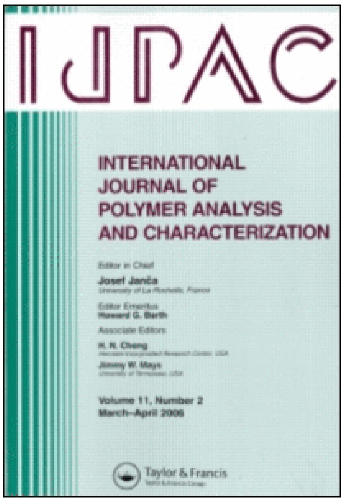

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Linear Low Density Polyethylene Thermal Fractionation by DSC Technique

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Abstract: Crystallization of linear low density polyethylene was studied through DSC analyses. Melting peak resolution was determined in order to establish the effect of crystallization conditions on polymer thermal fractionation. The isothermal number, fractionation window, and annealing time were varied, and suitable crystallization conditions were evaluated based on the sharpness of the DSC endothermic curve. The results confirmed that the selection of the thermal fractionation conditions is very important to control the multiple melting peaks number. The polyethylene endothermic curve profile changed significantly according to the crystallization conditions.

Keywords: Crystallization; DSC; LLDPE; Thermal fractionation

INTRODUCTION

Linear low density polyethylenes (LLDPE) with up to 20 mol% of α-olefins have been developed in the past two decades by using

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metallocene catalyst, besides those having from 2 to 5 mol% of α-olefins obtained by using Ziegler-Natta catalysts.[1] The intra- and intermolecular structure heterogeneity of a given LLDPE or polyethylene copolymer results from the comonomer insertion mode in the growing chain[2,3] and depends on the catalytic system and polymerization conditions. It is well known that incorporation of α-olefins in the polyethylene backbone produces LLDPEs with short (SCB) or long (LCB) chain branches.

The properties of a semicrystalline polymer—thermodynamic, spectroscopic, physical, and mechanical—depend on the details of crystal structure and morphology that develop from the melt. Understanding the crystallization mechanism is a key to understanding these properties. Crystallization studies[4,5] are generally conducted under isothermal conditions, since the use of a constant temperature permits easier theoretical treatment and limits the thermal gradients within the samples.

Thermal fractionation by differential scanning calorimetry (DSC) has been used to evaluate the LLDPE molecular structure[6,7] since crystallites with different sizes and order are a consequence of the polymer structure heterogeneity and molecular weight distribution. Thermal fractionation consists in polymer crystallization from the melt through successive cooling and annealing followed by a further heating of the polymer, which melts in multiple peaks. The multiple peaks correspond to different types of crystallites due to diverse fractions of molecules having differences in the size and content of the branches as well as in the molecular weight. At present, two main hypotheses have been proposed to account for the multiple melting behavior of polyesters under investigation: (i) melting and recrystallization processes occurring during the calorimetric run and (ii) the existence of different crystal structures.[8]

The melting behavior of copolymers suggests that the melting peaks come from the different crystal populations, which are formed from chains with different crystallizable lengths, after being annealed for a certain time.[9] Thermal fractionation induces molecular segregation due to the chain segments' ability to crystallize at a specific temperature according to the macromolecule size and comonomer distribution in the chains.[10,11] LLDPE samples after being held 30 min at 130°C and successively cooled and annealed until they reached 90°C presented several melting peaks when reheated from 30° to 200°C.[12] Thermal fractionation of an ethylene/1-butene copolymer (4.2 mol% of butane) through seven isothermals, starting from 128°C with fractionation windows of 6°C and annealing time of 120 or 150 min, took about 17 h.[13,14] Varga et al.[15,16] reported that a well-defined endothermic curve for a LLDPE sample was obtained by using fractionation windows of 3°C and annealing time of 120 min. Chen et al.[17] evaluated and proposed the best onset crystallization temperature for blends of LLDPE/VLDPE (very low density polyethylene) by following the effect of initial crystallization temperature on the shape and position of the melting peaks. On the other hand, Shanks and Amarasinghe[18] obtained endothermic curves with similar resolution using isothermals from 116° to 24°C, fractionation windows of 4°C, and annealing time of 50 or 100 min. Therefore, the annealing time used in DSC thermal fractionation method varies from 50 to 600 min taking into account all the possible differences in polymer structure, molar mass, polydispersity, and comonomer content.

Following this view, herein a detailed investigation of the effect of the crystallization conditions on the melting peak resolution is reported, by analyzing the variation of the DSC endothermic curve profile due to the fractionation window, isothermal number, and annealing time used in the thermal fractionation of an LLDPE sample.

