Chemical Composition Distribution and Molecular Weight Distribution Determination of Ethylene, 1-Butene Linear Low-Density Polyethylene (LLDPE)

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Two ethylene, 1-butene copolymer samples, obtained by heterogeneous Ziegler-Natta catalysis and two obtained by homogeneous zirconium-based catalysis, were characterized. Fractionation, based mainly on crystallinity, was carried out by means of temperature-rising elution fractionation using an analytical custom-built apparatus (A-TREF). This technique provided a continuous representation of TREF distribution from the detector signal. In addition, a simple and inexpensive off-line sampling method to collect eluted fractions, as low as 0.3 mg, suitable for composition determination by infrared microspectroscopy and subsequent gel permeation chromatography fractionation is reported. The experimental results showed that all the samples studied were compositionally heterogeneous, and that their A-TREF profiles reflect the nature of the parent catalyst system.

Keywords: Linear low-density polyethylene, temperature-rising elution fractionation (TREF), gel permeation chromatography, infrared microscopy, chemical composition distribution.

INTRODUCTION

Linear low-density semicrystalline polyethylene copolymers (LLDPE), being heterogeneous materials with respect to both composition and molecular weight, require a combination of different techniques to measure their

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bivariant distribution. Several reviews[1-5] have been published on analytical methods currently under development for the characterization of these copolymers. The aim of this work was to develop an experimental procedure to obtain information on the molecular structure and homogeneity of the chains in LLDPE on an analytical scale.

Two ethylene, 1-butene copolymer samples obtained by heterogeneous MgCl$_2$-supported Ti catalysis (Mg-Ti) and two obtained by homogeneous zirconocene-based catalysis (Zr-based) were fractionated by analytical temperature-rising elution fractionation (A-TREF) and subsequently analyzed by infrared microspectroscopy (IMS) and gel permeation chromatography (GPC).

The TREF technique, which separates polymer molecules on the basis of their solubility differences, was carried out using a custom-built apparatus on an analytical scale. This apparatus provided a continuous representation of the TREF distribution from the detector signal. In addition, a simple and inexpensive off-line sampling method to collect eluted fractions, as low as 0.3 mg, suitable for the IMS determination and successive GPC fractionation was set up.

EXPERIMENTAL

The samples were fractionated by A-TREF and the resulting fractions were analyzed by IMS to determine short-chain branching (SCB), which is indicated as methyl groups per 100 carbons (CH$_3$/100 C) or 1-butene wt%, and by GPC to measure molecular weight distribution (MWD). Fractions collected from analytical TREF were characterized by IMS and GPC.

Samples

Four ethylene, 1-butene copolymers have been studied. Samples A and B were obtained by MgCl$_2$-supported Ti catalyst system; samples C and D were obtained by two different homogeneous zirconocene based catalysts. The properties of the samples are reported in Table I.

Analytical TREF

Each LLDPE sample was dissolved at 135°C in o-dichlorobenzene (ODCB) stabilized with 2,6-di-t-butyl-p-cresol (BHT). Each solution (0.25 g/dL) was deposited on a steel column (250 × 9.7 mm) packed with solid

TABLE I   Intrinsic viscosities (IV), xylene solubles (X.S.), 1-butene contents (wt%) and molecular weight parameters (M_i) of LLDPE copolymers.

Sample	IV (dL/g)	X.S. (wt%)	1-butene (wt%)	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	M_w/M_n	Catalytic system
A	1.88	10.2	8.0	28500	131800	359100	4.62	Mg-Ti
B	1.79	10.6	7.5	27400	127000	367600	4.64	Mg-Ti
C	1.53	3.80	9.9	41800	89700	152900	2.15	Zr-based
D	2.04	0.30	4.9	47700	123100	235500	2.58	Zr-based

silica beads (150–250 μm) and the injection volume was approximately 4 mL. The column was placed in an oven at 135°C and cooled to 25°C in about 16 h and 50 min. During the slow and controlled cooling of the solution, the copolymer was crystallized on the solid silica beads. In this way, a selective crystallization of the polymer chains was obtained as a function of their branching degree. Then, after an equilibration delay of 30–60 min at 25°C, the temperature was raised with a linear gradient (1°C/min) and the polymer was eluted with ODCB at a flow rate of 0.8 mL/min. The dissolution temperature program was initiated once a stable baseline was achieved and the refractive index detector signal was recorded on a strip-chart recorder.

