

# Branching Measurement by Analytical TREF: A Fully Quantitative Technique

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## SYNOPSIS

Conversion of analytical TREF data to accurate branching distributions of polyethylene requires a calibration of branching frequency as a function of elution temperature. It has been found that the elution temperature of a semicrystalline polymer such as polyethylene depends on molecular weight, branch content, branch length, and branch clustering. It stands to reason that every polymer will have its own unique relation of branch frequency and elution temperature. Ideally, the polymer would be fractionated by a preparative TREF technique and the fractions analyzed by NMR or IR to determine branch frequency with respect to elution temperature. This method is tedious and time-consuming. An alternative method is described here to determine the relation between branch frequency and TREF elution temperature and to generate a calibration from analytical TREF data only. A two-detector system is used to simultaneously measure both concentration and branching frequency as a function of elution temperature. Each polymer is analyzed using analytical TREF data alone, eliminating the need for preparative TREF fractionation and NMR analysis of the fractions. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Conventionally, analytical TREF data are converted to branching distributions via a calibration curve relating the number of branches to elution temperature of the polymer.<sup>1-3</sup> Extensive studies relating branching to the crystalline melting temperature of polymer fractions have been done for various polyolefins.<sup>4-18,20-25</sup> All these studies concluded that one calibration curve is insufficient to fully describe the crystallizability distributions of the various polyethylenes studied. The findings of these studies indicate that several factors affect the crystalline melting point of polyethylene molecules.

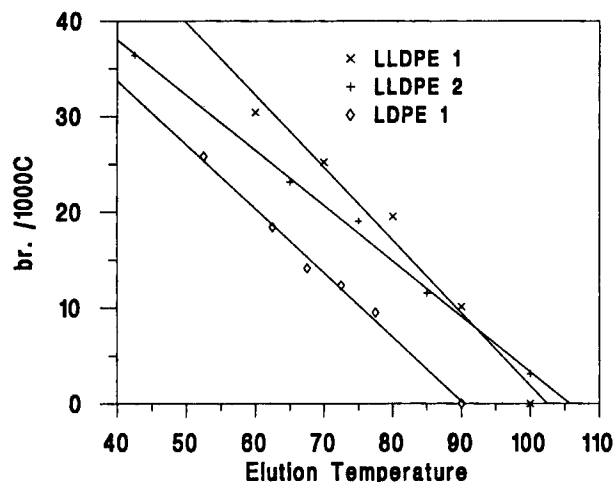
Although the branching frequency of the polymer molecules has the greatest effect on the crystalline melting point, there are several aspects of the polymer structure that also have a marked effect on the crystalline nature of the polymer. The structural characteristic that has the least effect on the crys-

tallizability of polymers is molecular weight.<sup>3-5</sup> The other two structural characteristics that contribute to the crystalline melting point of the polymer molecules are length of the branches and distribution of the branches on the main polymer chains.

Studies in which LLDPE polymers with different branch lengths were analyzed indicate that branch length has a significant effect on the crystalline nature of polymer molecules.<sup>3,6,7</sup> In these studies, various polymer samples, each produced with a different comonomer, were fractionated by differences in crystalline melting point. The resulting fractions were then analyzed to determine branching frequency and it was found that longer branches had a larger effect on the melting point than did shorter ones. The cause of this is believed to be the ease of incorporation of shorter branches into the crystal lattice.<sup>6</sup> The shorter branches apparently cause less disruption of the crystal lattices and produce a smaller depression of the crystalline melting point of the fully linear polymer.

It was also discovered that LLDPEs with the same comonomer type had different crystalline melting behaviors.<sup>8-10</sup> This behavior was believed to

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**Figure 1** Calibration curves of branching and elution temperature for LLDPE 1, LLDPE 2, and LDPE 1. The data were generated from  $^{13}\text{C}$ -NMR analyses of preparative TREF fractions.

be caused by variations in the clustering of branches on the main polymer chains.

A number of studies have been done in which polymer fractions were analyzed by  $^{13}\text{C}$ -NMR to determine sequence distributions.<sup>11-16</sup> These studies concluded that sequence distributions deviated from those predicted by first-order Markovian schemes and that LLDPE polymers may have some blocky character.<sup>11-13</sup> Two causes of blockiness have been proposed in the literature. The presence of hetero-

geneous sites on the organometallic catalysts<sup>11-13</sup> and the diffusion of monomer through the polymer particles<sup>14,15</sup> have both been hypothesized to cause blockiness. Experimental evidence in which different polymerization techniques were studied support the significance of a diffusion mechanism for the formation of blocks.<sup>16</sup> In the cited work, one catalyst system was studied with a low-pressure polymerization process and a high-pressure process. With the low-pressure process, the amount of branch clustering was found to be higher than with the high-pressure process when working with the same catalyst.

