

Comparison of Analytical and Preparative TREF Analysis: A Mathematical Approach to Correcting Analytical TREF Data

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SYNOPSIS

Analysis of analytical temperature rising elution fractionation (TREF) data involves conversion of elution temperature information to branching information via a calibration curve relating the two. The curve is generated by analysis of polymer fractions recovered using preparative TREF techniques. In preparative TREF a stepwise temperature ramp is used to recover these fractions so that samples with sharp branching distributions are obtained. A continuous temperature ramp, as in analytical TREF, produces samples that differ in branching properties from the stepwise ramp at the same temperatures. The analytical TREF data can be corrected for these differences by an iterative computer program so that a calibration curve generated by preparative techniques can be used to convert the analytical TREF data to branching distributions. Analytical TREF results should be corrected for fraction overlap before relating these data to polymer properties. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Temperature rising elution fractionation (TREF), is an analytical technique that is used to measure branching distributions of semicrystalline macromolecules such as polyethylene and ethylene vinyl acetate copolymers.^{1,2} The method involves dissolving the polymer in a suitable solvent at high temperature and loading the resulting solution onto a column containing an inert support. The column is slowly cooled, allowing the polymer molecules to crystallize out of solution onto the inert support in layers according to their crystalline melting points. The process is then reversed with solvent flow going through the column. This causes the polymer molecules to elute from the column in the reverse order of the sequence in which they crystallized onto the support. The most branched or least crystalline molecules are removed first, followed by successively less branched species as the elution temperature is slowly increased.

Elution of the TREF columns can be done in either of two possible ways. The most common and fastest way is to raise the temperature continuously with solvent flow going through the column to remove the polymer from the support as it goes into solution.³⁻⁵ This is the analytical TREF mode. In this technique the effluent is monitored by an infrared (IR) detector tuned to the carbon-hydrogen stretching frequency at 3.41 microns. The raw data are obtained as a plot relating IR response to elution temperature which can be reduced to a plot relating IR response to the number of branches in the sample. This is achieved by using a calibration curve of number of branches versus elution temperature to convert the elution temperature axis of the raw data plot to one in terms of number of branches.^{2,3,6} This calibration curve is obtained from information about polymer fractions collected by operating the system in a preparative mode.

In preparative TREF, a stepwise temperature ramp is used rather than a continuous one to prevent mixing of fractions.⁷⁻⁹ These fractions are then analyzed by carbon-13 nuclear magnetic resonance (NMR) or IR to determine the amount of branching present.^{2,10,11} This information is then used to gen-

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erate the calibration curve of branching versus elution temperature. The fractions may optionally also be characterized by size exclusion chromatography.

If a calibration curve generated in this manner is to produce accurate branching distributions, fractions recovered by operating the system in either a continuous mode or a stepwise mode should necessarily have the same compositions over similar temperature ranges. We have found that this is not generally the case. Polymer samples recovered by these two methods over the same temperature ranges differ from each other in a number of ways. Properties include molecular weight distributions, the amount of polymer recovered and more importantly, the amount of branching present. It is believed that these differences reflect mixing in the large interstitial volume characteristic of TREF columns. Polymer that goes into solution at one particular temperature elutes over a large volume and exits the column over a temperature range rather than at the single temperature at which it went into solution. Because of this overlap of dissolved fractions, conventional analytical TREF curves may be in error.

It is possible to correct the analytical TREF raw data mathematically for the error caused by this effect by using an iterative computer program. Several items of information are required to do this. These include the delay time between the column outlet and the IR detector. A mathematical function that accurately describes the shape of the elution profile of polymer as it exits the column is also needed. This function must account for the fact that polymer that goes into solution across the length of the column at one temperature will elute from the column with a distinctive shape caused by increasing band broadening effects as the eluent travels inside the column.

The elution profile shape will be the same for polymer that goes into solution at different temperatures but will differ in height because of differences in concentration. One other piece of information that is required is the change in density of the solvent as the temperature is raised from ambient to the highest elution temperature. The effects of this change on the mathematical function described above must also be accounted for. This information is required since the solvent is pumped at ambient temperature but the temperature in the column and the detector is continuously increasing, thus causing an increase in flow rate inside the column.

Correction of the data obtained by analytical TREF is essential if a calibration curve relating elution temperature to number of branches is to be used, since the information required to generate this cal-

ibration curve is obtained from polymer fractions recovered by preparative TREF. The computer program reported here has been applied to linear low-density polyethylenes (lldpe) made with different types of comonomers as well as low density polyethylenes (ldpe).

EXPERIMENTAL

All polymer samples used in the TREF analysis were injected into stainless steel columns (25 × 250 mm packed with silanized silica gel) as 0.5% by weight solutions in 1,2,4-trichlorobenzene (TCB) at 150°C. These columns were cooled at a rate of 1.5°C per hour from 110°C to ambient. This rate of cooling has been shown to give the maximum resolution when separating polymers on the basis of differences in crystalline melting point.^{1,3,12} Due to the extreme length of time required to deposit the polymer out of solution onto the packing, a separate oven that can accommodate four columns was used for this purpose.