The principle of the A-TREF apparatus is shown in Figure 1. The solvent is kept in the reservoir and heated at 140°C to eliminate dissolved gases. To avoid pump damage a filter is placed in the solvent line before the pump to remove particulate matter. The solvent from the outlet of the pump is directed into a bellow to dampen flow pulses. The flow is split in the reference and in the sample column by means of two valves. The column compartment is a gas chromatographic (GC) oven with a temperature programmer. Both the sample and the reference column are packed with solid silica beads. The sample solution is injected into the sample column with a syringe and a six-port valve is used to switch the eluent stream.

The eluted solution flows from the column sample to the sample side of the differential refractometer where it is detected and then expelled into the waste container. In the same way the solvent flows from the column reference to the reference side of the refractometer. The difference between the refractive index of the solvent and the refractive index of the eluted solution represents the detector signal. The detector sends the signal to a strip-chart recorder. The refractive index detector is taken from a Waters 200 GPC instrument (Waters, Milford, Massachusetts, USA).
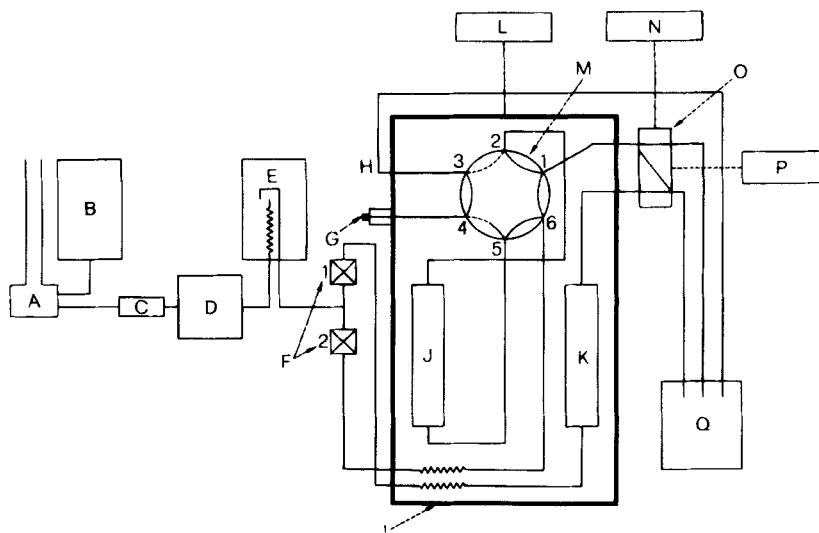
FIGURE 1 Scheme of the A-TREF apparatus: (A) solvent degasser; (B) solvent reservoir; (C) filter; (D) pump; (E) bellows; (F) reference and sample flows valves; (G) sample inlet; (H) sample overflow; (I) insulated oven; (J) sample column; (K) reference column; (L) temperature programmer; (M) sample loop; (N) temperature controller; (O) differential refractometer; (P) strip-chart recorder; (Q) waste.

Sampling Method

Fractions of 4 mL eluted by A-TREF are collected at the detector output in a stainless-steel column (4-mm ID and 250 mm long) with a stainless-steel filter (pore size of 0.2 μm) at the bottom end. The polymer is precipitated by addition of excess acetone and methanol mixture (ratio 1:1) and then filtered and dried under a nitrogen flow. Then the polymer is removed from the filter as a film and analyzed with an infrared microscope. This "off-line precipitation method" generates solvent-free polymer fractions and the resultant spectra are free from solvent interferences. Further advantages are:

(i) The calibration of SCB vs. elution temperature, for the TREF system, is directly obtained.

(ii) The use of antioxidants during fractionation is possible because they remain soluble and are removed when methanol is added.

(iii) Infrared spectra, suitable for quantitative analysis, can be obtained with very small amounts of polymer (e.g., lower detection limit is about 0.3 mg).

Other "off-line" methods based on solvent stripping, could be affected by the presence of antioxidants and, in addition, they require quite complex and expensive mechanical devices.[6]

