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Development of an Automated Cross-Fractionation Apparatus (TREF-GPC) for a Full Characterization of the Bivariate Distribution of Polyolefins

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Summary: A compact automated instrument has been developed for measuring the bivariate distribution by TREF fractionation and subsequent GPC analysis of the fractions in a single run. The configuration of this instrument and its operation principles are covered here. High resolution TREF fractionation of HDPE and fast methods with overlapped GPC injections are also discussed. Future developments, such the addition of comonomer or molar mass sensitive detectors, as well as operation in GPC – TREF mode for broad MWD resins are outlined.

Keywords: fractionation of polymers; gel permeation chromatography (GPC); microstructure; polyolefins; temperature rising elution fractionation (TREF)

Introduction

Advances in polyolefin catalyst research and manufacturing processes, such as multiple reactor technologies, have resulted in quite complex end products that can be accurately tailored to different applications by producing carefully designed microstructures in terms of molecular weight distribution, chemical composition distribution, and how the comonomer is incorporated as a function of the molecular weight. This trend will continue in the future and is already challenging the polyolefin characterization technology which needs to account for the different distributions of a given product and for their interdependency. The full characterization polyolefin microstructure can be achieved by defining a two dimensional distribution with molecular weight and chemical composition as independent variables, which constitutes the so-called bivariate distribution.

Single dimension fractionation techniques have been widely used for both determining the molecular weight distribution (MWD) by gel permeation chromatography[1] and the chemical composition distribution (CCD) by temperature rising elution fractionation (TREF)[2,3] or crystallization analysis fractionation (CRYSTAF).[3,4]

In order to elucidate the relationships between structural parameters, different methods have been developed using several online detectors coupled single dimension analytical techniques. Examples of these techniques include the determination of comonomer distribution across the MWD by fixed band[5] or Fourier transform[6] infrared detectors coupled to GPC, or the measurement of molecular weight along the CCD by addition of molar mass sensitive detectors to TREF[7,8] or CRYSTAF[9,10] instruments. Although being powerful tools, those methods cannot provide all the information on polyolefin microstructure, as they are based on fractionation according to one microstructural distribution and the simultaneous measurement of only average values of the other distribution, thus loosing significant information in the process.

The direct measurement of the two-dimensional distribution by cross-fractionation in terms of both molecular weight and

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chemical composition is the most comprehensive way to obtain the full definition of polyolefin microstructure. This goal can be achieved by coupling the CCD fractionation by TREF and the MWD fractionation by GPC to measure the bivariate MWD-CCD for the polymer. The method can be further extended by the use of multiple detectors after the cross-fractionation process

Possibly due to the lack of the appropriate instrumentation and high effort required, this comprehensive approach has not been widely used until recently, despite of its potential. Preparative fractionation followed by analysis of the fractions has been the preferred method when trying to elucidate this bivariate distribution, but this procedure is both time consuming and quite complex, taking from days to weeks before the results are available. A description of this method and its application was given by Wild, starting with a preparative fractionation by TREF followed by off-line GPC analysis of the fractions.[11] The first attempt to automate an analytical system for cross-fractionation of polyolefins was presented by Nakano and Goto,[12] who combined a crystallizability fractionation device with a commercial GPC instrument. Recently, an in-house cross-fractionation system has also been described,[13] having increased throughput by using multiple TREF ovens.

A new bench-top, fully automated instrument for cross-fractionation of polyolefins has now been developed based on the combination of a high resolution TREF system (TREF-300, Polymer Char)[9] with a compact dedicated GPC subsystem built as an isothermal oven holding the columns and detectors. The standard procedure to achieve the cross-fractionation of the polymer samples consists of TREF fractionations performed in discontinuous isothermal steps with subsequent on-line GPC analysis of the TREF fractions and IR detection of the polymer. Details of the operation principles, hardware configuration, and data processing are covered in this paper, together with different application examples.

Experimental Part

A schematic diagram of the new cross-fractionation instrument is shown in Figure 1. It was build by modifying the design of a TREF 300 unit (Polymer ChAR, Spain) which incorporates an oven used for sample preparation and a high precision TREF column oven. Other components are: syringe pump, HPLC pump, high temperature isothermal oven (GPC oven) in which the injection valve, a multi-position selection valve and the GPC column set are placed. A dual band IR4 infrared detector (Polymer ChAR, Spain) is used as the concentration detector.

Inside of the TREF oven, a set of five stainless steel vessels with internal filters and magnetic stir bars is used for dissolution of the up to 5 different samples that can be analyzed sequentially. Solvent is added to the vessels through a syringe pump, while the TREF oven is heated typically to 150 °C. Once the polymer sample is fully dissolved, an aliquot is taken from the vessel through its internal filter and loaded into the TREF column by using again the syringe pump, moving the injection valve to the ‘‘load’’ position. Depending on the sample heterogeneity and number of fractions required, typically 1 to 3 milligrams of material are loaded into the TREF column.

The polymer in the TREF column is then crystallized, typically at 0.5 °C/min with no flow, keeping the injection valve in ‘‘load’’ position during the crystallization process. Meanwhile, a stand-by flow of solvent is maintained through the GPC columns. The flow rate is increased, typically to 1.0 mL/min at a pre-defined stabilization time prior to the first injection. Figure 2 shows a typical temperature profile followed by the TREF oven along the full cross-fractionation analysis, where dissolution, crystallization, and stepwise elution are identified.

Once the polymer has been crystallized and the fractions having different crystallinities have been segregated into the TREF column, a discontinuous elution process is followed at increasing temperature steps. At

