

# Characterization of Fractionated LLDPE by DSC, FTIR, and SEC

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## SYNOPSIS

Samples of ethylene/1-butene copolymer were fractionated according to chemical composition by preparative temperature rising elution fractionation (TREF) in the range of 27–117°C. The resulting fractions were submitted to DSC, SEC, and FTIR analyses. For each fraction, the methyl group content, melting temperature, crystallinity, average molecular weight, and molecular weight distribution were determined. From the results, it was found that the melting temperature increased linearly with the extraction temperature in the range of low temperatures and remained constant at high temperatures. Similar behavior was observed for crystallinity. It was also verified that the first two fractions showed a higher degree of supercooling than the fractions extracted at higher temperatures. These results were explained by the existence of a heterogeneous intermolecular distribution of comonomer molecules. In a general way, the comonomer units, present at higher concentrations in the low temperature fractions, tended to destroy the crystalline order of the polymer. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

The molecular structure of linear low density polyethylene (LLDPE) has been investigated from different points of view, such as the average content of comonomer, the intramolecular comonomer sequence distribution, and the distribution of comonomer among polymer chains, in addition to average molecular weights and molecular weight distribution.

The final properties of LLDPE are strongly affected by its chemical composition. Mirabella et al.<sup>1</sup> found that LLDPE had significantly higher values of fracture toughness than HDPE and LDPE resins, because of its extreme compositional heterogeneity.

In order to study these heterogeneities, several authors<sup>2–6</sup> have fractionated LLDPE according to molecular size and/or to chemical composition by solvent gradient elution fractionation (SGEF) and temperature rising elution fractionation (TREF) techniques, respectively.

Mirabella and Ford<sup>2</sup> reported for LLDPE a strikingly melting behavior different from that of LDPE and HDPE, characterized by a broad and multimodal curve. After fractionation by TREF, such behavior is attributed to a broad and multimodal short chain branching distribution (SCBD).

Wild et al.<sup>3</sup> used an improved TREF system for the segregation of tubular and autoclave LDPE resins, high and low density resins produced by low pressure processes, and copolymers of ethylene with vinyl acetate and ethyl acrylate. The results show that the TREF procedure is slightly influenced by molecular weight in the normal high polymers range. Also, cocrystallization effects between unlike macromolecular species were negligible.

Usami et al.<sup>4</sup> also reported results from samples of LLDPE, manufactured by four different processes, and fractionated by TREF. After SEC, <sup>13</sup>C-NMR, DSC, and FTIR analyses, LLDPE samples, produced under different conditions of temperature, pressure, and solvent, showed the same characteristic bimodal SCB distribution, while HP-LDPE exhibited a single-peak distribution. From the values of reactivity ratio determined for each fraction by <sup>13</sup>C-NMR, two kinds of active sites in the catalyst particle were identified. Finally, Usami et al.<sup>4</sup> con-

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cluded that the two peaks observed in TREF curves were caused by the two different types of sites, one producing an alternating character, and the second a random behavior in the polymerization.

The purpose of this work was to study the melting and crystallization behaviors of the fractions and to correlate them with FTIR and SEC data.

## EXPERIMENTAL

### Materials

Ethylene/1-butene copolymer, G 7047 Natural 7, was kindly supplied in granular form by Union Carbide Chemical and Plastics Corporation, Victoria, Texas, USA. It was a low-pressure product produced in a gas-phase reactor using Ziegler–Natta catalysts. Union Carbide has reported that the sample was an antioxidant modified resin with the following characteristics: density = 0.918 g/cm<sup>3</sup> (ASTM-D 1505) and melt index = 1.0 g/10 min (ASTM-D 1238).

### Size Exclusion Chromatography (SEC)

The average molecular weights and molecular weight distribution of the whole polymer and fractions were determined by standard techniques on a Waters 150 ALC gel permeation chromatograph, operating at 135°C, using 1, 2, 4 TCB as solvent with a flow rate of 1.0 mL/min. The column used was a PL–Gel 10 μm mixed bed with porosity ranging from 10<sup>3</sup> to 5 × 10<sup>7</sup> Å. Solution concentrations were within the order of 0.05–0.01% w/v.