Springer et al.<sup>17</sup> did a detailed literature search of the relationship between melting point and branching content for ethylene-1-butene copolymers studied by various authors.<sup>3,17,18,20-24</sup> Their work showed that no two polymers had the same relationship between melting point and branching frequency even though all the polymers were polymerized with the same comonomer.

It would appear that no two polymers have the same relationship between branching frequency and crystalline melting point. Other factors that affect the melting point are molecular weight, branch length, and clustering of branches that could be caused by the catalyst system or the polymerization process. To confirm this, calibration curves of branching frequency and melting point were compared for LLDPE 1, LLDPE 2, and LDPE 1 (Fig. 1 and Table I) (see Appendix 1 for descriptions of

**Table I** Branching Frequencies Determined by  $^{13}\text{C}$ -NMR Analyses of Preparative TREF Fractions from LLDPE 1, LLDPE 2, and LDPE 1<sup>a</sup>

Elution Temperature (°C)	Average Branching (LLDPE 1)	Average Branching (LLDPE 2)	Average Branching (LDPE 1)
42.5	—	36.4	—
52.5	—	—	25.8
60.0	30.4	—	—
62.5	—	—	18.4
65.0	—	23.1	—
67.5	—	—	14.1
70.0	25.2	—	—
72.5	—	—	12.3
75.0	—	19.0	—
77.5	—	—	9.5
80.0	19.5	—	—
85.0	—	11.5	—
90.0	10.1	—	0
100.0	0	3.1	—

<sup>a</sup>The temperatures listed are the midpoints of the temperature ranges over which the fractions were collected.