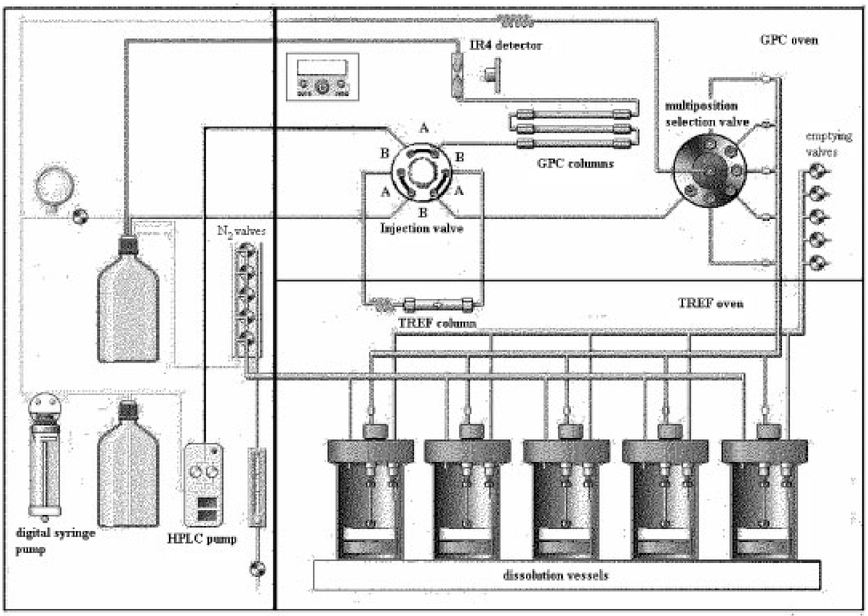

Figure 1.
Schematic diagram of the new automated crossfractionation instrument. Injection valve shown in ''load'' position A; ''inject'' position marked as B.

each temperature, and after a given dissolution time, the injection valve is switched to the ''inject'' position in order to allow the solvent to elute the dissolved polymer from the TREF column. Once that fraction is eluted, the injection valve is closed again to ''load'' position so that the flow through the TREF column is stopped. Then, the oven temperature is increased to start dissolving the fraction that will be eluted in the next step.

Following that process, different TREF fractions with increasing crystallinity are injected into the GPC columns, where they are fractionated this time according to molar mass. An IR4 infrared detector is used to record the final chromatograms continuously, as depicted in Figure 3, where the raw IR detector and oven temperature signals from a real experiment are plotted. It must be noted that each of the peaks in the IR detector signal is in fact a full GPC

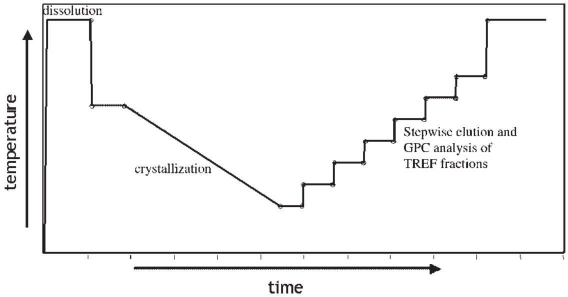

Figure 2.
Temperature profile followed by the TREF oven in a typical cross-fractionation experiment with indication of the different processes.

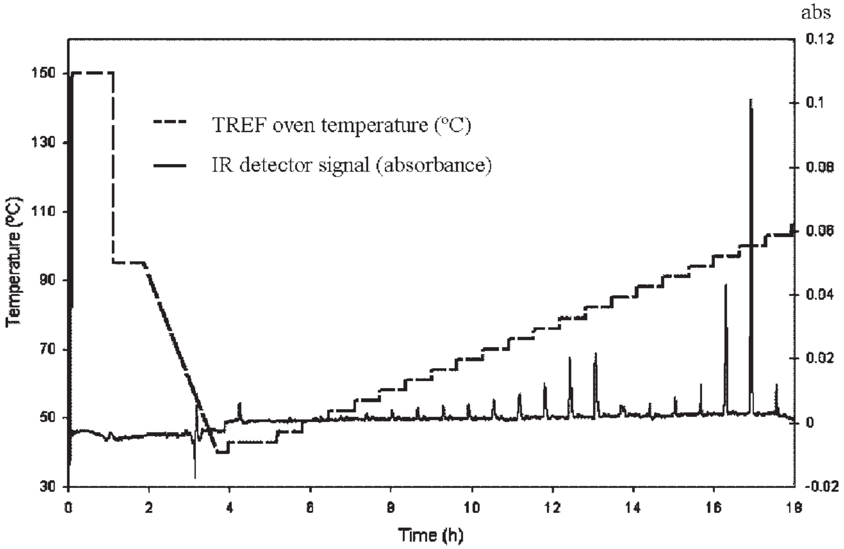

Figure 3.
IR detector signal and TREF oven temperature collected during a full cross-fractionation run.

chromatogram of one of the TREF fractions; therefore the MWD of each narrow-CCD fraction is obtained.

The dissolution and injection processes are illustrated in Figure 4, with an expanded view of the temperature and IR absorbance recorder signals plot. The dashed horizontal arrow indicates the dissolution time of the polymer fraction within the TREF column. The solid downwards arrow shows the injection. Solvent flows through the TREF column for a time long enough to elute all the species dissolved at that temperature. The injection valve is closed as indicated by the solid upwards arrow.

At that time, the TREF oven temperature is increased to that of the next fractionation step. Meanwhile, the TREF polymer fraction travels through the GPC columns, being fractionated by molar mass, producing the peak in the IR detector signal indicated by the circle in Figure 4.

An interesting improvement has been implemented in this system to allow for the injection of one fraction before the previous one has completely exited the GPC columns, hence reducing the overall analysis time. In Figure 5, a direct comparison of standard and overlapped injection analyses is provided. In a period of three hours,

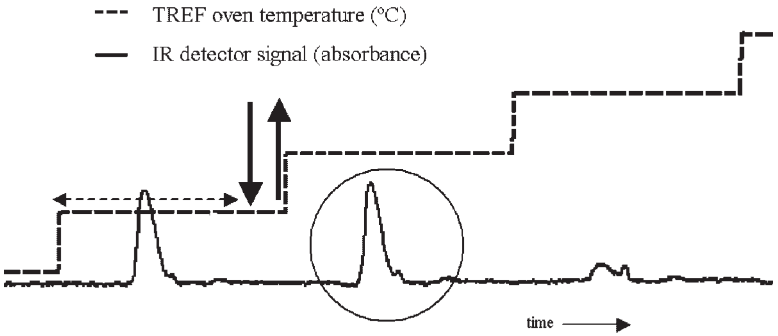

Figure 4.
Detailed view of the injection process.