Polystyrene standards were used for calibration purposes, and by using the Mark–Houwink and the hydrodynamic volume equations, the molecular weights, with respect to polystyrene, were converted to polyethylene.

The Mark–Houwink constants ( $k$ ;  $\alpha$ ), generally used for HDPE, were also adopted for LLDPE, since neither the backbone mobility nor its molecular size are significantly affected by the presence of SCBs in LLDPE. The values taken from literature<sup>7</sup> for polystyrene (PS) and polyethylene (PE) were:

$$\text{PS: } k = 1.72 \times 10^{-4} \text{ dL/g; } \alpha = 0.67.$$

$$\text{PE: } k = 9.54 \times 10^{-4} \text{ dL/g; } \alpha = 0.64.$$

### Thermal Analysis

Thermal analysis was carried out using a differential scanning calorimeter, Perkin–Elmer DSC-2. Samples of 5–10 mg were sealed in aluminum pans and

were subjected to heating–cooling cycles. Previous thermal effects were minimized by initially heating the samples until melting. The samples were then slowly cooled to room temperature to favor crystallization from the melt. Subsequently, the second heating–cooling cycle was recorded, providing endothermic (melting) and exothermic (crystallization) curves.

The heating and cooling rates were 10°C/min and the range of temperatures examined was between 20°C and 140°C.

The heat of fusion was estimated from the area measured under the endothermic curve by means of a planimeter. Indium was used as standard ( $T_m = 156.6^\circ\text{C}$ ;  $\Delta H_f = 6.8 \text{ cal/g}$ ). The degree of crystallinity was then obtained from the ratio between the fusion heats of the sample and 100% crystalline polyethylene ( $\Delta H_{100\%}$ ). A value of 66.2 cal/g was obtained from the literature for  $\Delta H_{100\%}$ .

### Branching Analysis

The degree of short chain branching (SCB) was determined by infrared spectroscopy, using the methyl group absorption band at 1378 cm<sup>-1</sup>. All spectra were recorded on a Perkin–Elmer infrared spectrometer, FT–IR 1710. The measurements were carried out under the following conditions: number of scans: 100; resolution: 4 cm<sup>-1</sup>; signal/noise ratio: > 0.1%  $T$ ; wavenumber range: 2000–600 cm<sup>-1</sup>.

The quantitative measurement of methyl contents was performed according to a method reported in the literature.<sup>8</sup> Calibration was carried out using NBS-1476 as standard with a methyl content of 1.46/100 C.

All data were expressed as the number of branches per 100 carbon atoms. The relative error of this method was approximately 8%.

The comonomer molar concentration ( $[X_{C_4}]$ ) was determined from the total CH<sub>3</sub>/100 C, by just applying some corrections. Both lateral and terminal methyl groups contribute to the absorbance of the band at 1378 cm<sup>-1</sup>. Since the use of Ziegler–Natta catalysts almost completely inhibit the occurrence of intra- and intermolecular reactions, the presence of lateral methyl groups was supposed to be a result of the comonomer molecules.

Therefore, the number of comonomer methyl groups ( $C$ ) can be obtained from the number of total methyl groups ( $N$ )—calculated from 1378 cm<sup>-1</sup> absorption—and terminal methyl groups ( $T$ )—calculated from the number average molecular weight, as follows:

$$C = N - (k_t/k_c)T \quad (1)$$

where  $(k_t/k_c)$  is the ratio between the absorption coefficients, relative to terminal and lateral methyl groups at  $1378 \text{ cm}^{-1}$ , respectively.

This equation is based on the assumption that both chain ends are methyl groups.

