Fractionation and thermal behaviour of linear low density polyethylene

P. Schouterden and G. Groeninckx
Laboratory of Macromolecular Structural Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200 F, B-3030 Louvain, Belgium

and B. Van der Heijden and F. Jansen
Olefin Plastics R&D, Dow Chemical (Nederland) B.V., P.O. Box 48, 4530 AA Terneuzen, The Netherlands

(Received 3 February 1987; revised 24 March 1987; accepted 15 April 1987)

An ethylene/1-octene copolymer has been fractionated by molecular weight using successive solution fractionation (s.f.f.). The fractions obtained and the original copolymer were analysed with respect to the short chain branching distribution using analytical temperature rising elution fractionation (a.t.r.e.f.). A bimodal, very wide branching distribution is observed, both for the non-fractionated polymer and for the s.s.f. fractions. A decrease of the average degree of branching with increasing average molecular weight of the fractions is observed. The melting behaviour of isothermally crystallized samples was studied using differential scanning calorimetry (d.s.c.). The low-temperature melting endotherm is caused by the melting of small crystals, composed of very strongly branched molecules. The endotherms above the isothermal crystallization temperature are caused by the melting of thicker crystals, composed of weakly branched molecules.

(Keywords: linear low density polyethylene; fractionation; short chain branching distribution; thermal behaviour; molecular segregation)

INTRODUCTION

Linear low density polyethylene (LLDPE) is a copolymer of ethylene and an alpha-olefin, e.g. propene, 1-butene, 1-hexene and 1-octene. The chain microstructure of ethylene/alpha-olefin copolymers depends on the following basic parameters: the type of comonomer used, the comonomer (or branch) content, the distribution of the comonomer along the molecules, and the molecular weight of the polymer. These parameters influence the physical properties (i.e. viscoelastic, mechanical, optical and melting properties) through their control of crystallinity and semicrystalline morphology.

The crystallization and melting behaviour of non-fractionated LLDPE is very complex[1]. The d.s.c. melting curve of an isothermally crystallized specimen ($T_c = 105°C$) of 1-octene LLDPE reveals several melting endotherms in a temperature interval between 50 and 130°C (*Figure 1*). A certain fraction of the copolymer (segregated fraction) is not able to crystallize at crystallization temperature $T_c = 105°C$. Part of this segregated material, however, crystallizes during cooling at temperatures markedly lower than the original crystallization temperature. During a subsequent d.s.c. heating scan (*Figure 1*), the crystallized segregated fraction melts over a broad temperature range below T_c (endotherm I); the crystalline structure formed at T_c gives rise to multiple melting endotherms above T_c (endotherms II and III). This segregation phenomenon has already been observed for non-fractionated propene, 1-butene and 1-octene LLDPE copolymers[1].

The segregation process, which occurs both during isothermal and dynamic crystallization, is caused by the fact that LLDPE samples are very heterogeneous on the molecular level on account of a broad distribution of the short comonomeric side branches; as a consequence, the thickness and internal perfection of the crystals will differ considerably and give rise to an inhomogeneous semicrystalline morphology. Several authors[2–5] have investigated the ethylene sequence distribution for some LLDPEs using ^{13}C n.m.r. and concluded that the short chain branches are non-randomly distributed along the chains. Very recently, Mathot *et al.*[6,7] have fractionated LLDPE using two methods which are fairly different in character: the direct extraction and the crystallization/dissolution method. From these data, the authors concluded that an intermolecular heterogeneity of the comonomer distribution exists. Wild *et al.*[8] have fractionated LDPE and 1-butene LLDPE using an analytical temperature rising elution fractionation (a.t.r.e.f.) system and showed that these copolymers exhibit extremely wide short chain branching (*SCB*) distributions. Such *SCB* distributions will result in an inhomogeneous distribution of crystal thickness and perfection upon crystallization.

In this paper, fractionation of a 1-octene LLDPE, followed by an investigation of the thermal behaviour is presented. Such experimental data provide information about the complex molecular structure and consequently the complex crystalline morphology of LLDPE.