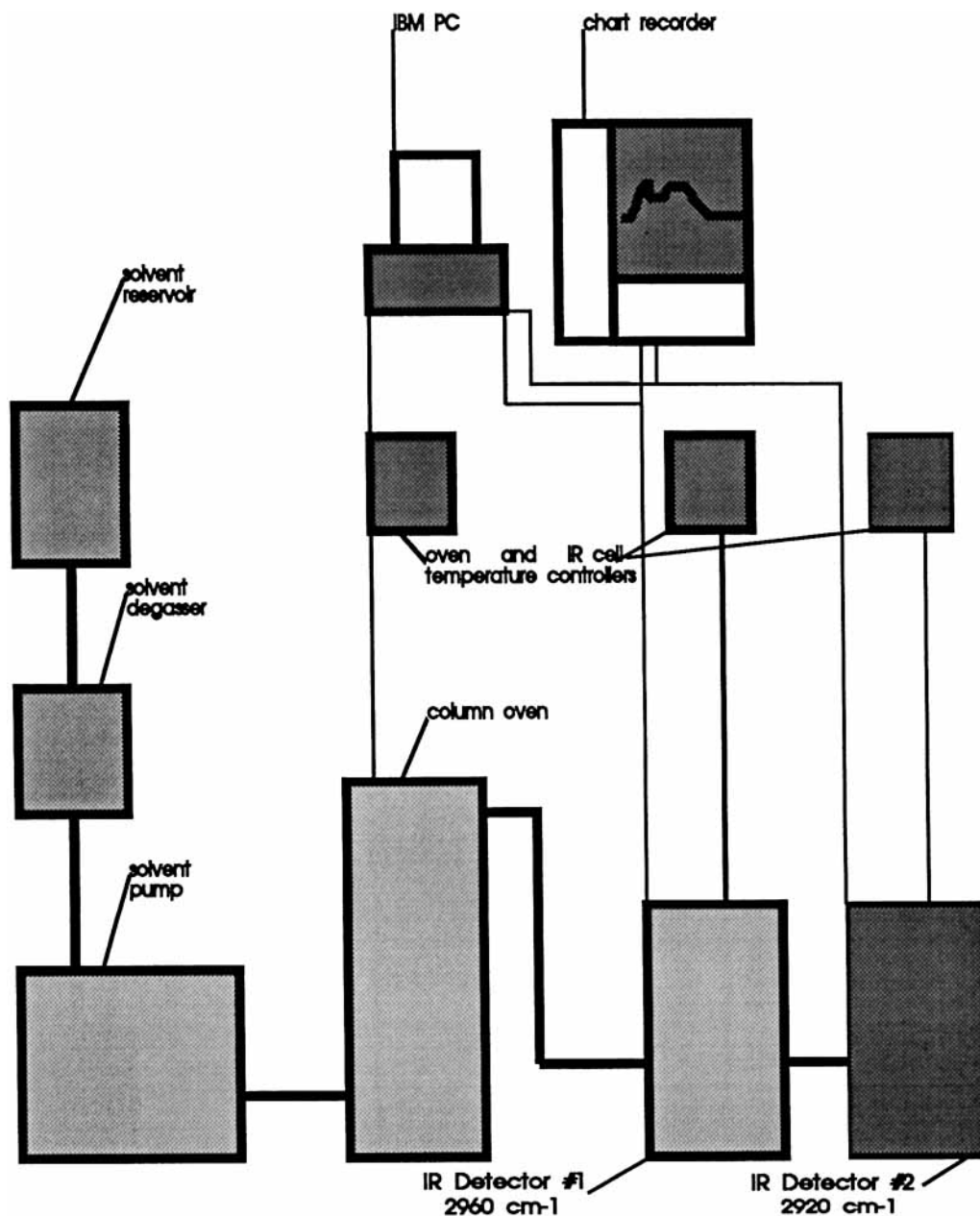


Figure 2 Column elution apparatus.

the polymers). Significantly different crystalline melting behavior with respect to elution temperature was exhibited by all three of the polymers.

It was concluded that to convert analytical TREF data to branching distributions a separate calibration curve is required for each polymer that is analyzed. It is possible to do this by branching content analyses of preparative TREF fractions or, more efficiently, by using a dual infrared detector system to measure branching directly from analytical TREF data. A technique is presented here for generating

calibration curves measuring branch frequencies from analytical TREF data alone by using a double IR detector system.

## EXPERIMENTAL

### Analytical and Preparative TREF

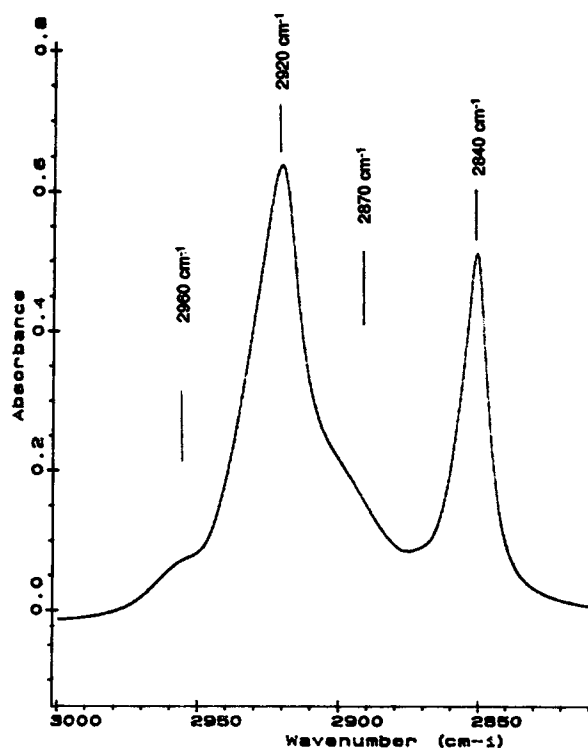
Procedures for loading columns with polymer samples and details of analytical and preparative TREF analyses are described elsewhere.<sup>19</sup> This reference

details polymer concentrations for both analytical and preparative TREF as well as elution profile and column cooling information.

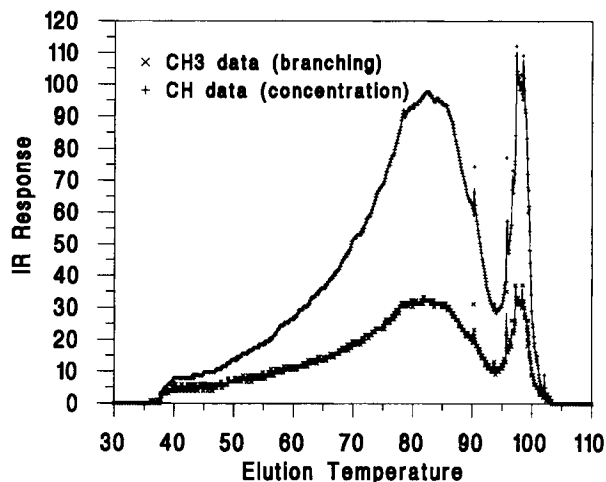
### Apparatus

The apparatus used to elute the columns (Fig. 2) consists of a solvent reservoir, an on-line degasser, an SEC solvent pump, a small forced-air oven to encase the column, two infrared detectors for measuring polymer concentration and branching, and a PC for data collection and temperature control of the column oven. The programs used for temperature control, data collection, and data analysis are all in-house programs.

