Characterization of Linear Low Density Polyethylene by Temperature Rising Elution Fractionation and by Differential Scanning Calorimetry

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SYNOPSIS

In this article we consider characterization of the branching distribution of LLDPE by analytical TREF and by DSC techniques. Qualitatively, both methods yield parallel information, provided that the DSC samples are prepared at very slow cooling rates. Analytical TREF provides more quantitative information, however, in that the mass fraction of material with different branch levels can be estimated. Full characterization of a polyethylene requires the use of a preparative TREF technique, in which fractions dissolved at preselected temperatures are investigated for branching with high resolution ^{13}C NMR and for molecular weight distribution, with high temperature SEC analyses.

INTRODUCTION

LLDPE is made by the copolymerization of ethylene with α-olefins, such as 1-butene, 1-hexene, and 1-octene, producing a backbone of ethylene units with short side chains. These branches affect crystallinity and properties such as density, crystalline melting point, rigidity, hardness, permeability, and chemical resistance.[1] The catalysts used in the manufacture of LLDPE appear to have more than one active site, resulting in varying interactions between the ethylene and comonomer during a polymerization reaction.[2] This gives rise to multimodal branching distributions.

The diversity of the various polyethylene grades is primarily a result of variations in distributions of molecular weight and branches of various types. In the past, the majority of molecular characterizations performed on polyethylenes have been concerned with analyses of molecular weight averages and distributions. Since the advent of LLDPE, it has been noted that such semicrystalline polymers may exhibit different physical properties although the density, melt flow index, molecular weight averages, and distributions are found to be the same. Such observations suggest the need for a complementary method to aid in the elucidation of the molecular structure of these polymers. Techniques such as solution viscometry for the determination of long chain branching[1] and ^{13}C NMR for the determination of overall short chain branching levels[3-4] have been developed. ^{13}C NMR analyses of short chain branching yield average values rather than distributions. This type of analysis is therefore limited in the case of LLDPE because most commercial polymers of this type exhibit broad, multimodal short chain branching distributions that are not adequately described by an average number of branches per 1000 backbone carbons.

A fractionation technique, based on the level of short chain branching, was first described by Desreux and Spiegels in 1950.[5] This technique, currently known as Temperature Rising Elution Fractionation (TREF), takes advantage of the differing crystallizabilities of molecules due to variations in chain branching levels to achieve fractionation. The power of this method was not fully appreciated nor used prior to the commercialization of LLDPE. In the past decade, however, TREF has been recognized as a powerful tool for the structural analysis of

LLDPEs and their blends. As a result, the technique has been refined by a number of researchers.[6-15]

TREF equipment is not commercially available at present. One purpose of this article is to describe a TREF instrument and the accompanying software and to illustrate its capacity with reference to several commercial LLDPEs.

TREF analyses can be performed in the analytical or preparative modes. In the latter version, fractions are collected according to their relative crystallinities and are analyzed separately for branching character (^{13}C NMR) and molecular weight distributions (SEC). Analytical TREF is a necessary precursor to preparative analyses, in order to determine the appropriate temperature regimes for the various fractions. DSC analyses are a possible alternative to analytical TREF characterizations, since both provide a profile of relative amounts of material with differing crystallinities. This is in terms of melting temperatures for the DSC method and solution temperatures for the TREF. Since DSC apparatus is much more widely available than TREF equipment, it was of interest to compare the information provided by both techniques. We show here that DSC and analytical TREF data are qualitatively similar, but that the latter gives more quantitative information.

EXPERIMENTAL

Materials

Four commercial linear low-density polyethylenes, labelled A through D, were utilized in this study. All four were ethylene–octene copolymers with six carbon short chain branches. Molecular weight averages and distributions were similar for all four. Polymers A through C exhibited melt indices of approximately 1 g/10 min, with D having a significantly lower melt index of 0.85 g/10 min. Resins A through C were pure polymers without additives. Resin D contained some fluorocarbon elastomer processing aid. Resins A and B were further characterized by analysis of TREF fractions using GPC and ^{13}C-NMR (i.e., preparative TREF).

Temperature Rising Elution Fractionation

TREF profiles were generated using an instrument built at the University of Waterloo. The instrumental setup consists of an HPLC pump, an Omega temperature controller that can maintain a specified temperature within 0.1°C, a stainless steel elution

oven and a Miran 1A–CVF infrared detector. The IR detector was set at a fixed wavelength of 3.41 μ to detect the C–H stretch of the polyethylene. The temperature controller and IR detector are interfaced to a personal computer with software to collect and analyze the data (Fig. 1). The columns utilized in the system were stainless steel columns (1.27 cm diameter, 30.5 cm length) loaded with 100–200 mesh silica. The silica was silanized using trimethylchlorosilane, as described by Kelusky and Fyfe[16] prior to loading into the column. The silanation procedure was necessary to provide a nonpolar, inert support for the deposition of the polyethylene fractions. Samples were dissolved in 1,2,4 trichlorobenzene containing 0.1% Irganox 1010 antioxidant. Injection into the TREF column loaded with trimethylchlorosilane treated silica gel took place at 150°C. The samples were subsequently cooled according to the following program:

150–135°C in 30 min,
135–125°C in 2 h,
125–25°C in 67 h.

