Evaluation of the heterogeneity in linear low-density polyethylene comonomer unit distribution by differential scanning calorimetry characterization of thermally treated samples

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A new procedure for analysing the structure of linear low-density polyethylene (LLDPE) based on differential scanning calorimetry (d.s.c.) has been developed. LLDPE with heterogeneous and homogeneous distributions of comonomer units have been annealed in stages at decreasing temperatures starting from the melt. With this new procedure, it has been possible to show on d.s.c. thermograms the appearance of various families of macromolecules in the case of heterogeneous copolymers. In the case of more homogeneous copolymers, various families are still present in the material but in a smaller number. Furthermore, using the various melting peaks that appeared on the d.s.c. thermogram during the heating of the annealed polymer and with the help of a calibration curve, it has been possible to determine qualitatively the composition of the LLDPE.

(Keywords: linear low-density polyethylene; differential scanning calorimetry; distribution of comonomer units; structure determination; Ziegler–Natta catalyst)

INTRODUCTION

In the last decade linear low-density polyethylene (LLDPE) has become one of the most widely produced polymers in the world. In comparison with the other types of low-density polyethylene, such as the radically produced high-pressure low-density polyethylene (HP-LDPE), LLDPE exhibits better thermal and mechanical properties.

LLDPE is a copolymer and possesses short-chain branching (SCB) due to the incorporation in the polymeric chain of α-olefins (propene, 1-butene, 1-hexene, 4-methyl-1-pentene, etc.) used as comonomers. It has been shown[1–11] that such LLDPEs often exhibit high heterogeneity in the inter- and intramolecular distribution of comonomer units (DCU) along the polymer chains. Since the final mechanical and thermal properties of the resulting materials are closely related to the homogeneity of the samples, various methods to characterize intra- and intermolecular monomer sequence distributions have been developed.

The most widely used methods for the characterization of intermolecular heterogeneity are fractionation procedures, such as direct extraction by solvent/non-solvent mixtures (extraction depending mainly on molar masses) and crystallization/dissolution fractionation procedures (temperature-rising elution fractionation, etc.) for a fractionation based on the difference in crystallinity due to variable chemical composition of the polymeric chains.

The temperature-rising elution fractionation (t.r.e.f.) technique is based on the crystallization/dissolution procedure and gives polyethylene fractions of different chemical composition extracted according to their degree of crystallinity: polyethylene is first dissolved in hot solvent (mostly xylene, *o*-dichlorobenzene (DCB), trichlorobenzene (TCB)) and then deposited during slow cooling on an inert support (sand, glass beads, Chromosorb p, silica gel, etc.). The most crystalline fraction precipitates first on the support whereas the least crystalline and more soluble one is the last to be deposited. The polymer fractionation is carried out by solvent extraction at stepwise increasing temperatures.

The largest drawbacks of this fractionation technique are the length of time needed for a complete analysis and the high cost of implementation. Even if not as complete as the t.r.e.f. method, a quicker and easier method for the analysis of LLDPE, able to give information on the molecular structure and homogeneity of the chains, would be of great interest. Thus the possibility to characterize such molecular heterogeneity parameters by means of d.s.c. after submitting the polymer to a suitable thermal treatment has been examined. As for t.r.e.f. the method consists of a stepwise crystallization of the polyethylene chains by successive annealing at decreasing temperatures starting from the melt and the subsequent analysis by d.s.c. of the melting behaviour of the treated sample.

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The results obtained according to this procedure for various LLDPE are presented and discussed in the present paper.

EXPERIMENTAL

Materials

LLDPE samples. The LLDPEs used in this study were prepared by copolymerization of ethylene and 1-hexene. The polymerization takes place in a batch reactor in solution in isododecane at 160°C and under 5 bar of ethylene. The reaction time was 1 min. Various Ziegler–Natta type catalysts based on titanium (commercial $TiCl_3$–$\frac{1}{3}AlCl_3$), vanadium (7 h ball-milled VCl_3 from Aldrich. Co) or zirconium (7 h ball-milled $ZrCl_4$ from Aldrich. Co) were used in order to get polymers of different molecular structures and distributions of comonomer units (DCU) along the chains. The catalytic systems were obtained by combination of the heterogeneous transition-metal salt and aluminium triethyl in a ratio from 1/4 to 1/10.