EXPERIMENTAL SECTION

An LLDPE commercial grade, ethylene-1-butene copolymer having short chain branching ($-CH_2-CH_3$) and produced with heterogeneous Ziegler-Natta catalyst (Spherilene process) was supplied by Ipiranga Petroquímica S.A. (Brazil). The LLDPE sample has 1.5 mol% of comonomer, polydispersity of 3.6, and average molar masses of $M_n = 32.6\,\mathrm{Kgmol^{-1}}$, $M_w = 117\,\mathrm{Kgmol^{-1}}$, and $M_z = 305\,\mathrm{Kgmol^{-1}}$.

The thermal fractionation of the LLDPE was carried out by using a differential scanning calorimeter DSC 2010 (TA Instruments) equipped with refrigerated cooling accessory. The temperature was calibrated by the onset melting temperature of high purity indium standards. The DSC furnace was purged with nitrogen during the measurements of the samples (approximately 10 to 14 mg) encapsulated in aluminium pans. Samples of the LLDPE were analyzed under six standard procedures (series) aiming to evaluate the multiple melting peaks as a function of the crystallization conditions. In each experiment, a fresh specimen was used since long-term melt-crystallization was performed according to each series. The endothermic pattern curves are always those obtained in the second heating run. Repeated runs for a given sample under long-term conditions produced endothermic curve profiles with excellent reproducibility, which can be seen in the curves with no differences in the profile and heat fusion. The heat of fusion (ΔH_m) of the crystalline phase was calculated from the area of the DSC endothermic peak, and the crystallinity of the thermal fractionated samples was estimated from the ΔH_m data by assuming that ΔH_m^0 (100% crystallinity) is $290\,\mathrm{J.g^{-1}}$.[9]

Table 1 summarizes the DSC measurement conditions carried out for all series described as follows. The first procedure or series consisted in heating and cooling the sample without annealing in order to obtain the exothermic and endothermic curves and crystallization and melting

Table 1. DSC experiment conditions used in LLDPE thermal fractionation

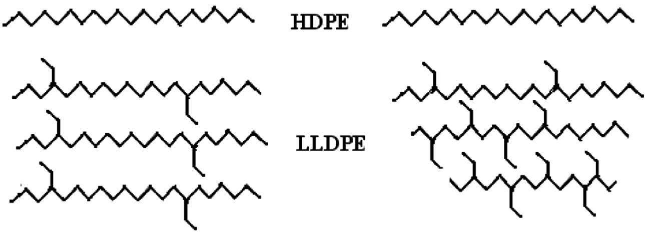
Series number	Thermal treatment	Fractionation windows (°C)	Isothermal temperatures (°C)	Annealing times (min)
1st	• Heat to 180°C at 10°C/min	No	No	No
2nd	• Held at 180°C for 5 min	5	100–95–90	60
3rd	• Cooling jump to the isothermal temperature • Followed or not by successive jumps up to the last isothermal	No	128 118 108 98	60 and 100 60 and 100 60 and 100 100
4th	• Cooling to 20°C at 10°C/min	10	128–118–108–98–88	100
5th	• Reheating to 180°C for the endothermic curve profile	6	124–118–112–106–100	100
6th		10	128–118–108–98	60–70–80–90

peak temperature ranges used as reference. The LLDPE samples were heated to 180°C (about 50°C above fusion temperature) at a rate of 10°C/min, held there for 5 min to eliminate the previous thermal history, then cooled at a rate of 10°C/min to 20°C. Finally, the samples were reheated at a rate of 10°C/min to 180°C (second scan).

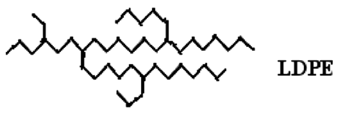
The second series consisted in the sample being heated to 180°C, held there for 5 min, and then rapidly quenched by a jump to 100°C, followed by successive jumps with fractionation windows of 5°C. The sample was maintained for 60 min at each temperature. Finally, the sample was cooled to 20°C and reheatedto 180°C at a rate of 10°C/min. The third series consisted in isothermal crystallization at different temperatures. The melt polyethylene at 180°C was cooled by a jump to a specific temperature (128°, 118°, or 108°C) selected between the end-set temperature of the melting peak (T_m) and the apex temperature of the crystallisation peak (T_c). After being annealed for 60 or 100 min, the sample was cooled to 20°C and reheated to 180°C at a rate of 10°C/min. Isothermal crystallization at 98°C using annealing time of 100 min was also performed. In the fourth series, the LLDPE sample, after being heated and held at 180°C for 5 min, was cooled by a jump to 128°C. Isothermal crystallizations were performed by successive annealing and cooling through three to five isothermals using fractionation windows of 10°C and annealing time of 100 min. After the last isothermal, the sample was cooled to 20°C and reheated to 180°C at a rate of 10°C/min. In the fifth series, the LLDPE sample was crystallized as in the fourth series through five isothermals starting from 124°C by using fractionation windows of 6°C and annealing time of 100°C. In the sixth series, the sample was crystallized through four isothermals starting from 128°C with fractionation windows of 10°C, running experiments with annealing times of 60, 70, 80, and 90 min.