The apparatus used to elute the columns, depicted in Figure 1, consists of a solvent reservoir, an SEC solvent pump, a small oven to encase the column and an infrared detector for measuring the concentration of polymer in the eluent. Commercial infrared detectors may leak when used with TCB at high temperatures. The detector cell may require rebuilding. Data acquisition and temperature control are achieved with an IBM PC. The analytical TREF data and fractions were collected by continuously heating the columns from ambient to 110°C at a rate of 10°C an hour with a solvent flow rate of 1.0 mL/min. The preparative TREF data and fractions were collected using a stepwise temperature ramping program where the temperature was held constant until all the dissolved polymer eluted from the column before proceeding to a higher temperature.

The weight fractions of polymer recovered for each temperature range were determined for both the analytical and the preparative TREF analyses. In the case of the analytical TREF data, shown in Figure 2(a), the weight fractions were determined by dropping perpendicular lines to the baseline at the appropriate temperatures and comparing the areas under the IR response curve for each temperature range. In the case of the preparative data, the amount of polymer recovered in different temperature ranges was determined by comparing the areas under the IR response curves over the appropriate temperature ranges shown in Figure 2(b).

The molecular weight distributions were mea-

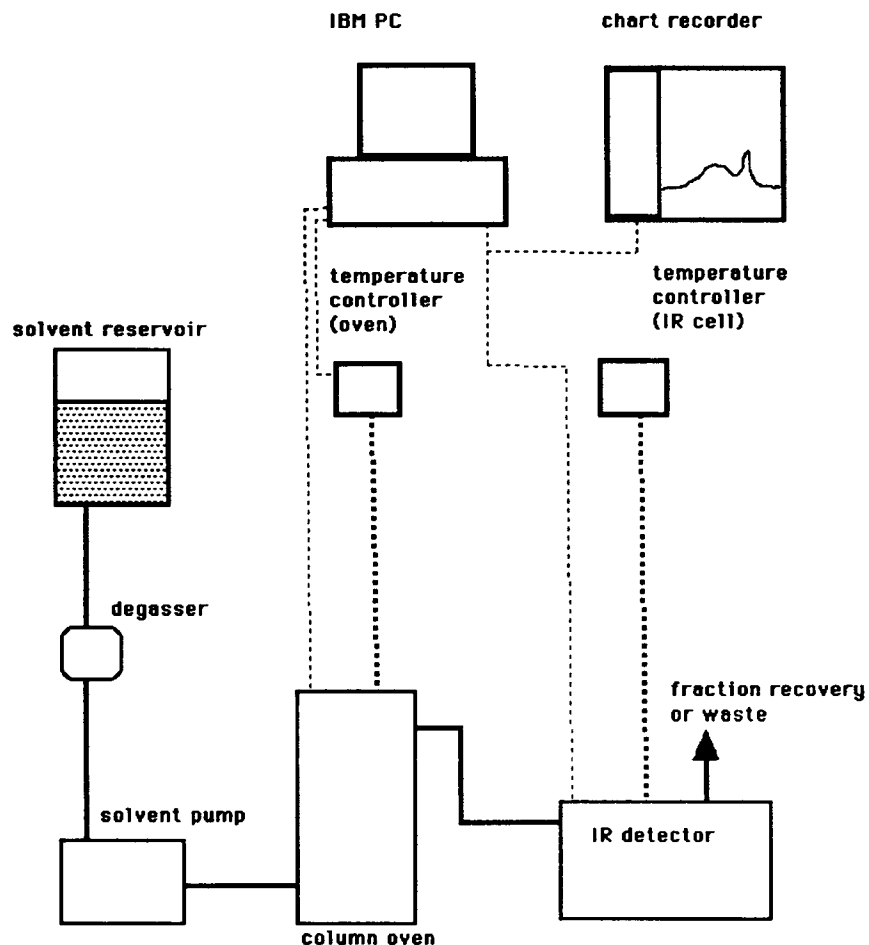


Figure 1 TREF elution apparatus.

sured with a high temperature GPC operating at 145°C using TCB as the mobile phase. A Jordi styrene-divinylbenzene linear mixed-bed column was used with a reported molecular weight range of 100–20,000,000.¹³ The concentration of polymer in the SEC eluent was determined with a differential refractive index detector. Number average molecular weights were determined using an on-line viscosity detector (Viscotek). Weight-average molecular weights were determined with an on-line low-angle laser light scattering detector (LDC Milton Roy). The amount of branching in the fractions and the whole polymer was determined with a 300 MHz nuclear magnetic resonance spectrometer. The ¹³C spectra were obtained at 130°C using a 90° pulse angle and a 12.5-s relaxation delay time from 60% by weight polymer in TCB solutions in 5 mm o.d. NMR tubes.

The elution profiles of the TREF columns were determined by loading the columns with 0.1% by weight solutions of heptane in TCB and then eluting

at 25°C with a flow rate of 1 mL/min of TCB. Shown in Figure 3 are the overlaid normalized elution profiles for five different TREF columns. Due to the similarity in shape of the profiles it was considered valid to use one average profile to describe the elution profiles of all the columns. The shape of this average profile was described mathematically by fitting two polynomials as shown in Figure 4. The delay time between the column and the detector was assumed to be the time elapsed from the beginning of the data collection to the first steep rise in IR response, labelled T1. The first polynomial was fitted to the curve stretching from the end of the delay time to the highest point of the profile, labelled T2 (Fig. 4). The second polynomial was fitted to the remaining part of the profile stretching from T2 to T3. The correlations of fit for the two polynomials were 0.998 and 0.995, respectively.