The polymers so prepared were precipitated in a mixture of hexane/methanol containing a few drops of concentrated HCl. The copolymers were then filtered off and washed several times with hexane and methanol and finally dried for 48 h under vacuum at 50°C. However all the copolymers obtained in these conditions were found to be highly heterogeneous with respect to DCU. A commercial ethylene/1-butene copolymer, 'Tafmer', from Mitsui Petrochemical Industries, was used as a sample of a probably less heterogeneous LLDPE.

Fractionation of LLDPE by solvent extraction. Fractionations of LLDPE of various SCB were performed by extracting polymer samples in a Kumagawa extractor, under nitrogen, with a series of solvents of increasing boiling point, i.e. pentane, hexane, heptane, octane. Polymers were recovered by solvent evaporation under vacuum.

Blends of LLDPE. Heterogeneous LLDPEs of known monomer unit composition were prepared by mixing, at 150°C (in the melt state), a homopolyethylene and a Tafmer LLDPE on the one hand, and two fractions of relatively homogeneous molecular structure but of different SCB that were obtained by solvent extraction fractionation of an ethylene/1-hexene copolymer on the other hand.

Polymer characterization

Determination of the short-chain branching (SCB). The average number of CH_3 groups per 1000 C was determined by *FT*i.r. using the 1378 cm^{-1} absorption band according to ASTM procedure D2238-68.

D.s.c. analysis. Two distinct d.s.c. procedures have been employed, as follows.

Method A is the most common one used for analysis of partially crystalline polymers. First, 4 to 8 mg of polyethylene are melted at 170°C for 5 min and then cooled at 10°C min^{-1} to 0°C. This temperature was maintained for 5 min and the sample heated at 10°C min^{-1} up to 160°C. The melting endotherm and enthalpy were recorded using a Mettler TA 3000 d.s.c. apparatus.

Method B is inspired by the t.r.e.f. procedure. First, 5 to 10 mg of polymer in a d.s.c. crucible are melted at 150°C under nitrogen for 20 min. Then the polymer sample is successively annealed (under nitrogen) at decreasing temperatures starting from the melt. Temperature stages were separated from each other by about 10°C. In the present set of experiments the annealing temperatures were 125, 113, 97, 87, 78, 69, 55 and 25°C. The time for each annealing step was about 12 h. Then the cooled sample was heated at 5°C min^{-1} and the melting endotherms and enthalpies were recorded as for method A.

RESULTS AND DISCUSSION

The d.s.c. thermograms of ethylene/1-hexene copolymers with various SCB and of homopolyethylene are presented in *Figure 1*, according to procedure A. The most significant differences observed in the thermal behaviour of the linear polyethylene and copolymers of increasing SCB are:

(i) a decrease of the melting enthalpy, accompanied by a slight shift (< 10°C) of the melting peak maximum to lower temperatures; and

(ii) an asymmetric broadening (peak tail) of the melting peak in the low-temperature range.

As may be seen in *Figure 2*, using an expanded scale for each sample, the peak shape cannot be directly

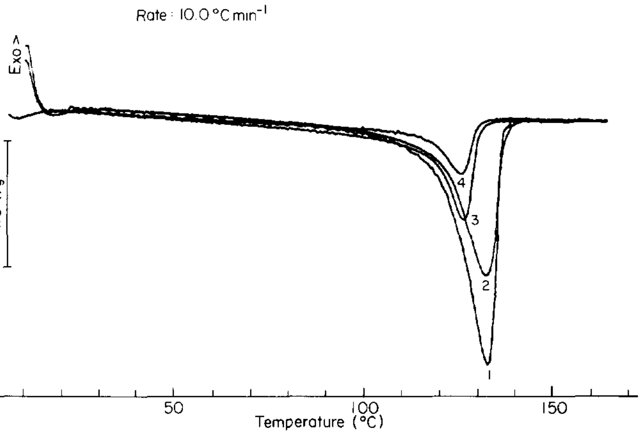

Figure 1 Variation of the d.s.c. thermograms as a function of SCB for heterogeneous ethylene/1-hexene polymers. The curves are as follows: (1) homopolyethylene, 7.739 mg, SCB = 0.7, $\Delta H = 156\,J\,g^{-1}$; (2) copolymer, 8.847 mg, SCB = 12.5, $\Delta H = 108\,J\,g^{-1}$; (3) copolymer, 6.238 mg, SCB = 22.5, $\Delta H = 93\,J\,g^{-1}$; (4) copolymer, 4.462 mg, SCB = 36, $\Delta H = 60\,J\,g^{-1}$

