Molecular, thermal and morphological characterization of narrowly branched fractions of 1-octene linear low-density polyethylene: 1. Molecular and thermal characterization

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A 1-octene linear low-density polyethylene (LLDPE) with a bimodal short-chain branching (SCB) distribution has been fractionated with respect to the SCB content using preparative temperature-rising elution fractionation (PTREF). The average SCB content of the fractions obtained ranges from 2.9 to 28.2 branches per 1000 C atoms. Their weight-average molecular weight decreases with increasing degree of branching, while the polydispersity remains rather broad. The fractions exhibit a broad single melting endotherm in contrast to the multiple melting endotherms of the unfractionated copolymer. Dynamic crystallization of the fractions from the melt results in two separate exotherms.

(Keywords: linear low-density polyethylene; temperature-rising elution fractionation; short-chain branching; melting behaviour; crystallization behaviour)

INTRODUCTION

Linear low-density polyethylene (LLDPE) is a copolymer of ethylene and an α-olefin (e.g. propene, 1-butene, 1-hexene, 1-octene). The Ziegler–Natta catalyst used during polymerization gives rise to linear polyethylene chains with the comonomer incorporated as short-chain branches. The physical properties of LLDPE are influenced by the average molecular weight and molecular-weight distribution, the type of branching (i.e. the type of comonomer used), and the average short-chain branching content and distribution. The heterogeneous composition of LLDPE makes a systematic study of the structure–property relations very difficult.

Fractionation of LLDPE with respect to the short-chain branching content and the molecular weight provides a powerful tool to investigate the influence of the complex chain microstructure of the copolymer on the morphology-induced properties. Wild *et al.*[1] have fractionated LLDPEs using the analytical temperature-rising elution fractionation (ATREF) technique and demonstrated a very wide bimodal short-chain branching distribution of these copolymers. Schouterden *et al.*[2] fractionated 1-octene LLDPE with respect to the molecular weight using a successive solution fractionation (SSF) method, followed by fractionation according to the short-chain branching content using an ATREF system. It was shown that both strongly branched and weakly branched molecules are present in all the molecular-weight fractions, but that the relative amount of the strongly branched molecules decreases with increasing molecular weight.

In this paper, we present a preparative-scale fractionation of a 1-octene LLDPE with respect to the short-chain branching content using a temperature-rising elution fractionation (TREF) system. Fractionation on a preparative scale allows one to investigate the influence of the short-chain branching content and distribution on the crystallization kinetics, the semicrystalline morphology and melting behaviour of the fractions. Molecular characteristics, especially the short-chain branching distribution, and the thermal behaviour of the fractions are presented in this paper.

Recently, a mechanism for the crystallization of LLDPE and its fractions has been proposed by Wilfong and Knight[3], based on the non-random incorporation of the comonomer in the copolymer chains. Although most of our experimental results are in agreement with this study, some of the statements with respect to the proposed crystallization mechanism have to be reconsidered, based on the electron microscopy study[4] presented in part 2 of this series. A morphological study will be published[5] in part 3.

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EXPERIMENTAL

Analytical and preparative temperature-rising elution fractionation

The 1-octene LLDPE used in this study was fractionated in a TREF system. This type of fractionation consists of two different steps: the selective crystallization of the copolymer chains as a function of their branching degree during a slow and controlled cooling of a dilute solution of the copolymer, followed by elution of the copolymer as the temperature is subsequently raised. This fractionation is based on the crystallizability of the copolymer and, as a consequence, is directly related to the amount and distribution of the comonomer.

In the analytical TREF system a small column loaded with glass beads, having a diameter of 800 μm, is filled with a dilute solution (1 wt%) of the copolymer in 1,2,4-trichlorobenzene (TCB). The column is immersed in a thermostatic bath at 160°C and cooled to 25°C at a rate of 2°C h^{-1}. During the cooling of the dilute solution, the copolymer crystallizes on the glass beads, forming a thin layer with a gradient of increasing short-chain branching content starting from the glass surface. During the elution step, the temperature is raised in a continuous way, and the amount of eluted material is detected by i.r. absorption of the 2940 cm^{-1} wavenumber, corresponding to the antisymmetric stretching of the CH bonds.

The preparative TREF system consists of two large columns mounted in series (*Figure 1*). The columns are loaded with glass beads having a diameter of 2 mm, leaving a total free volume of 650 ml. The same cooling procedure was followed as for the ATREF system.