The second infrared detector is connected in series to the first detector (Fig. 2). The first detector in the series was a variable wavelength detector tuned to measure a C—H stretching band of methyl groups ( $\text{CH}_3$ ) at  $2960\text{ cm}^{-1}$ , while the second detector in the series was a fixed wavelength infrared detector tuned to a C—H stretching band of methylene groups ( $\text{CH}_2$ ) at  $2920\text{ cm}^{-1}$ . It was not possible



**Figure 3** The  $2800\text{--}3000\text{ cm}^{-1}$  absorbance range of polyethylene. The  $2960$  and  $2870\text{ cm}^{-1}$  absorbance bands are attributed to C—H stretching in methyl groups, whereas the  $2920$  and  $2840\text{ cm}^{-1}$  absorbance bands are from C—H stretching in methylene groups.



**Figure 4** Raw data for LLDPE 1. The upper trace (+) is polymer concentration and the lower trace (X) is branching.

to measure the symmetrical deformation vibration  $\delta_s(\text{CH}_3)$  of the methyl groups at  $1378\text{ cm}^{-1}$  since 1,2,4-trichlorobenzene, which is the carrier solvent for the polymer, is opaque at this wavelength. There exist several stretching modes for both types of C—H groups (methyl and methylene) in the  $2800\text{--}3000\text{ cm}^{-1}$  wavelength range (Fig. 3). Both the  $2960$  and  $2870\text{ cm}^{-1}$  bands are attributed to C—H stretching frequencies of methyl groups ( $\text{CH}_3$ ), whereas the  $2920$  and  $2840\text{ cm}^{-1}$  bands are attributed to C—H stretching frequencies of methylene groups ( $\text{CH}_2$ ). The absorbance band at  $2960\text{ cm}^{-1}$  was used to measure the amount of branching in the column eluent, whereas the absorbance band at  $2920\text{ cm}^{-1}$  was used to measure the concentration of polymer.

### DATA ANALYSIS

The goal here is to convert the raw data (Fig. 4) to an accurate branching distribution. To do this, the lower trace,<sup>†</sup> which contains the branching information, must be manipulated to yield a calibration of branching frequency as a function of elution temperature that is unique to the polymer being analyzed. Once this calibration is found, it can be used to convert the upper trace<sup>†</sup> (polymer concentration) to a branching distribution.

On first inspection of the raw data (Fig. 4) obtained from the detector tuned to the absorbance

<sup>†</sup> Both sets of raw data must be corrected for the temperature/time lag of the columns using a method described elsewhere.<sup>19</sup> This correction is necessary since polymer that goes into solution at a specific temperature elutes over a temperature range.

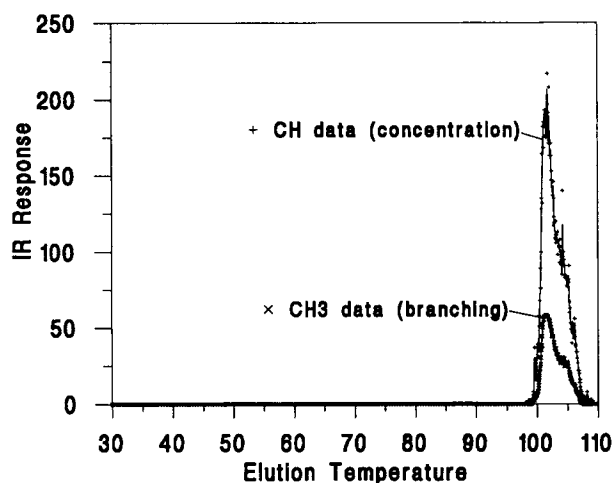
band at  $2960\text{ cm}^{-1}$  (C—H stretching in methyl groups—lower trace), several problems become immediately apparent. The first is that the absorbance band at  $2960\text{ cm}^{-1}$  resides on the shoulder of the absorbance band at  $2920\text{ cm}^{-1}$  (C—H stretching in methylene groups). This is caused by the large amount of methylene groups present in the structure of polyethylene in comparison to methyl groups. The contribution to the absorbance band at  $2960\text{ cm}^{-1}$  from the one at  $2920\text{ cm}^{-1}$  must be eliminated before the data can be converted to a calibration curve.