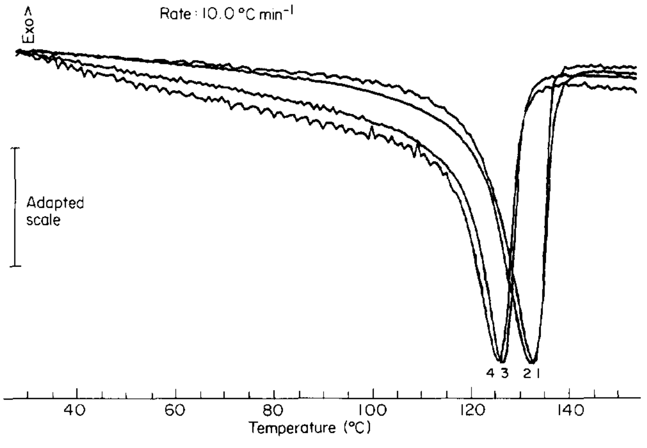

Figure 2 Comparison of melting peak tails of copolymers with various SCB. An adapted expanded scale is used for each copolymer so that the melting peak shape can be more easily compared. See *Figure 1* for details of curves

correlated to the amount of incorporated comonomer. In fact the presence of a peak tail is mostly observed with non-fractionated copolymers that have a heterogeneous molecular structure (DCU). This therefore suggests that melting peak broadening results from the presence of families of macromolecules—or blocks of monomer units—of various SCB, which could have syncrystallized during cooling, thus giving a continuous melting curve during the heating phase.

When using the staged cooling procedure (method B), several well resolved melting endotherms are obtained during the heating cycle for the copolymers (*Figure 3*), whereas only a single melting peak is observed for the homopolyethylene (*Figure 4*). These observations suggest separate crystallization of various types of copolymer crystallites during the staged cooling process. A similar observation has been made by Schouterden *et al.*[6,7] when annealing heterogeneous LLDPEs at a temperature of 105°C: during subsequent d.s.c. heating, several melting peaks were obtained above the annealing temperature whereas a broad and unresolved endotherm was observed below it. As may be seen in *Figure 3* this segregation can be pursued down to low temperature by annealing the copolymer at stepwise decreasing temperatures. Since a similar process could not be induced with a homopolyethylene ($SCB < 1$), this phenomenon was tentatively interpreted as the formation, due to heterogeneity in comonomer unit distribution, of crystallites of different thickness and internal perfection giving rise to an inhomogeneous semicrystalline morphology.

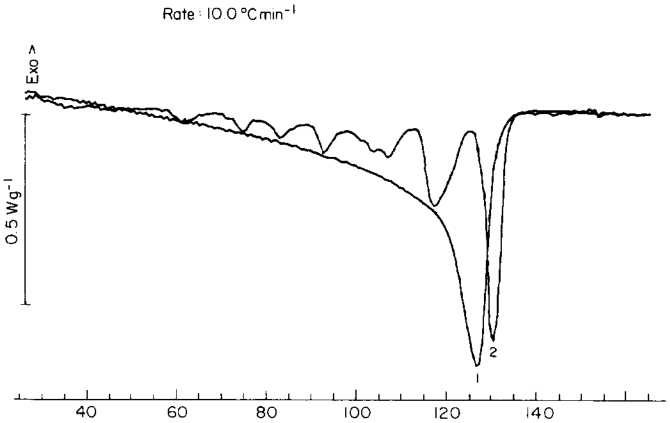

Figure 3 Comparison of the thermograms obtained by methods A and B for an ethylene/1-hexene copolymer (titanium catalyst). $M_w = 310\,640$, $M_n = 39\,020$, $SCB = 26.5$. Curve (1), method A, $\Delta H = 84.7\ J\ g^{-1}$; curve (2), method B, $\Delta H = 110.4\ J\ g^{-1}$