The cooling cycle was followed by elution of the column over a temperature range of 25–110°C. Two modes of elution were used as follows: (1) Continuous flow elution, consisting of elution at 1 mL/min as the oven and solvent is being heated at +10°C/hour. This elution yields what we term an analytical TREF trace. This analysis provides the overall short chain branching distribution of the polymer in question. Sample concentration for this method was approximately 0.007 g/mL. (2) An alternative is a preparative TREF technique, using stop flow elution to recover narrow branched fractions for further characterization by GPC and ^{13}C NMR. In this case, sample concentration was increased to approximately 0.025 g/mL to ensure that the fractions were large enough for subsequent analyses. Stop flow elution consists of raising the temperature of the oven to the upper temperature of a desired range, holding the column in a static state for approximately 10 min followed by elution until output from the IR detector returns to the baseline. The column is then heated to the next temperature and the process repeated. Typical ranges used in this study were as follows: 25–55°C, 55–65°C, 65–75°C, 75–85°C, 85–95°C, and 95–105°C. (These ranges should be adjusted for different polymers, depending on the guidance provided by prior analytical TREF analyses.) The fractions were then recovered by precipitation in cold absolute ethanol followed by vacuum
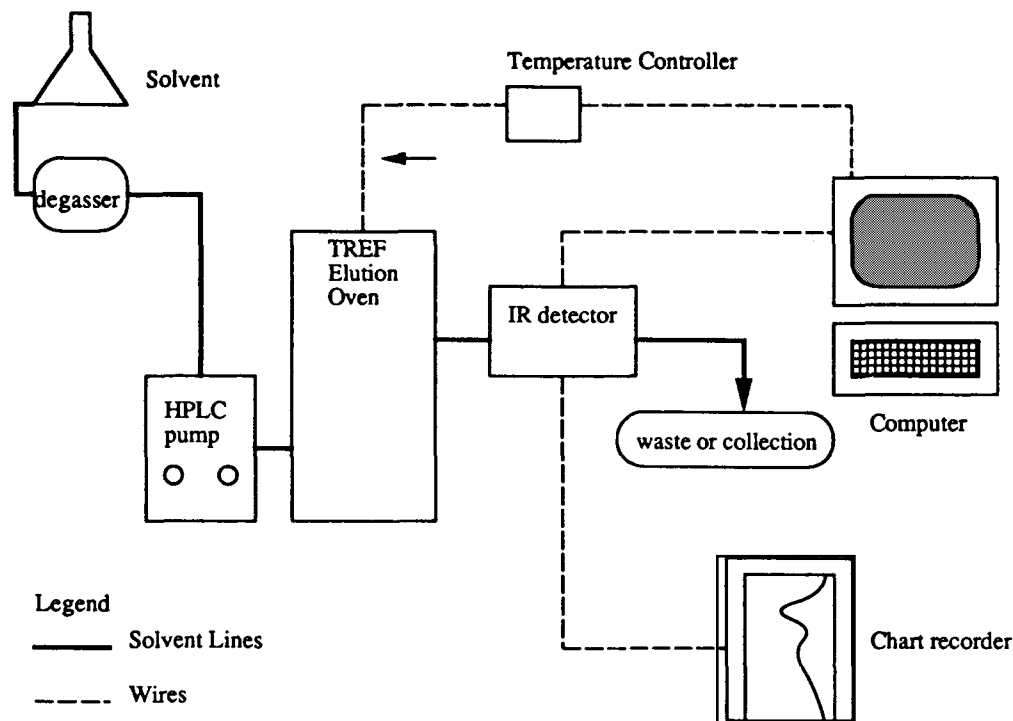
Figure 1 TREF Schematic.

filtration onto a 0.5 μ PTFE filter. Samples were dried at 60°C under vacuum for 24 h to drive off any residual solvent.

Software

The software package used to collect and analyze the TREF data was developed for this specific system. The programs were written in QuickBasic and were designed to perform the following functions:

1. Data collection: The computer is interfaced with both the temperature controller and the IR detector. Through the program, the rate of temperature increase can be controlled. The number of data points collected is optional and the data collected includes the IR signal and the corresponding temperature.
2. Data smoothing: This program allows for the smoothing of any spurious spiking in the trace caused by air bubbles or particulate contamination. The program is such that distortion of the shape of the elution profile can be avoided.
3. Data Analysis/Normalization: This program allows the user to determine a baseline and

to calculate the weight percent of any given fraction by area comparison. The area under the elution curve can also be normalized to any desired number using this program. This permits the comparison of polymer solutions of different concentrations.