Short-Chain Branching Determination by Infrared Microspectroscopy

Films of approximately 0.3–0.5 mg were removed from the filter after the precipitation and were analyzed in transmission mode using a Nic-Plan microscope (Nicolet Instruments Corp. Madison, Wisconsin, USA) interfaced to a Nicolet 5SXC Fourier-transform infrared spectrophotometer. IR spectra were collected with a rectangular field of view at the sample plane of $60 \times 60 \ \mu m$. Measurement time of 2 min was used at 4 cm^{-1} nominal resolution. To obtain the height of the absorbance band from CH_3 groups of 1-butene (1378 cm^{-1}), the spectra were curve fitted in the range 1395–1330 cm^{-1} using four mixed Lorentz-Gauss functions (Figure 2). In the range 1395–1330 cm^{-1} four bands are present. One, centered at about 1375 cm^{-1}, arises from CH_3 symmetrical bending. Another one, centered at about 1364 cm^{-1}, arises from CH_2 scissoring. Two weaker bands at about 1353 cm^{-1} and at about 1340 cm^{-1} (shoulder) arise from CH_2 twisting and wagging vibrations.[7] Sum Gauss and Lorentz peakshape is the most common function to fit the absorption bands of solid state samples:[8]

$$PEAK(X) = H(1-F)\exp\left(\frac{(X-C)^2}{(W/1.665)^2}\right) + \frac{HF}{1+4(X-C)^2/W^2}$$

where C is the center position of the peak, H is the peak height, W is the full width at half maximum and F is the Lorentz fraction ($F = 0$ Gauss peakshape, $F = 1$ Lorentz peakshape). A baseline is subtracted before fitting. The same initial fit parameters were used for all spectra. Lab-Calc*** (Galactic) software was used. Since band intensity also depends on the thickness of the film, the area of the combination absorption bands between 4482-3950 cm^{-1} is used for spectrometric normalization of film thickness.

A linear calibration between A(1378 cm^{-1})/A(4482-3950 cm^{-1}) and SCB content was obtained ($R^2 = 0.99$) by analyzing molded film of ethylene, 1-butene copolymers as standard reference material (1-butene content 3–30 wt%) previously measured by ^{13}C-nuclear magnetic resonance spectroscopy (NMR).
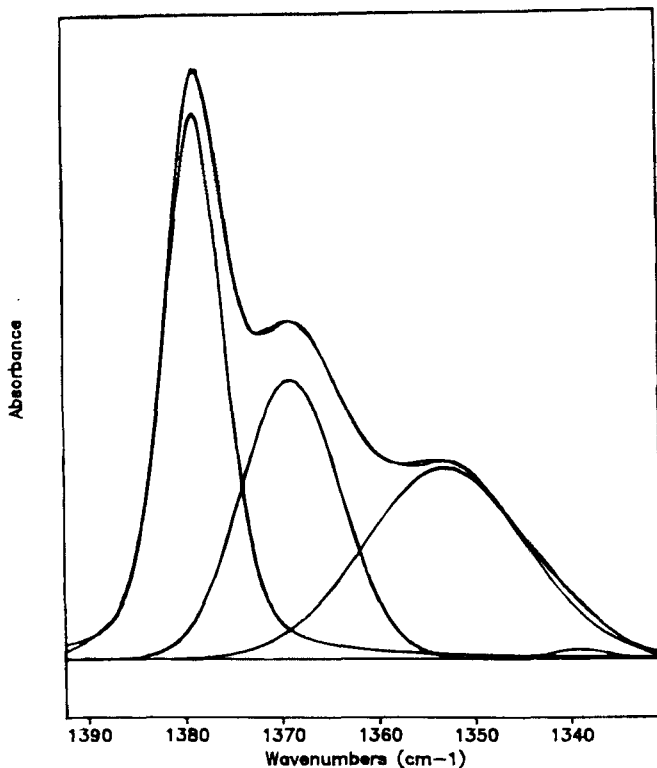
FIGURE 2   Curve fitting of IR Spectrum (1395-1330 cm^{-1}) from sample A fraction 55–65°C.

Xylene Solubility

The determination of the xylene soluble content of each sample was carried out dissolving a weighed amount of sample in o-xylene at 135°C. The solution was cooled down under controlled conditions to 25°C so that the sample insoluble fraction was precipitated. Then the precipitate and the solution were separated by filtration on paper. After filtering, the solution was evaporated to dryness at 140°C, dried in an oven at 70°C and weighed.

Viscometry

The IV of the samples was measured using an Ubbelhode modified capillary viscosimeter and a Sematech Cinevisco system (39 Chemin du Terron, Nice, France) for the automatic recording of the flow time to the accuracy

of 0.01 s. The measurements were made in tetrahydronaphthalene at 135°C. The silicon oil thermostatic bath was regulated to 0.1°C. The calculations were performed using the Huggins equation and taking into account the kinetic energy correction. Elapsed time from preparation of the polymer solution to final viscosity measurement was always less than 2 h.