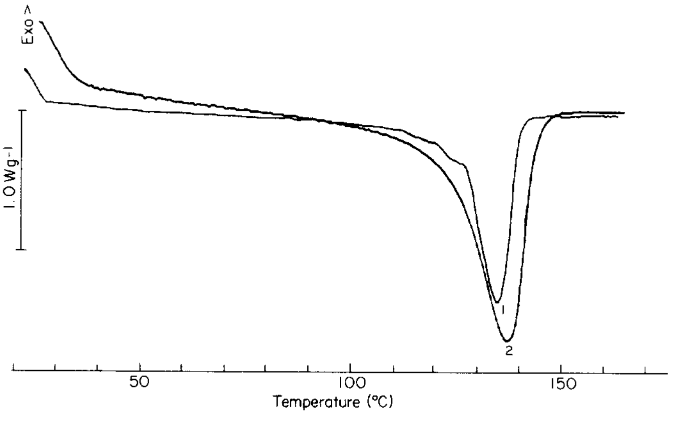

Figure 4 Homopolyethylene treated according to methods A and B (zirconium catalyst). $M_w = 845\,340$, $M_n = 202\,641$, $SCB = 0.8$. Curve (1), method A; curve (2), method B

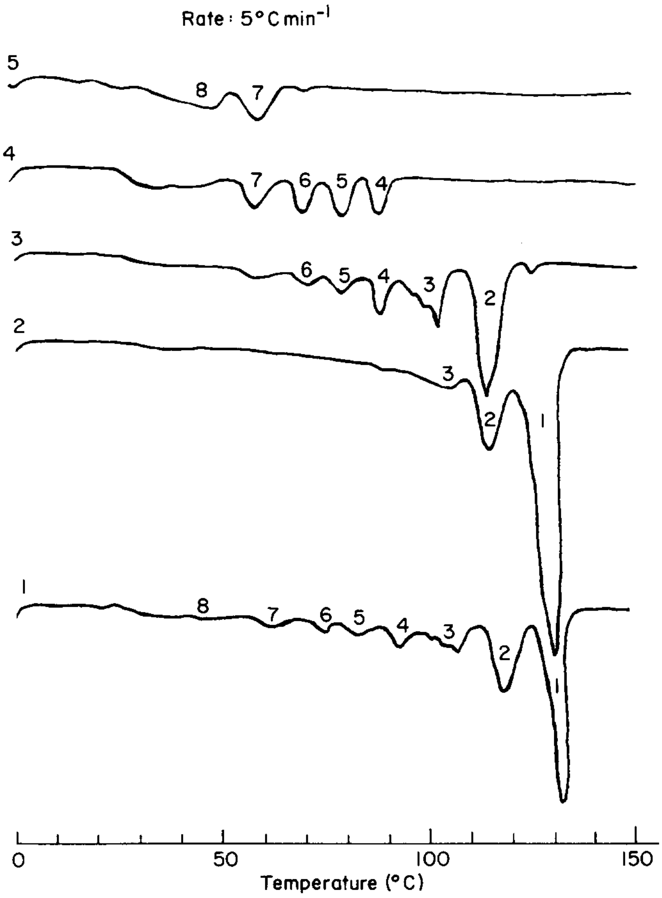

Figure 5 D.s.c. thermograms according to procedure B of an ethylene/1-hexene copolymer and its fractions obtained by solvent extraction. The curves are as follows: (1) non-fractionated polymer, 7.494 mg, $\Delta H = 110.4\ J\ g^{-1}$, $SCB = 26.5$; (2) octane-soluble fraction, 7.601 mg, $\Delta H = 134.8\ J\ g^{-1}$, $SCB = 8$; (3) heptane-soluble fraction, 10.434 mg, $\Delta H = 85.2\ J\ g^{-1}$, $SCB = 27$; (4) hexane-soluble fraction, 5.726 mg, $\Delta H = 46.7\ J\ g^{-1}$, $SCB = 49$; (5) pentane-soluble fraction, 6.925 mg, $\Delta H = 20.3\ J\ g^{-1}$, $SCB = 56$

In order to check this hypothesis further and also in an attempt to correlate the observed thermogram shapes with the molecular structure of the ethylene/α-olefin copolymers, a series of comparative d.s.c. analyses of non-fractionated and fractionated LLDPEs of various origins and molecular heterogeneities have been performed.