4. File adding: This allows the user to determine the shape of a polymer blend by digitally adding the files of the individual polymers in the desired proportions.
5. Plotting option: This option interfaces with a Roland digital plotter and allows superimposition of up to six TREF profiles.

DSC

DSC measurements were made on a Perkin-Elmer DSC-4 with a TADS software package to collect and analyze the data. Samples were prepared from the whole polymer by pressing at 170°C for 10 min under 20,000 lbs force. The samples were subsequently subjected to a controlled cooling rate of 1.5–3°C/hour. Samples, 5–10 mg, were sealed in aluminum sample pans for analysis. Endotherms were generated at a heating rate of +10°C/h over a range of 40–170°C.

Table I   Molecular Characteristics (Whole Resin)

Polymer	MI g/10 min	Density g/mL	Branches/ 1000 C	$\bar{M}n$	$\bar{M}w$ ($\times 10^{-3}$)	$\bar{M}z$	$\bar{M}w/\bar{M}n$	Sn[a]	Sw[a]	Percent[b] High Density
A	0.94	0.932	8.3	23	66	147	2.9	31.4	73.1	21.0
B	1.07	0.923	16.1	23	70	175	3.0	32.9	85.7	14.4
C	0.92	0.929	9.6	22	66	150	3.0	31.1	74.5	16.4
D	0.82	0.931	8.6	20	68	176	3.4	31.0	85.7	25.5

[a] Standard deviations of number and weight distributions, respectively.
[b] From TREF analyses.

Melt Index

Melt index measurements were performed as outlined in the ASTM 1238 under 190°C/2.16 kg conditions and reported as g/10 min.

SEC

Molecular weight measurements were carried out using a high temperature GPC with a differential refractometer, LALLS (low angle laser light scattering) detector and differential viscometer, all on line. 1,2,4 trichloro benzene, containing 0.1% Irganox 1010 antioxidant, was used as the solvent for the system and in sample preparation. Samples ranged in concentration from 1–2 mg/mL with injection volumes varying from 175–250 mL. The system was maintained at 145°C throughout all analyses. Sample dissolution was achieved by rotation of samples at 160°C for 24–72 h. The higher crystallinity fractions required 72 hour dissolution times and were therefore dissolved in 0.2% Irganox in trichlorobenzene. Molecular weight averages reported in Tables I and II were calculated from the differential viscometer data.

^{13}C NMR

^{13}C NMR spectra were obtained on a Bruker AC 300 MHz spectrometer operating at 75.43 MHz. The spectra were recorded at high resolution using inverse gated conditions and a 90° pulse of 12 microseconds with a 12 second delay. Samples were run in 1,2,4 trichlorobenzene at 120°C in 10 mm tubes for the whole polymer, and 5 mm tubes for the fractions, as there was not a large amount of polymer per fraction. Sample preparation consisted of swelling the polymer in trichlorobenzene at 150°C for 0.5 h, followed by insertion into the NMR without cooling. Satisfactory spectra were obtained in approximately 2000 scans. The short chain branch frequency was calculated from the relative areas of the CH_2 peaks at 29.99, 34.5, 30.5, and 27.3 ppm, the CH peak at 38.1, and that of the 3B6 carbon at 32.2 ppm, yielding a measure of short chain branches per 1000 backbone carbons.[17]

Density Measurements

Density measurements were made on whole polymer samples that ranged in weight from 0.6–1 g. These

Table II   Molecular Characteristics (TREF Fractions)