RESULTS AND DISCUSSION

The molecular structures of the high (HDPE) and low (LDPE) density polyethylenes as well as their copolymers, known as linear low density polyethylene (LLDPE), are sketched in Figure 1. Both HDPE and LLDPE are obtained by the polymerization process using Ziegler-Natta (Z-N) or metallocene catalysts, and the LDPE is produced by free radical polymerization. It is well known that LLDPE obtained by heterogeneous Z-N catalysts exhibits higher polydispersities (M_w/M_n) and heterogeneous comonomer distribution in the polyethylene chains than the metallocenic polyethylene.[1–3] In the former, chains with lower molar mass have higher comonomer incorporation and vice versa, while in the latter, the comonomer incorporation in the chains is rather homogeneous, as can be seen qualitatively in the given structures, in Figure 1.



(a) Metallocene (b) Ziegler-Natta



(c) Free radical

Figure 1. Molecular structure of linear and branched polyethylenes produced with (a) metallocene and (b) Ziegler-Natta catalysts and (c) branched polyethylene produced by free radical polymerization.

Although the polyethylene copolymers have the same density, they show different properties as a consequence of the chain microstructure and average molar mass and polydispersity. The melting point and the degree of crystallinity of a given polyethylene depend on the chain structure. The branch type and the distribution in the chains affect the polymer crystallization. Thus, thermal fractionation of a given LLDPE can favor distinct crystallites or a thickness of well-ordered lamellae, which, when reheated, produce an endothermic curve with multiple melting peaks that can be considered as the fingerprint of the polymer. Polymer crystallization is a transition phase that is a consequence of the intra- and interchain heterogeneity, which plays an important role in polymer processing; therefore, it is valuable to know and differentiate the various LLDPEs. On the other hand, LLDPE chemical structure characterization is very laborious, and its thermal fractionation seems to be practical and copes very well with the polymer structure.

The LLDPE employed in this work has low comonomer content, and it was used for a systematic study in order to evaluate the effect of the thermal fractionation conditions on producing sharp multiple melting peaks. As already reported,[19] the endothermic curve profile of thermal fractionated LLDPE changes significantly with the melt crystallization conditions. Figure 2 shows the endothermic and exothermic curves of the LLDPE sample analyzed as described in the first series without annealing or thermal fractionation. The melting peak onset (T_{onset}) and

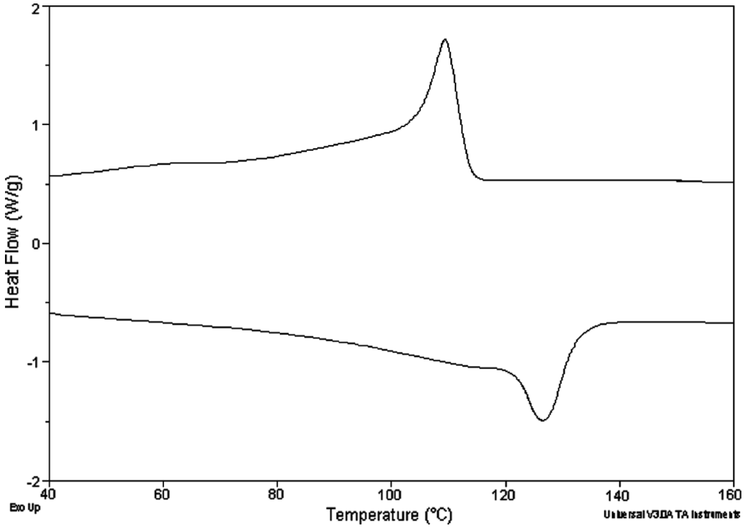


Figure 2. LLDPE exothermic curve and endothermic curve without sample annealing.

end-set (T_{endset}) temperatures were 72° ± 1° and 138° ± 1°C, respectively, and the apex of the endothermic peak (T_m) was 126° ± 1°C. The T_{onset} and the T_{endset} of the crystallization peak were 72° ± 1°C and 115° ± 1°C, respectively, and the apex of the crystallization peak (T_c) was 109° ± 1°C. Based on both temperature intervals and on data from the literature,[12–18] the temperature range to be used in the LLDPE thermal fractionation was set from 128° to 88°C. In this temperature interval, from T_m to below T_c there is a balance between the melting and recrystallization process, since the melting onset and the crystallization end set are coincident and equal to 72° ± 1°C. The fractionation windows used in this interval for the LLDPE crystallization procedures were 5°, 6°, or 10°C with annealing time ranging from 60 to 100 min, as can be seen in the procedures described in Table 1.