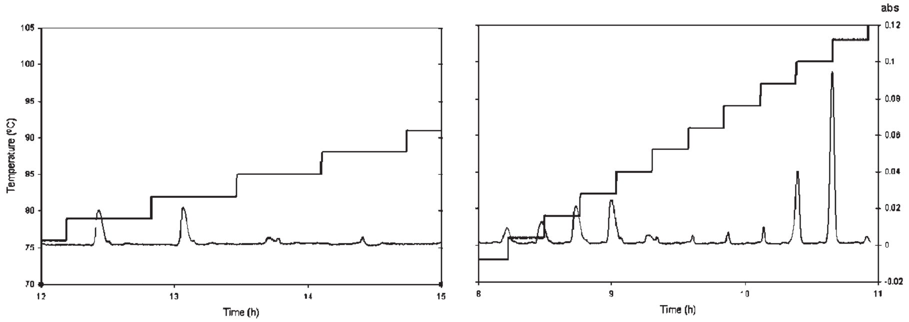

Figure 5.
Comparison of standard GPC injections (left side) versus overlapped GPC injections (right side). In a period of three hours, a larger number of fractions are analyzed in the second case, resulting in shorter analysis time or increased resolution.

only four TREF fractions are analyzed in the first case, while up to eleven fractions can be analyzed when overlapping the injections. This feature can be exploited either to reduce the cross-fractionation time or to increase the resolution of the method by generating more TREF fractions in a given time. No loss of quality in the results was observed by the authors using this technique, probably due to the low concentration of the fractions effectively injected into the GPC columns and also due to the stability of the IR detector along the multiple injection process.

Data Processing

The IR detector generates a continuous signal from which the software automatically separates the individual chromatograms synchronized by the injection signal. This process can be visualized in Figure 6. A series of raw chromatograms, together with their elution temperatures is stored in a raw data file, which is used for further processing.

Every chromatogram is baseline-corrected and integrated in order to obtain the molecular weigh distribution (MWD) based on a polystyrene-standard calibration curve of the GPC columns. Such calibration is generated beforehand by injecting a set of mixtures of narrow distribution polystyrenes to the GPC columns, following the same injection process as for the cross-fractionation analysis, and using the TREF column as injection loop. The different molecular weight averages can be computed after the MWD is acquired, such as the weight, number and z-average molecular weights (M_w, M_n, M_z), as well as

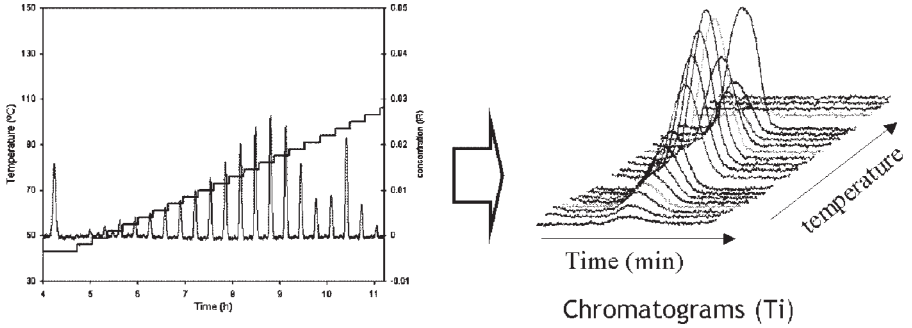

Figure 6.
Continuous raw IR signal (left) and separated chromatograms (right) obtainned as first step in the processing of the cross-fractionation raw signals.

Table 1.
Standard conditions for cross-fractionation analysis of polyethylene samples.

Solvent	1,2 ortho dichlorobenzene with 300 ppm antioxidant (BHT)
Dissolution	60 minutes at 150 °C at 200 rpm stirring inside the stainless steel vessels
Sample weight loaded into TREF column	1.6 mg
Crystallization rate	0.5 °C/min
Elution	24 fractions from 40 °C to 120 °C, temperature step every 3 °C, overlapped GPC injections with 19 minutes inter-injection time
GPC analysis flow rate	1 mL/min
GPC column set	3 PLGel 10 micron mixed columns (Polymer Laboratories Inc.)

polydispersity index (*PDI*). The weight fraction at each temperature is also computed by comparing the area of every single chromatogram to the total area.

That set of MWDs measured at different temperatures are combined with their respective weight fractions to generate a 3D plot representing the bivariate composition-molar mass distribution of the sample. Numerical interpolation smoothing spline algorithms are used in this step, in an approach similar to that described by Nakano and Goto.[12]

The whole sample MWD is also recovered as the weighted sum of the MWD of individual fractions according to their weight fractions. The reconstruction of the TREF profile of the whole sample is a more complex process. It is based on constructing a discontinuous TREF cumulative curve with the progressive sum of the weights of the fractions at each elution temperature, starting with the soluble fraction at the initial temperature and ending with the total weight at the final temperature. The first derivative of the smoothed interpolation line of the cumulative curve constitutes the reconstructed TREF profile.

Results and Discussion

In order to demonstrate the operation of this new cross-fractionation instrument and to show its capabilities, a series of polyethylene samples have been analyzed and the results are presented in this section.

The standard cross-fractionation conditions used are summarized in Table 1, resulting in an overall analysis time of roughly 11 hours per sample for a quite reasonable number of fractions and very good resolution.

Blend Analysis

A two component blend of metallocene polyethylenes was first used to evaluate the resolution of this method. The description of the components in the blend is summarized in Table 2.

A view of the 3D plot of the bivariate distribution of this blend is shown in Figure 7, together with its contour plot. The logM axis was obtained with the GPC calibration curve, while the temperature axis corresponds to the elution temperatures of the different TREF fractions. The elution temperature can be related to comonomer content considering that high crystalline materials eluting at high temperature have little or no comonomer, while increasing levels or comonomer reduce crystallinity and result in lower TREF temperatures. The height of the surface plot represent the relative IR absorbance signal, directly related to concentration at every molar mass-temperature point, so it represents the amount of material having a given molar mass and eluting at a given temperature.

Table 2.
Description of metallocene polyethylene blend components.

Component	Density (g/cm^3)	MI	Weight percent
A	0.957	19.6	50%
B	0.921	0.25	50%

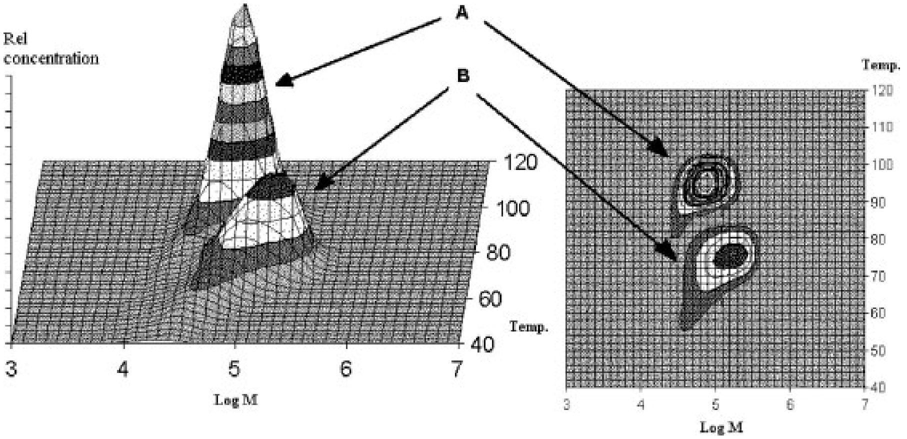

Figure 7.
3D-surface plot (left) and 2-dimensional contour plot (right) of a metallocene polyethylene blend.