Alternatively, it was possible to model the flow in the columns by considering the band broadening effects across the length of the column. The maxi-

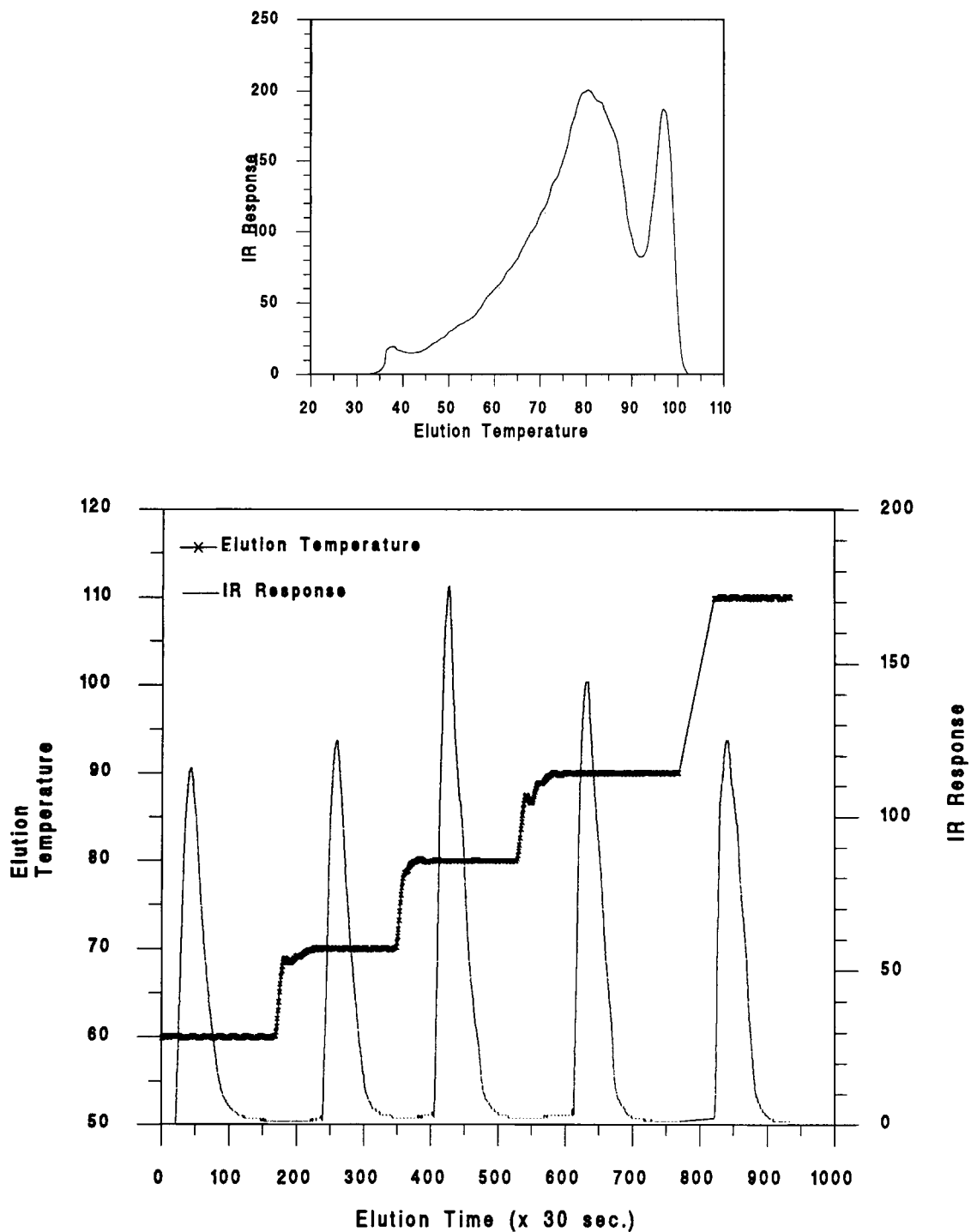


Figure 2 (a) Analytical TREF analysis of lldpe 2 (continuous temperature ramp). (b) Preparative TREF analysis of lldpe 2 (stepwise temperature ramp).

mum band broadening effects were measured by injecting a slug of heptane in the inlet to the column to measure the spreading of the material. It was assumed that the spreading effects were linear across

the length of the column, ranging from zero at the outlet of the column where plug flow behavior is exhibited to a maximum amount at the inlet. When all the spreading effects were calculated and added