The 1-octene LLDPE sample was fractionated into a fraction, A0, and eight other fractions, A1 to A8, as shown in *Figure 2*. The fraction A0 consists of non-crystallizable material and was obtained at 25°C by eluting the column with TCB at a flow rate of 20 cm^3 min^{-1}, until the i.r. detector could no longer detect any polymer. The column was then stabilized at 30°C for 2 h and eluted with TCB in a similar way.

The temperature was subsequently increased by 3°C to 33°C, and the column was again stabilized for 2 h. The polymer eluted between 30°C and 33°C is fraction A1. The next fractions were obtained in a similar way and consist of molecules that were eluted over a

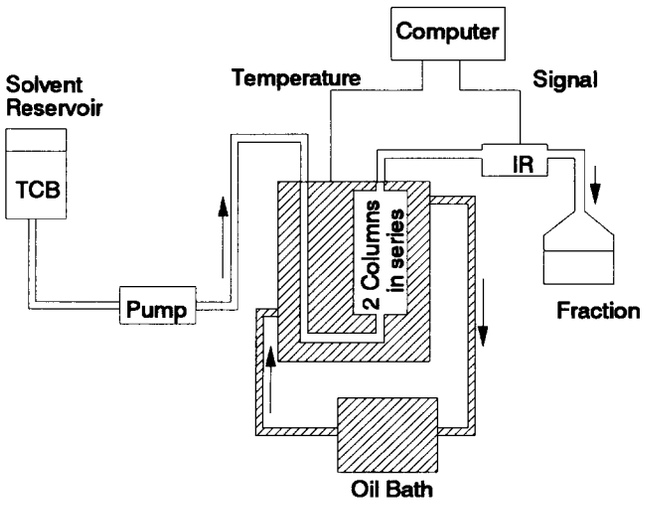

Figure 1 Preparative TREF set-up

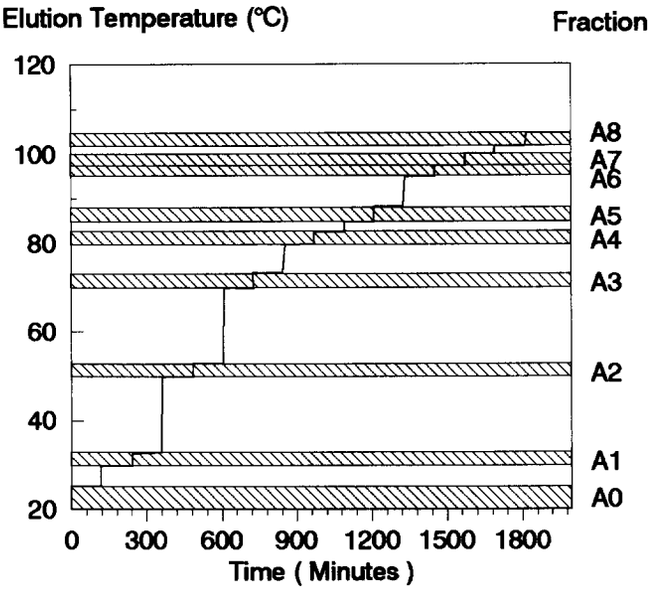

Figure 2 Temperature profile of the column during the elution step of the fractionation as a function of time

temperature interval of 3°C. The upper limit temperature of the elution interval of the fractions A2 to A8 was 53, 73, 83, 88, 98, 100 and 105°C, respectively. It should be noted that fraction A7 only covers an interval of 2°C, between 98 and 100°C.

During elution the fractions were collected and subsequently precipitated by adding an excess of acetone as a non-solvent to the TCB solution; they were finally filtered on a glass filter and dried in a vacuum oven at 50°C for 3 days.

This fractionation scheme gives rise to fractions obtained over a small elution temperature interval of 3°C. The fractionation step itself should therefore not have any influence on the degree of intermolecular heterogeneity. This is not the case when the polymer is fractionated into fractions obtained within different temperature elution intervals.

Only very small amounts of each fraction have been obtained owing to the very narrow fractionation intervals (between 10 mg for fraction A0 and 900 mg for fraction A4). The yield of fractions A0, A1 and A8, obtained at 25, 33 and 105°C respectively, was too poor to consider further complete investigation.

LLDPE sample used and characterization techniques

An ethylene/1-octene LLDPE sample (LLDPE A) polymerized in solution, having a density of 0.920 g cm^{-3} and a melt index of 1.0, has been fractionated using the PTREF system.