Ethylene/1-hexene copolymers prepared from various catalysts have been fractionated using solvents of increasing boiling point (pentane, hexane, heptane and octane). It has been shown that fractionation proceeds mainly according to the crystallization parameters of the chains and not to the molecular weights[11]. In the present case this was corroborated by SCB values of the fractions, and s.e.c. measurements.

The non-fractionated polymer and the corresponding fraction have been thermally treated and analysed according to procedure B. *Figure 5* shows the thermograms obtained after treatment B for a copolymer prepared with a titanium catalyst. As may be seen, the thermogram of the crude copolymer is resolved into a series of at least seven peaks.

Though there is some partial overlap demonstrated by the presence of common melting peaks for two successive polymer fractions, the endotherms differ from one fraction to another. The fact that some melting peaks are present in a given fraction and not in others tends to support the idea that they correspond to different polymer families that have been separated in the fractionation procedure: for example, the disappearance of peaks 1 to 6 in the pentane-soluble fraction, of peaks 1 to 3 in the hexane-soluble fraction, and of peaks 1, 7 and 8 in the heptane-soluble fraction can be noted. Therefore, each endotherm may be considered to be representative of a 'homogeneous' (in SCB and DCU) set of macromolecules or blocks.

In order to check that peak formation could not result from the syncrystallization of macromolecules families (or block of monomer units) of different SCB in various proportions, blends of two polymers or fractions of various SCB have been prepared.

The resulting heterogeneous polymer mixtures were thermally treated according to method B. The first blend was made of a hexane fraction ($\mathrm{SCB}=49$) and an octane fraction ($\mathrm{SCB}=8$) of a vanadium-prepared polyethylene ($\mathrm{SCB}=25$). As can be seen in *Figure 6*, only the melting peaks corresponding to those observed in the initial fractions are observed in the thermogram of the blend. No additional peak, particularly melting peak 4 characteristic of the heptane-soluble fraction, is observed in the thermogram.

The second blend was obtained by mixing an homopolyethylene ($\mathrm{SCB}<1$) and an ethylene/1-butene Tafmer copolymer (*Figure 7*). As for the previous mixture, no additional peak other than those present in the thermograms of the two separate polymers is observed.