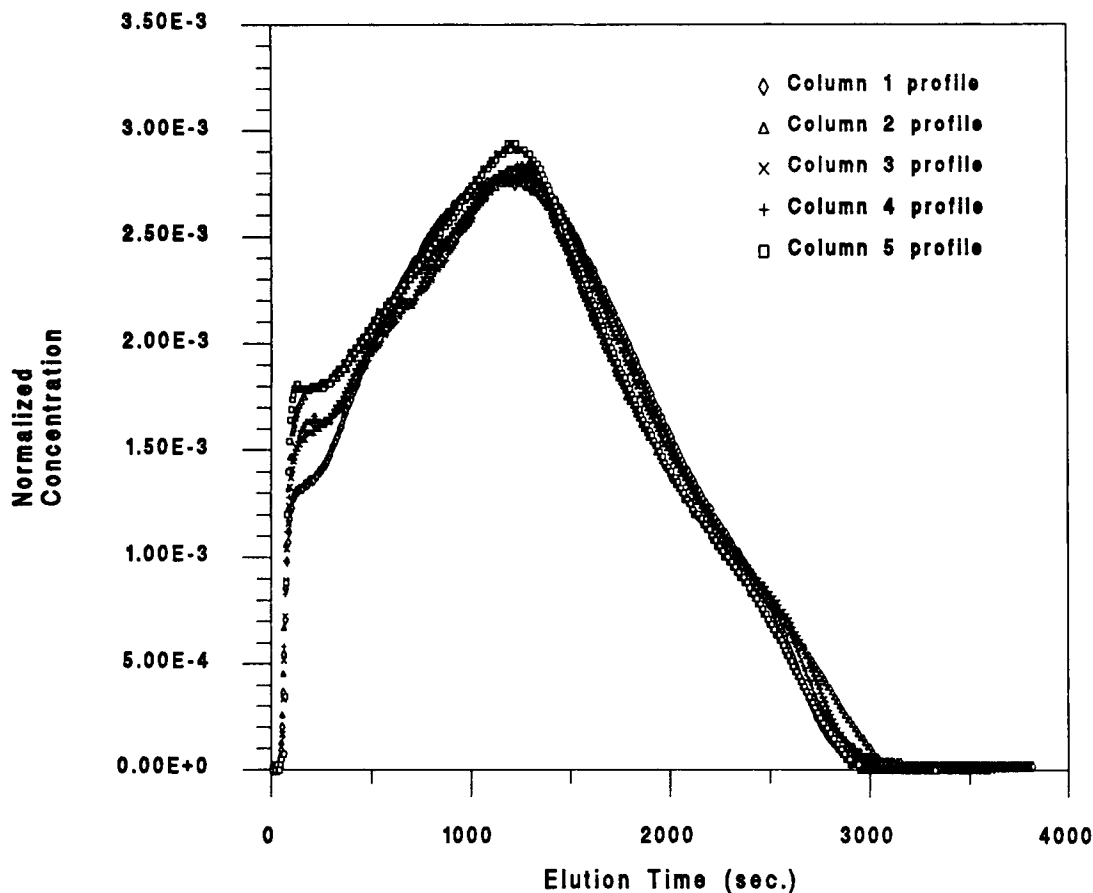


Figure 3 Heptane in TCB elution profiles for five TREF columns.

together using a gaussian function to describe the band broadening, a profile of the same shape as that in Figure 4 was the result. It was decided to use the two polynomials in the computer program in place of the band broadening model because the latter model required a large amount of computing each time it was applied.

The polymers used in this research were:

1. lldpe 1, an ethylene-butene copolymer produced by a gas phase process
2. lldpe 2, an ethylene-octene copolymer produced by a slurry process
3. ldpe 1, an ethylene homopolymer produced by an autoclave process

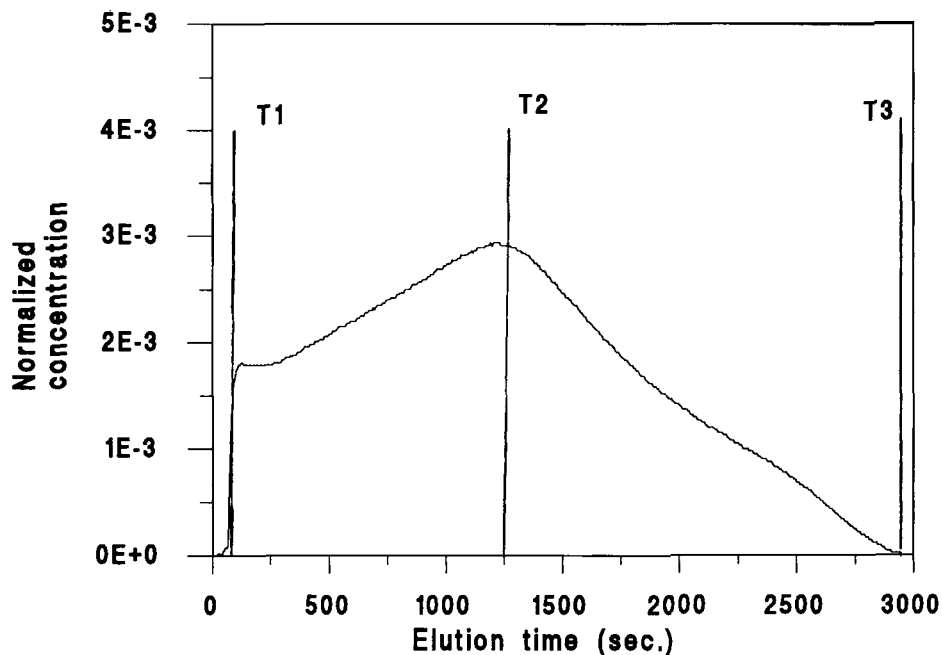
RESULTS

Comparison of Analytical and Preparative TREF

The Introduction section stressed the importance that the polymer fractions collected over the same

temperature ranges by the two techniques have identical compositions. Shown in Table I are the amounts of polymer recovered over various temperature ranges for lldpe 1 and ldpe 1. Both comparisons indicate the same trends. The preparative technique which is correct by virtue of its mode of operation, indicates that the analytical data show too little polymer eluted at low temperatures and too much at higher solvent temperatures.