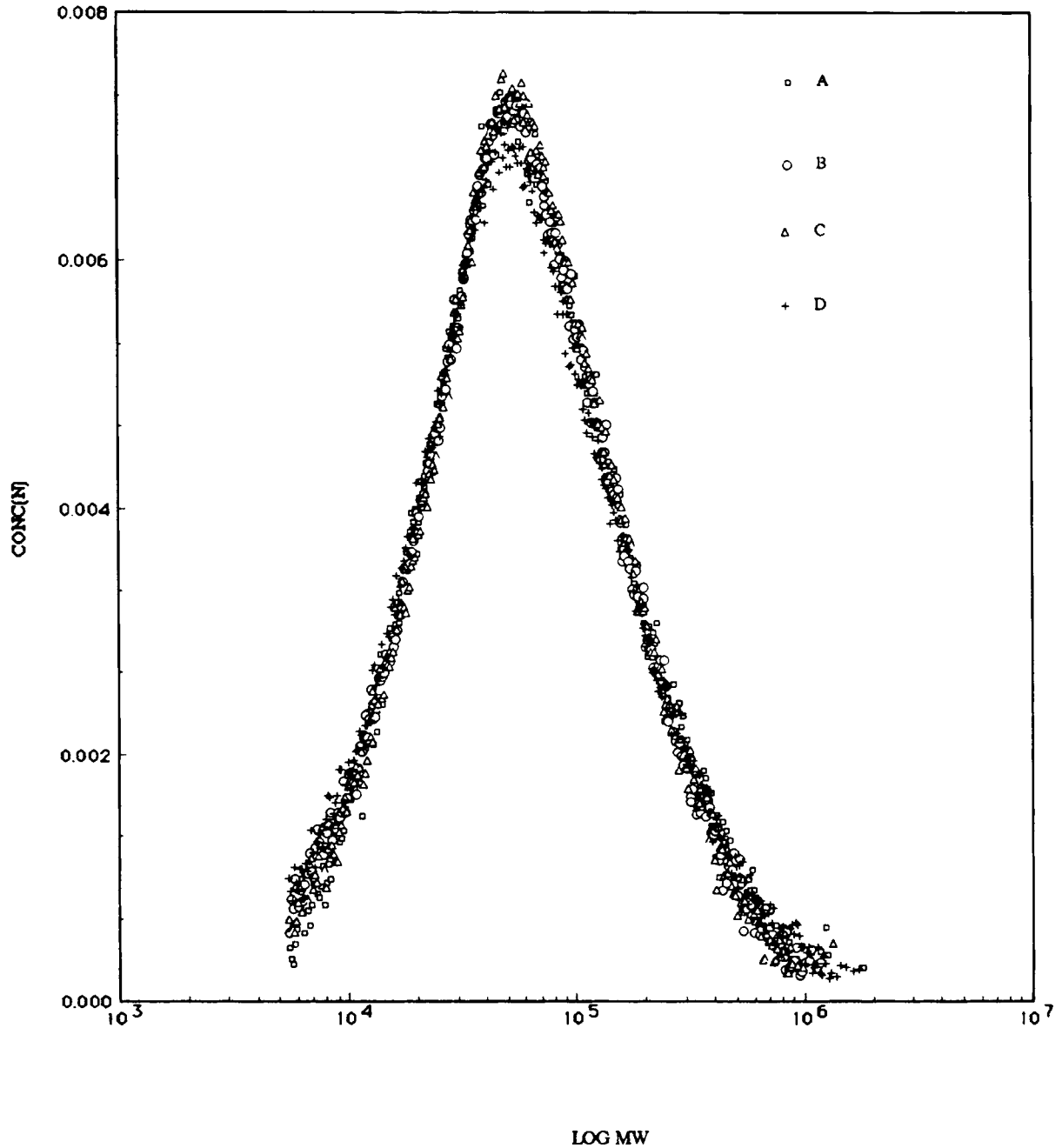| Fraction	Temperature Range °C	Branches/1000 C	$\bar{M}n$	$\bar{M}w$ ($\times 10^{-3}$)	$\bar{M}z$	$\bar{M}w/\bar{M}n$
Polymer A						
5 (Polymer A)	85–95	8.9				
6 (Polymer A)	95–105	4.4 (4.5, rerun)				
1 (Polymer B)	25–55	—	18	48	151	2.7
2 (Polymer B)	55–65	29.7	24	54	180	2.3
3 (Polymer B)	65–75	25.4	30	79	236	2.6
4 (Polymer B)	75–85	20.9	37	95	375	2.6
5 (Polymer B)	85–95	9.7	45	103	459	2.3
6 (Polymer B)	95–105	0	55	134	493	2.4

Figure 2   Molecular weight distributions from SEC using universal calibration.

were prepared by melting at 170°C for 20 min in a circular mold followed by a 1.5°C/h cooling program. This was done to ensure that each sample had the same thermal history. Densities were determined using a specific gravity device with reagent grade acetone as the suspending liquid.

All samples were protected from oxidation by adhering aluminum foil covers.[18]