The number of the comonomer methyl groups can be readily converted into comonomer molar concentration, using the following equation:

$$[X_{c4}] = \frac{2N}{1 - 0.02N} \quad (2)$$

In addition to the absorption at  $1378 \text{ cm}^{-1}$ , the presence of comonomer molecules can also be identified in the spectra through the internal methylene rocking vibration at  $770 \text{ cm}^{-1}$ , relative to the absorption of ethyl groups attached to backbone.

The fractions and the whole polymer were prepared as  $150\text{--}300 \mu\text{m}$  thick films, obtained by compression molding at  $140^\circ\text{C}$ . The thickness of the films was measured by means of a micrometer and the density was obtained by the density-gradient column method.

### Fractionation

According to a method reported in the literature,<sup>9</sup> a previous weighed sample (8 g) was dissolved in *o/p*-xylene at  $120^\circ\text{C}$  until complete dissolution was achieved, in order to provide a 4.5% w/v solution. The polymeric solution was then rapidly cast onto the heated column, which had been filled with an inert support (Celite 535), at the same temperature of the solution. After casting, the system was naturally cooled to room temperature.

The separation process was initiated by adding 500 mL of xylene at constant temperature. In each fraction, the extracted material was collected after all xylene had been added to the column.

The extraction temperature was raised stepwise in  $10^\circ\text{C}$  intervals over the range of  $27\text{--}117^\circ\text{C}$ ; therefore, ten fractions were obtained. The extraction time was controlled by the flow rate of the eluted fractions. Three fractionation tests were performed. In the first one, all fractions were extracted in 90 min, while in the others, the extraction time for the first three fractions was duplicated to assure the elution of the material which was soluble at low temperatures.

The resulting fractions were recovered by reprecipitation using methyl alcohol as nonsolvent, filtered and dried in a vacuum oven at  $50^\circ\text{C}$  overnight. The dry material was weighed to provide the frac-

tions' weight distribution curves and then was submitted to SEC, FTIR, and DSC analyses.

## RESULTS AND DISCUSSION

### Fractions Weight Distribution

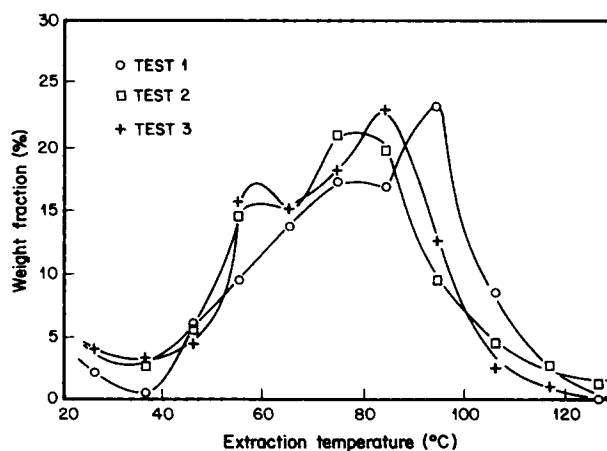
The fractions weight distribution curves, obtained from the three fractionation tests, are shown in Figure 1, where it can be seen that:

1. In all tests, the profiles are similar, with the copolymer molecules being extracted for the most part at approximately  $80^\circ\text{C}$ .
2. Until the polymer was exhausted in the column, the amount of material eluted at a given temperature in the second and third tests was always greater than in the first test. This result indicates that, by allowing the system to remain in the first three temperatures for a longer period, the molecules' solubilization was favored in the subsequent temperatures. This reflects the strong effect of time on the solubilization process of the chains. From the distinct results, it can be concluded that the desired equilibrium was not reached.