The molecular weight distributions for the fractions from lldpe 1 in Table II show higher molecular weights at the low-temperature end and lower molecular weights at the high-temperature end for the preparative technique as compared with the analytical technique. Both trends that are observed are in keeping with the model proposed in the Introduction that polymer elutes over a temperature range in analytical TREF, rather than at the temperature at which it went into solution. The effect is even more pronounced when comparing the branching in the fractions collected by both analytical and preparative TREF techniques. The branching results for



Polynomials:

#1 T1 - T2

$$y = 1.544E-3 + 2.124E-6 \cdot T + 8.384E-8 \cdot T^2 - 6.857E-10 \cdot T^3 + 2.731E-12 \cdot T^4 - 4.543E-15 \cdot T^5 \quad r^2 = 0.995$$

#2 T2 - T3

$$y = -4.028E-2 + 5.884E-4 \cdot T - 3.060E-6 \cdot T^2 + 7.616E-9 \cdot T^3 - 9.234E-12 \cdot T^4 + 4.379E-15 \cdot T^5 \quad r^2 = 0.998$$

Figure 4 Average elution profile for the five TREF columns and the mathematical description of the shape of the profiles (two 5th degree polynomials).

lldpe 1 in Table III show a large difference in branching between the fractions collected by both methods.

To check the validity of the branching results, the branching frequencies were normalized using the amounts of polymer recovered, and then summed together. The sum for both the analytical and the preparative techniques should be equal to the amount of branching measured by ^{13}C analyses of the whole polymer. The whole polymer contained 18.6 branches per 1,000 carbons while the preparative and analytical techniques indicated 18.8 and 19.2 branches per 1,000 carbons, respectively.

This difference in branching illustrates the need to correct the analytical data before using these results to relate elution temperature to branching. If the effects noted are not corrected, branching distributions generated from a calibration curve will be inaccurate, since the polymer fractions used to

generate the calibration are recovered using preparative techniques in which the elution temperature intervals do not correspond to those in the analytical TREF method.

Theory for Data Correction

As mentioned, it was found that when solute is evenly distributed in solution in the column and then eluted off, the shape of the elution profile is the same for different columns (Fig. 3) with the same dimensions and packing. This profile can be described mathematically by two polynomials. The area underneath the profile will be equal to the amount of polymer that went into solution at a given temperature. This area, (A_T) can be found by integrating the polynomial, (F) over the temperature range that the polymer elutes over ($T_i - T_f$), and multiplying this by a constant (C_T) proportional to the concen-

Table I Comparison of Weight Fractions of lldpe 1 and ldpe 1 Obtained by Preparative TREF and Analytical TREF

Fraction No.	Temperature Range (°C)	Preparative Data (wt %)	Analytical Data (wt %)
lldpe			
1	25-60	23.5	15.6
2	60-70	15.9	13.0
3	70-80	18.2	18.1
4	80-90	20.8	25.2
5	90-110	21.6	28.1
ldpe			
1	25-60	16.5	12.2
2	60-70	13.3	9.2
3	70-75	15.2	8.5
4	75-80	26.8	18.5
5	80-85	24.3	35.0
6	85-110	4.8	15.9

tration of the polymer that went into solution at the temperature of interest. The temperature range that the polymer elutes over is determined by the time required for the polymer to exit the column which is labelled T1 - T3 in Figure 4.

$$A_T = C_T \int_{T_i}^{T_f} F$$

This area, A_T can be calculated for each elution temperature. The sum of these areas is equal to the area underneath the entire IR response curve (A_{IR}) for the polymer when it is eluted from 25 to 110°C.

$$A_{IR} = \sum_{T=25}^{110} C_T \int_{T_i}^{T_f} F$$

To correct the analytical TREF data for time lag the concentration constants, C_T are required to calculate the amount of polymer that goes into solution at each temperature which is equal to A_T . This constant can be calculated for each temperature from the analytical TREF data. It is possible by using the polynomials to estimate how much polymer went into solution at each temperature in the analytical TREF profile. The value of the concentration constant at any temperature can be calculated by summing the contribution to IR response at the temperature of interest from all polymer that went into solution at lower temperatures. This sum is then subtracted from the IR response and the difference is used to calculate the concentration constant at that temperature. The IR response curve can then be reconstructed by calculating A_T at each temper-

Table II Comparison of Molecular Weight Distributions of Polymer Fractions of lldpe 1 Recovered by Both Preparative and Analytical TREF Analysis

Fraction No.	Temperature Range (°C)	Preparative Data M_n, M_w	Analytical Data M_n, M_w
1	25-60	17,260	14,050
		69,760	62,300
2	60-70	20,210	18,150
		79,570	73,130
3	70-80	22,090	22,170
		99,070	85,950
4	80-90	24,410	25,560
		97,780	112,560
5	90-110	34,430	36,230
		124,710	148,350

Table III Comparison of Branching in Polymer Fractions of lldpe 1 Recovered by Both Preparative and Analytical TREF Analysis

Fraction No.	Temperature Range (°C)	Preparative Data (No. Branch/1,000 C)	Analytical Data (No. Branch/1,000 C)
1	25-60	36.4	53.4
2	60-70	23.1	30.6
3	70-80	22.3	17.4
4	80-90	9.0	11.8
5	90-110	3.1	5.3

ature using the polynomials and the concentration constants.