The distribution of the comonomer in each fraction has been determined using the ATREF system. From the ATREF curves, a number-average elution temperature T_n has been calculated and translated in terms of an average short-chain branching content, using the calibration curve used for ATREF (elution temperature vs. short-chain branching content).

High-temperature gel permeation chromatography (g.p.c.) was performed on a Waters 150C apparatus to determine the molecular-weight distribution of the unfractionated sample and the fractions.

The crystallization and melting behaviour was studied by differential scanning calorimetry (d.s.c.), using a

Perkin–Elmer Delta Series DSC-7. Cooling and heating rates were both 5°C min^{-1} and the sample weight was between 4 and 6 mg. The degree of crystallinity was calculated from the heat of fusion by integration of the area under the normalized melting peak; a value of 293 J g^{-1} was used as the reference melting enthalpy for 100% crystalline polyethylene.

All the samples of the different fractions were heated to 150°C for 10 min in order to destroy the thermal history. For the study of the crystallization behaviour, the samples were cooled from 150 to 0°C at a rate of 5°C min^{-1}. Subsequently, the melting behaviour was obtained by heating the samples at a rate of 5°C min^{-1} from 0 to 150°C.

RESULTS AND DISCUSSION

Molecular characteristics

The unfractionated 1-octene LLDPE is characterized by a bimodal short-chain branching (SCB) distribution: a narrow mode consisting of molecules with a very low branching content and a very broad mode containing the branched chains. Fractions A7 and A8 obtained at the highest elution temperatures (100 and 105°C) consist only of molecules that belong to the narrow mode. The other fractions will consist of molecules that belong to the broad branched mode. The molecular characteristics (average molecular weight, polydispersity and average short-chain branching content) of the unfractionated 1-octene LLDPE sample and the fractions are summarized in *Table 1*.

Figure 3 shows the elution profiles of the different fractions as measured by an improved analytical TREF system; these curves can be translated in terms of short-chain branching distributions. Fractions A7 and A8, eluted at 100 and 105°C respectively, show a single narrow peak with a maximum at 101°C, corresponding to a homogeneous population of almost unbranched molecules. All the other fractions studied (A6, A5, A4, A3 and A2) exhibit a broader short-chain branching distribution that shifts to higher branching contents (lower elution temperatures). The SCB distributions of all the fractions, even A7 and A8, exhibit a tail towards higher branching contents, indicating that segments having a markedly higher branching content with a much lower crystallizability exist within each fraction. It has been suggested recently that octene can be incorporated in a non-random manner into the ethylene/1-octene copolymer, resulting in blocks of ethylene and poorly crystallizable segments having a much higher octene content[3]. This blockiness of comonomer has also been claimed for an ethylene/1-butene copolymer[6].

Table 1 Elution temperature range T_{el}, number-average molecular weight $\bar{M}_n$, weight-average molecular weight $\bar{M}_w$, polydispersity D, and average short-chain branching content SCB of the fractions and the unfractionated LLDPE A

Fraction	T_{el} (°C)	$\bar{M}_n$	$\bar{M}_w$	D	SCB (CH_3/1000 C)
A1	30–33	4800	19100	3.98	–
A2	50–53	14600	49300	3.37	28.2
A3	70–73	32900	94000	2.86	20.4
A4	80–83	46400	128200	2.76	14.8
A5	85–88	53100	146200	2.75	11.5
A6	95–98	72200	176300	2.44	6.4
A7	98–100	114500	252000	2.20	3.2
A8	102–105	123000	269000	2.19	2.9
LLDPE A		31000	114000	3.67	9.7