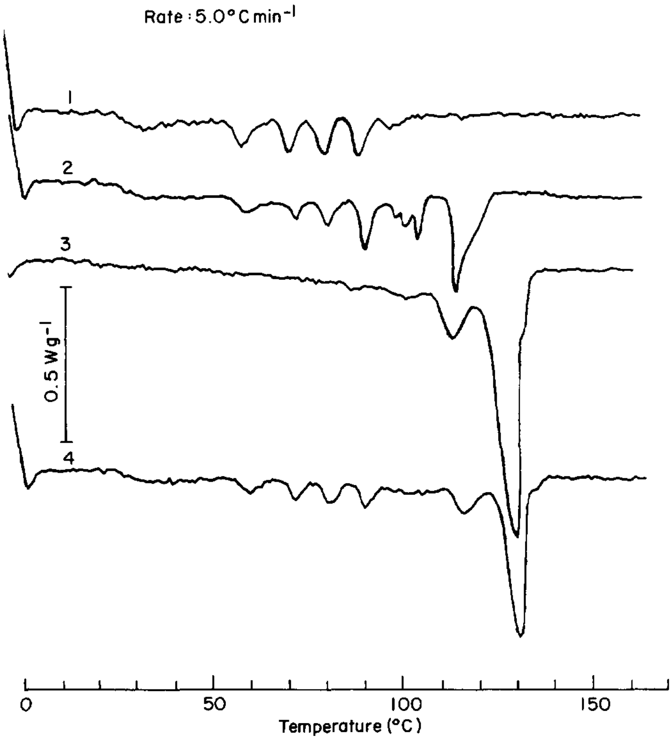

Figure 6 Thermograms of various fractions of an ethylene/1-hexene copolymer and of a blend of two fractions: (1) hexane-soluble fraction, 4.80 mg, $\Delta H=37.9\,\mathrm{J\,g^{-1}}$; (2) heptane-soluble fraction, 4.629 mg, $\Delta H=91.8\,\mathrm{J\,g^{-1}}$; (3) octane-soluble fraction, 5.080 mg, $\Delta H=127.5\,\mathrm{J\,g^{-1}}$; (4) octane-soluble fraction (60%) + hexane-soluble fraction (40%), 5.960 mg, $\Delta H=91.6\,\mathrm{J\,g^{-1}}$

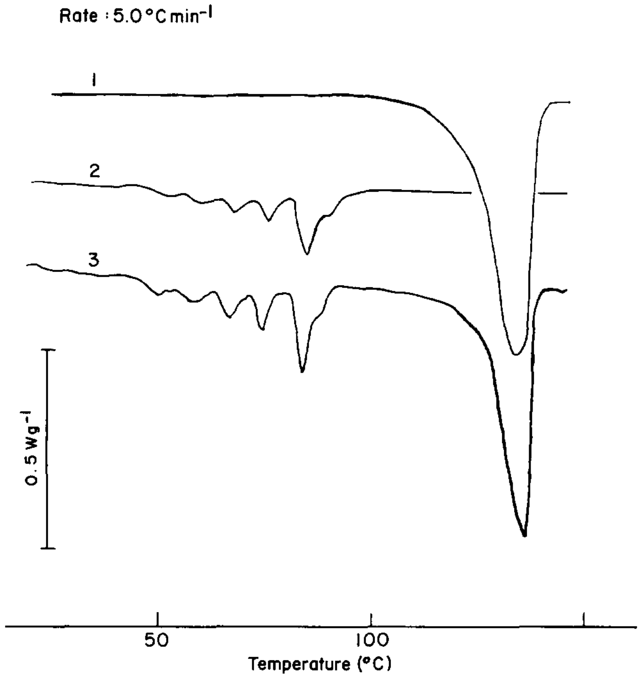

Figure 7 Thermograms according to procedure B: (1) homopolyethylene (zirconium catalyst), 3.185 mg; (2) Tafmer, 5.502 mg; (3) blend of 53 wt% of (1) and 47 wt% of (2), 6.021 mg

Therefore, it may be concluded that each melting peak formed is representative of a distinct family of macromolecules (or block of monomeric units), with different SCB or DCU, and that the parameters that govern the crystallization of macromolecules of a given family are relatively similar. On this basis it can be assumed that each copolymer family is homogeneous in composition and comonomers unit distribution, and it becomes possible to correlate the melting peak temperatures with a short-chain branching value, provided that a calibration curve giving the melting peak temperatures of homogeneous copolymers as a function of their SCB is available. Such a calibration curve could be established from homogeneous copolymer fractions obtained from t.r.e.f. and characterized by i.r. and d.s.c. Relationships between the melting temperature and the degree of SCB for an ethylene/1-hexene and an ethylene/1-butene copolymer, established from data of ref. 8, are shown in *Figure 8*. The relations between melting peaks and SCB can be described by the following equations:

$$T(^\circ\mathrm{C})=-1.84\times\mathrm{SCB}+136 \qquad (1)$$

for ethylene/1-hexene copolymers and

$$T(^\circ\mathrm{C})=-1.6\times\mathrm{SCB}+136 \qquad (2)$$

for ethylene/1-butene copolymers.

Figure 9 shows the thermogram of the ethylene/1-butene copolymer (Tafmer); SCB values indicated on the figure correspond to calculated values according to equations (1) and (2) respectively for the various polymer families revealed by their melting peak.