The 3D graph on the left side of Figure 7 already gives a clear idea of the separation and of the main structural features of the blend components. Having higher density, component A has an elution temperature around 95 °C, higher than the lower density component B, while its molar mass is shifted to lower values, as expected by their respectives MIs. Component A has narrower composition distribution, resulting in a higher 3 dimensional peak. A certain tailing can also be seen in both components in the direction of lower TREF temperatures and molar masses. This last effect, as well as the relative positions in the temperature-LogM plane are more clearly seen in the contour plot.

The MWD of the fractions, weighted according to their relative amounts, are presented in Figure 8 (thin lines), while the summation of all of them, which constitutes the distribution for the whole sample, is presented with a thicker line in Figure 8.

For comparison purposes, and in order to validate the procedure followed to

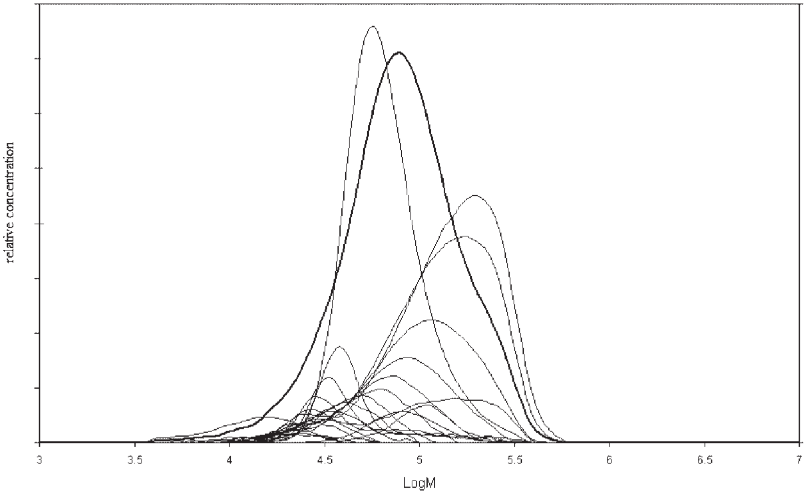

Figure 8.
Weighted MWD curves from all the fractions measured at every elution temperature (thin lines) overlaid with the recovered MWD of the polyethylene blend (thicker line).

recover the original MWD from the fractions, a special analysis was performed in which the whole sample was injected from the TREF column to the GPC columns in the same manner as the fractions were injected. In this way, a direct GPC analysis of the whole sample was performed and the resulting MWD was overlaid in Figure 9 with the recovered MWD. Given the number of individual fractions that were measured and integrated independently, it is remarkable how similar the two results are.

The chemical composition view is obtained by reconstructing the TREF profile from the individually recovered weights of the fractions. This curve is presented in Figure 10, in which the higher resolution achieved in the comonomer dimension is clearly seen, in comparison with the typical lower resolution in the molar mass dimension. The high quality of the recovered TREF curve is quite comparable to that directly obtained with analytical TREF.

Figure 10 also plots the M_w of the fractions as a function of the chemical composition distribution. In this case, the high density material has a lower average molar mass than the lower density one. At the same time, it is also seen that there is a trend of decreasing M_w with increasing comonomer content or lower TREF elution temperatures for both materials.

Similar information can be obtained by coupling molar mass sensitive detectors such as laser light scattering or viscometer detectors to an analytical TREF instrument.[8–10] However, this information is much more evident in the 3D surface and contour plots, which can only be directly measured by this cross-fractionation technique. It is important to emphasize the tremendous power of having the full MWD at each elution temperature, which allows the determination of the polydispersity and other parameters of interest.

Linear Low Density Polyethylene (LLDPE)

A commercial LLDPE was run in this cross-fractionation unit using the same conditions summarized in Table 1. The 3D surface and contour plots are presented

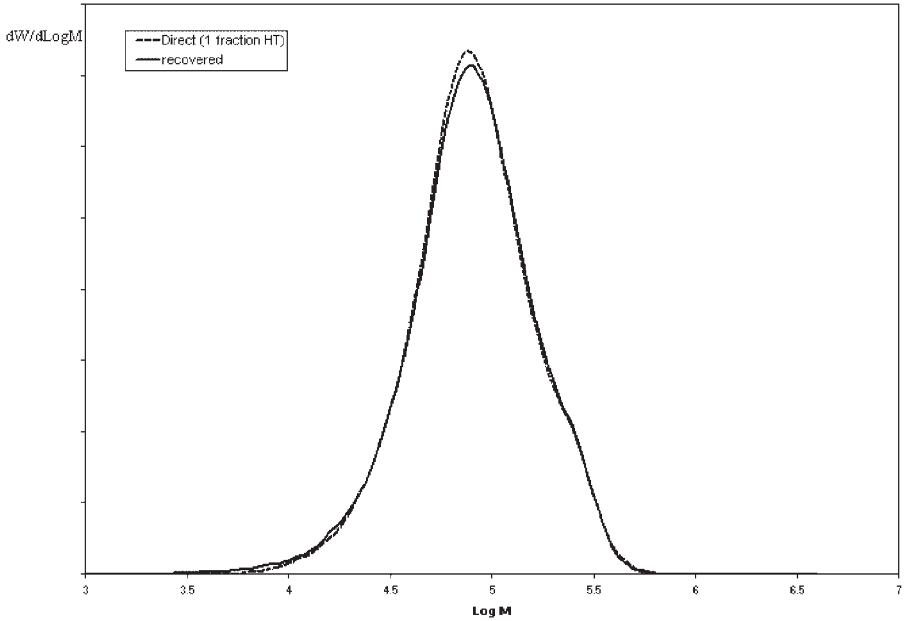

Figure 9.
Overlay of directly measured MWD of the whole polyethylene blend with the recovered MWD after the cross-fractionation process.