0032-3861/87/122099-06$03.00

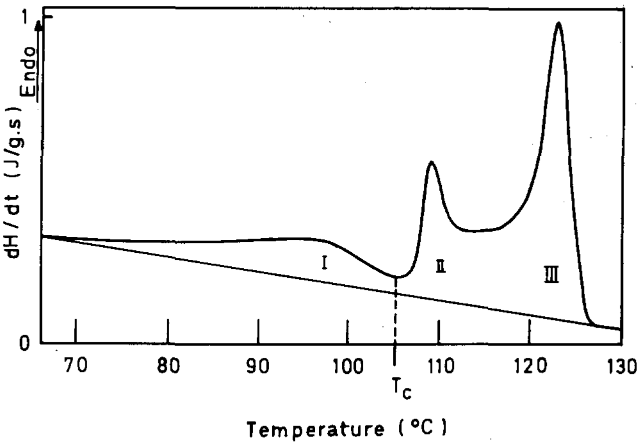

Figure 1 D.s.c. trace of a non-fractionated 1-octene LLDPE, isothermally crystallized at $T_c = 105$°C

EXPERIMENTAL

For the fractionation study, an ethylene/1-octene sample (polymerized in solution), containing an average of 10.3 side branches per 1000 carbon atoms in the main chain, and with weight-average molecular weight $\bar{M}_w = 120\,000$ and polydispersity $\bar{M}_w/\bar{M}_n = 3.95$ was used.

For the fractionation with respect to molecular weight, the successive solution fractionation (s.s.f.) technique[9–11] was used because it yields very narrow molecular weight distribution fractions under easy operating conditions. In order to determine the distribution of the short chain branches over the molecules, an improved analytical temperature rising elution fractionation (a.t.r.e.f.) method, described by Wild *et al.*[12], was applied. The oil bath (Julabo Ultratherm F30), which controlled the temperature of the polymer solution during the fractionation processes, was digitally programmable (Julabo PRG) and kept at a temperature constant to within ±0.1°C.

Prior to the differential scanning calorimetry (d.s.c.) experiments, the original specimen and all fractions obtained were heated up to 150°C for 10 min in order to destroy the thermal history, followed by isothermal crystallization at $T_c = 105$°C for 17 h. This treatment was carried out under nitrogen atmosphere. Finally, the specimens were cooled to room temperature. For the d.s.c. experiments, a Perkin-Elmer DSC-2C was used.

High temperature gel permeation chromatography (g.p.c.) on a Waters instrument was performed to establish the molecular weight distribution of the original sample and of the fractions.

FRACTIONATION PROCEDURES

Fractionation towards molecular weight using the s.s.f. method

Successive solution fractionation (s.s.f.) is based on the temperature dependence of the solubility of a polymer as a function of its molecular weight. The procedure consisted of the following steps. A 1 wt% solution was prepared at high temperature in a vessel, V (see *Figure 2a*). The solution was cooled down linearly to an isothermal temperature between 90 and 130°C. This temperature has to be constant for several hours to establish the equilibrium between the polymer-rich and polymer-lean phase. Afterwards, the polymer-lean phase was pumped via a filter, F, into a recipient, R. The solvent of the polymer-lean phase was evaporated off and the material precipitated by adding methanol. The fraction was separated on a glass filter, washed with methanol and finally dried in a vacuum oven.

Vessel V was filled with cyclohexanone to the original level and the same procedure repeated for the next fraction (of higher molecular weight) at a higher isothermal temperature (*Figure 2b*). During fractionation, nitrogen was purged through the solution and an antioxidant added to inhibit oxidative degradation of the polymer. G.p.c. analysis proved that no degradation or crosslinking of the polymer occurred, even for the high molecular weight fractions, which remained for very long times at high temperatures.

Determination of the short chain branching distribution using the a.t.r.e.f. method

In the a.t.r.e.f. method, fractionation of ethylene copolymers is obtained on the basis of their crystallizability, which is directly related to the degree of short chain branching. The a.t.r.e.f. fractionation consisted of two steps: slow cooling of a dilute solution of the polymer, giving rise to crystallization on a surface, followed by continuous elution of the dissolved polymer during a simultaneous, controlled temperature increase.

