tempera-

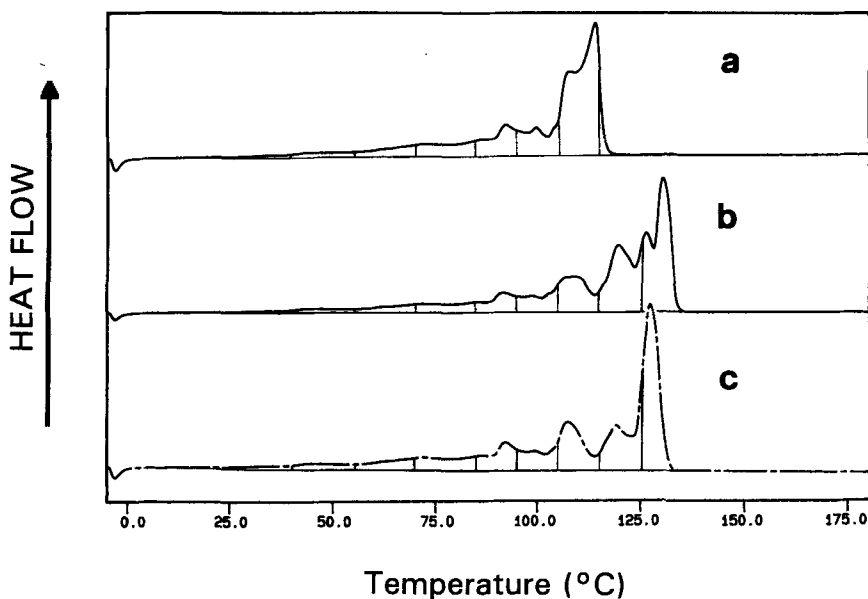


FIGURE 2 Melting endotherms of the sample after TFC treatment: a) Sample 1. b) Sample 2. c) Sample 3.

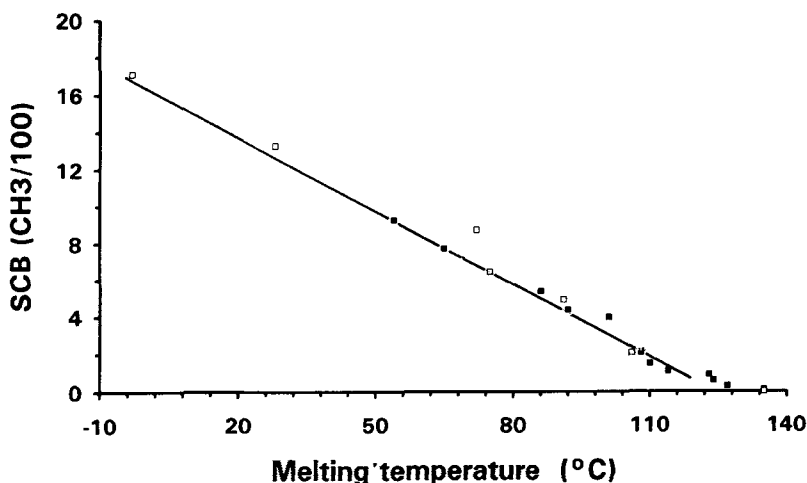


FIGURE 3 Plot of the peak melting temperature as a function of SCB ($\text{CH}_3/100\text{C}$) of LLDPE: ■ fractions from TREF of polymer with narrow CCD; □ data from reference 14.

ture axis of the thermograms with the crystallite thickness by using the equation of Thomson and Gibbs (see appendix) or with the 1-butene content. This is reasonable if we suppose that the thickening of the lamella stops at the chain folding, particularly in correspondence to the 1-olefin monomer and/or sequences (size exclusion model [12]). Because the use of the Thomson and Gibbs equation is probably an oversimplification of the crystallization phenomenon, we tried to get an empirical relation between melting temperature (T_m) and SCB content. A calibration curve, T_m vs. SCB, was performed by analyzing narrow polymer fractions (see experimental section).