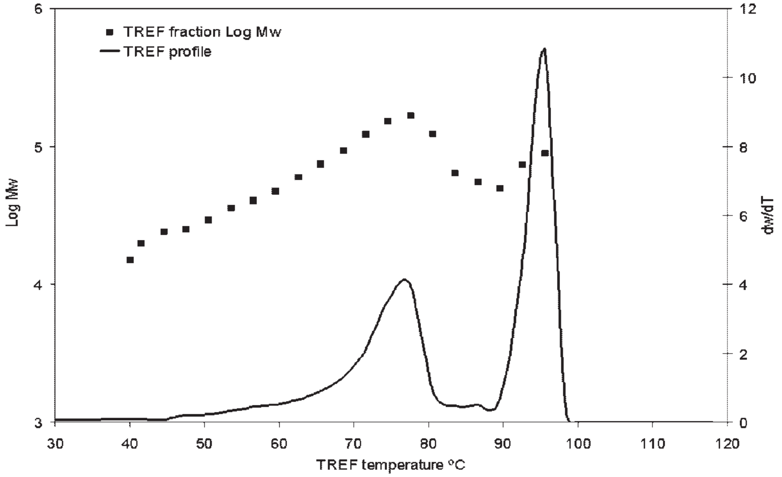

Figure 10.
Reconstructed TREF profile (solid line) based on the weight fractions collected at each elution temperature and weight average molecular weight (M_w) of the individual fractions (dots) as a function of elution temperature.

in Figure 11. In this case, the soluble fraction, amounting to approximately 5 wt% of the sample, is represented as a separate smoothed peak. The contour plot clearly shows the direct dependency of TREF elution temperature and molar mass, in good agreement with previous publications,[11] demonstrating the relative higher comonomer incorporation in the shorter polymer chain, while the less short chain branched fractions (sometimes referred to as homopolymer) exhibits the highest molar mass.

Those observations can be confirmed in the reconstructed TREF view, overlaid with the M_w of the fractions, as presented in Figure 12. We have also overlaid two independent analysis in Figure 12 to show the good reproducibility of this automated analytical instrument and the reliability of the numerical reconstruction of the TREF profiles. The M_w values show more scatter in the temperature ranges with lowest weight fractions because of the lower detector signal to noise ratio in these areas.

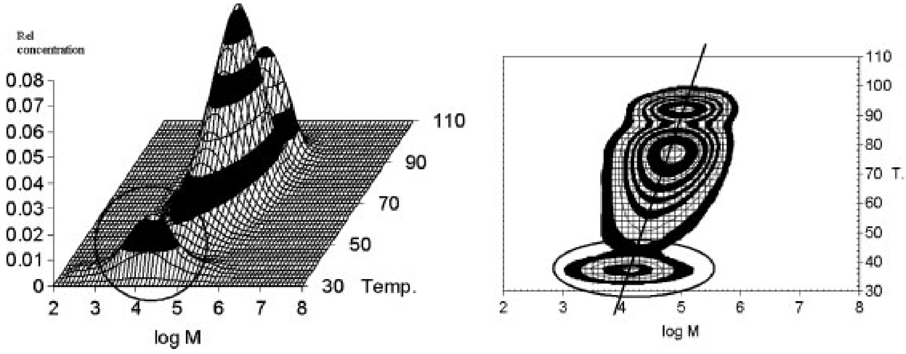

Figure 11.
3D-surface plot (left) and 2-dimensional contour plot (right) of a LLDPE sample including the representation of the soluble fraction as a separate peak. A trend line is added to the contour plot to indicate the direct relation of elution temperature to molar mass.

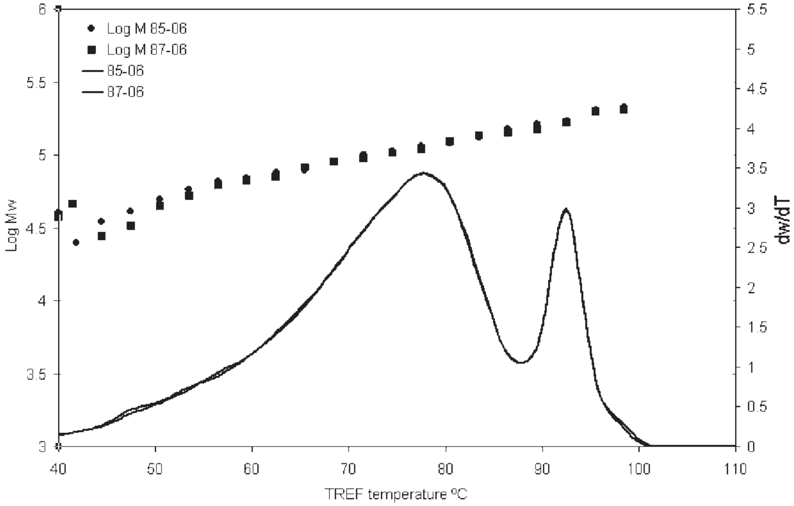

Figure 12.
TREF profile and M_w plot for a LLDPE sample. Two independent cross-fractionation analyses are overlaid to demonstrate the good reproducibility of this technique.

Polyethylene Resins Made in Multiple Reactors

Another commercial product that has a broad and complex chemical composition distribution, in this case produced presumably by a multiple reactor process, was analyzed using the cross-fractionation instrument under the same conditions as in the previous sections. The 3D plots in Figure 13 show a peculiar structure in which three different populations can be identified.

One of the remarkable characteristics of this product is the highly short chain branched component eluting in the range of 55 to 70 °C showing a higher molecular weight than that of the more crystalline population eluting at higher temperatures. This product is a good example of materials with very heterogeneous and multimodal chemical composition distributions. This can also be seen very clearly the reconstructed TREF profile shown in Figure 14.