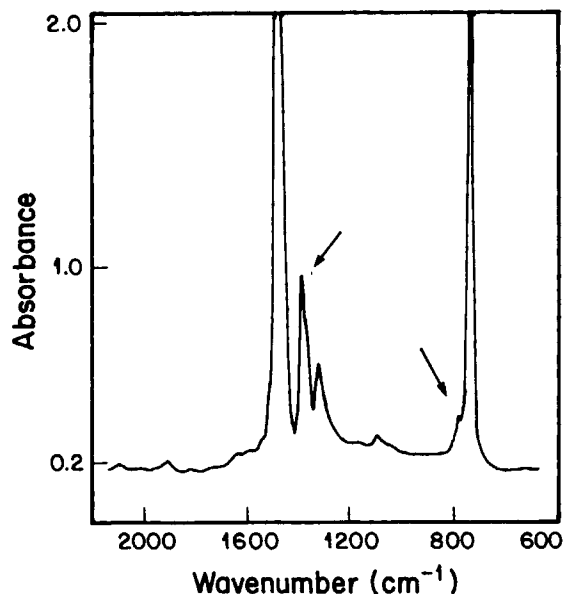
### Content of Methyl Group

Prior to the measurement of the methyl group content for each fraction, the spectrum of the unfractionated sample was recorded for comparison purposes.

Figure 2 shows the spectrum of LLDPE before fractionation. Observed are either the  $1378 \text{ cm}^{-1}$



**Figure 1** Weight fraction distribution of ethylene/1-butene copolymer.



**Figure 2** FT-IR spectrum of ethylene/1-butene copolymer. Film thickness: 230  $\mu\text{m}$ .

band, relative to lateral and terminal methyl groups, or the  $770\text{ cm}^{-1}$  peak, which is assigned to the vibration of ethyl groups attached to the backbone.

Since the occurrence of branches in LLDPE, due to chain transfer reactions, is supposed to be inhibited by the catalyst, these bands can be attributed to the ethyl groups formed during the 1-butene copolymerization. Consequently, these bands can be used to measure the comonomer concentration in the copolymer.

The number of total methyl groups ( $N$ ) was then determined from the absorbance of the methyl band

at  $1378\text{ cm}^{-1}$ . From the value of  $\bar{M}_n$ , the number of terminal methyl groups ( $T$ ), relative to the original sample, was calculated to be equal to  $0.08\text{ CH}_3/100\text{ C}$ , and the subtraction of the terminal methyl groups from the total methyl groups produced 1.67 comonomer methyl groups per 100 carbon atoms.

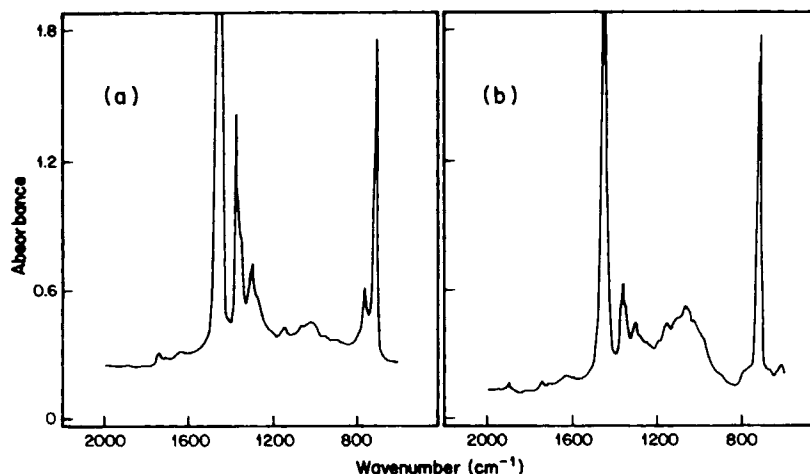
$$\text{From eq. (2), } [X_{c4}] = 3.4\%.$$

After the spectroscopic characterization of the unfractionated sample, the spectrum of each fraction was recorded and the comonomer methyl groups were determined. The spectra from the fractions, extracted at  $27^\circ\text{C}$  and  $107^\circ\text{C}$ , are illustrated in Figures 3(a) and 3(b), respectively. In the former, both the  $1378\text{ cm}^{-1}$  and  $770\text{ cm}^{-1}$  peaks are strong and sharp, while in the latter, these bands appear just as a shoulder. These differences are an indication of a heterogeneous intermolecular distribution of the comonomer molecules.