The experimental apparatus is shown in *Figure 3*. A column was filled with glass pearls of diameter 800 μm. Prior to the a.t.r.e.f. experiment, the column was filled with a 1 wt% solution of the polymer in 1,2,4 trichlorobenzene (TCB) at high temperatures. The polymer crystallized upon slow cooling to room temperature, giving a polymer layer on the glass pearls. This layer was inhomogeneous in composition because the weakly branched molecules crystallize at a higher temperature than the more branched molecules. Thus, the glass pearls were coated with a polymer layer which showed a gradient of increasing amount of short chain branching in the direction from the glass pearl towards the surface of the polymer layer.

For the a.t.r.e.f. experiment, the column was submerged in a temperature-controlled oil bath. A

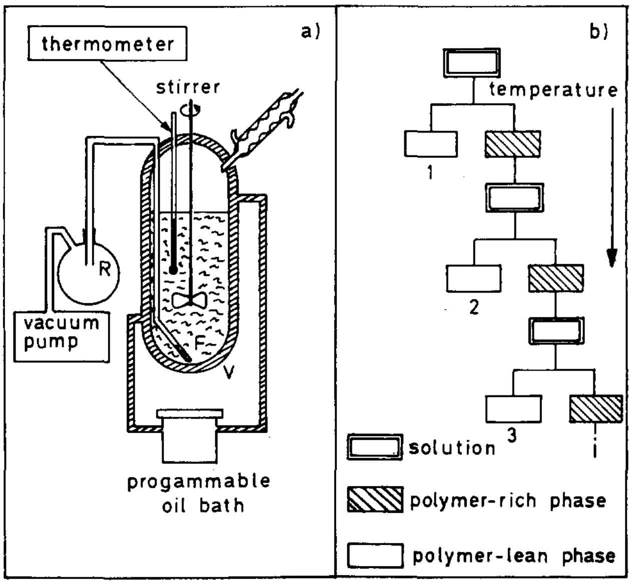

Figure 2 (a) Successive solution fractionation (s.s.f.) system. (b) Principle of successive solution fractionation (s.s.f.)[11]

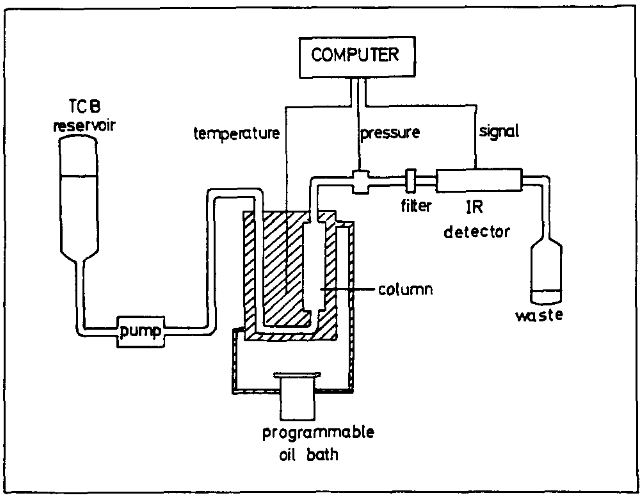

Figure 3 Analytical temperature rising elution fractionation (a.t.r.e.f.) system

pumping system provided a flow of solvent (TCB) through the column. During the linear heating programme, the polymer is dissolved in the solvent flow in the reverse order to that in which it has crystallized, i.e. the more branched molecules, which are located at the surface of the polymer layer, will dissolve at low temperatures, followed by the weakly branched molecules at higher temperatures. The amount of polymer which eluted from the column during the linear temperature increase was measured using an infra-red detector (the detector was heated to prevent crystallization in the measuring cell during the run). The i.r. detector measured the absorbance index at a wavenumber of 2850 cm^{-1}, which is the response of C–H_2 bonds. The temperature, pressure and analogue detector signal were digitized by an A/D converter and processed by a computer. From the results a curve was plotted of the amount of polymer detected as a function of elution temperature.

A calibration curve of the number of short chain branches as a function of the elution temperature has to be established if quantitative data are required. As pointed out by Wild[12], no standards of narrow branching distributions are available. For this study, standards were prepared using the fractions of an ethylene/1-octene copolymer eluted for every 5°C temperature interval. For these fractions, the average degree of short chain branching was determined using a Fourier-transform infra-red (*FT*i.r.) apparatus. A linear relationship was found between the methyl content and the elution temperature (*Figure 4*).