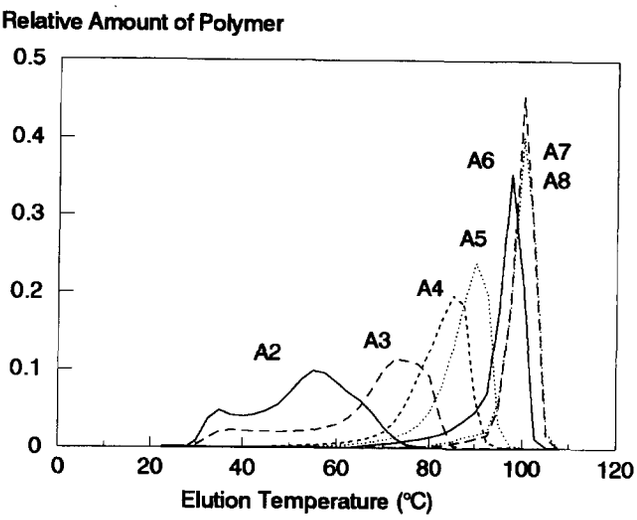

Figure 3 ATREF curves of the fractions

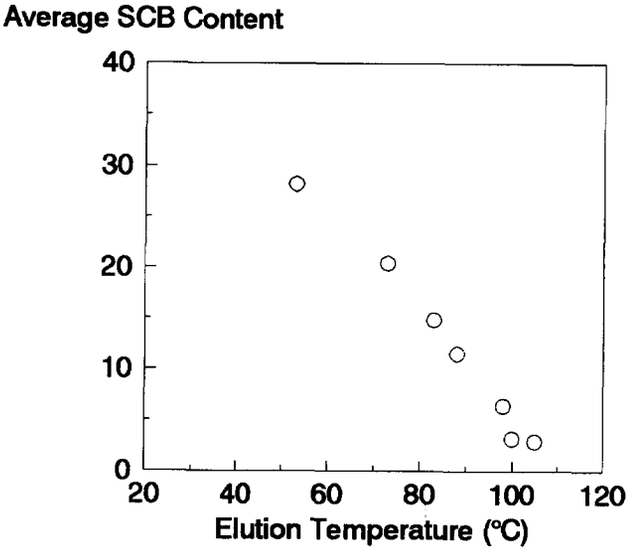

Figure 4 Average SCB content of the fractions as a function of the elution temperature

The average short-chain branching content of the fractions decreases from 28.2 branches per 1000 carbon atoms for the fraction eluted at 53°C (A2), to 2.9 branches per 1000 carbon atoms for the fraction eluted at 105°C (A8). The relation between the elution temperature T_{el} of the fractions and the average short-chain branching content is shown in *Figure 4*.

For all fractions, a broad molecular-weight distribution has been observed (*Figure 5*). The polydispersity index $\bar{M}_w/\bar{M}_n$ decreases with decreasing SCB content of the fractions. The overall molecular weight of the fractions ranges from less than 500 to more than 2×10^6.

An interesting correlation is found between the average short-chain branching content and the number- and weight-average molecular weights of the fractions (*Figure 6*). A decrease of the average short-chain branching content results in a concomitant increase of the molecular weight. Similar observations were also presented by other

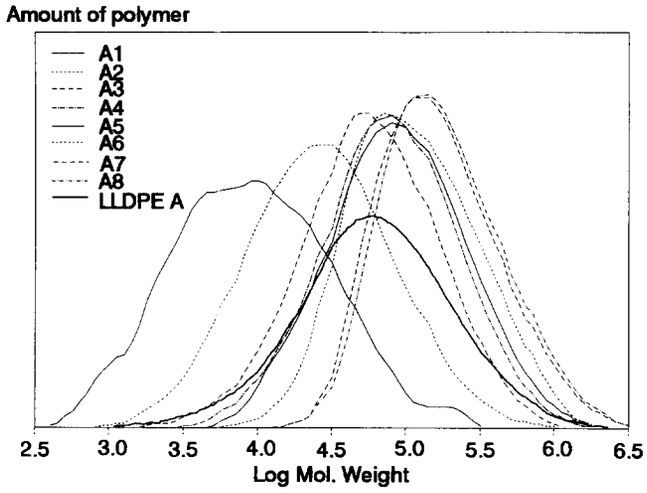

Figure 5 Molecular-weight distribution of the fractions and LLDPE A

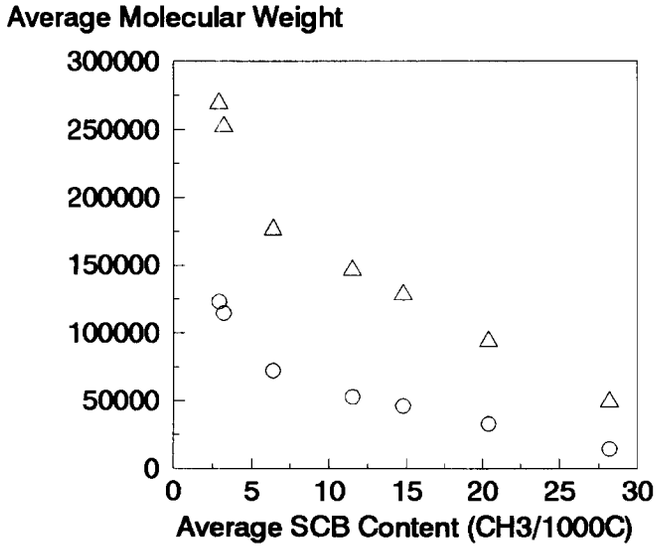

Figure 6 Number-average (△) and weight-average (○) molecular weights as a function of the SCB content