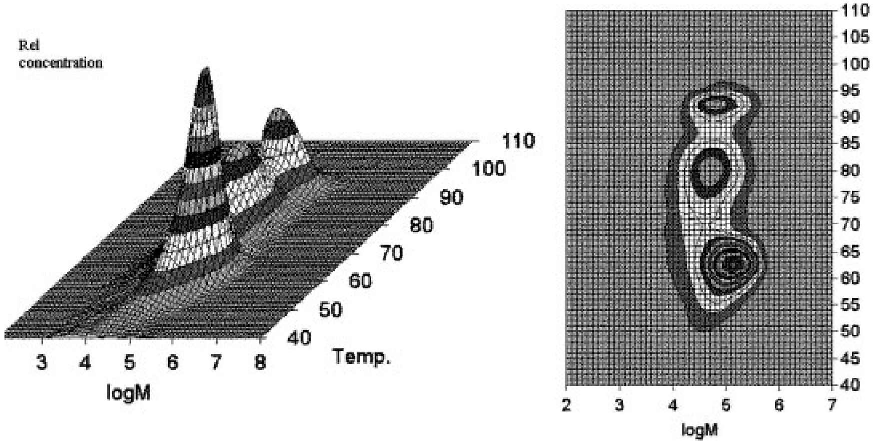

Figure 13.
3D-surface plot (left) and 2-dimensional contour plot (right) of a multiple reactor polyethylene sample.

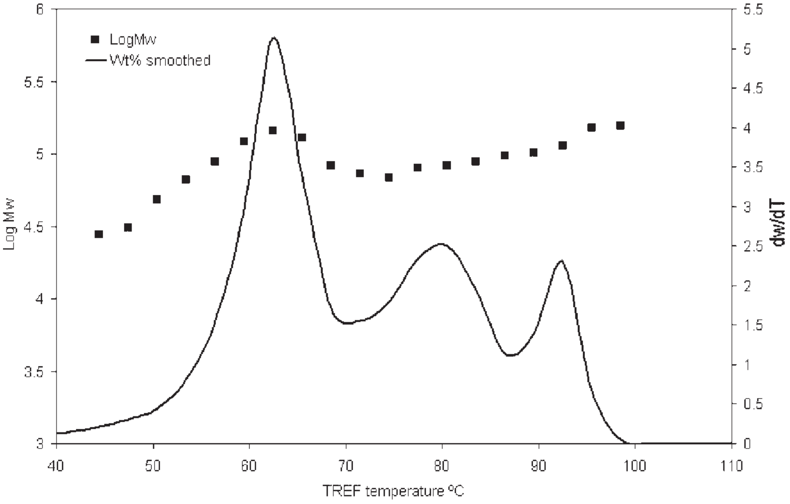

Figure 14.
TREF profile and M_w plot for a multiple reactor polyethylene sample.

On the other hand, the MWD analysis of the whole sample measured by GPC would provide little information on its structural complexity. In fact, the MWD of this product is basically unimodal, showing a small high molecular weight shoulder, as can be visualized from the surface and contour plots of Figure 13 due to the overlapping of the molecular weight distributions of the different polymer populations.

Distribution of Comonomer as a Function of MWD of HDPE Pipe Grade Resins

A higher resolution method was used for the analysis of high density resins because of their narrow chemical composition distribution due to the low amount of comonomer present in the copolymer. At the same time, a very good definition of the bivariate distribution in the 3D plot was required to obtain all the comonomer distribution information. Analysis conditions are summarized in Table 3.

In the lower temperature range from the 60 °C to 82 °C, TREF fractions were taken every 2 °C so that enough material was eluted to produce a detectable chromatogram. Fractions were taken every 1 °C from 82 °C to 100 °C in order to obtain the best temperature resolution and gather the maximum information from the cross-fractionation process.

Figure 15 presents the 3D surface and contour plots after the high resolution cross-fractionation analysis of a pipe grade

Table 3.
High resolution conditions for cross-fractionation analysis of HDPE samples.

Solvent	1,2 ortho dichlorobenzene with 300 ppm antioxidant (BHT)
Dissolution	60 minutes at 150 °C at 200 rpm stirring rate inside stainless steel vessels
Sample weight loaded into TREF column	1.6 mg
Crystallization rate	0.1 °C/min
Elution	27 fractions from 60 °C to 105 °C, temperature step every 1-2 °C, overlapped GPC injections with 19 minutes inter-injection time
GPC analysis flow rate	1 mL/min
GPC column set	3 PLGel 10 micron mixed columns (Polymer Laboratories Inc.)

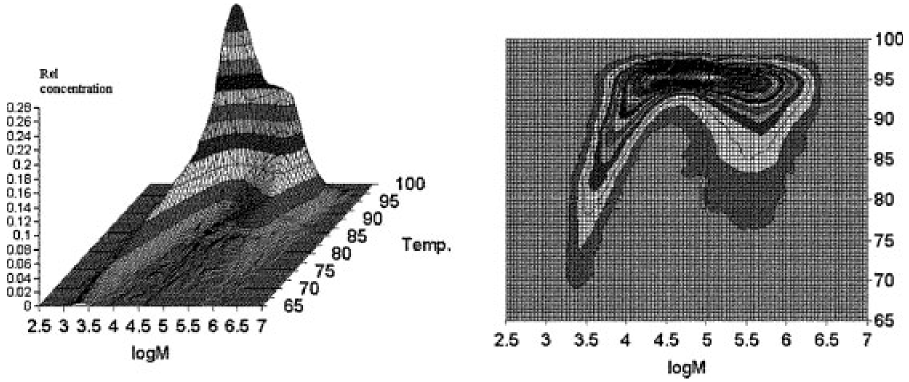

Figure 15.
3D-surface plot (left) and 2-dimensional contour plot (right) of a HDPE pipe grade resin.

HDPE sample. This HDPE is a reverse comonomer composition resin, in which a low level of comonomer was added to the higher molecular weight components in order to achieve the desired end product properties.

Figure 15 clearly shows the heterogeneity of this product. The pronounced tailing towards lower elution temperatures in the low molecular weight range is explained by the effect of the chain ends which act as a source of crystal defects as described by Nieto et al.[14] and produce a depression in TREF elution temperatures. The fact that for molecular weights lower than 10,000 there is a rather sharp decrease in TREF temperatures is also in good agreement with Nieto's observations based on CRYSTAF analysis of narrow-MWD polyethylene fractions and paraffins. This low molecular weight effect on TREF elution temperatures can be compensated in the processing software when translating the TREF temperature axis into the comonomer weight percent in order to produce the two dimensional distributions of molar mass and comonomer composition.

On the other hand, the higher molar mass fractions from Log M from 5 to 6 show a broad TREF elution temperature range produced, in this case, by the addition of comonomer in that area of the molar mass distribution.

In the TREF view plot (Figure 16), M_w values are rather uniform for most all temperatures, decreasing only at lower temperatures because of the low molar mass tail observed in the two dimensional plots. The different contributions to the TREF temperature decrease by either comonomer addition or low molar mass species are clearly seen in this two-dimensional plot measured with the cross-fractionation instrument. They would not be detected by one-dimensional techniques, even with multiple detectors.