Two other points that must be addressed are the effects of polymer concentration on the data and the conversion of the resulting signal axis to one in terms of average branching frequency. Concentration effects in the branching data must be negated to obtain an IR signal representative of the average amount of branching independent of the amount of polymer. The three points mentioned will be considered in the next sections.

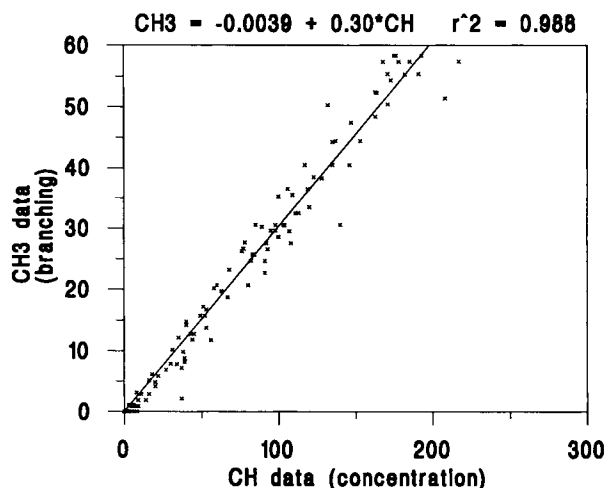
### Isolation of Branching Data

The obvious way of isolating the branching data is to discover how the absorbance band at  $2920\text{ cm}^{-1}$  (concentration) affects the absorbance band at  $2960\text{ cm}^{-1}$  (branching) when there are no effects of branching present. This relationship can then be used to isolate the branching information. This was done by analyzing a high molecular weight linear polyethylene (Appendix 1).

The information obtained by the two detectors (Fig. 5) can then be used to obtain a plot of the  $2960\text{ cm}^{-1}$  data as a function of the  $2920\text{ cm}^{-1}$  data (Fig.



**Figure 5** Raw data from an analytical TREF analysis of a high molecular weight, linear polyethylene (HDPE 1).



**Figure 6** The  $2960\text{ cm}^{-1}$  absorbance band ( $\text{CH}_3$  data) as a function of the  $2920\text{ cm}^{-1}$  absorbance band (CH data) for a high molecular weight, linear polyethylene.

6). This function is used to eliminate the concentration effects of the  $2920\text{ cm}^{-1}$  absorbance band on the  $2960\text{ cm}^{-1}$  absorbance band using eq. (1).

$$A_{\text{CH}_3} = A_{2960} - (-0.0039 + 0.3A_{2920}) \quad (1)$$

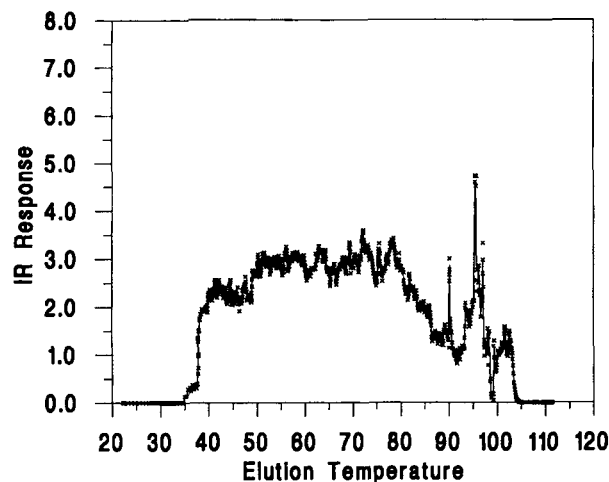
In eq. (1),  $A_{\text{CH}_3}$  is the absorbance signal at  $2960\text{ cm}^{-1}$  without the effects of the  $2920\text{ cm}^{-1}$  absorbance band,  $AB_{2960}$  is the raw data from the branching detector, and  $AB_{2920}$  is the raw data from the concentration detector. When this equation was applied to a polymer that had branching (LLDPE 1), a plot (Fig. 7) was found that was not linear as expected. This was because the signal is dependent on the amount of polymer and not only on the average amount of branching.

### Concentration Effects

The data in Figure 7 can be converted to be representative of the average amount of branching by dividing by the concentration of polymer ( $2920\text{ cm}^{-1}$  absorbance band data). This conversion was done for LLDPE 1 (Fig. 8). A linear plot was obtained over most of the elution temperature range. This is expected since the plot of branching with respect to elution temperature is linear for LLDPE 1 (Fig. 1). The one step remaining to generate a calibration curve for the polymer is to convert the signal data to real branching information.