RESULTS AND DISCUSSION

Ethylene/1-octene copolymer was fractionated by successive solution fractionation (s.s.f.) into 11 fractions (*Figure 5*). G.p.c. analysis (*Table 1*) confirmed an increasing molecular weight for a higher equilibrium temperature (or fraction number). Fractions 8 and 9 showed an anomaly and were not used for further analysis. The equilibrium temperatures were chosen in such a way that the polydispersity index $\bar{M}_w/\bar{M}_n$ was relatively constant for all fractions.

The original non-fractionated specimen and the nine s.s.f. fractions were analysed with respect to the distribution of the side branches between the molecules,

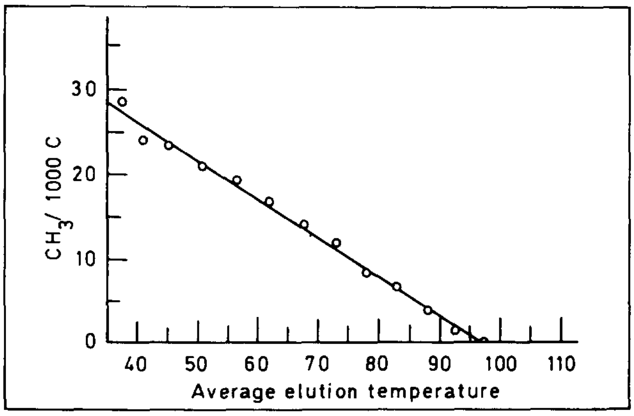

Figure 4 Calibration curve for the a.t.r.e.f. system. Methyl content (number of CH_3 groups/1000 C atoms in the backbone) as a function of the elution temperature

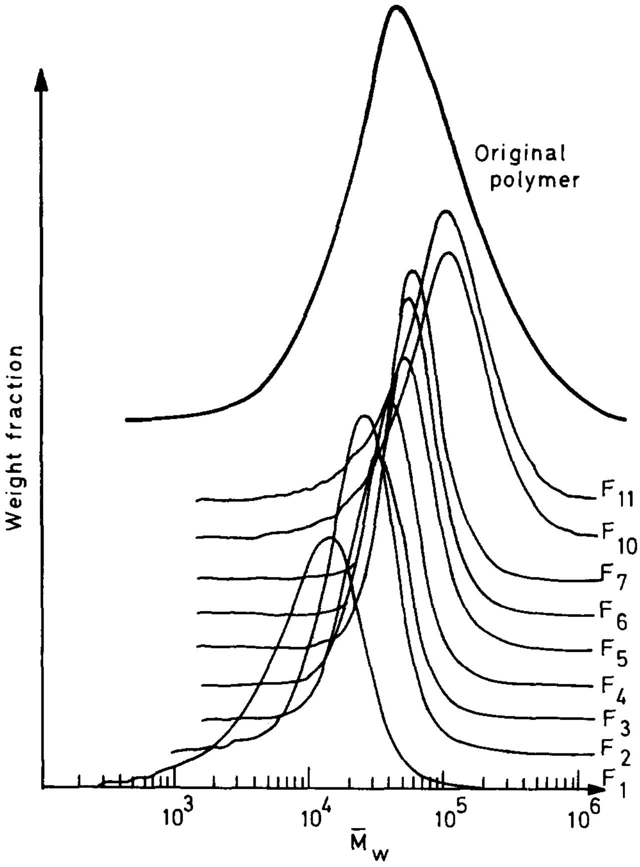

Figure 5 G.p.c. curves of the original copolymer and of the s.s.f. fractions obtained

Table 1 Molecular weight and polydispersity of the s.s.f. fractions of a 1-octene LLDPE

Fraction number	Weight-average molecular weight ($\bar{M}_w$)	Number-average molecular weight ($\bar{M}_n$)	Poly-dispersity index ($\bar{M}_w/\bar{M}_n$)
1	14900	5400	2.76
2	30400	18400	1.65
3	37500	27900	1.34
4	49100	37300	1.32
5	68100	51500	1.32
6	73500	58500	1.26
7	81300	62700	1.30
10	141700	72900	1.94
11	395800	235900	1.68