Gel Permeation Chromatography Measurements

Molecular weight parameters and molecular weight distribution (MWD) for all the samples were measured using a Waters 150C ALC/GPC instrument (Waters, Milford, Massachusetts, USA) equipped with three mixed-gel columns GMHXL-HT (TosoHaas GmbH, Stuttgart, Germany). The dimensions of the columns were 300×7.8 mm and the "pore size" designations of the column packing were in the range from 20 to 250000 Å. The solvent used was ODCB and the flow rate was kept at 1.0 mL/min. Solution concentrations were 0.1 g/dL in ODCB with 0.1 g/L added BHT and the injection volume was 300 μL. All the measurements were carried out at 135°C. GPC calibration for copolymers is complex, as no well-characterized narrow MWD standard reference materials are available for 1-butene copolymers. Thus, a universal calibration curve was obtained using 10 polystyrene standard samples with molecular weights ranging from 980 to 3,040,000 and the data treatment was carried out taking into account the average composition of each sample and respective fractions using a linear combination of Mark-Houwink constants K for polyethylene and poly-1-butene:

$$K_{EB} = (100 - x_B)K_{PE} + x_B K_{PB}$$

where K_{EB} is the constant of the copolymer, K_{PE} (3.8×10^{-4} dL/g) and K_{PB} (1.8×10^{-4} dL/g) are the constants of polyethylene and poly-1-butene respectively, x_E and x_B are the ethylene and the 1-butene wt% content measured by IMS. The Mark-Houwink exponents α (0.725) are the same for polyethylene and poly-1-butene. Even though the molecular parameters obtained were only an estimate of the hydrodynamic volume of each copolymeric chain, they allowed a relative comparison to be made.

RESULTS AND DISCUSSION

The fractions soluble below 25°C in ODCB are not reported.

The significant differences in A-TREF profiles, shown in Figure 3, observed among the polymers obtained with the two different catalytic systems (Mg-Ti vs Zr-based) are:

(i) Mg-Ti copolymers (samples A and B) show characteristic broad and bimodal curves.

(ii) For the Zr-based copolymers (samples C and D) there is a shift of the TREF profile to lower temperatures. An increasing comonomer content gives rise to a greater shift to lower elution temperature.

(iii) In the Zr-based copolymers, there is no longer a sharp peak at about 100°C attributed to the linear homopolyethylene; in other words all the chains contain 1-butene.

Copolymers C and D were "scouting" samples and their broad A-TREF profiles confirm that optimized synthesis conditions were not reached. Therefore, they do not completely represent the Zr-based family.

In Figure 4 the correlation between methyl content ($CH_3/100$ C) and elution temperature for all the samples is reported. As expected, the $CH_3/100$ C decreases as elution temperature increases and this confirms that TREF behavior is controlled by SCB.
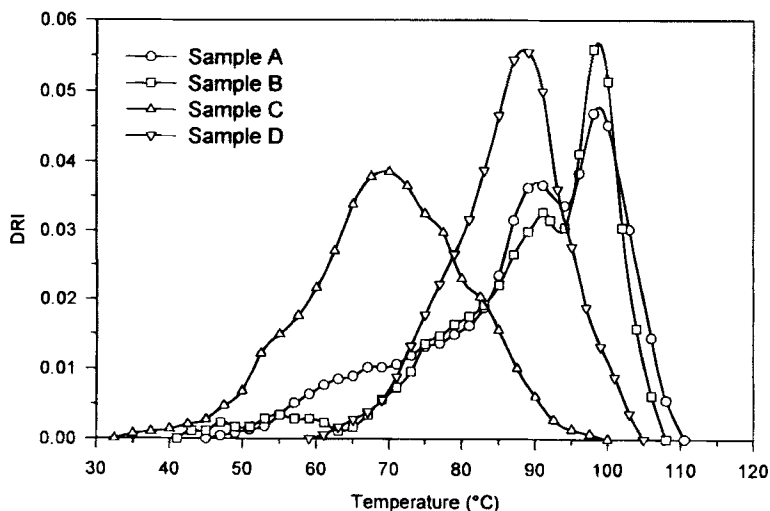