RESULTS

The great diversity between various polyethylenes is the result of variations in molecular weight and branching distributions. Table I shows the molecular weight and branching data pertaining to the four LLDPE resins considered in this investigation. All resins show very similar molecular weight averages,
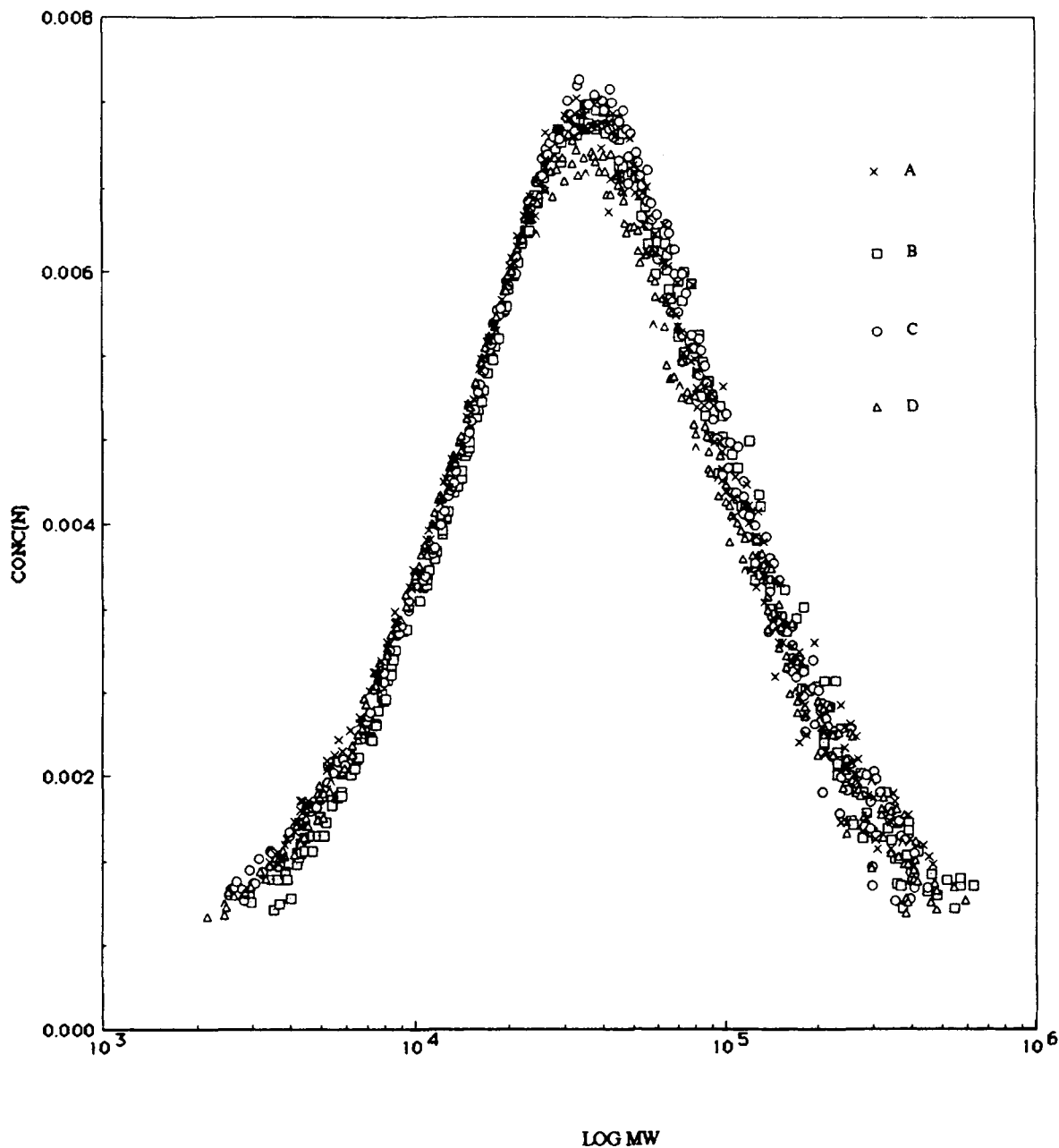
Figure 3 Molecular weight distributions from SEC using a continuous viscometer detector.

which are identical within the limits of our measurement techniques. Figures 2–4 show the molecular weight distributions of the four polymers, from universal calibration, continuous viscometer, and LALLS data, respectively. The LALLS is very sensitive to higher molecular weight species and insensitive to smaller polymers. This is seen in Figure 4, where the data degenerate into noise at molecular weights much less than 100,000. (All data are pre-

sented here as points, rather than smoothed curves, in order not to disguise uncertainties, particularly in the tails of the distributions.) It is evident from these plots that there is no appreciable difference in the molecular weight distributions of these polymers.