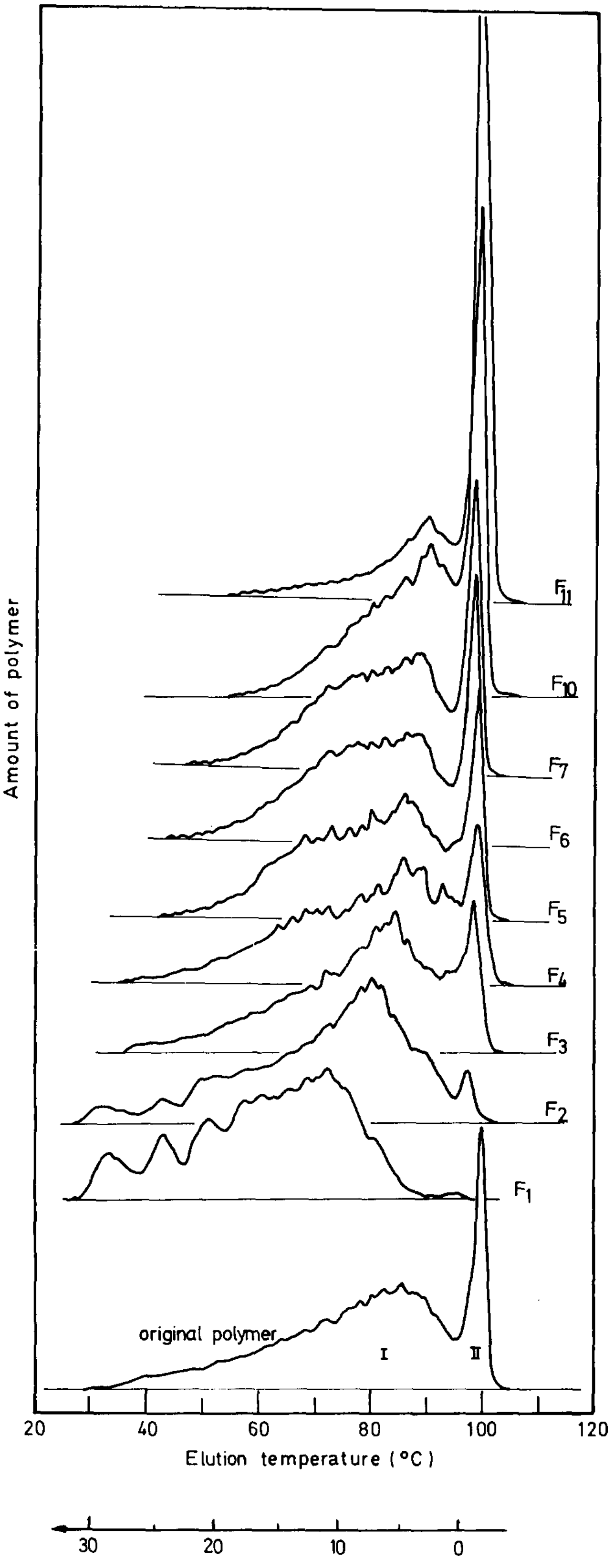

Figure 6 A.t.r.e.f. curves for the original non-fractionated polymer and the s.s.f. fractions

using the a.t.r.e.f. method. In *Figure 6*, the amount of polymer detected by the i.r. detector is plotted as a function of the elution temperature, for the original sample and the s.s.f. fractions. Using the calibration curve, the elution temperature can be substituted by the methyl content. The non-fractionated sample and all fractions obtained, except fraction F1, exhibited a bimodal *SCB* distribution. The ratio of the area of peak II (at high elution temperatures, or low degree of branching) to the total area (peak I and II) is plotted against weight-average molecular weight in *Figure 7*. As can be seen from *Figures 6* and *7*, the high molecular weight fractions contain less short chain branches than the low molecular weight fractions. Also, the lower the molecular weight of the fractions, the broader the *SCB* distribution and the higher the average content of short chain branches.