Figure 16 also shows how the polydispersity index depends on the TREF elution temperature. PDI increases dramatically as the temperature is reduced, from initial values of approximately 5 at high temperatures to about 30 at low temperatures, due to the bimodality of the measured chromatograms.

In the case of these HDPE products with broad MWD it has been of great interest to study the molar mass view and also to add the comonomer distribution information to it. An approach to investigate this problem using the cross-fractionation information in the 3D plots is outlined in the following paragraphs.

The recovered MWD for the whole sample is shown in Figure 17. The MWD is clearly bimodal and the question now is to determine the range across this broad MWD in which comonomer is present.

In this study we start by realizing that for every molar mass value, a TREF-like profile is obtained from the 3D surface plot,

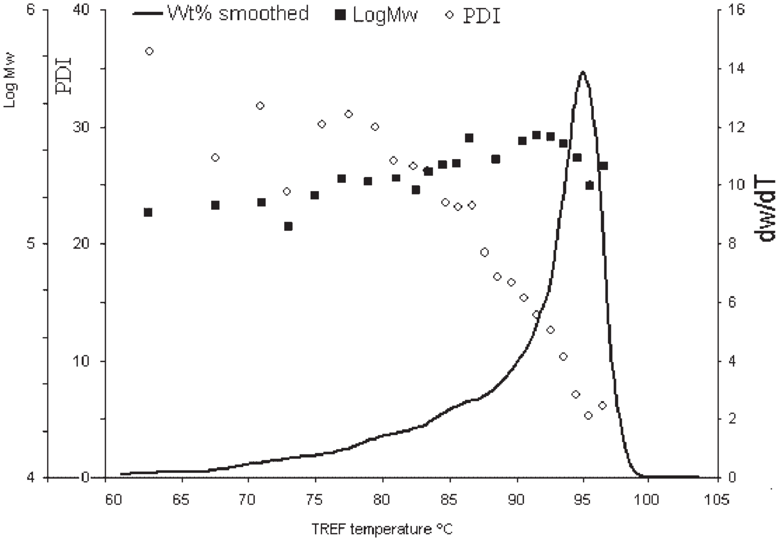

Figure 16.
TREF profile and M_w and PDI plots for a HDPE pipe grade resin.

representing the TREF profile of a very narrow molecular weight fraction. Figure 18 helps visualizing this approach by presenting a surface plot cut in the direction of the TREF temperature axis, highlighting the equivalent TREF curve at log M value of 5.5.

For the generated TREF curve, the weight average elution temperature, T_w, is computed with the equation:[4]

$$T_W = \frac{\sum c_i \cdot T_i}{\sum c_i} \tag{1}$$

Similar TREF curves and T_w averages can be obtained for every molar mass value to generate a T_w versus Log M plot. The

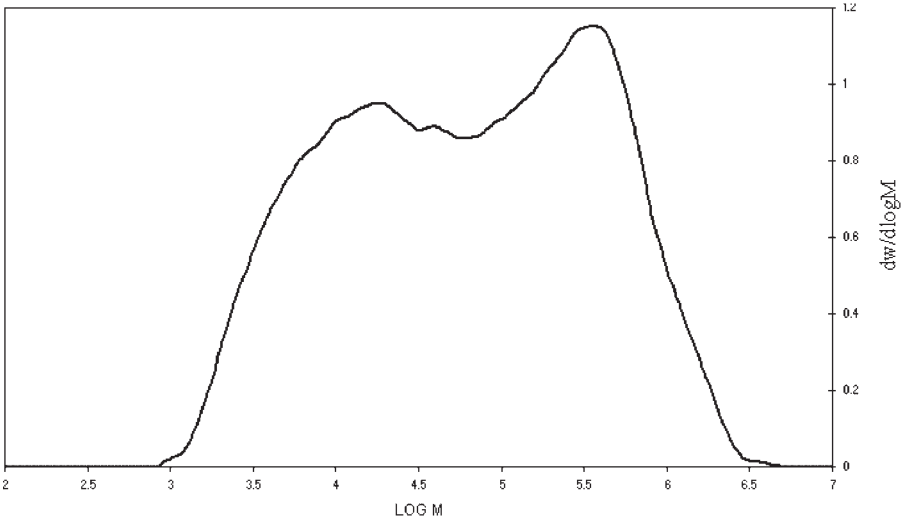

Figure 17.
Recovered MWD of the whole HDPE sample by a weighted sum of the individual MWDs based on their respective weight fractions.

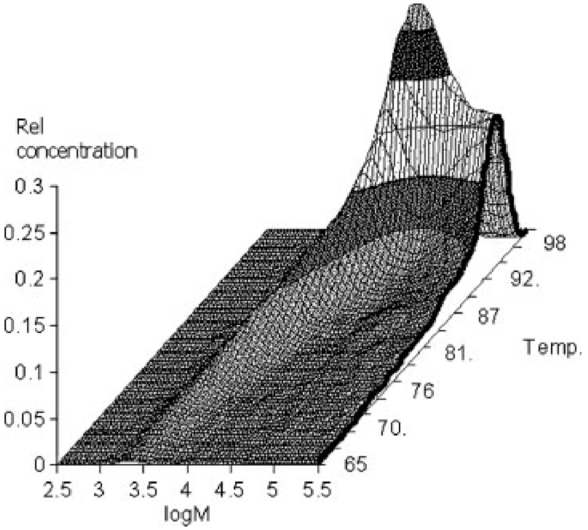

Figure 18.
3D surface plot of a HDPE sample with a cut view produced at LogM = 5.5 in the direction of the temperature axis. The highlighted edge of the surface plot represents a TREF profile at that molar mass value.

resulting data series is overlaid with the MWD curve in Figure 19.