As can be seen, the Tafmer copolymer, though almost homogeneous, gives a thermogram resolved into several peaks, again suggesting the presence of various sets of macromolecules. According to equation (2), the SCB of macromolecules (or blocks) varies from 25 to 55. A t.r.e.f. fractionation of Tafmer was therefore attempted in order to confirm these observations. The elution temperature diagram is presented in *Figure 10*. Main weight fractions

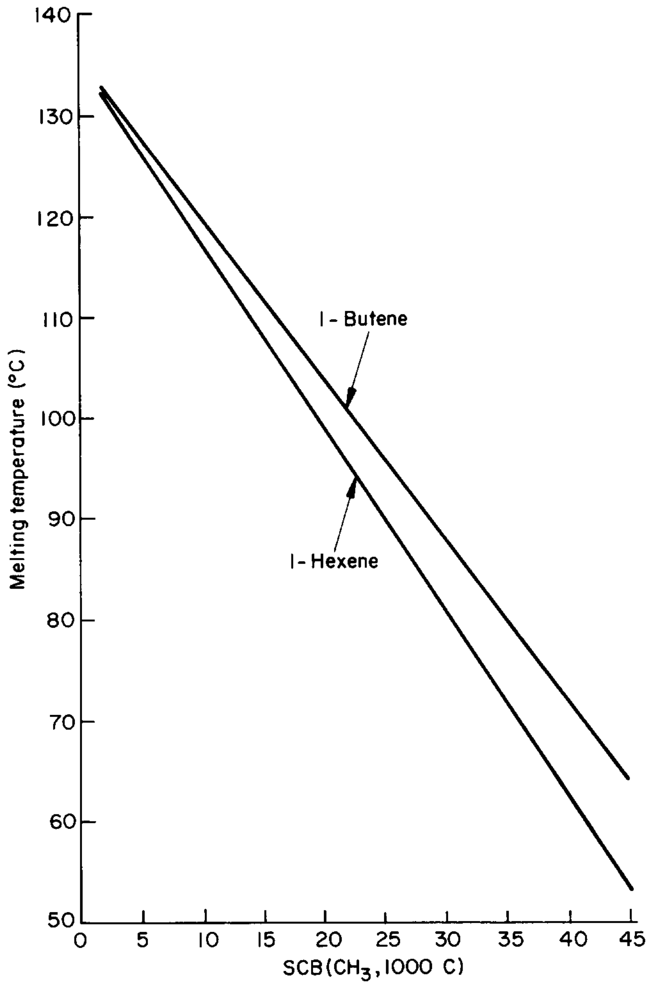

Figure 8 Relationship between melting temperature and degree of short-chain branching for cross-fractions of various ethylene/α-olefin copolymers (ref. 8)

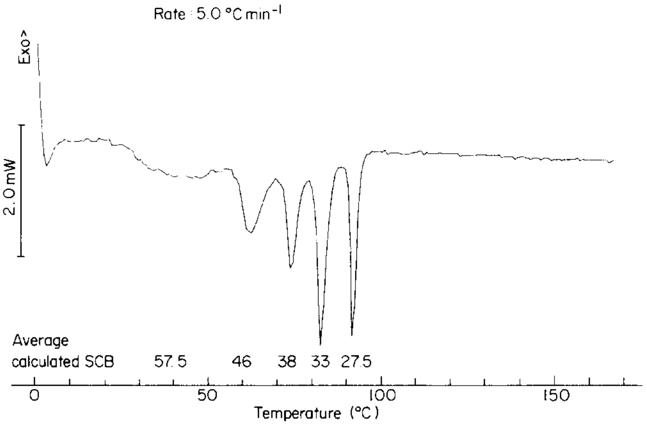

Figure 9 Thermogram of a Tafmer copolymer obtained by method B (7.605 mg)

are extracted at elution temperatures ranging from 22 to 60°C. As may be seen from the calibration curve given in *Figure 11* and plotted from data of ref. 4, such elution temperatures correspond to copolymers with SCB values between 25 and 55, in very good agreement with the