authors[3,7,8]. *Figure 6* also illustrates the huge intermolecular heterogeneity of LLDPE. Extrapolation of the relationship between SCB content and molecular weight to higher SCB contents indicates that the probability of finding molecules with more than 35 branches per 1000 main-chain C atoms is very low. This can be an explanation of the very low amounts of polymer eluted at 25 and 33°C.

The molecular characteristics of the fractions obtained make it clear that the fractionation using PTREF was very effective. Fractions A7 and A8 consist of a homogeneous population of very weakly branched molecules. The fractions obtained at lower elution temperatures consist of molecules with broader distributions of the short-chain branches and of the molecular weight. These results are a clear illustration of the complex chain microstructure of unfractionated 1-octene LLDPE.

Melting behaviour

Unfractionated LLDPE copolymers are characterized by a complex melting behaviour involving broad endotherms (*Figure 7a*). The thermal history and the intermolecular heterogeneity of the copolymer, which both depend on the type, amount and distribution of the branches as well as on the molecular weight, determine the morphology and consequently the thermal behaviour[9–11]. The multiple melting endotherms of unfractionated LLDPE can be attributed to the melting at high temperatures of crystals composed of very weakly branched molecules, while the melting of crystals composed of more branched molecules results in a broad melting endotherm at lower temperatures. As already mentioned, the thermal history is of great importance for the morphology and the melting behaviour. The melting endotherms of the fractions, crystallized during cooling at 5°C min^{-1}, are less complex (*Figure 7b*). The fractions are still melting over a broad temperature range but exhibit a single melting peak. The peak and end melting temperatures of the fractions shift to lower temperatures with increasing average short-chain branching content. The results deduced from the melting endotherms are summarized in *Table 2*.

Fractions A8, A7 and A6 (eluted at 105, 100 and 98°C respectively), which consist of weakly branched molecules, have a higher peak maximum and end melting temperature than the unfractionated copolymer LLDPE A. This might be an indication that co-crystallization occurs in the unfractionated copolymer between the weakly branched molecules and the ethylene-rich segments of molecules having a higher average branching content.

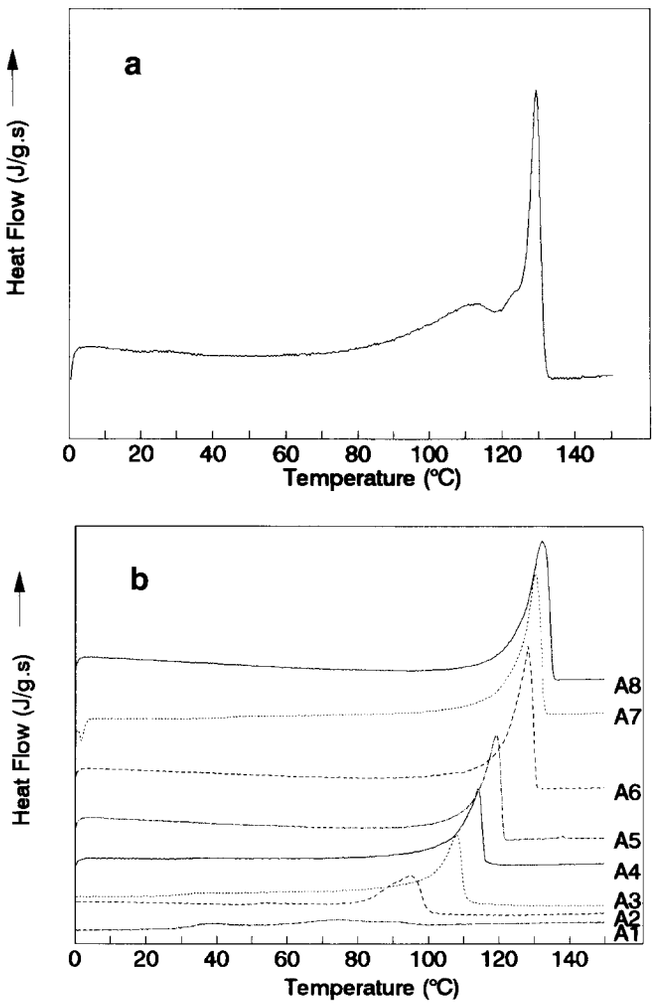

Figure 7 Melting endotherms of (a) the unfractionated LLDPE A and (b) the fractions