The original specimen and the fractions were isothermally crystallized from the melt at $T_c = 105°C$ for 17 h (under nitrogen atmosphere) and subsequently cooled to room temperature. A d.s.c. scan was recorded at a heating rate of 5°C min^{-1} between 40 and 140°C. The melting curves are shown in *Figure 8*. All fractions, except the fraction with the highest average molecular weight (fraction 11), still show a crystallized segregated phase (endotherm I below T_c). *Figure 9* plots the crystallinities of the original crystallized phase X_{T_c} (endotherms II, III and eventually IV), the crystallized segregated phase X_s (I) and the total crystallinity X_{tot} as a function of weight-average molecular weight $\bar{M}_w$. The total crystallinity of the fractions increased for $\bar{M}_w$ in the range 15 000–80 000. At higher $\bar{M}_w$ the total crystallinity decreased very slightly.

The crystallinity of the original formed phase X_{T_c} increased with increasing $\bar{M}_w$, due to a decrease in the average degree of branching, while the crystallinity of the

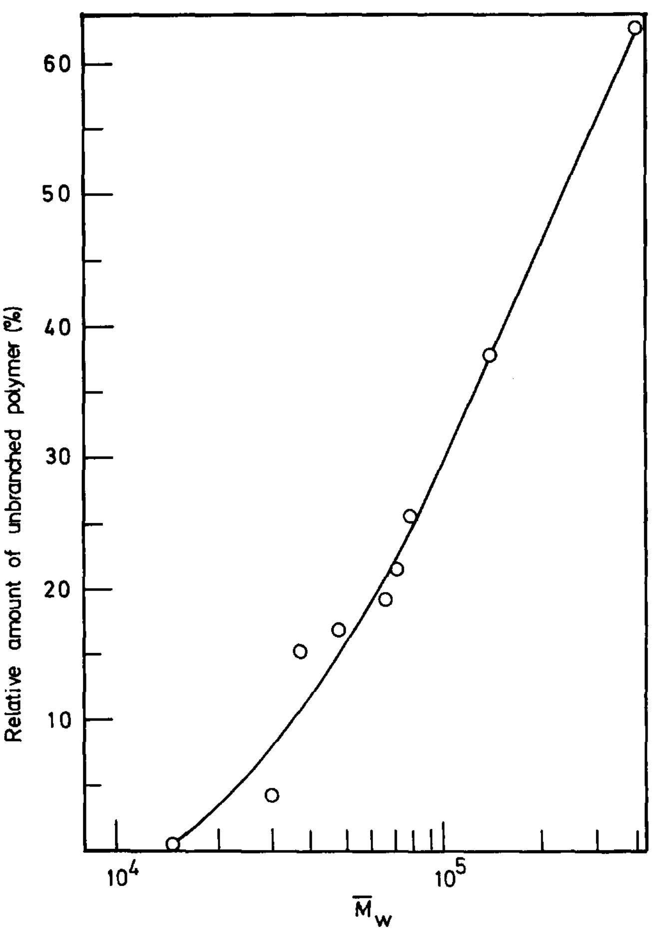

Figure 7 Amount of very weakly branched polymer as a function of $\bar{M}_w$

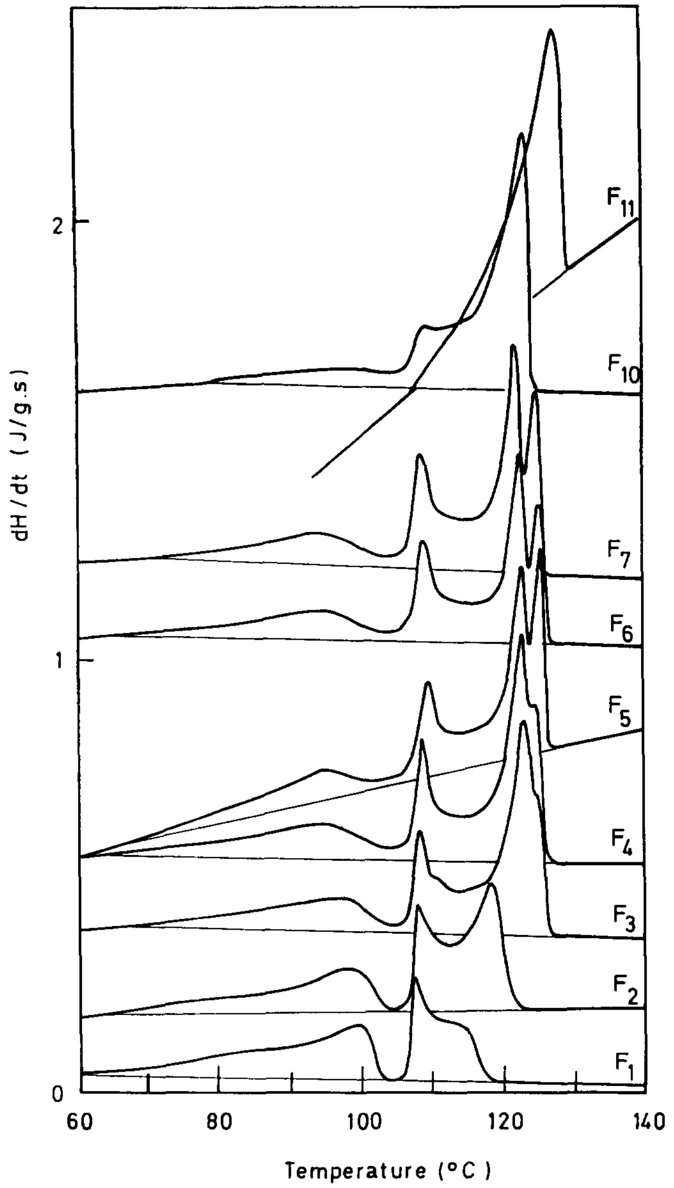

Figure 8 D.s.c. curves of the s.s.f. fractions, isothermally crystallized at $T_c = 105°C$

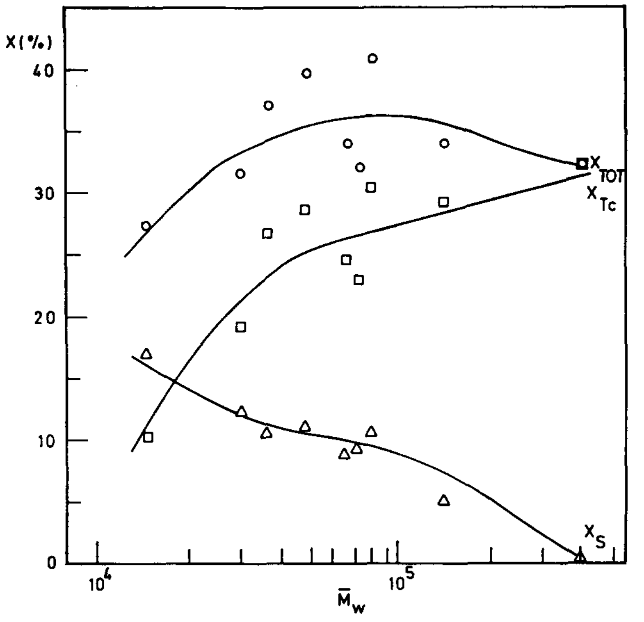

Figure 9 Total crystallinity (X_{tot}), crystallinity of the crystallized segregated phase (X_S) and of the original crystalline phase formed at $T_c(X_{T_c})$ for the s.s.f. fractions