Figure 3 shows the endothermic curve of the LLDPE sample fractionated as described in the second series, in which the melt polyethylene was cooled by a jump to 100°C, then successively annealed for 60 min and cooled with fractionation windows of 5°C until it reached 90°C. The endothermic curve obtained presents a main melting peak with apex (T_m) at about 120°C, displaced to lower values compared to the sample without annealing, and also two weaker peaks at lower temperatures. In this procedure, even using an annealing time twice as long as the 30 min employed by Wolf et al.[12] in LLDPE thermal fractionation, the endothermic curves present neither good resolution nor well-defined

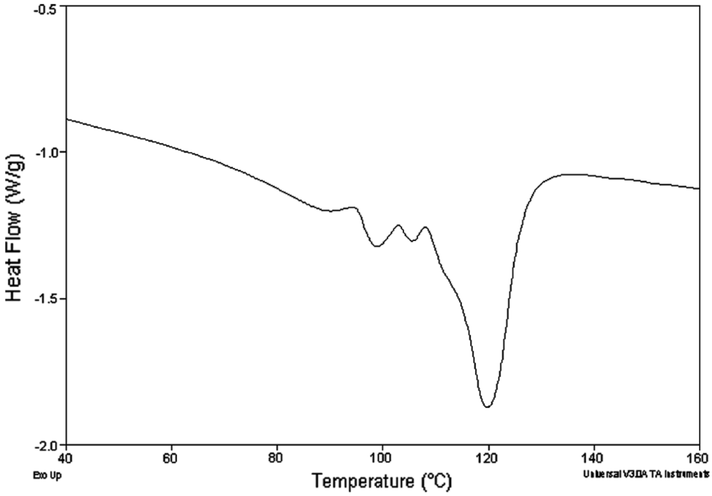


Figure 3. LLDPE endothermic curves of samples crystallized from 100°C to 90°C with fractionation windows of 5°C and annealing time of 60 min.

multiple peaks. Nevertheless, the smaller peaks reveal that under this condition there was molecular segregation, and some crystallites or lamellae could be formed in temperatures lower than 100°C, probably due to the more branched LLDPE chains having lower average molar mass.

The endothermic curves of LLDPE samples crystallized under isothermal conditions at 128°, 118°, or 108°C, with annealing time of 60 min as described in the third series, are shown in Figure 4. The lower the isothermal or annealing temperature, the higher the number of melting peaks in the endothermic curve. Multiple melting peaks are a consequence of the sample fractionation, and lower temperatures seem to favor molecular segregation as a function of the chain's ability to crystallize at a specific temperature. The dependence of the melting peak position and intensity on the annealing or isothermal temperature was also observed for semicrystalline aliphatic polyesters.[8] When the LLDPE sample was annealed at the highest temperature or 128°C (Figure 4, curve a), only one large melting peak was observed in the endothermic curve. On the other hand, when the sample was annealed at 118°C (Figure 4, curve b), two well-defined melting peaks were observed. However, when the annealing temperature was even lower (108°C) an endotherm having a broader melting peak with a shoulder was followed by a new discrete peak at lower temperature (Figure 4, curve c). The new peak suggests that

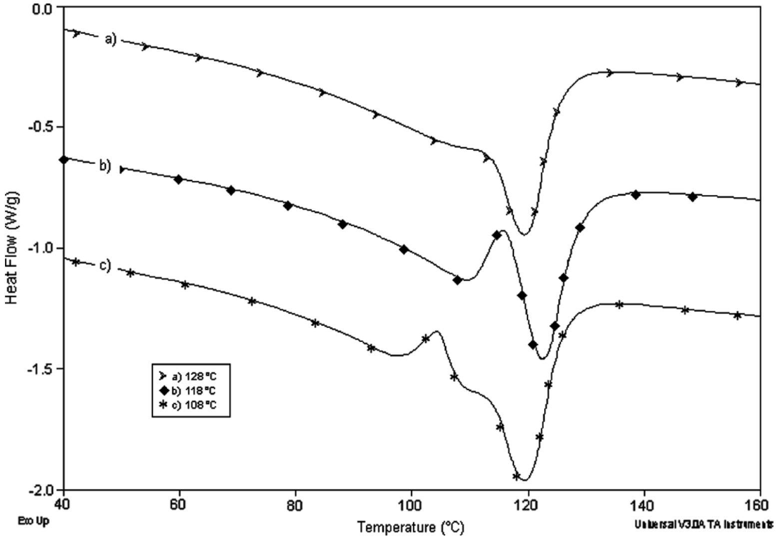


Figure 4. LLDPE endothermic curves of samples annealed for 60 min at a) 128°C, b) 118°C, and c) 108°C.