Table 2 Elution temperature range T_{el}, enthalpy of fusion ΔH_u, crystallinity χ_c, onset temperature T_{onset}, and peak temperature T_{peak} of the melting endotherms of the fractions and the unfractionated LLDPE A

Fraction	T_{el} (°C)	ΔH_u (J g^{-1})	χ_c (%)	T_{onset}[a] (°C)	T_{peak} (°C)
A1	30–33	32.8	11.2	–	74.1
A2	50–53	67.4	23.0	82.5	95.2
A3	70–73	99.7	34.0	99.7	106.7
A4	80–83	99.2	33.8	108.1	114.1
A5	85–88	119.2	40.7	111.8	119.2
A6	95–98	148.7	50.7	122.3	128.0
A7	98–100	141.8	48.4	124.8	130.0
A8	102–105	156.8	53.5	124.2	132.1
LLDPE A		108.7	37.1	117.5	121.1

[a] Onset temperature of the highest-temperature melting peak

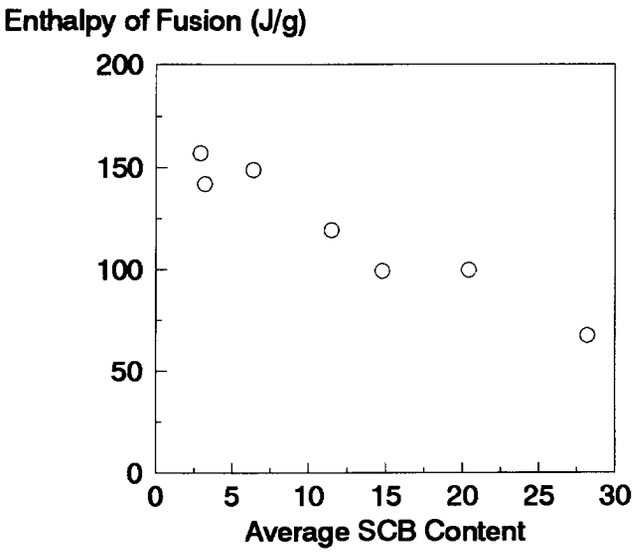

Figure 8 Enthalpy of fusion ΔH_u of the fractions as a function of the SCB content

The branches present in these co-crystallized molecules restrict the formation of thick lamellae having high melting temperatures.

The enthalpy of fusion of the fractions, calculated from the area under the melting endotherm, strongly depends on the short-chain branching content (*Figure 8*). The crystallinity χ_c varies from about 11% for the highly branched fractions to about 53% for the almost unbranched fractions. An intermediate value of about 37% is obtained for the unfractionated LLDPE (*Table 2*).

Crystallization behaviour from the melt

The unfractionated 1-octene LLDPE sample (LLDPE A) exhibits a sharp onset of crystallization at about 107°C (*Figure 9a*) and crystallizes over a range of about 80°C. The fractions (*Figure 9b*) exhibit a large high-temperature crystallization exotherm, shifting to lower temperatures with increasing comonomer content (*Table 3*). A second, much smaller exotherm can be detected for most fractions as the temperature is lowered by about 40°C with respect to the first crystallization exotherm. In a preliminary study, using fractions obtained over a broader elution interval, the lower-temperature exotherms were present in a more pronounced manner.

Such a twofold crystallization behaviour has also been observed recently by Wilfong and Knight[3] and has been tentatively ascribed to the separate crystallization of ethylene-rich and octene-rich segments of the copolymer chains. The authors based their conclusions on a transmission electron microscopy study of Hosoda[8], showing that unfractionated LLDPE copolymers exhibit long, straight, thick lamellae as well as very short, thin lamellae, branching off the thick ones. The long and thick