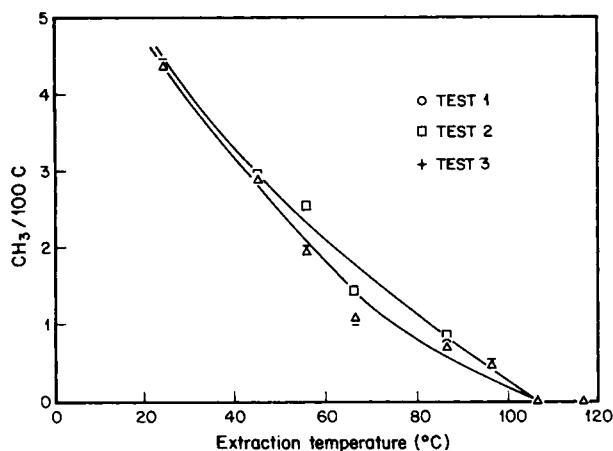
The quantitative analysis of methyl groups, through the  $1378\text{ cm}^{-1}$  band, corroborates the above, preliminary observation. As is shown in Figure 4, the comonomer distribution among the fractions is heterogeneous. It is more concentrated in the fractions extracted at low temperatures while, for extraction at high temperatures, the comonomer concentration is negligible.

Therefore, it can be suggested that the LLDPE sample used in this work consists of a mixture of ethylene/1-butene copolymer molecules with a wide range of 1-butene content, as well as molecules of ethylene homopolymer.

The explanation for such heterogeneous intermolecular distribution should be the same as that



**Figure 3** FT-IR spectrum of ethylene/1-butene copolymer. (a) extracted at  $27^\circ\text{C}$ , (b) extracted at  $107^\circ\text{C}$ .



**Figure 4** Relationship between the methyl group content and the extraction temperature of ethylene/1-butene copolymer.

proposed by Usami et al.,<sup>4</sup> that is, the existence of at least two kinds of active sites in Ti-based Ziegler-Natta catalysts. The first kind of active site, with an alternating character during the copolymerization, produced the chains extracted at low temperatures and characterized by a high comonomer content. The second type of site, with a random character, can be responsible for the low content comonomer chains extracted at high temperatures. In this case, since the overall concentration of 1-butene is relatively low as compared to ethylene, this site can also lead to ethylene homopolymerization.

### Molecular Weight Measurements

The average molecular weights and polydispersity of the fractions, obtained from the first and second

tests, are summarized in Table I, which also includes SEC results for the unfractionated sample.

It is shown in Table I that the fractions extracted at low temperatures showed slightly lower molecular weights than the fractions extracted at high temperatures. However, this discrepancy is not significant in view of the uncertainties present in a high-temperature SEC analysis.

The polydispersity of the fractions were close to the value obtained for the unfractionated sample. Thus, it can be concluded that the temperature rising elution fractionation technique is not effective in segregation according to molecular size. Fractions obtained from TREF are similar in chemical composition, but different in size.

This result seems to be consistent with the conclusion reached by Wild et al.,<sup>3</sup> which predicts that in the high-molecular-weight region ( $> 10^4$ ), the temperature of separation is essentially independent of the molecular weight.

### Thermal Characterization

In addition to the chemical structure analysis, the fractions were also characterized with respect to their melting ( $T_m$ ) and crystallization ( $T_c$ ) temperatures, degree of crystallinity ( $X_c$ %), and degree of supercooling ( $T_m - T_c$ ).