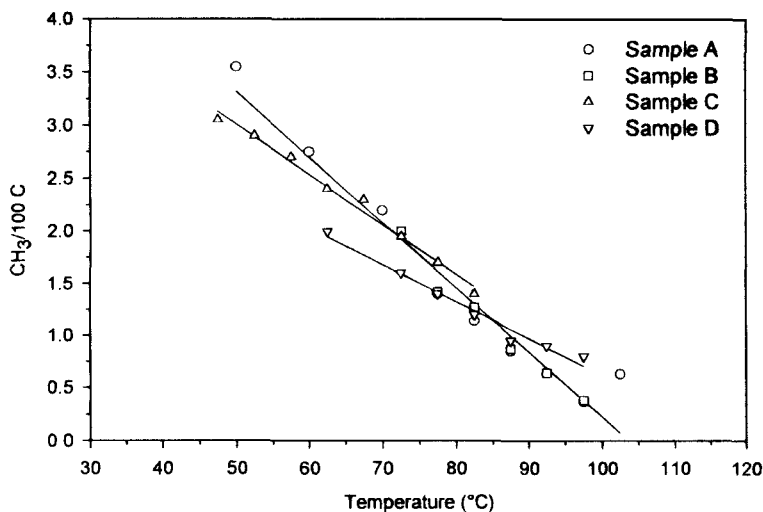FIGURE 3   A-TREF profiles relative to the ODCB insoluble fraction at 25°C for all the samples.

FIGURE 4   Correlation between methyl content ($CH_3/100$ C) and elution temperature for all the samples.

For Mg-Ti samples (samples A and B), the two sets of data are quite well overlapped which indicates that the two samples, produced with similar catalysts and reaction conditions, consist of macromolecules with the same comonomer distribution along the chains and thus are eluted at the same temperature (T_e). The data are interpolated in a linear manner (least-squares method), as generally accepted in the related literature, by the following equation:

Samples A and B: $n° \, CH_3/100 \, C = 6.40 - 0.061 \times T_e(°C)$ ($R^2 = 0.98$)

In the case of the Zr-based samples (samples C and D), the data can be described by two different relationships that are in turn different from the above reported for Mg-Ti based samples. This behavior is a consequence of the different comonomer distribution along the chain indicating a different nature, that is, different copolymerization statistics of the catalysts used:

Samples C: $n° \, CH_3/100 \, C = 5.38 - 0.047 \times T_e(°C)$ ($R^2 = 0.99$)

Samples D: $n° \, CH_3/100 \, C = 4.17 - 0.036 \times T_e(°C)$ ($R^2 = 0.99$)

In sample C, a given SCB content induces a lower crystallinity decrease than in sample D, which can be attributed to a different microstructure. In

other words, there is no "universal" calibration for TREF, as each catalyst system gives rise to a characteristic microstructure.

Figures 5–8 report the MWD curves for whole samples and several selected fractions. It is interesting to note that:

(i) Samples from the Zr-based catalytic system have a narrower MWD than Mg-Ti samples.

(ii) For Zr-based samples, the fractions eluted at higher temperatures give rise to a shift towards higher molecular weights as reported in Figure 7 and 8.

Figures 9 to 12 offer a detailed summary of both chemical-composition and molecular weight distribution of the copolymers. It is interesting to note that:

(i) Samples A and B are characterized by a sharp peak relative to both the lowest SCB content and the highest molecular weight. This is a common feature of all the LLDPE produced with Mg-Ti catalysts and is generally attributed to the unmodified, or slightly modified, linear homopolyethylene.

(ii) Samples C and D are characterized by a relatively broad dissolution profile indicating heterogeneous SCB and molecular weight parameters.

(iii) Each sample shows that the highest molecular weight chains have the lowest SCB content (1-butene content) and therefore the highest elution temperature.

(iv) Samples C and D show a variation in weight-average molecular weight (M_w) with the elution temperature, whereas in samples A and B, it is almost constant over the whole range of chemical composition studied. Thus, an influence of molecular weight on the position and slope of the SCB vs temperature curves cannot be excluded.