The program requires a normalized analytical TREF data file as shown in Figure 2 (a). At the first data point where there is an IR response greater than zero the program calculates the concentration constant for that temperature by dividing the IR

response (IR_T) by the mathematical function that describes the elution profile.

$$C_T = \frac{IR_T}{F(T)}$$

At each successive data point (T_P), the program

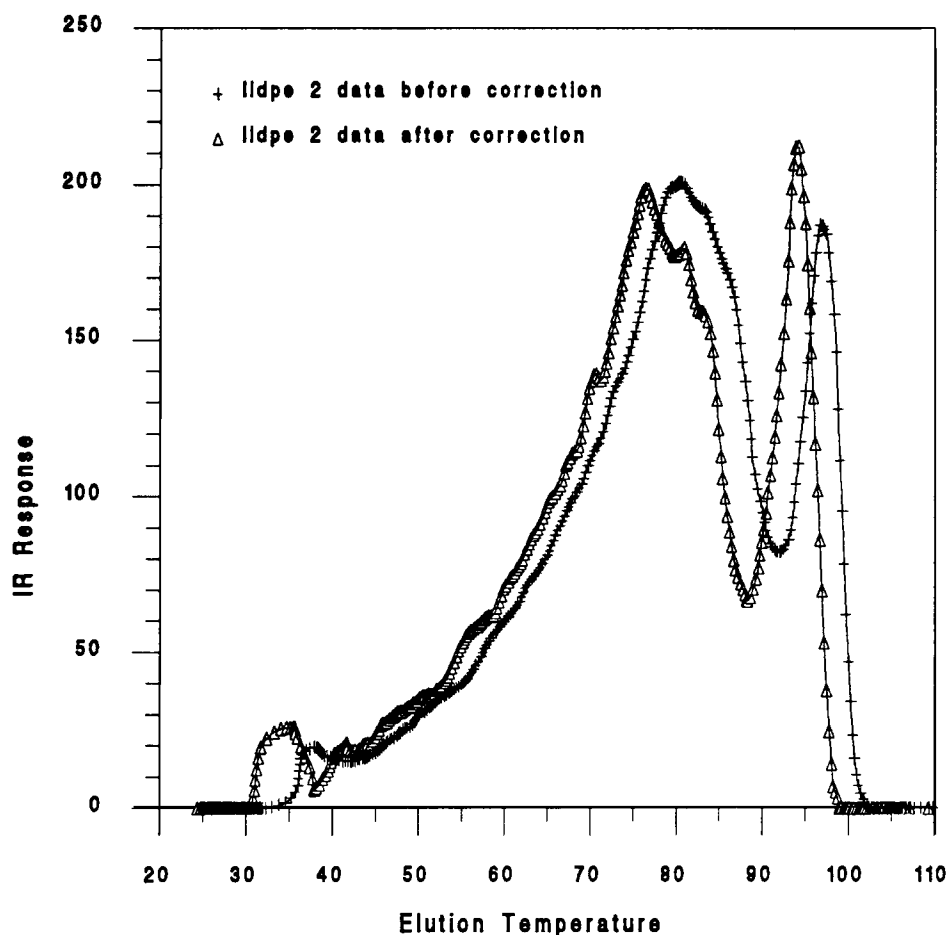


Figure 5 Analytical TREF analysis of lldpe 2 before and after fraction overlap correction.

calculates the contribution to IR response from each data point before the one of interest (IR_{sum}), using the concentration constants calculated earlier and the mathematical function.

$$A_{IR} = \sum_{T=25}^{T_p} C_T F(T)$$

After subtracting the contribution to IR response from previous data points, the program calculates a new concentration constant by dividing this difference by the mathematical function.

$$C_T = \frac{IR_T - IR_{sum}}{F(T)}$$

After calculating all the concentration constants, the program uses these and the polynomials to calculate how much polymer went into solution at each temperature.

Other considerations that are taken into account are the time delay between the column and the detector and the change in density of TCB between ambient and 110°C (an 8.05% change). This change in density is accounted for in the time delay and the width as well as the height of the mathematical function of the elution profile. The change in all three is proportional to the change in density of the solvent since all three were measured at ambient conditions. This density change must be accounted

for because throughout the analysis the solvent is being pumped at 25°C, resulting in a constant mass flow rate but the flow in the column and the detector is steadily increasing because the solvent density is decreasing with increasing temperatures.