The values for the short chain branches per 1000 backbone carbons, listed in Table I, reflect the shape of the branching distributions generated by TREF
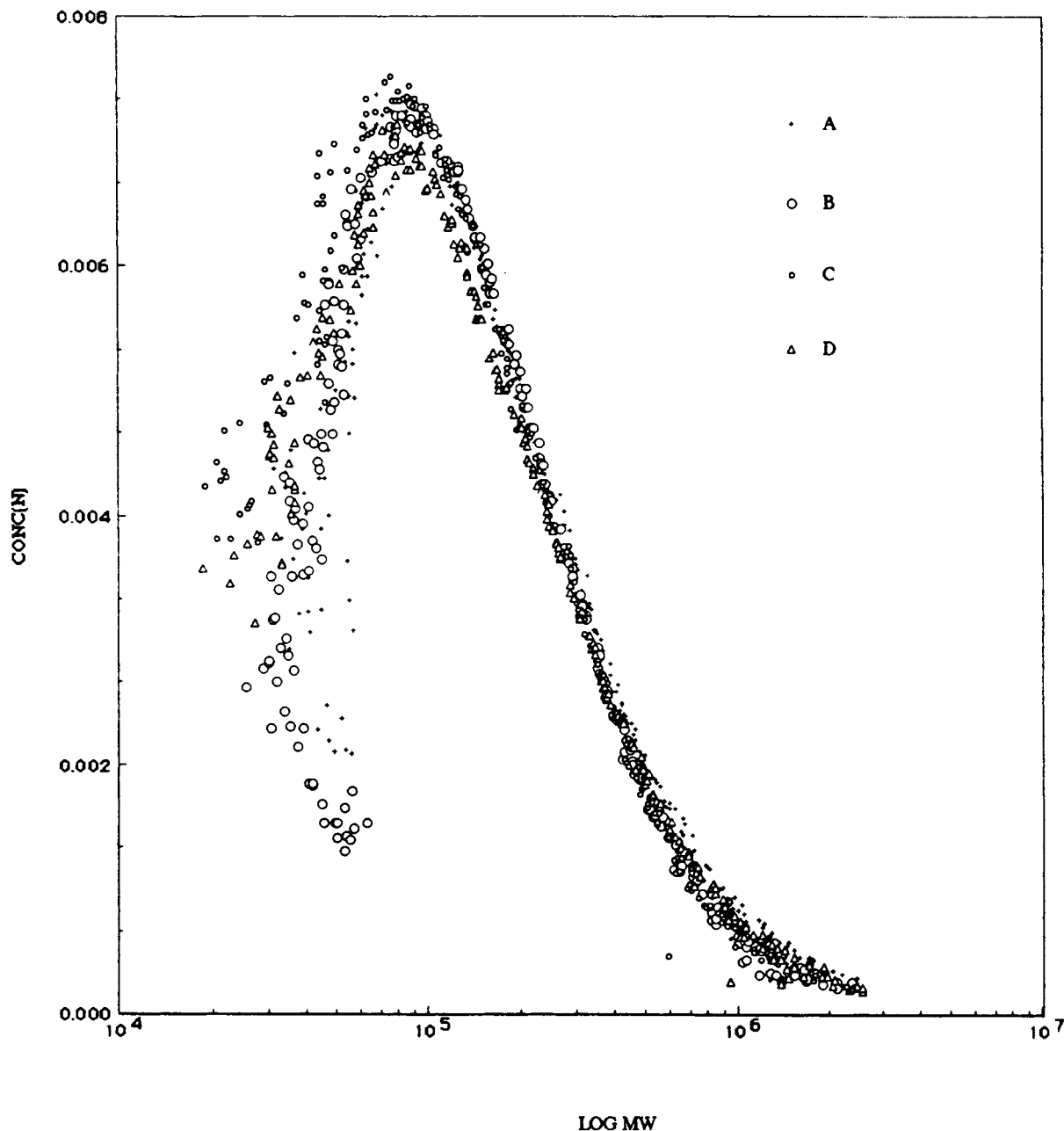
Figure 4   Molecular weight distributions from SEC using a LALLS detector.

analysis (Fig. 5). The relative amount of branching in descending order is B > C > A = D. (Note that short and long branches cannot be distinguished in these cases); ^{13}C NMR at present does not differentiate between six carbon and longer branches.[17] This order is reflected in the TREF traces as resins A and D exhibit very similar distributions, C shows a slightly broader distribution and Resin B appears to have the broadest distribution of solution tem-