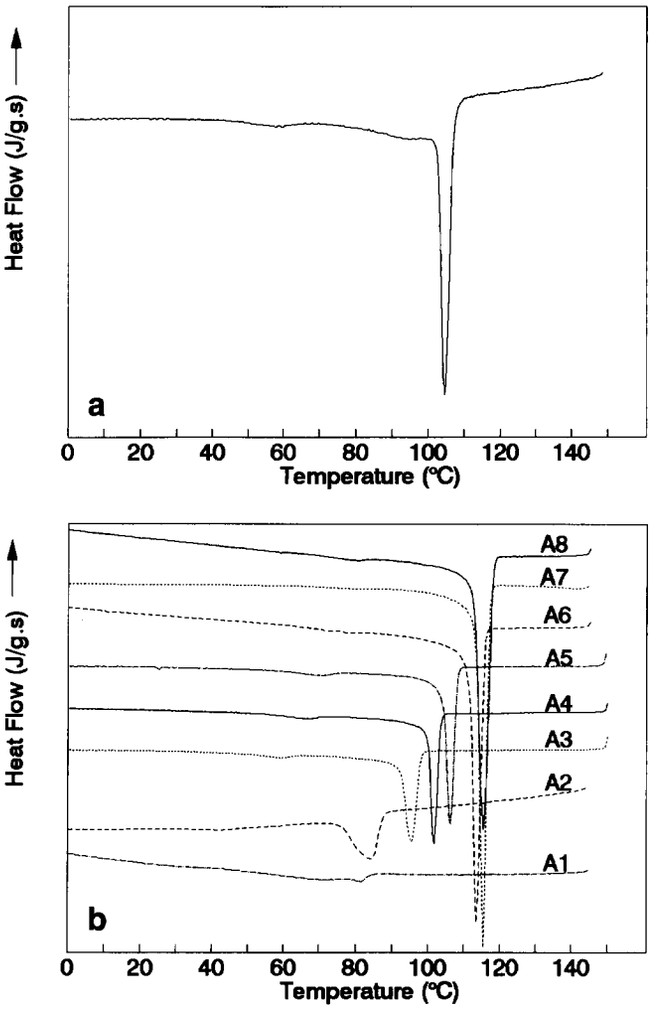

Figure 9 Crystallization exotherms of (a) the unfractionated LLDPE A and (b) the fractions

Table 3 Elution temperature range T_{el}, enthalpy of crystallization ΔH_c, onset temperature of crystallization T_{onset}, and peak temperature T_{peak} of the first crystallization exotherm of the fractions and the unfractionated LLDPE A

Fraction	T_{el} (°C)	ΔH_c (J g^{-1})	T_{onset} (°C)	T_{peak} (°C)
A1	30–33	−33.1	85.2	67.9
A2	50–53	−68.0	88.3	84.7
A3	70–73	−115.2	97.8	95.3
A4	80–83	−100.0	103.4	101.6
A5	85–88	−138.0	108.5	106.6
A6	95–98	−168.7	116.0	113.9
A7	98–100	−146.0	117.7	116.0
A8	102–105	−180.7	118.4	115.7
LLDPE A		−126.6	107.0	104.6

lamellae would result from the ethylene-rich segments of the LLDPE molecules, whereas the octene-rich segments would crystallize into the short and thin lamellar branches. However, a detailed TEM study[4] on the fractions considered in this paper clearly shows that the lamellar population existing in each fraction corresponds nearly to a Gaussian distribution where only the mean and standard deviation are influenced by the SCB content. Only for the unfractionated LLDPE could a bimodal lamellar population be detected.

CONCLUSIONS

A preparative-scale fractionation of 1-octene LLDPE with respect to the short-chain branching content using a PTREF system has been realized. Each fraction was collected over a narrow elution interval of 3°C. The average short-chain branching content of six fractions analysed (A8 to A2) ranges from 2.9 and 28.2 branches per 1000 carbon atoms, compared to an average value of 9.7 for the unfractionated 1-octene LLDPE sample. Fractions A8 and A7, eluted at 105 and 100°C, respectively, can be considered as homogeneous populations of very weakly branched molecules. The SCB distributions of the other fractions (A6, A5, A4, A3 and A2) become broader with decreasing elution temperature. The short-chain branching distributions of the fractions clearly illustrate the pronounced intermolecular heterogeneity existing in unfractionated LLDPE. The fractions also exhibit a broad molecular-weight distribution. The number- and weight-average molecular weight decreases with increasing average SCB content.

The melting endotherms of the fractions show single, but rather broad melting curves. The crystallization exotherms obtained during cooling from the melt exhibit one large peak at high temperatures and a second smaller peak at lower temperatures.

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