Program Results

The program was used to correct analytical TREF data for an ethylene octene copolymer labelled lldpe 2. The polymer was also fractionated by preparative TREF over a wide number of temperature ranges and the amount of polymer recovered in each range was measured. If the computer program works properly to correct the analytical data, the amount of polymer recovered over the various temperature ranges should be the same for both the preparative analysis and the corrected analytical analysis. Shown in Figure 5 are the original and corrected analytical TREF traces for lldpe 2. Shown in Table IV are the weight fractions for the preparative, analytical and corrected analytical analyses. The third column in the table is the amount of polymer obtained from the preparative TREF analysis and the fourth column represents the amount of polymer recovered from the corrected analytical TREF analysis. There appears to be good agreement between the corrected analytical and the preparative analysis with respect to the amount of polymer recovered by the two techniques.

Table IV Comparison of Analytical and Corrected Analytical Weight Fractions to Preparative Data of lldpe 2

Fraction No.	Temperature Range (°C)	Preparative Data (wt %)	Corrected Analytical Data (wt %)	Analytical Data (wt %)
1	20-30	0.0	0.0	0.0
2	30-40	3.5	3.1	1.6
3	40-50	5.2	4.4	3.5
4	50-60	9.2	8.8	7.2
5	60-65	6.7	7.1	6.0
6	65-70	8.8	9.4	8.0
7	70-74	9.1	9.9	8.6
8	74-78	11.5	12.9	10.7
9	78-82	13.3	12.4	13.2
10	82-88.5	14.3	13.0	18.6
11	88.5-92	5.1	5.6	5.3
12	92-94.5	6.5	6.4	3.7
13	94.5-98.5	6.9	6.9	10.8
14	98.5-110	0.0	0.0	2.8

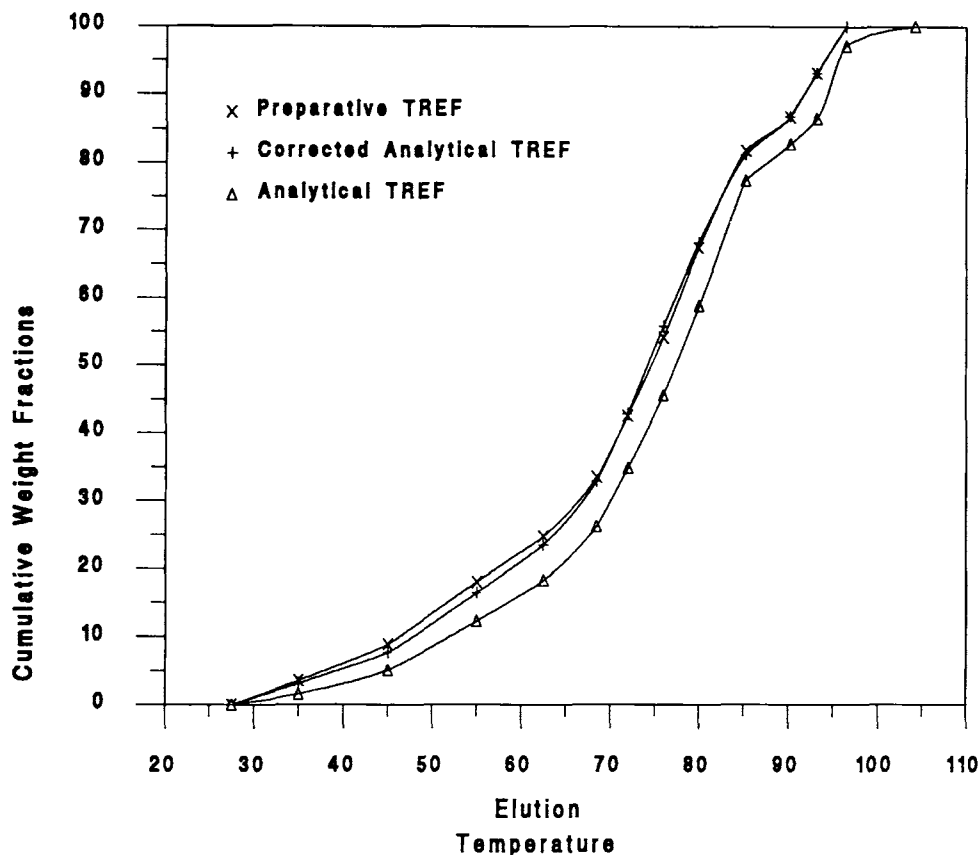


Figure 6 Cumulative weight distribution plots for lldpe 2 using preparative TREF data, corrected analytical TREF data and analytical TREF data before correction.

Shown in Figure 6 is a cumulative plot of the weight fractions of polymer recovered from the preparative TREF and both the analytical and the corrected analytical TREF. Both the preparative and the corrected analytical plots overlap well while the uncorrected analytical plot deviates considerably from the preparative data. This indicates that the program to correct the analytical data works well enough to use the corrected analytical data with a

calibration curve generated from fractions recovered by preparative techniques.