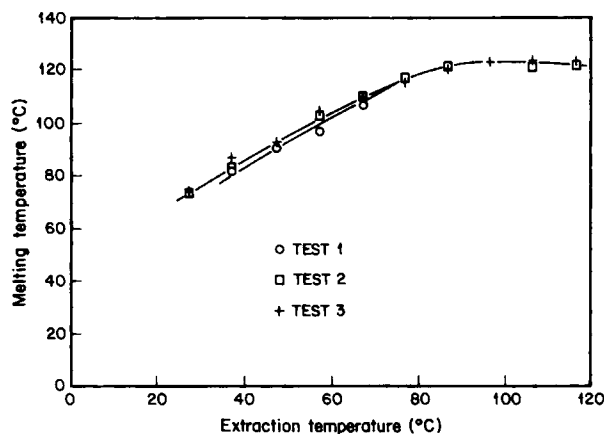
The melting temperature behavior, with respect to the extraction temperature, is shown in Figure 5. For comparison purposes, the DSC curve, related to the unfractionated sample, is illustrated in Figure 6, with the following results:  $T_m = 121^\circ\text{C}$ ,  $T_c = 106^\circ\text{C}$ ,  $X_c = 30\%$ ,  $T_m - T_c = 15^\circ\text{C}$ .

From Figure 5, one can verify that the melting temperature increased linearly with the extraction temperature in the low temperature range, and re-

**Table I**  $\bar{M}_w$ ,  $\bar{M}_n$ , and  $\bar{M}_w/\bar{M}_n$  of Fractionated Ethylene/1-Butene Copolymer<sup>a</sup>

Extraction Temperature (°C)	Experiment 1			Experiment 2		
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
27	90,000	13,960	6.4	73,110	15,530	4.7
37	98,500	21,850	4.5	83,180	21,700	3.8
47	102,100	24,540	4.1	94,270	23,080	4.1
57	113,200	33,800	3.4	105,130	28,690	3.7
67	128,600	35,910	3.6	124,300	40,780	3.1
77	110,600	34,180	3.2	113,700	38,360	3.0
87	158,200	39,610	4.0	145,200	42,720	3.4
97	123,500	35,090	3.5	103,600	31,760	3.3
117	116,100	33,410	3.5	120,600	32,720	3.7

<sup>a</sup> Unfractionated sample:  $\bar{M}_w = 106,000$ ,  $\bar{M}_n = 25,000$ , and  $\bar{M}_w/\bar{M}_n = 4.3$ .



**Figure 5** Melting temperature as a function of the extraction temperature of ethylene/1-butene copolymer.

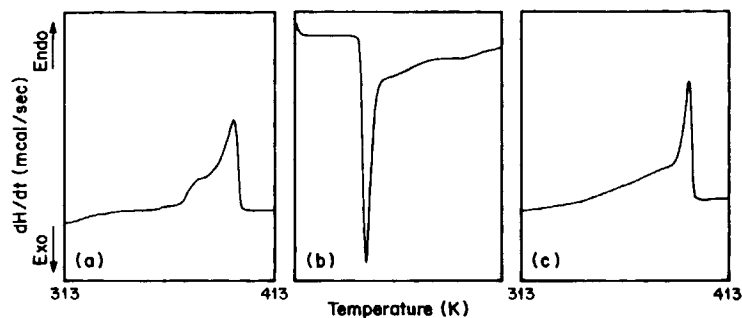
mained constant at the high temperature region, with a difference of 3°C higher than the melting temperature of the unfractionated polymer.

Even for the high-temperature fractions, in which the comonomer concentration was low, the melting temperature of HDPE was not reached.

From the work of Flory et al.<sup>10</sup> and the data of Wilfong and Knight,<sup>11</sup> comonomer molecules, which are at low concentrations in these fractions, are still able to reduce their melting temperature.

The relationship between melting and extraction temperatures is in agreement with the results obtained for the intermolecular comonomer distribution. Fractions, extracted at low temperatures, showed more drastic reductions in  $T_m$ , due to the high concentration of comonomer molecules, which reduces the crystalline order of the polymer.

Figure 6 shows that the melting range, presented by the original sample, was broad, as compared to the relatively narrow molecular weight distribution. The melting temperature profile explains this fact.



**Figure 6** DSC curves of ethylene/1-butene copolymer. (a) first heating, (b) cooling, (c) second heating.

The crystals are composed of small and imperfect crystallites with thin lamellae, which are under the strong influence of the comonomer molecules and, therefore, melt at low temperatures.