peratures. This order is maintained in the properties that are related to crystallinity, specifically density (Table I) and ΔH_{melt} (enthalpy of melting, Table III). Comparison of the analytical TREF profiles of the four resins under consideration to the DSC endotherms shows that the differences in the TREF profiles are reflected in the shape of the endotherms. Resins B and C, exhibiting broader branching distributions, also have multimodal melting endo-
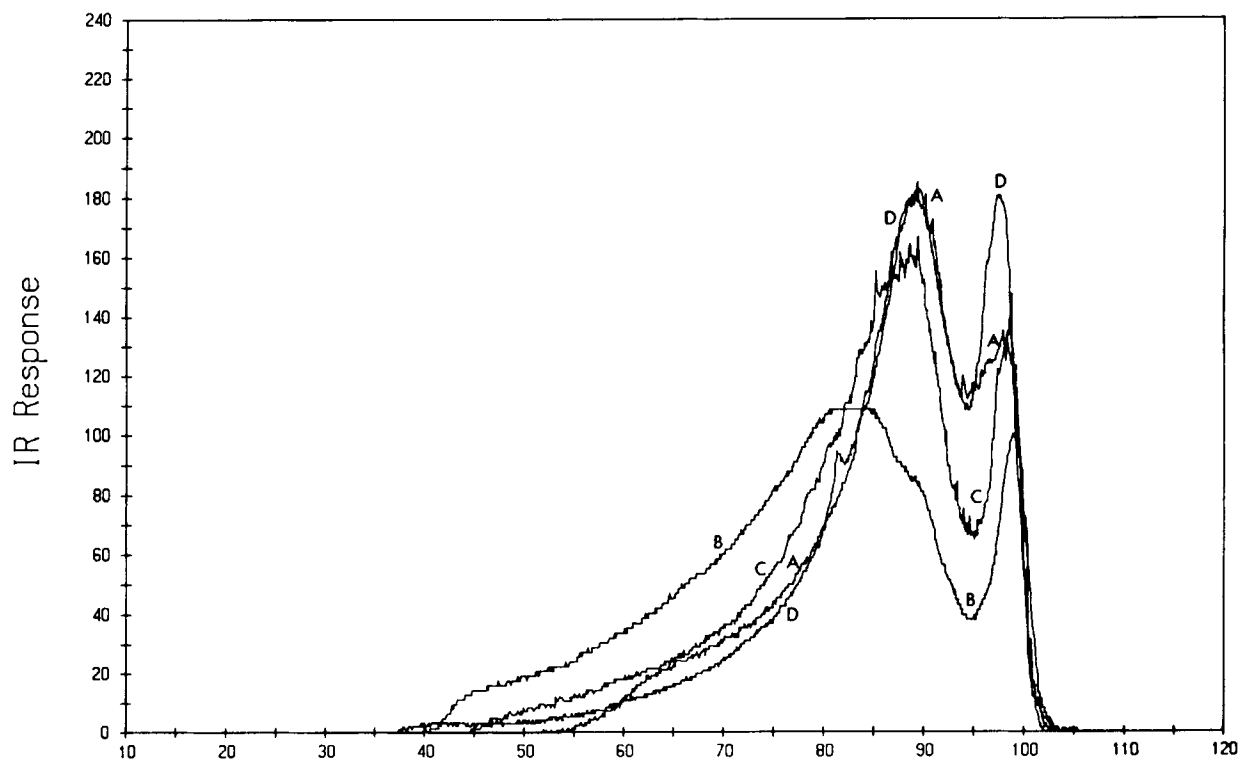
Figure 5   Analytical TREF traces.

therms (Fig. 6). This is particularly evident with respect to Resin B, where the endotherm shows melting taking place over a very broad temperature range. The shape of the TREF curves also enables the prediction of order of ΔH_{melt}, as the resins exhibiting higher degrees of short chain branching also exhibit lower ΔH_{melt} values (Table III).

It is also evident that the cooling rate has a significant effect on ΔH_{melt} (Table III). By reducing the cooling rate from 3 to 1.5°C/h, the measured crystallinity increases, as expected.

Percent crystallinity of the samples cooled at $-1.5°C/h$ was determined from both the densities and the ΔH_{melt} as follows: the enthalpy of fusion of perfectly crystalline polyethylene was taken to be 289 J/g and that of amorphous material to be zero[19] and the following equation was used:

$$\Delta H_{(meas'd)} = x289 J/g \qquad (1)$$

where

$$x = \% \text{ crystallinity}$$

The wt % crystallinity was calculated from the density measurements as follows:

$$w_c = \rho_c(\rho - \rho_a)/\rho(\rho_c - \rho_a) \qquad (2)$$

taking the density of the amorphous polyethylene (ρ_a) to be 0.853 g/cm^3 and that of the perfectly crystalline polyethylene (ρ_c) to be 1.00 g/cm^3.[20] As expected, these values are not identical, but they do exhibit the same trends. The difference is a result of the method of measurement, since different calculations take advantage of different manifestations of the short chain branching distribution.

The percent high density (HD) polyethylene numbers listed in Table I were calculated from the analytical TREF traces as described by Bibee and

Table III   Crystallinity, DSC Data (Whole Resin)

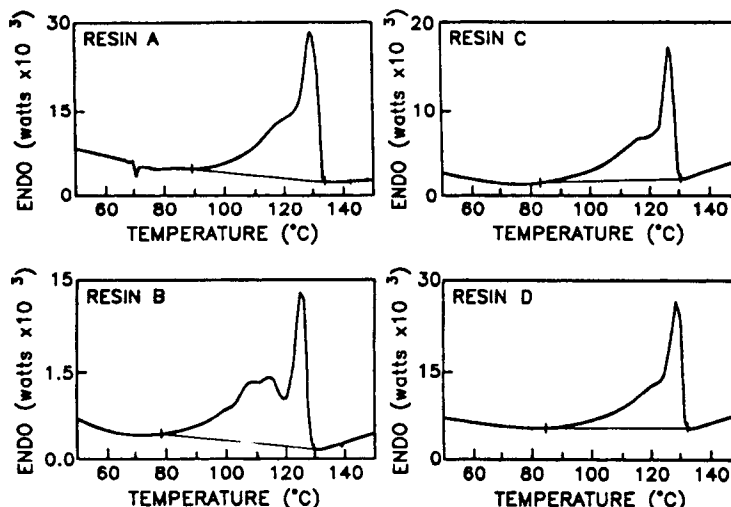| Polymer | Percent Crystallinity | | ΔH_{melt} (J/g) | |
	Density	DSC	3°C/h	1.5°C/h
A	58	48	114	140
B	52	34	76	97
C	56	41	94	119
D	57	49	123	143

Figure 6   DSC traces: samples cooled from the melt at 1.5°C per h.