The results are shown in Figure 3 and Table II. On the same figure data of Krigas [14] are also reported concerning model copolymers obtained from anionic polymerization of 1,3-butadiene and subsequent hydrogenation. As seen, these data fit in well with ours. From the values of Table II, a fairly good correlation was obtained (correlation coefficient = 0.987).

$$\text{SCB}(\text{CH}_3/100\text{C}) = 15.64 - 0.12 \cdot T_m \quad (1)$$

It should be emphasized that the intramolecular comonomer distribution in the polymer depends on the catalytic system from which it originated [15–17]. In our case the samples used for the calibration curve showed the same characteristics of the samples studied by Krigas, [14] where the 1-butene units are randomly distributed and isolated as confirmed by ^{13}C NMR analysis. Samples in which some 1-butene sequences are present, a positive deviation from the linearity should be expected due to the fact that sequences of 1-butene units act on the polymer chain as a single unit [11].

In order to characterize the DSC melting zones in terms of 1-butene content for each partial area of the thermogram, a mean value of the melting range was calculated and then by using Equation (1), the average SCB was obtained. The results are reported in Table III.

TABLE II
 Experimental relation between melting temperature and SCB content in LLDPE from fraction
 of polymer having an homogeneous comonomer distribution

T_m (°C)	135	127	124	123	114	110	108	101	92	86	65	54
SCB (CH ₃ /100C)	0.1	0.3	0.6	0.9	1.1	1.5	2.1	4.0	4.4	5.4	7.8	9.3

TABLE III
Calculated average SCB (CH₃/100C) content for each DSC zones

Zone	Melting Range (°C)	SCB (CH ₃ /100C)	Average SCB (CH ₃ /100C)
A	{ 135 125 }	{ 0.1 0.6 }	0.3
B	{ 115 105 }	{ 1.8 3.0 }	1.2
C	{ 105 95 }	{ 3.0 4.2 }	2.4
D	{ 95 85 }	{ 4.2 5.4 }	3.6
E	{ 85 70 }	{ 5.4 7.2 }	4.8
F	{ 70 55 }	{ 7.2 9.0 }	6.3
G	{ 55 35 }	{ 9.0 11.4 }	8.1
H	{ 35 0 }	{ 11.4 15.6 }	10.2
K	{ 0 }	{ 15.6 }	13.5

By applying common mathematical mean calculations, average 1-butene contents could be obtained as following:

$$D_{n-1} = \frac{\sum h_i / C_{4i}}{\sum h_i / C_{4i}^2} \quad (2)$$

$$D_n = \frac{\sum h_i}{\sum h_i / C_{4i}} \quad (3)$$

$$D_w = \frac{\sum h_i C_{4i}}{\sum h_i} \quad (4)$$

$$D_z = \frac{\sum h_i C_{4i}^2}{\sum h_i C_{4i}} \quad (5)$$

$$D_{z+1} = \frac{\sum h_i C_{4i}^3}{\sum h_i C_{4i}^2} \quad (6)$$

where h_i is the area of the zone i given by melting of crystalline lamellae

TABLE IV
Chemical comonomer distribution calculated from DSC thermogram after the thermal fractionated crystallization (TFC) treatment of 3 different LLDPEs (1-butene) and their fractions