It is well established[2,3,15] that T_w is correlated to the methyls groups per 1000 carbons (CH_3/1000C), even for molecular weights down to 1000 (either coming from short chain branches or chain ends) by a linear inverse function; consequently, a

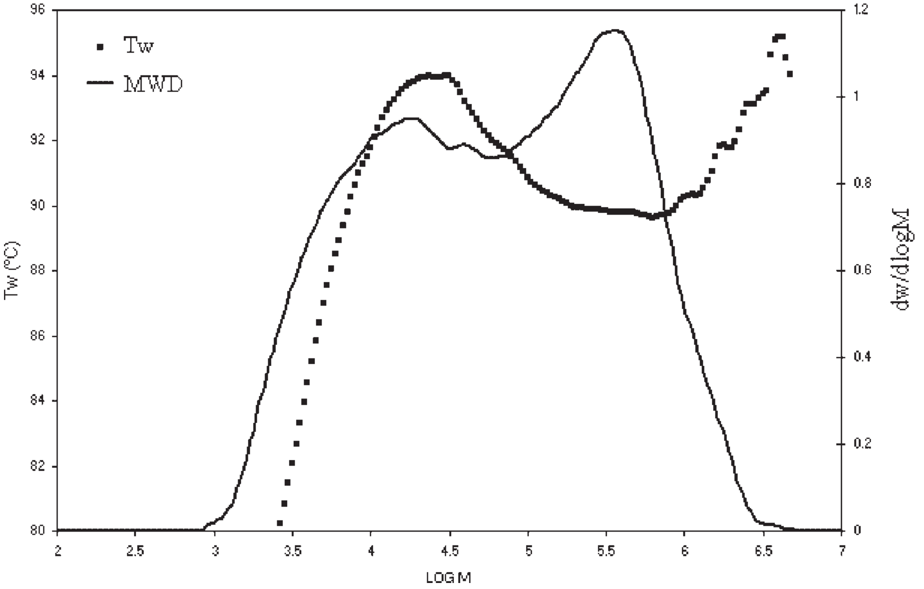

Figure 19.
MWD of a HDPE sample and T_w averages as a function of molecular weight. The values of T_w decrease sharply for molecular weights lower than 10,000 due to chain end effects in TREF fractionation. T_w decreases in the high molecular weight range due to comonomer incorporation.

linear calibration curve can be developed to translate T_w values into CH_3/1000C. Although work is being conducted to obtain an accurate calibration curve for this method, in order to show the potential of this approach, a simulated T_w –CH_3/ 1000C calibration curve was used in this work to obtain the methyl frequency as a function of molecular weight.

A correction for the effect of chain ends based on molecular weight was applied to obtain the short chain branch frequency (SCB/1000C) along the MWD (Figure 20). Provided the type of comonomer is known, as it is usually the case, the comonomer weight percent can be directly computed from the SCB frequency.

This result proves that the cross-fractionation instrument operating as TREF–GPC can provide the same information as online or offline GPC-IR techniques. A higher precision is expected from the cross-fractionation method because precision is not related to detector signal-to-noise ratio but to the TREF separation mechanism which is known to be highly reproducible.

An alternative approach, starting with fractionation by molecular weight and then analyzing the narrow-MWD fractions by TREF may seem more suitable for those broad MWD samples. However, provided that the bivariate distribution is accurately measured, there should be no difference in using TREF or GPC as the primary fractionation method, and the choice of cross-fractionation configuration should be made according to convenience and available instrumentation.

Conclusions

A new automated compact cross-fractionation instrument has been developed with special attention to efficiency, flexibility and robustness. The main hardware components, as well as operation principles, have been described in some detail, together with a special feature for producing overlapped GPC analysis of TREF fractions.

A series of application examples has been presented for different types of

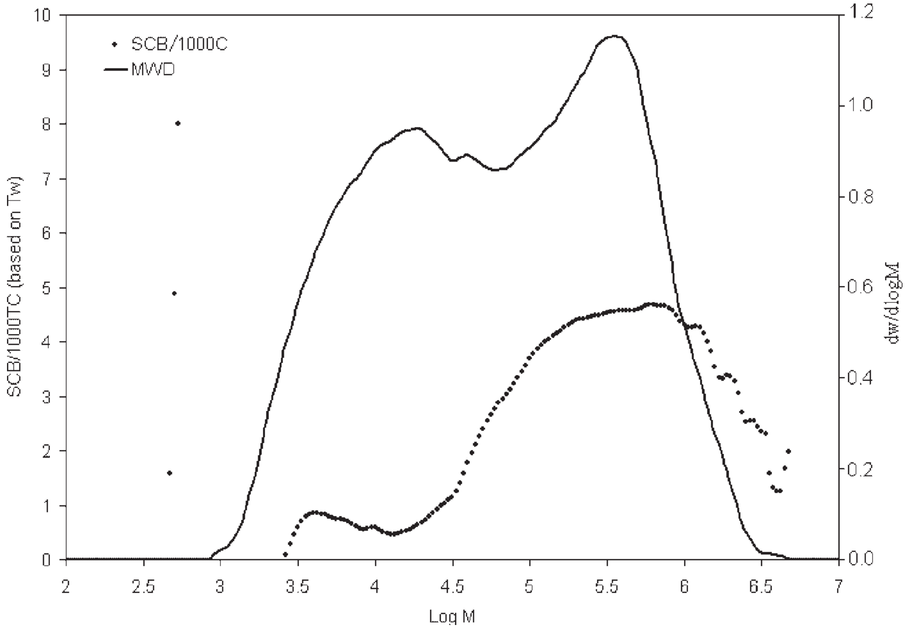

Figure 20.
Short chain branch (SCB) frequency along the MWD obtained from the cross-fractionation data, showing that the higher molecular weight material has the higher SCB frequency due comonomer incorporation.

polyethylene samples to demonstrate the resolution and comprehensive information produced by this instrument. Other analytical methods with slower crystallization rates down to 0.01 °C/min, sub-ambient temperatures for less crystalline polymers, higher elution temperatures for polypropylene, or different flow rates are easily programmed through the virtual instrumentation software user interface.

This cross-fractionation instrument also proves to be a very powerful tool for obtaining the SCB distribution along the MWD for the most demanding applications of pipe grade HDPE resins having very little comonomer incorporated. An approach for measuring the distribution of comonomer along the MWD for HDPE products based on cross-fractionation data obtained by TREF fractionation and GPC analysis has been studied and its feasibility established using the instrument and analysis conditions described in this work.

Addition of other detectors online will still increase the amount of information generated by this cross-fractionation instrument. A methyl sensitive head can be incorporated to the IR detector in order to measure the methyl groups concentration and, as a result, the comonomer weight percent directly both for polyethylene and polypropylene copolymers. Future developments also include coupling viscometer and light scattering detectors to this instrument, which will provide absolute molecular weight and long chain branching detection as well as the possible adaptation to work in reverse mode as GPC fractionation followed by the TREF analysis of the GPC fractions.

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