Dohrer.[21] A vertical line was dropped down to the baseline from the minimum between the linear and more branched peaks. The relative areas of each were measured using the aforementioned software. Bibee and Dohrer suggest that a lower value of percent HD represents a more uniform intermolecular distribution of the comonomer among polymer chains. Resin B stands out in this calculation with the lowest fraction of high density polyethylene at 14.4%, followed by C at 16.4%, A at 21.0%, and D showing the highest proportion of high density polyethylene at 25.5%. Observation of the analytical TREF trace of Resin B (Fig. 5) verifies this calculation, as it has the broadest elution range and also the lowest HD percentage.

Table II shows the results of the GPC and ^{13}C NMR analysis of fractions obtained by stop flow temperature rising elution fractionation. It should be noted that there is an unquestionable trend for increasing molecular weight as a function of elution temperature for these samples. It is interesting to observe that the branch content of the high density fraction of Resin A, at approximately 4.4 short chain branches, is significantly higher than that measured for the high density fraction of resin B, which exhibited no peak at 32.2 ppm. It is possible that the high density peak of Resin B is "purer" than that of resin A as the minimum between the branched and the high density peak is much more pronounced for resin B as compared to A. Further investigations would be required to confirm this correlation. A plot of branch frequency as a function of elution temperature shows a linear relationship (Fig. 7). Sim-

ilarly, a plot of molecular weight vs. elution temperature shows a linear trend (Fig. 8). These relations may not be valid, however, for LLDPEs made with other catalyst systems.

CONCLUSIONS

It is apparent that temperature rising elution fractionation is a valid technique for the determination of branching distributions in LLDPE. The technique has been refined such that it can be used as a reliable method to elucidate the nature of the branching distribution of LLDPE and to provide fractions for de-
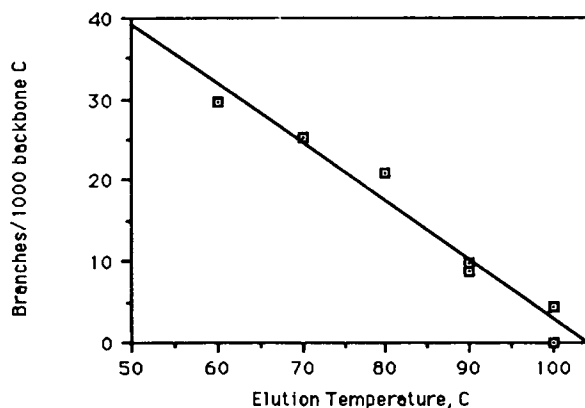

Figure 7   Calibration curve, branch frequency vs. elution temperature for ethylene-co-1-octene LLDPE.
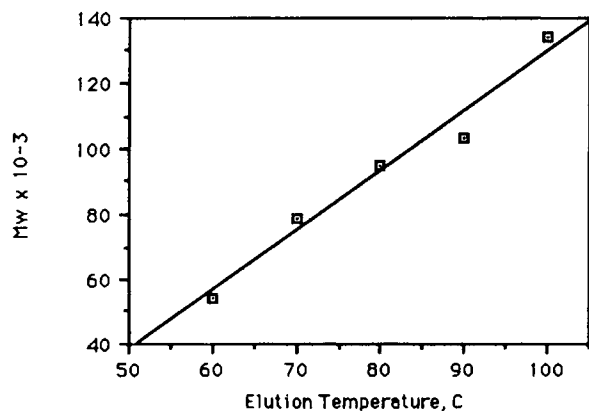
Figure 8 Molecular weight vs. elution temperature for ethylene-co-1-octene LLDPE.

tailed characterization. Physical properties that are a function of short chain branching, such as ΔH_{melt} and percent crystallinity, can be accurately ranked by comparing branching distributions.

Detailed characterizations of branched fractions show that molecular weight increases and short chain branch frequency decreases as a function of increasing TREF elution temperature. DSC analyses of samples that have been crystallized slowly give much of the same qualitative information as analytical TREF in terms of estimating the breadth of the branch distribution. One major advantage of TREF analyses is the ability to determine percent by weight of fractions since the data is generated in the form of a mass distribution. By contrast, the intensity of the DSC response is a product of the amount of material melting at a particular temperature and the ΔH_{melt} of that material. In order to translate a DSC endotherm into a weight distribution, the ΔH_{melt} for each fraction would have to be measured and the DSC response corrected for the differing enthalpies of melting. It is only by operating TREF in a preparative mode, and collecting and characterizing fractions, that the full power of the technique can be utilized.

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