### Conversion of Branching Signal to Branching Frequency

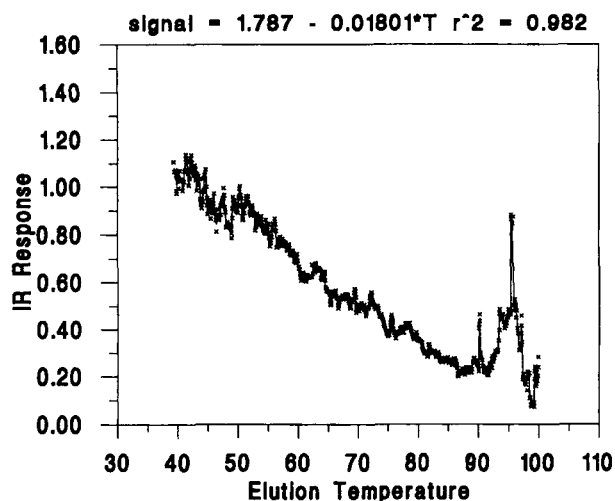
The method for this conversion requires knowledge of the branching frequency of a polymer as a function



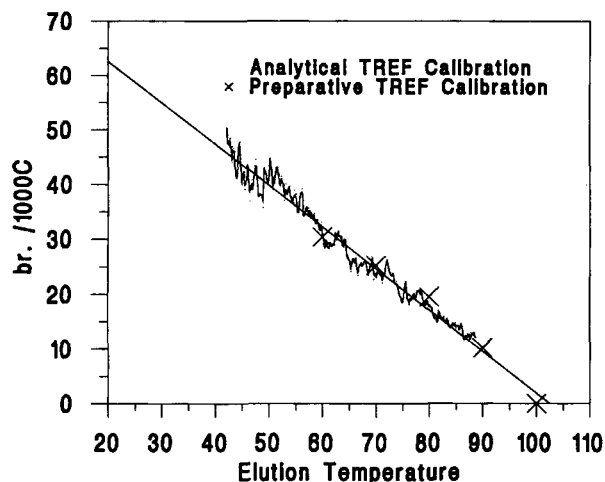
**Figure 7** Branching data for LLDPE 1 from the 2960  $\text{cm}^{-1}$  detector (branching) deconvoluted from the 2920  $\text{cm}^{-1}$  data (concentration) using eq. (1).

of elution temperature. This involves fractionating a polymer by preparative TREF for branching analysis by  $^{13}\text{C}$ -NMR to obtain a true calibration of branching frequency and elution temperature. The polymer is then analyzed by the technique outlined in the previous sections to generate a calibration of signal ( $S$ ) and elution temperature (Fig. 8). The two functions are then used to convert the signal data ( $S$ ) generated from other polymers to average branching data ( $br_{1000\text{C}}$ ).

$$br_{1000\text{C}} = S \frac{(74.5 - 0.75T)}{(1.787 - 0.0180T)} \quad (2)$$



**Figure 8** Branching data for LLDPE 1 from Figure 7 divided by the concentration data (2920  $\text{cm}^{-1}$  detector).



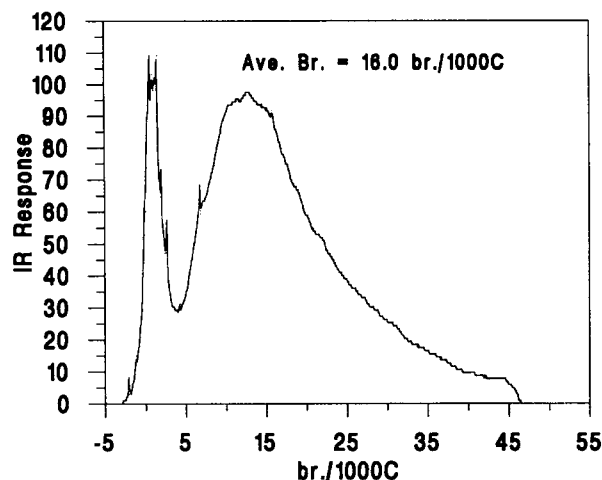
**Figure 9** Calibration curves for LLDPE 1 generated by analytical TREF and preparative TREF techniques.

The numerator in eq. (2) is the relationship between branching frequency and elution temperature ( $T$ ) for LLDPE 1 generated from preparative TREF data fractionation, while the denominator is the relationship between signal ( $S$ ) and elution temperature ( $T$ ) for LLDPE 1 generated from the analytical TREF analysis.