As shown in Figure 7, the first two fractions showed higher values of supercooling degree, as compared to the remaining fractions and the unfractionated sample. This quantity indicates how far the crystallization process has deviated from equilibrium conditions.

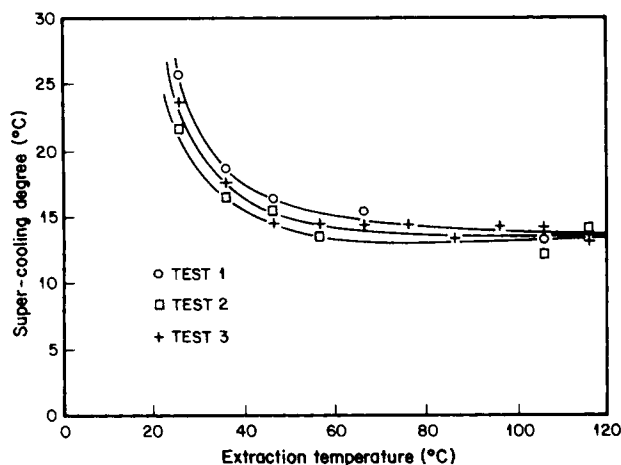
In the first two fractions, it can be suggested that the crystallization would have occurred far from equilibrium, probably due to the effects caused by the high comonomer concentration in these fractions.

In order to obtain more information about the melting and crystallization processes, the DSC curve of each fraction was carefully examined. Figure 8 illustrates the DSC curves obtained from the first test.

It is obvious that the fraction, extracted at room temperature ( $T = 27^\circ\text{C}$ ), showed two well-defined peaks during the first heating. According to Usami's theory, the first peak should be assigned to the melting of the crystalline species, which are produced by a specific kind of active site and are characterized by a high comonomer concentration. On the other hand, the second peak should be attributed to the melting of crystals with a low comonomer concentration, probably produced by another type of site.

The fraction extracted at 37°C showed similar behavior, but in this case, the area under the first peak was small as compared to the second peak. This result is consistent with the fact that the comonomer concentration in this fraction was not as high as in the 27°C fraction.

However, for both fractions, only one *broad* peak was detected in the DSC curves, corresponding to



**Figure 7** Supercooling degree ( $T_m - T_c$ ) as a function of extraction temperature of ethylene/1-butene copolymer.

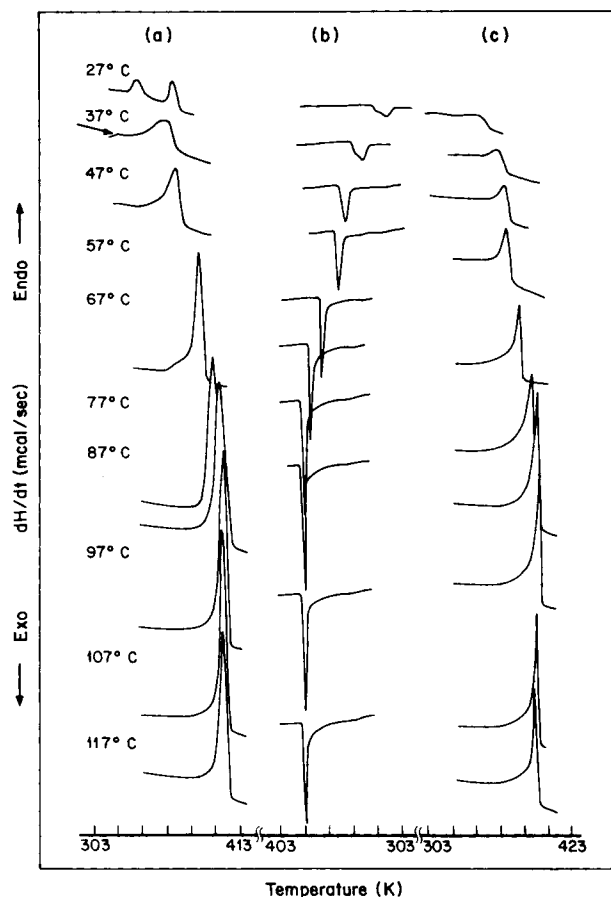
the second heating, in contrast with the first heating. This is in accordance with the assumption that solution crystallization is more effective than melt crystallization in revealing the presence of the various components.<sup>12</sup> Solution crystallization provides superior separation of the different crystalline species, especially in the lower crystallinity region. It is also probable that during slow cooling from the melt, the high-comonomer concentration species have been cocrystallized with those characterized by a low comonomer concentration.