To ensure that the correction method works on all types of polymers the above experiment was repeated on two other types of polyethylenes. These were an ethylene-butene copolymer labelled lldpe 1 and a low-density polyethylene labelled lldpe 1. In these cases a smaller number of fractions were recovered, to save experimental time. The results of

Table V Comparison of Analytical and Corrected Analytical Weight Fractions to Preparative Data of lldpe 1

Fraction No.	Temperature Range (°C)	Preparative Data (wt %)	Corrected Analytical Data (wt %)	Analytical Data (wt %)
1	25-60	23.5	22.6	15.6
2	60-70	15.9	14.5	13.0
3	70-80	18.2	18.8	18.1
4	80-90	20.8	21.5	25.2
5	90-110	21.6	22.5	28.1

Table VI Comparison of Analytical and Corrected Analytical Weight Fractions to Preparative Data of Idpe 1

Fraction No.	Temperature Range (°C)	Preparative Data (wt %)	Corrected Analytical Data (wt %)	Analytical Data (wt %)
1	25-60	16.5	15.6	12.2
2	60-70	13.3	11.2	9.2
3	70-75	15.2	13.9	8.5
4	75-80	26.8	30.3	18.5
5	80-85	24.3	24.4	35.6
6	85-110	4.5	4.8	15.9

these experiments are shown in Tables V and VI. It appears that the program works equally well on all types of semicrystalline polymers, even ones with very different branching distributions such as in the case of Idpe 1 shown in Figure 7.

CONCLUSION

In order to use a calibration curve relating number of branches to elution temperature produced from

preparative TREF fractions to generate branching distributions from analytical TREF data it is necessary that the analytical data be corrected for time lag associated with the volume of the columns. It has been shown here that there are significant differences in compositions of polymer fractions collected over the same temperature ranges by analytical and preparative TREF methods. Comparative data on weight percent of polymer recovered, molecular weight measurements, and branching anal-

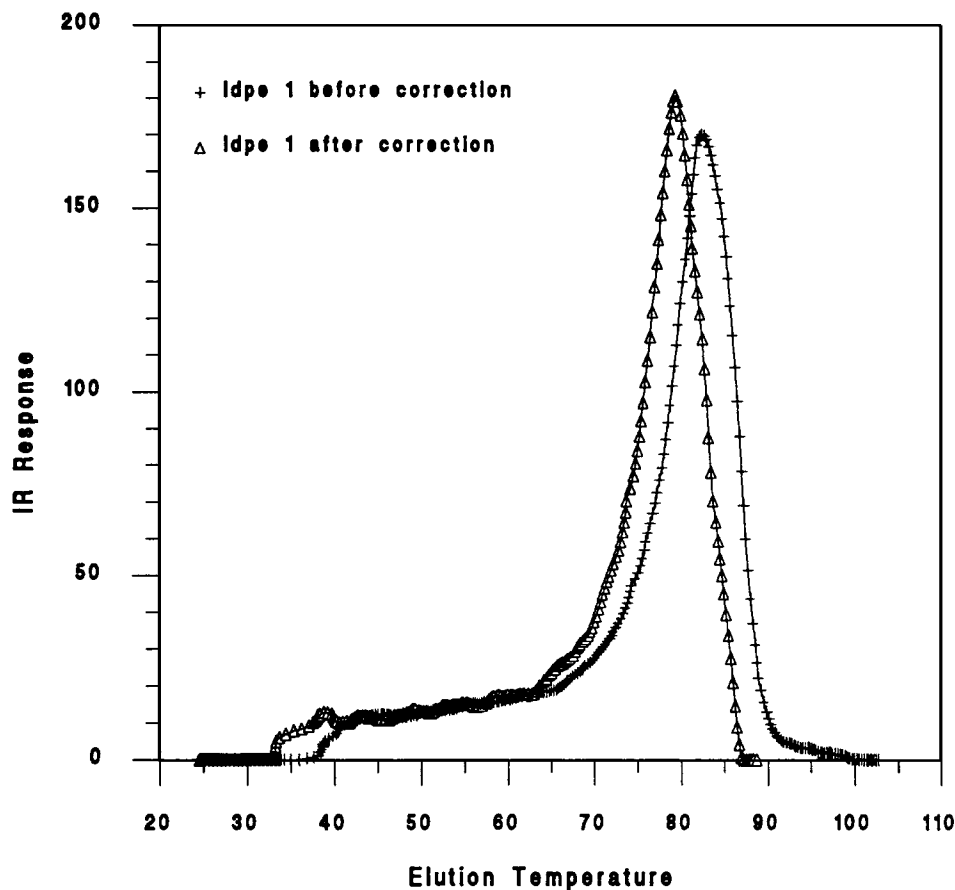


Figure 7 Analytical TREF analysis of Idpe 1 before and after fraction overlap correction.

yses of the polymer fractions all support this conclusion.

It is possible to correct analytical TREF data if the TREF columns all have a common elution profile. This was shown to be the case by eluting heptane in TCB from the different columns with the same dimensions, to discover the shape of the elution profiles, which was similar for all the columns. A computer program was written using a mathematical description of the elution profile to eliminate the band-broadening effects inherent in analytical TREF and to simulate the ideal case in which all the polymer instantly exits the column as soon as it goes into solution.

The correction method works equally well for various linear low and low-density polyethylenes. It appears to be generally useful to obtain accurate branching distributions by using the corrected analytical TREF data.

This work was supported by the Natural Sciences and Research Council of Canada and The Ontario Centre for Materials Research.

The authors also thank J. Pronovost, who designed and constructed the infrared detector cell used in this research.

All programs used in this research are available upon request to the authors. The computing language is QuickBasic. An IBM compatible system is required with Hercules Graphics capabilities.

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Received December 26, 1991

Accepted February 20, 1992