CONCLUSIONS

The main advantage of the reported experimental procedure is the possibility to characterize fractions on an analytical scale. The experimental results showed that all samples studied were compositionally heterogeneous as a consequence of the different content and sequence distribution of 1-butene along the chains. In addition, samples can be clearly distinguished accord-
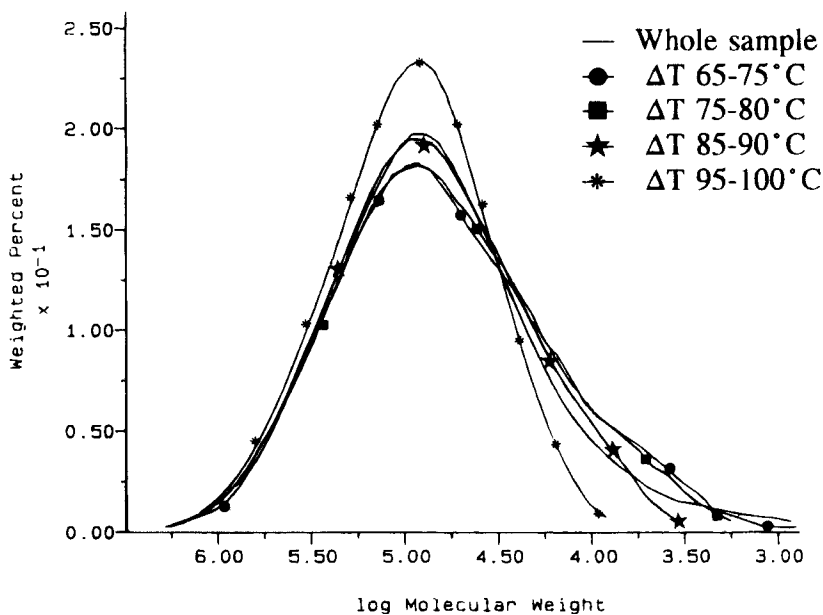
FIGURE 5   Molecular weight distribution curves of the whole samples A and its selected A-TREF fractions.
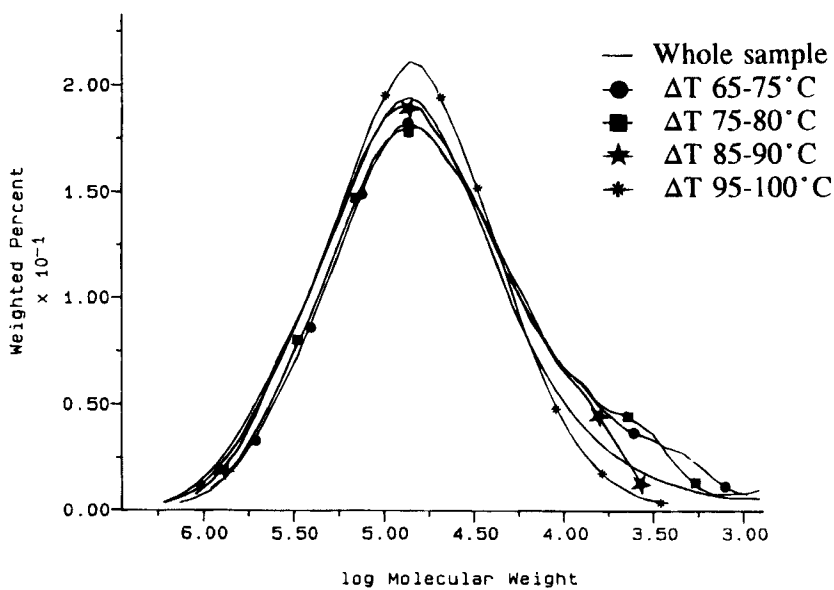