When the signal data for LLDPE 1 are analyzed using the above technique, the data are converted to average branching frequency (Fig. 9). The linear portion of this plot yields a calibration curve of branching frequency and elution temperature that is unique to the polymer being analyzed. The function of the plot can then be used to convert the data obtained from the detector tuned to the absorbance band at 2920  $\text{cm}^{-1}$  (concentration detector) to a branching distribution (Fig. 10). Average branching can also be calculated from this branching distribution using eq. (3):

$$Br_{\text{ave}} = \frac{\sum_{T=25}^{110} [B(T)IR(T)]}{\sum_{T=25}^{110} IR(T)} \quad (3)$$

In the above equation,  $Br_{\text{ave}}$  is the average amount of branching per 1000 carbons;  $B(T)$ , the calibration of branching and elution temperature for the polymer; and  $IR(T)$ , the IR response at each temperature from the detector tuned to the 2920  $\text{cm}^{-1}$  absorbance band (concentration detector).



**Figure 10** Branching distribution and average branching frequency for LLDPE 1 using the calibration in Figure 9.

### BRANCHING METHOD EFFICIENCY

LLDPE 1 was analyzed in triplicate to determine the reproducibility. Three calibration curves of branching and elution temperature were generated from the analysis:

$$\text{Analysis 1} \quad br_{1000C} = 74.90 - 0.75T \quad (4)$$

$$\text{Analysis 2} \quad br_{1000C} = 75.91 - 0.77T \quad (5)$$

$$\text{Analysis 3} \quad br_{1000C} = 74.16 - 0.75T \quad (6)$$

$$\text{Calibration from preparation data (Fig. 1)} \quad br_{1000C} = 74.50 - 0.75T \quad (7)$$

All three calibrations were essentially the same as the true calibration generated from the prepar-

ative TREF fractionation. Branching distributions were generated using the above calibrations and average branching frequencies were calculated to be 16.0, 16.8, and 16.6 branches per 1000C. The true average branching frequency determined by  $^{13}\text{C}$ -NMR was 16.3. The average branching frequency determined by analytical TREF (16.5 *br*/1000C) was in good agreement with  $^{13}\text{C}$ -NMR analysis. The reproducibility of the technique is good and the average branching can be determined within  $\pm 0.4$  branches per 1000 carbons.

A number of other octene/ethylene copolymers (LLDPE 3 and 4) were analyzed by analytical TREF and the average branching frequencies (Table II) were in good agreement with  $^{13}\text{C}$ -NMR analysis of the whole polymers.

The technique for generating calibration curves from analytical TREF data works well for ethylene/octene copolymers (LLDPE 1, 3, and 4). This is because the IR signal-to-branching calibration was determined using an ethylene/octene copolymer. This IR signal-to-branching frequency calibration could be affected by the differences in extinction coefficients of C—H stretching on methyl groups of different branch lengths. The extinction coefficients represent how strongly molecular groups absorb with respect to their structural environment in the macromolecule. It is well documented that, in the case of polyethylene, methyl groups on short branches absorb more strongly than do methyl groups on longer branches.<sup>17,18,26-29</sup> This is evidenced by extinction coefficients derived for ethyl (0.59), butyl (0.70), and hexyl (0.76)<sup>26</sup> branches from the absorbance band at  $1378 \text{ cm}^{-1}$  in the infrared spectrum of polyethylene.

To check the extent of this effect, calibration curves were generated from analytical TREF data for LLDPE 2 and LDPE 1 and compared with the true calibration curves (Figs. 11 and 12). It would

**Table II** Average Branching Frequencies for Various Polymers Determined by  $^{13}\text{C}$ -NMR and Analytical TREF Analysis

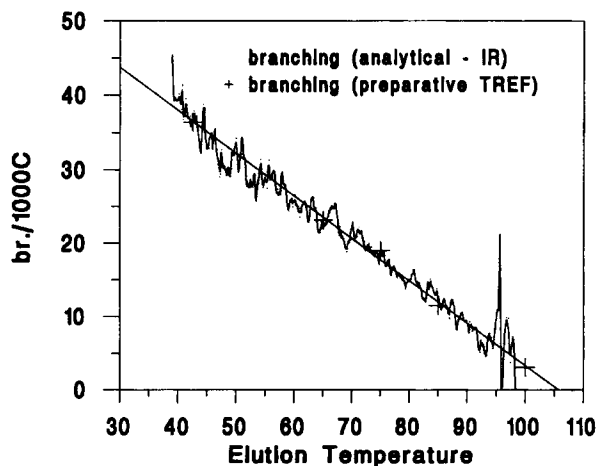
Polymer	Av Branching Frequency (TREF)	Av Branching Frequency ( $^{13}\text{C}$ NMR)
LLDPE 1	16.0, 16.8, 16.6-16.5	16.3
LLDPE 2	14.8	15.2
LLDPE 3	16.4	16.8
LLDPE 4	11.0	11.4
LDPE 1	13.6	13.8
LDPE 2	14.0	14.3
LDPE 3	17.3	17.3
LDPE 4	17.9	17.6