a crystallite fraction could be formed if lower isothermals were employed. The temperature dependence of the thickness of well-ordered lamellae in high density polyethylene investigated by small-angle X-ray scattering suggested that a reversible transition occurs at the lateral surface of crystals[5] under isothermal conditions. Thus, the reversible process can reduce the crystallite size, and subsequent annealing at lower temperatures can induce crystallites of progressively lower size and, thus, endothermic curves with multiple melting peaks.

Figure 5 shows the endothermic curves of the LLDPE samples annealed at the same temperatures as before (Figure 4), but for 100 min as described also in the third series. The sample annealed at 128° and 118°C (Figure 5, curves a and b) showed endothermic curve profiles quite similar to those of the sample annealed for 60 min (Figure 4, curves a and b). Thus, at these temperatures a longer annealing time did not influence the sample crystallization behavior. On the other hand, the sample annealed at 108°C showed two well-defined melting peaks (Figure 5, curve c), quite different from the broad melting peak obtained for the sample annealed for 60 min (Figure 4, curve c), showing that longer annealing time clearly favors the growth of a second fraction of crystallites. Nevertheless, the sample annealed at 98°C presented a large melting peak (Figure 5, curve d) displaced to lower temperature, and sample fractionation was not favored. During the heating of the sample

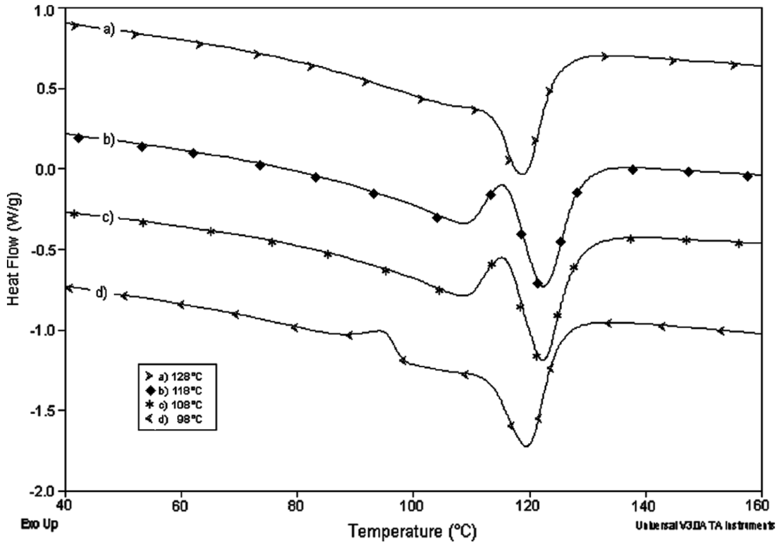


Figure 5. LLDPE endothermic curves of samples annealed for 100 min at a) 128°C, b) 118°C, c) 108°C, and d) 98°C.

an exothermic peak can be observed showing that some recrystallization must have occurred. By annealing the LLDPE at 118°C (above the T_c) or at 108°C (T_c of the non-annealed sample) for 100 min two distinct crystallite fractions were formed, and the main peak shifted to higher temperature due to more perfect crystallites or thicker crystalline lamellae made up of higher molar mass chains with low comonomer content.

Effect of Isothermal Number on Melting Behavior

The LLDPE endothermic curves obtained as a function of isothermal number, varying from three to five according to the thermal treatment, with fractionation windows of 10°C and annealing time of 100 min (described in the fourth series), are shown in Figure 6. The higher the number of isothermals, the higher the number of melting peaks. When the LLDPE sample was successively annealed and cooled starting from 128°C, annealing temperatures as low as 98° and 88°C still favored the chain segments' molecular segregation, and distinct crystallite fractions were formed. According to the literature,[20] more branched LLDPE macromolecules having low molar mass still have mobility to crystallize from solution at low temperatures when the temperature decreases continuously. Under the thermal condition described in the fourth series,