FIGURE 6   Molecular weight distribution curves of the whole samples B and its selected A-TREF fractions.
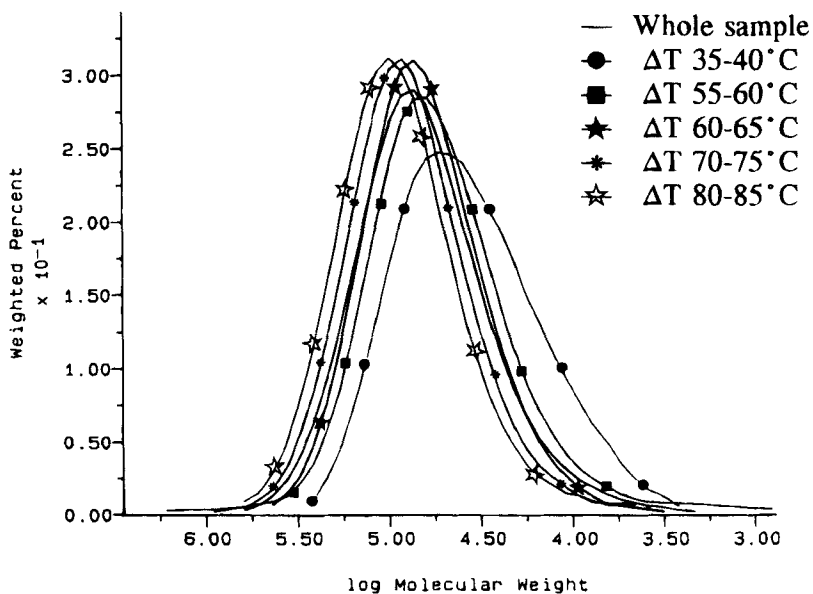
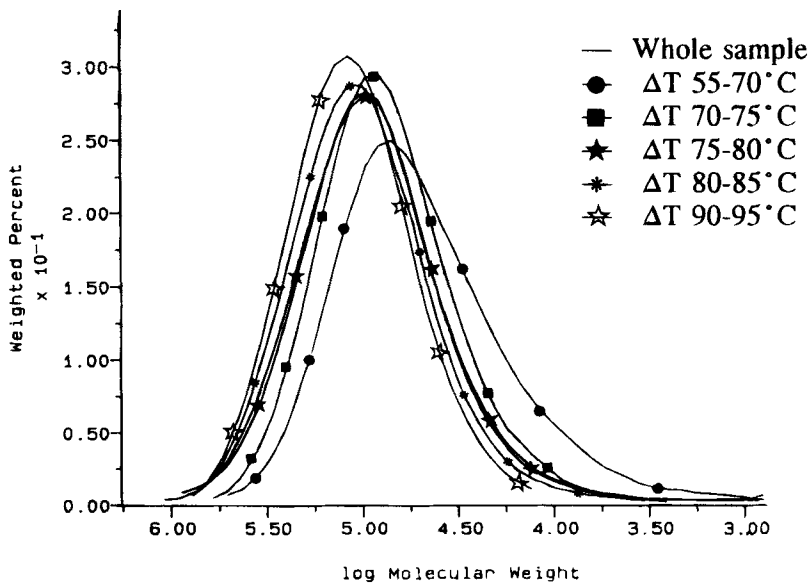FIGURE 7 Molecular weight distribution curves of the whole samples C and its selected A-TREF fractions.

FIGURE 8 Molecular weight distribution curves of the whole samples D and its selected A-TREF fractions.
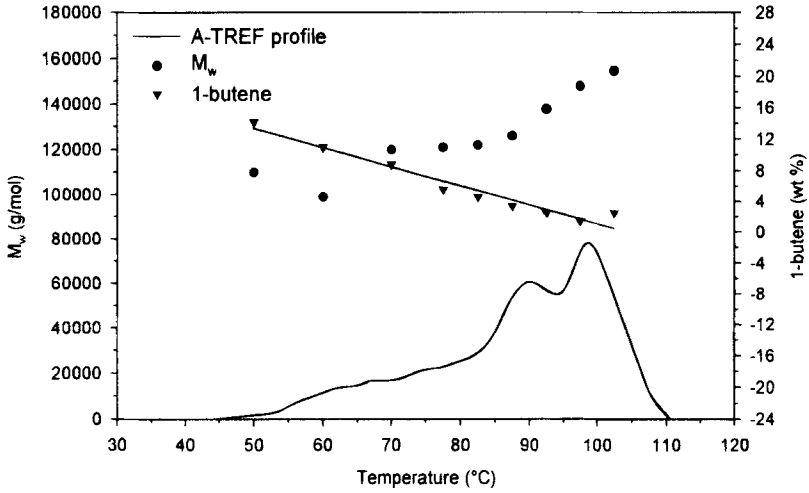
FIGURE 9   A-TREF profile of sample A, weight-average molecular weight (M_w) and 1-butene content of its fractions.
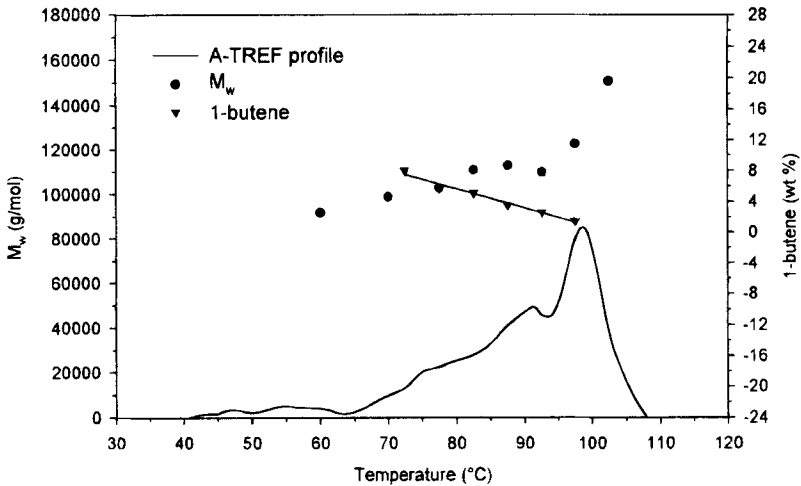