appear that the difference in extinction coefficients for the C—H stretching ( $2960\text{ cm}^{-1}$  absorbance band) is not as great when compared to the C—CH<sub>3</sub> stretching ( $1378\text{ cm}^{-1}$  absorbance band) extinction coefficients. The average branching frequencies determined by analytical TREF analysis of LLDPE 2 and several LDPE polymers (Table II) would indicate that the signal to branching calibration generated from LLDPE 1 is accurate for all branch lengths.

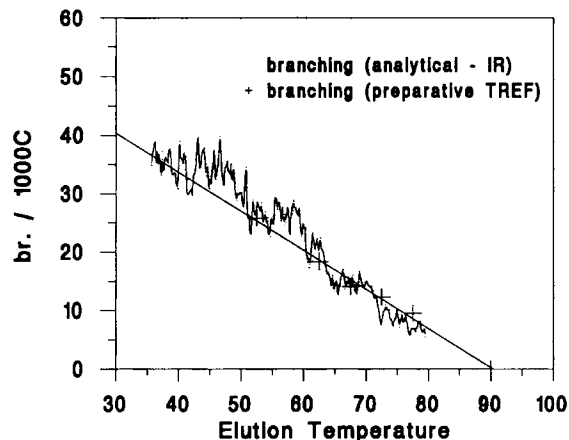
## CONCLUSION

Branching frequency as a function of elution temperature varies for every polyethylene. This relation can be generated from analytical TREF data by use of a second detector tuned to the C—H stretching absorbance ( $2960\text{ cm}^{-1}$ ) in methyl groups. This absorbance band can be isolated from the  $2920\text{ cm}^{-1}$  absorbance band (concentration data) using a correction generated from a high molecular weight, linear polyethylene. A signal related to the average branching frequency as a function of elution temperature is obtained by dividing the data by the concentration data. The signal data are converted to average branching frequency data using information generated from preparative TREF fractionation and  $^{13}\text{C}$ -NMR analysis of a polymer with a broad branching distribution. The same signal-to-branching conversion was found to be valid for all branch lengths.

The technique for generating calibration curves from analytical TREF data is valid for all types of polyethylenes and branching distributions generated



**Figure 11** Calibration curves for LLDPE 2 generated by analytical TREF and preparative TREF techniques.



**Figure 12** Calibration curves for LDPE 1 generated by analytical TREF and preparative TREF techniques.

from these calibrations yield average branching frequencies comparable with  $^{13}\text{C}$ -NMR analyses of the corresponding whole polymers. This technique eliminates the need for preparative TREF fractionation and IR/ $^{13}\text{C}$ -NMR analysis of fractions.

The technique outlined could be improved and simplified by replacing the present solvent (1,2,4-trichlorobenzene) by one that is more transparent to infrared absorption in the regions where polyethylene has useful characteristic infrared bands. Research is underway in our laboratory toward this objective.

This research was supported by the National Sciences and Engineering Research Council of Canada. Some of the equipment used was funded by a grant from the Ontario Centre for Materials Research.

## APPENDIX 1: POLYMER DESCRIPTIONS

1. LLDPE 1 ethylene–octene copolymer produced by a slurry process
2. LLDPE 2 ethylene–butene copolymer produced by a gas-phase process
3. LLDPE 3 ethylene–octene copolymer produced by a slurry process
4. LLDPE 4 ethylene–octene copolymer produced by a slurry process
5. HDPE 1 linear, high molecular weight polymer  $M_n = 188,000$ ,  $M_w/M_n = 2.4$ . The absence of branching was confirmed by  $^{13}\text{C}$ -NMR
6. LDPE 1 a linear low-density polyethylene produced by a high-pressure autoclave process
7. LDPE 2 a linear low-density polyethylene produced by a high-pressure autoclave process



8. LDPE 3 a linear low-density polyethylene produced by a tubular reactor process
9. LDPE 4 a linear low-density polyethylene produced by a tubular reactor process

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Received February 5, 1993

Accepted June 22, 1993