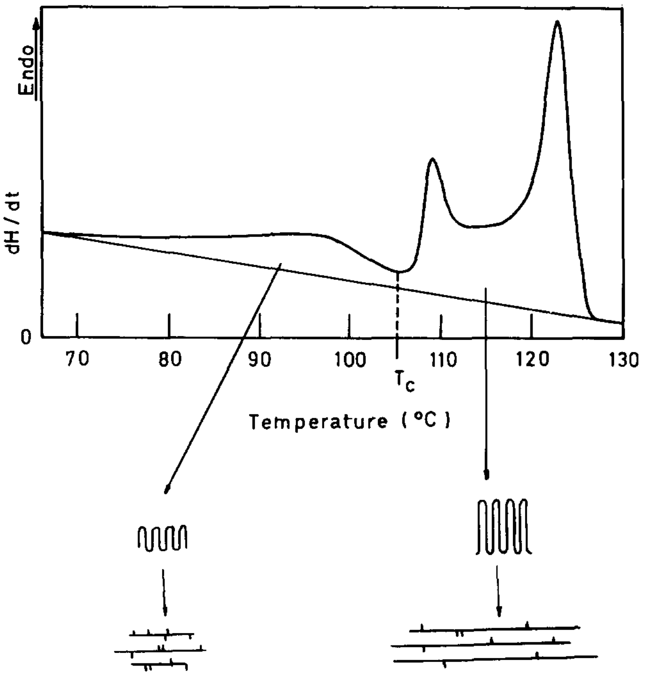

Figure 10 Schematic representation of the molecular structure and morphology of the crystals in LLDPE

crystallized segregated phase decreased. The highest fraction (F11) no longer showed a crystallized segregated phase. This observation may be ascribed to the lower degree of branching of the higher molecular weight fractions, which gives rise to a lower amount of segregated material upon crystallization.

It is clear that a higher degree of branching is responsible for a higher amount of segregated material, an observation already made for unfractionated specimens using d.s.c. and synchrotron radiation measurements[1]. Thus, it is clear that an increasing comonomer content must give rise to the formation of smaller crystals. A schematic representation of these results is given in *Figure 10*.

With respect to the complex melting behaviour above T_c, the present results give no definite answer regarding the origin of endotherms II, III and IV. It seems probable that these endotherms reflect the melting of lamellar crystals (formed at T_c), differing in size and perfection, as a result of the heterogeneous distribution in short chain branches. Fractionation according to *SCB* degree (preparative fractions) and a systematic morphological study of the preparative fractions will be necessary for an insight into the complex melting behaviour of LLDPE.

CONCLUSIONS

(1) Fractionation with respect to molecular weight, followed by a fractionation towards the comonomer distribution provides a very effective method to elucidate the complex chain microstructure of ethylene/alpha-olefin copolymers.

(2) In LLDPE specimens fractionated with respect to

molecular weight, the whole range of molecular weights contains a very wide comonomer distribution. This distribution has a bimodal character. Strongly branched and weakly branched molecules exist in every molecular weight fraction, but their relative amount decreases drastically with increasing molecular weight. The short chain branching distribution is broader for the lower molecular weight fractions. LLDPE should therefore be regarded as a physical blend of molecules with a wide distribution of comonomer over the total molecular weight range.

(3) D.s.c. analysis of LLDPE samples isothermally crystallized in the range 105–125°C provides fast and useful qualitative information regarding the short chain branching distribution.

REFERENCES

1 Schouterden, P., Groeninckx, G., Reynaers, H., Riekel, C. and Koch, M. H. J. *Polym. Bull.* 1985, **13**, 533

2 Hsieh, E. T. and Randall, J. C. *Macromolecules* 1982, **15**, 353

3 Hsieh, E. T. and Randall, J. C. *Macromolecules* 1982, **15**, 1402

4 Kimura, K., Yuasa, S. and Maru, Y. *Polymer* 1984, **25**, 441

5 Kimura, K., Sigemura, T. and Yuasa, S. *J. Appl. Polym. Sci.* 1984, **29**, 3161

6 Mathot, V. B. F. and Pijpers, M. F. J. *Polym. Bull.* 1984, **11**, 239

7 Mathot, V. B. F. in 'Polycon '84', Proceedings of the symposium on LLDPE, 9–11 May 1984, The Netherlands, PRI and SPE, pp. 1–14

8 Wild, L., Ryle, T. R. and Knobeloch, D. C. *Polym. Prepr. ACS* 1982, **23**(2), 133

9 Kamide, K. and Mizayaki, Y. *Polym. J.* 1980, **12**, 153

10 Kamide, K. and Mizayaki, Y. *Makromol. Chem.* 1975, **176**, 3455

11 Kamide, K., Mizayaki, Y. and Abe, T. *Br. Polym. J.* Dec. 1981, **13**, 168

12 Wild, L., Ryle, T. R., Knobeloch, D. C. and Peat, I. R. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 441