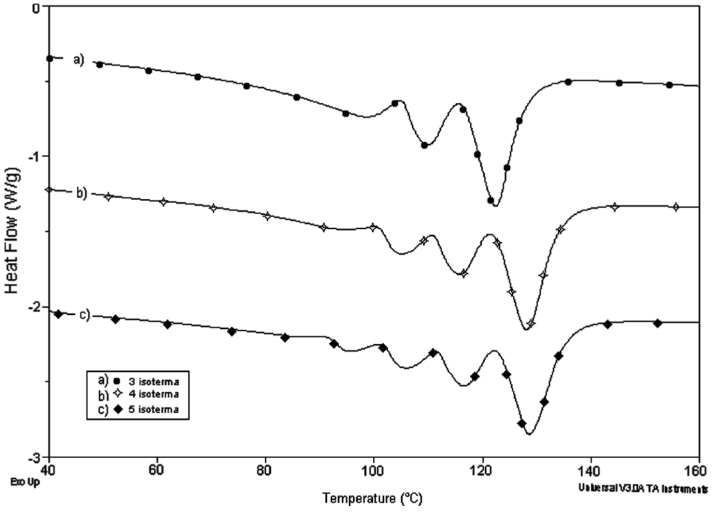


Figure 6. LLDPE endothermic curves of samples crystallized through a) three, b) four, and c) five isothermals using fractionation windows of 10°C and annealing time of 100 min.

the apex of the main melting peak (T_m) shifted to higher temperatures in accordance with higher isothermal numbers used. The LLDPE sample annealed through three isothermals (Figure 6, curve a) showed two well-defined melting peaks, at 122° ± 1°C (T_m) and at 110°C, and a very large and weak peak at 98°C. On the other hand, the sample annealed through four isothermals (Figure 6, curve b) showed three well-defined melting peaks, at 128° ± 1° (T_m), 116°, and 105°C. It is possible to infer from the latter endothermic curve that a fourth fraction of crystallites could have been formed at around 93°C. Thus, the runs with five isothermals improved the sample fractionation, and the LLDPE sample showed an endothermic curve with four well-defined melting peaks (Figure 6, curve c), at 129° ± 1° (T_m) and at 117°, 106°, and 95°C, with their areas reduced according to the temperature decrease. The main peak (T_m) shifting to higher temperatures can be explained as the result of crystallites of higher perfection or well-ordered lamellae of greater thickness[5] as a consequence of recrystallization or reorganization during the isothermal at subsequent temperatures of the longest chains with fewer branches. This happens because there is an equilibrium melting-recrystallization in the interval that could favor lamellar crystallites with an infinite and more homogeneous thickness due to the annealing time. In particular, isothermals below T_c can be considered as the typical annealing temperature and can be associated with the melting of ill-formed crystallites that grow at T_c among the larger crystals. The T_m of the main peak at higher temperatures can also be explained as a result of the melting and recrystallization of crystallites during the heating run, reorganizing themselves in comparison to those initially formed during isothermal crystallization, as already postulated in the literature.[8]

Thermal fractionation carried out in a single scanning with the highest number of isothermals through successive annealing and cooling, as the runs in the fourth series, was revealed to be efficient and time-saving, favoring sharp multiple peaks when compared to the endothermic curve of the sample annealed at a specific temperature. Thermal fractionation with a high number of isothermals seems to be much better for the LLDPE heterogeneity evaluation.

The ΔH_m of the LLDPE without annealing (Figure 1) was about $80 \pm 1\,\mathrm{J \cdot g^{-1}}$ and the crystallinity percentage was around 28 ± 1% calculated from the melting peak, considering the onset and end-set temperatures of 80° and 140°C, respectively. Table 2 shows ΔH_m and crystallinity percentage data of the LLDPE samples crystallized at different isothermals and annealing times (third series) and through different isothermal numbers with fractionation windows of 10°C and annealing of 100 min (fourth series). Although the endothermic curve profiles changed from run to run, there was no variation in the crystallinity of the samples with the thermal treatment, even when the sample was annealed at a specific

Table 2. LLDPE heat of fusion (ΔH_m) and crystallinity data of samples crystallized at different conditions

		Annealing time			
		60 min		100 min	
Run	Isothermal temperature (°C)	ΔH_m ($\pm 1\ \mathrm{J \cdot g^{-1}}$)	Crystallinity ($\pm 1\%$)	ΔH_m ($\pm 1\ \mathrm{J \cdot g^{-1}}$)	Crystallinity ($\pm 1\%$)
1	128	66	24	67	25
2	118	68	24	70	25
3	108	68	24	70	26
4	98	—	—	69	26
5	128–118–108*	—	—	71	24
6	128–118–108–98*	—	—	77	26
7	128–118–108–98–88*	—	—	76	26

*Fractionation windows = 10°C.

temperature for 60 or 100 min. Even though the crystallinity of the samples was always between 24% and 26%, the relative area of the multiple melting peaks changed according to the thermal fractionation or isothermal number. Even after being exposed to high temperatures for a long period of time during the analyses, the crystallinity of the LLDPE samples did not change from one experiment to another, showing good thermal stability.