FIGURE 10   A-TREF profile of sample B, weight-average molecular weight (M_w) and 1-butene content of its fractions.
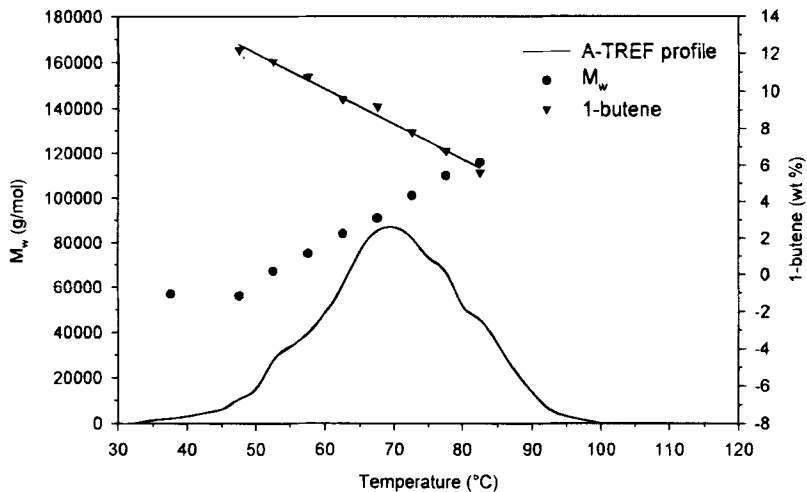
FIGURE 11   A-TREF profile of sample C, weight-average molecular weight (M_w) and 1-butene content of its fractions.
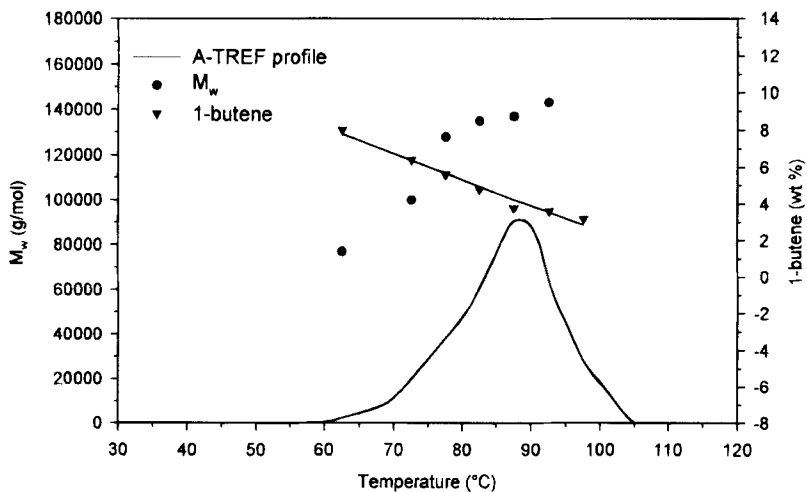

FIGURE 12   A-TREF profile of sample D, weight-average molecular weight (M_w) and 1-butene content of its fractions.

ing to their A-TREF profiles, which reflects the nature of the parent catalyst system. As indicated by IMS and GPC characterization, TREF is mainly controlled by SCB content and distribution, but the influence of molecular weight on elution temperature must also be considered. The developed A-TREF technique gave selective and reproducible results, which can be applied to any semi-crystalline polymers.

Acknowledgments

References

[1] L. G. Hazlitt, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **45**, 25 (1990).
[2] G. Glockner, *J. Appl. Polym. Sci., Appl. Polym. Symp.*, **45**, 1 (1990).
[3] L. Wild, *Adv. Polym. Sci.* **98**, 1 (1990).
[4] J. M. Vela Estrada and A. E. Hamielec, *Polym. React. Eng.*, **1**, 201 (1992/93).
[5] L. Wild, *Trends Polym. Sci.*, **1**, 50 (1993).
[6] L. M. Wheeler, *Appl. Spectrosc.*, **47**, 8 (1993).
[7] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*; Wiley & Sons: New York, NY, 1967.
[8] W. F. Maddams, *Appl. Spectrosc.*, **34**, 245 (1993).