Sample	Extraction Temperature (°C)	Fraction (wt %)	SCB (CH ₃ /100C)	D _{n-1}	D _n	D _w	D _z	D _{z+1}	D _{z+1} /D _{n-1}	D _{z+1} /D _n	D _z /D _n	D _w /D _n
1			1.5	2.56	3.16	4.26	6.06	8.12	13.7	2.6	1.9	1.3
1-1	55	26.6	2.0	2.02	2.76	3.98	5.68	7.50	3.7	2.7	2.1	1.4
1-2	70	50.0	1.5	2.64	3.42	4.42	5.61	6.86	2.6	2.0	1.6	1.3
1-3	80	23.1	1.1	1.50	1.97	3.01	4.59	6.09	4.1	3.1	2.3	1.5
2			2.5	0.36	0.69	2.61	6.01	8.44	23.5	12.2	8.7	3.8
2-1	55	12.9	6.5	4.10	5.05	6.24	7.53	8.75	2.1	1.7	1.5	1.2
2-2	70	9.1	2.3	1.76	2.45	3.71	5.37	6.94	3.9	2.8	2.1	1.5
2-3	80	24.5	1.5	0.35	0.55	1.30	2.76	4.08	11.6	7.5	5.0	2.4
2-4	90	48.5	0.35	0.32	0.40	0.93	2.65	4.19	13.2	10.4	6.6	2.3
2-5	110	5.1	-	0.32	0.44	1.54	5.61	8.59	26.7	19.4	12.6	3.5
3			2.0	0.36	0.74	2.93	6.09	8.06	22.4	10.8	8.2	3.9
3-1	55	34.3	4.0	2.93	4.21	5.64	7.04	8.28	2.8	2.0	1.7	1.3
3-2	70	44.7	0.9	0.40	0.82	2.44	5.05	7.30	18.3	8.9	6.1	3.0
3-3	80	19.9	0.6	0.34	0.54	1.62	4.11	6.07	17.7	11.3	7.6	3.0
3-4	90	1.1	-	0.32	0.41	0.90	2.35	3.73	11.6	9.1	5.7	2.2

consisting of copolymer chains having the C_{4i} mole content (expressed as $\text{CH}_3/100\text{C}$). Equations (2-6) represent mathematical averages and in particular D_{z+1} and D_{n-1} are most sensitive to the high and low C_{4i} content, respectively.

A collection of different LLDPEs can be characterized in terms of chemical composition distribution by a number, composition index (CI), alternatively defined as the ratio of two of the averages (Eqs. 2-6); for example: D_{z+1}/D_{n-1} , D_{z+1}/D_n , D_z/D_n or D_w/D_n . In this way, the lower the ratio, the narrower the CCD can be considered. The calculation method was tested on three different LLDPEs and on their fractions, Table IV. The samples showed different composition indices, as expected, for polymers obtained from different catalytic systems and polymerization conditions:

- Polymer 1 from homogeneous catalytic system had a very narrow CCD. For this polymer the CI is the lowest independently of the ratio of the average distributions considered.
- Polymers 2 and 3, from heterogeneous catalysts, with a broader CCD showed higher CI values and in particular 2 was higher than 3.

This CCD order is confirmed by examining the fraction analysis (see Table IV). In fact, the fractions of sample 1 have similar CI values, while samples 2 and 3 gave fractions with greatly different CI values. Although the fractions are narrower than the whole samples, as expected, CI increases as the overall SCB content decreases. This fact is due to the increasing uncertainty on the evaluation of h_i in the zones "H", and "K" for the fractions having low 1-butene content. For polymers from