The DSC curves, relative to the fractions extracted at 47 and 67°C, showed only one peak during the first heating, but a characteristic shoulder can still be observed, probably due to the presence of comonomeric units.

In contrast, the curves corresponding to fractions extracted above 77°C were smooth and showed only a sharp peak without any shoulder. This indicates that the crystallization process was not constrained and, therefore, occurred in a more homogeneous way. This probably occurred because the comonomer concentration was low in those fractions.

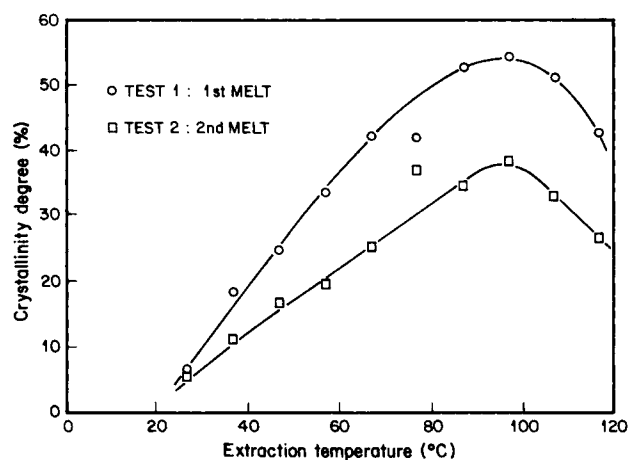
This result corroborates the assumption that the shoulder near 110°C, which was observed during the second melting of the original sample (Fig. 6), occurs because of the deleterious comonomer influence on the crystallization process.

As can be seen in Figure 9, the values obtained for crystallinity show a linear dependence on the extraction temperature, specifically in the range of low and medium extraction temperatures. This result can be explained by the progressive decrease of comonomer concentration with extraction temperature.



**Figure 8** DSC curves of the typical fractions from first TREF experiment. (a) first heating, (b) cooling, (c) second heating.

This behavior is in accordance with the fact that the higher branched species dissolve more easily than the unbranched and high crystalline species.



**Figure 9** Crystallinity degree as a function of extraction temperature of ethylene/1-butene copolymer.

However, at high extraction temperatures, a clear decrease in crystallinity was verified. Since the comonomer concentration was low in these fractions, and molecular weights were not high enough to prevent crystallization, this result can be attributed to lamellae thickness differences. As pointed out by Wilfong and Knight,<sup>11</sup> LLDPE copolymers exhibit two types of lamellae: long, thick, straight lamellae, associated with crystallization of the ethylene-rich portion of the LLDPE molecule, and short, thin lamellae, attributed to the subsequent crystallization of the molecular segments containing the butene comonomer.

Figure 9 illustrates that larger areas under DSC curves were observed during the first heating for all fractions, as compared with those corresponding to the second heating; that is, the sample crystallinity measured from the first melting curve was significantly higher than the second one. In contrast, the areas of the two heating cycles, obtained from the original sample, were similar.

The fractions were then submitted to a third heating cycle and the results were similar to the second heating. It was thus suggested that the distinct values of crystallinities, obtained from the first two heatings, were due to previous thermal effects developed during the fractionation steps.

These results should be explained by the assumption that crystallization from solution reduces intermolecular interactions (entanglements), which might interfere with the crystallization process. As reported in the literature,<sup>13</sup> crystallinity of several polymers can be greatly increased by residual solvent effects (induced-solvent crystallization).

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