Effect of Fractionation Windows on Melting Behavior

Figure 7 shows the endothermic curves of the LLDPE sample crystallized through five isothermals, annealing time of 100 min, and fractionation windows of 10°C (fourth series) (Figure 7, curve a) and 6°C (fifth series) (Figure 7, curve b). The sample cooled with fractionation windows of 10°C presented four well-defined melting peaks, whereas the sample fractionated with 6°C windows showed only two peaks. Therefore, fractionation windows of 10°C must be preferred, because a difference of only 6°C between the two annealing temperatures does not favor the growth of distinct crystallite populations if the sample is kept for only 100 min in each isothermal. On the other hand, Starck[13] reported that thermal fractionation of an LLDPE sample with fractionation windows of 6°C gave well-defined multiple melting peaks when longer annealing times (120 or 150 min) and seven isothermals were used. This reveals that the annealing time is a crucial point for an endothermic curve with good

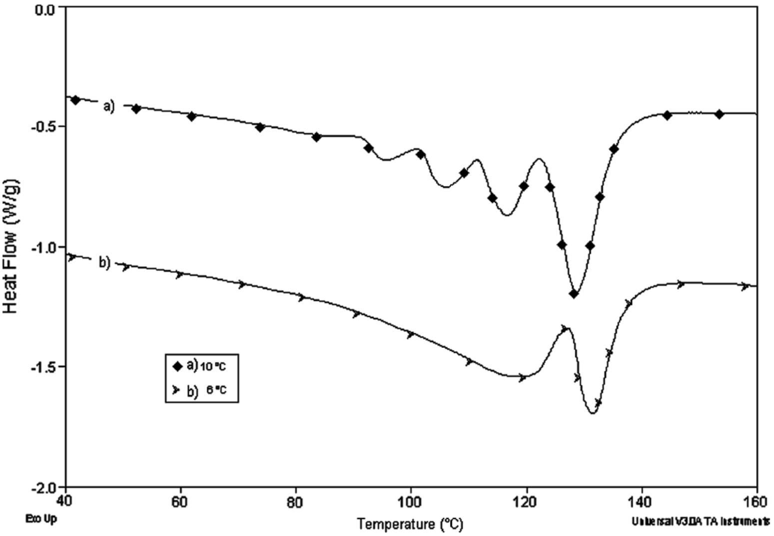


Figure 7. LLDPE endothermic curves of samples crystallized through five isothermals, annealing time of 100 min, and fractionation windows of a) 10°C and b) 6°C.

resolution when fractionation windows are not so large. Thus, wider fractionation windows must be used when annealing time not as long is employed if multiple melting peaks with good resolutions are pursued, such as those obtained in Figure 7, curve a. Fractionation windows of 3°C and annealing time of 120 min used in other studies[15,16] for LLDPE thermal fractionation did not favor endothermic curves with good profiles either. Therefore, results may change when choosing different fractionation windows or annealing times.

Effect of Annealing Time on Melting Behavior

Based on the results obtained with fractionation windows of 10°C, runs were carried out, as described in the sixth series, to evaluate the effect of the annealing time on peak resolution. Figure 8 shows the endothermic curves of the LLDPE samples annealed for 100, 90, 80, 70, or 60 min. The LLDPE fractionated with four isothermals showed similar melting curve profiles, having a broad melting peak and two more peaks. The melting peaks of the samples annealed for 100 (Figure 8, curve a), 90 (Figure 8, curve b), or 80 min (Figure 8, curve c) were well defined and did not show significant differences between them. On the other hand, annealing times