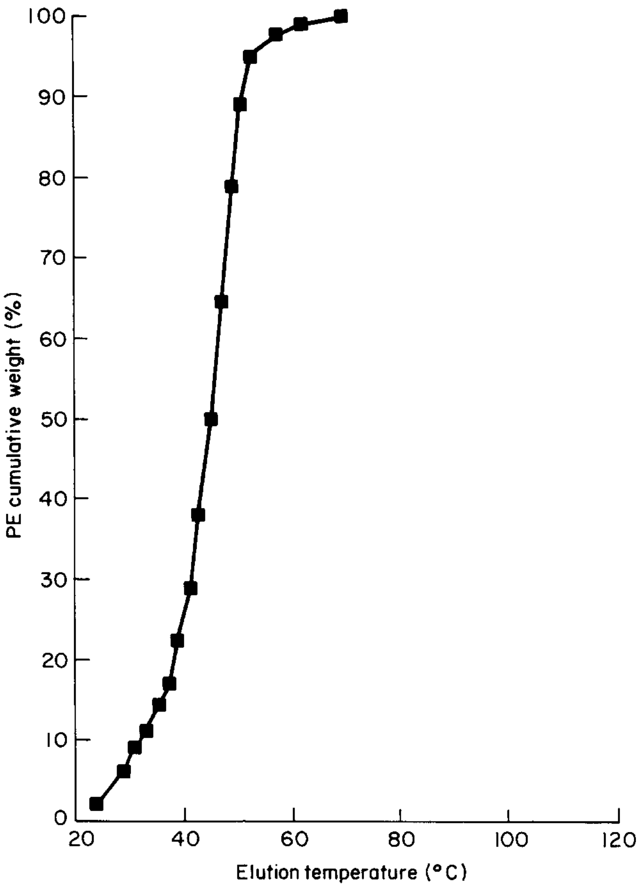

Figure 10 T.r.e.f. analysis of a Tafmer copolymer

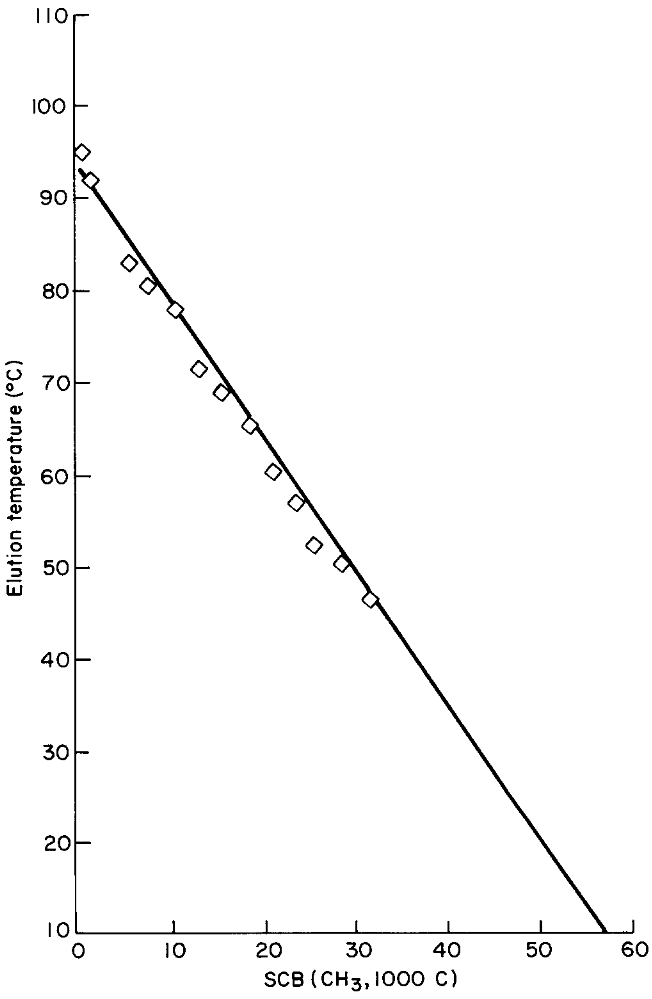

Figure 11 Calibration curve for calculating short-chain branching distribution from analytical t.r.e.f. data (ref. 4)

estimation made by d.s.c. This therefore corroborates the validity of method B.

CONCLUSIONS

The results presented in this paper show that the procedure consisting of successive annealings at decreasing temperatures of LLDPE samples, followed by d.s.c. analysis (method B), is useful to characterize the heterogeneity in monomer units distribution. It gives interesting and detailed information about the molecular structure of the chains.

Further studies are in progress to try to correlate the area of the various melting peaks with the amount of the corresponding polymer families; thus it would be possible also to obtain quantitative results about the various polymer families present in heterogeneous LLDPE.

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