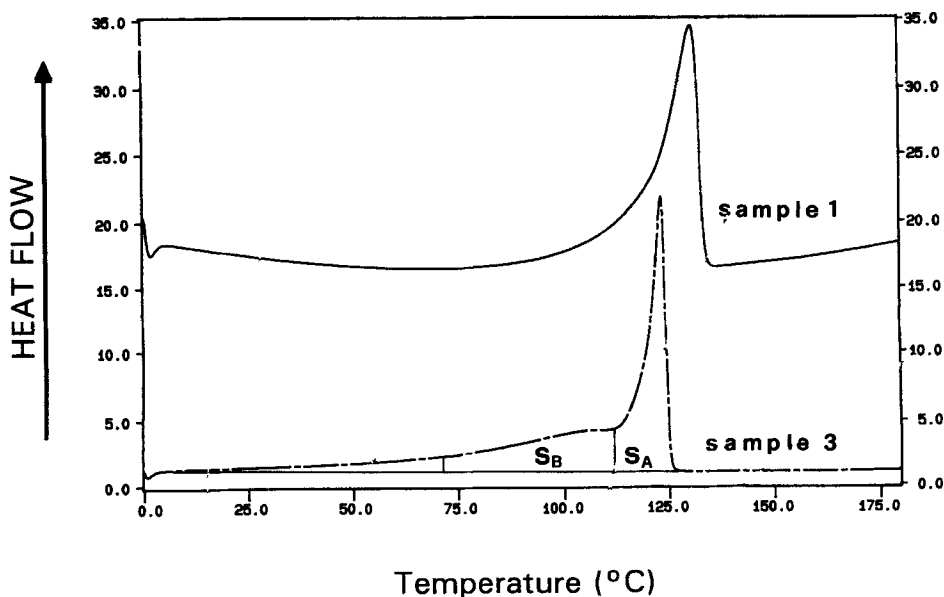


FIGURE 4 Melting endotherms obtained by applying the method proposed by Hosoda [8].

TABLE V

Comparison of the CCD determined by the distribution index (DI) following the Hosoda method [8] and the composition index (D_{z+1}/D_n) by the TFC method

Sample	DI	D_{z+1}/D_n
1	n.d.	2.6
2	n.d.	12.2
3	0.72	10.8

titanium-based catalysts, the effect is more evident and in one case (polymer 2), the fractions with the lowest 1-butene content seems to be even more dispersed than the whole polymer.

In conclusion, as the calculations greatly depend on the values of the areas of each zone, special care should be taken on evaluating the extremities of the thermograms. Hence it is clear that mean calculations, like D_{n-1} , should be avoided.

In our experiments we found a strong dependence on the isothermal crystallization conditions. In particular, good temperature control ($\pm 0.5^\circ\text{C}$) is required because minor changes on the T_c will be reflected in the shape of the subsequent endotherm and in the amount of area in that specific zone. To test the reproducibility of the method, several specimens of sample 2 were thermally fractionated at the same conditions. The dispersion coefficient, defined as $V = \pm s/\bar{X}$ where s is the standard deviation and \bar{X} is the mean value of the area h_i , changed significantly with the amount of area measured in each zone. Fluctuations from $V \cong 1$ for partial areas close to 0% to $V \cong 0.25$ for partial areas greater than 30% were found.

A comparison with other calculating methods involving the use of the DSC technique, highlights the larger applicability of TFC. For example, TFC works better than the semi-quantitative "distribution index" (DI) proposed by Hosoda [8], where DI was defined as the ratio between the peak area (S_a), due to the slightly modified polyethylene chain and the peak area (S_b) of the highly modified polyethylene chain, in slowly cooled LLDPE samples. In Figure 4, the thermograms of the second runs of samples 1 and 3, cooled at $1^\circ\text{C}/\text{min}$, are compared. A clear determination of the areas S_a and S_b is only possible for sample 3 as in sample 1 the area S_b is indeterminable. In Table V the comparison between DI and CI (D_{z+1}/D_n) are given for the three polymers.

CONCLUSION

The proposed TFC method permits quantitative evaluation of the chemical composition distribution in LLDPEs by a thermal treatment which is simpler and faster than the other known characterization methods. Four different ratios, D_{z+1}/D_{n-1} , D_{z+1}/D_n , D_z/D_n , D_w/D_n , to express the CCD were proposed. Tests on three LLDPEs evidenced D_{z+1}/D_n as the more selective number, while D_z/D_n as the most reliable.

Particular care should be taken, however, on considering averages like D_{z+1} and D_{n-1} , where small errors in the evaluation of the partial areas strongly affect the calculation. Moreover, an improvement could be achieved by dividing the thermograms into a larger number of zones, that is, operating a larger number of isothermal crystallizations.

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APPENDIX

The Thomson and Gibbs equation relates the lamella thickness to the melting temperature following:

$$T_m = T_m^0 \left(1 - \frac{2\sigma_e}{\Delta H_u L_c} \right)$$

where T_m^0 is the equilibrium melting temperature of the HDPE, σ_e is the top and bottom specific surface free energy of the lamella, ΔH_u and L_c are the molar melting heat, and the lamella thickness, respectively [18].

$$\sigma_e = 87 \text{ erg cm}^{-2}$$

$$\Delta H_u = 2.79 \cdot 10^9 \text{ erg cm}^{-3}$$

$$T_m^0 = 414 \text{ K}$$