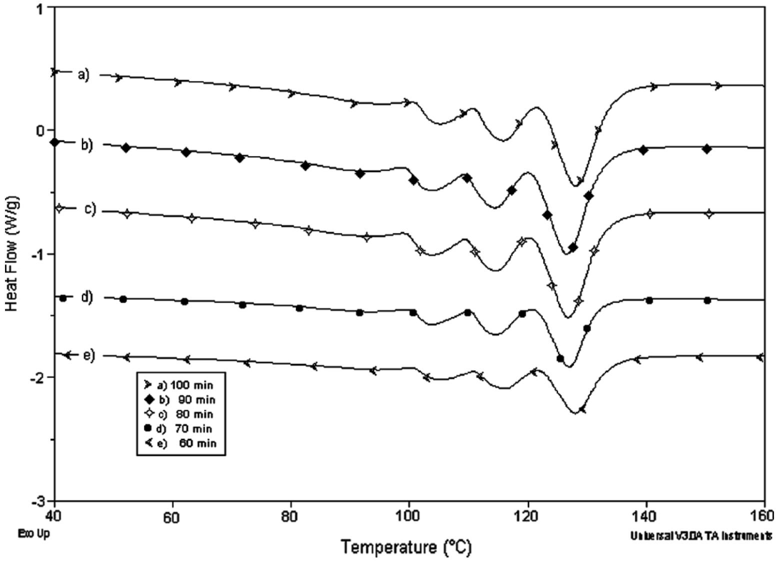


Figure 8. LLPDE endothermic curves of samples crystallized through four isothermals using fractionation windows of 10°C and annealing times of a) 100, b) 90, c) 80, d) 70, and e) 60 min.

of 70 min (Figure 8, curve d) and 60 min (Figure 8, curve e) were not long enough to favor the crystallization of different fractions of LLDPE molecules, and, therefore, the peaks are smaller and not as sharp. In our experiments, thermal fractionation of the LLDPE sample with good endothermic curve profiles was obtained by using fractionation windows of 10°C, annealing time at least of 80 min, and number of isothermals higher than or equal to four. It was also observed that the relative position and area of the multiple melting peaks in the DSC endotherm curve were affected when annealing time increased in the LLDPE thermal fractionation at a given temperature. This is expected since longer time favors crystallite growth and perfection.

The measured T_{onset} and T_m values of LLDPE melting peaks as a function of fractionation windows (6° or 10°C), isothermal number, and annealing time (60 to 100 min) of the runs having at least three isothermal temperatures are reported in Table 3. It was observed that the main melting peak occurs at higher temperatures when the LLDPE is thermal fractionated through different temperatures. The higher the isothermal number, the higher the T_m of the main peak for the same temperature interval from 80° to around 135°C (T_{endset}). The highest melting peak results from the most stable crystallite population, which is formed by the longest crystallizable chain length, as already

Table 3. T_{onset} and T_m values of LLDPE melting peaks as a function of thermal fractionation

			Melting peaks T_{onset}–T_m (°C)				
Fractionation windows (°C)	Number of isothermals	Annealing time (min)	5th	4th	3rd	2nd	Main
Reference							72–126
6	5	100	No	No	No	80–117	127–131
10	5	100	80–85	91–95	101–106	111–117	112–129
10	3	100	No	no	80–98	105–110	115–122
10	4	100	No	80–92	99–103	109–115	120–127
10	4	90	No	80–92	99–103	109–115	120–127
10	4	80	No	80–92	99–103	109–115	120–127
10	4	60	No	80–93	100–105	111–110	122–128

described.[9] The number of peaks in the endothermic curve is in accordance with the isothermal number used in the thermal fractionation procedure. Nevertheless, only two peaks were observed when the fractionation window was 6° instead of 10°C. It seems that 6°C is not enough to segregate different molecules of the LLDPE sample. For fractionations having the same number of isothermals and fractionation windows, changing annealing time from 100 to 80 min did not have an influence on the multiple melting peaks T_{onset} and T_m, but the peaks' areas decreased smoothly and the peaks were not as sharp. With annealing times of 60 min or lower, no well-defined peaks were obtained. Thermal fractionation studies of LLDPE with different structures, produced by different polymerization processes, are in progress in order to see the influence of branch type and content when determining the efficiency of thermal fractionation in relation to the crystallization conditions herein discussed.

CONCLUSION

Isothermal number, fractionation window, and annealing time, independently, have a strong effect on LLDPE crystallization, and for the same LLDPE sample many endothermic curve profiles were obtained. The apex of the main melting peak for the annealed sample with low isothermal number was very similar to the apex of the non-annealed sample and shifted to higher temperature when the isothermal number increased. The heat of fusion or the crystallinity percentage of the LLDPE samples crystallized at different thermal conditions did not change even when the process took 7 to 10 h. The ability of the sample to crystallize by fractionating rose with the increase of the number of isothermals due to the higher chain mobility of the macromolecules with low molar mass at lower temperature. In this work, the best thermal fractionation conditions for the LLDPE sample, producing sharp multiple melting peak curves with good profiles, resulted from the runs employing five isothermals, fractionation windows of 10°C, and annealing time of at least 80 min. Thus, in the thermal fractionation of different LLDPEs, since they are semicrystalline polymers with differences in their structure and molar mass, attention should be paid to physical characteristics and crystallization conditions, considering that both can affect the melting peak profile. In conclusion, the results herein reported confirm that the selection of the thermal fractionation conditions is very important in controlling the multiple melting peak number.

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