

Characterization of Branched Polyolefins by High Temperature GPC Utilizing Function Specific Detectors

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Introduction

Advances in polyolefin catalysis have opened the way for the development of polymers with tailored molecular architectures. Fully characterizing these structurally complex materials is a growing challenge in analytical chemistry, both as an important step in confirming the molecular structure of the materials and also as a tool to give insight into the mechanism of the polymerization reaction.

Gel permeation chromatography (GPC) is a relatively rapid method for the determination of polymer molecular weight and molecular weight distribution (MWD). The coupling of GPC with function specific detectors can significantly enhance the characterization of polyolefins by determining not only MWD but also the branching distribution. Online light scattering and viscosity detectors each measure parameters that can be related to the level of long chain branching. These two methods of detection have relative benefits and drawbacks depending on the molecular weight and level of branching in the polyolefin to be measured. The GPC system can also be coupled to FTIR providing spectral information as a function of elution time (and therefore, molecular weight) for studies of short chain branching distribution.

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Branching in Polyolefins

Branching in polymer systems can have many different architectures, dependent on the structure of the monomer and the synthetic method employed. For polyolefins, depending upon the catalyst type and level of comonomer incorporation, polymers can exhibit various conformations as illustrated schematically in Figure 1.

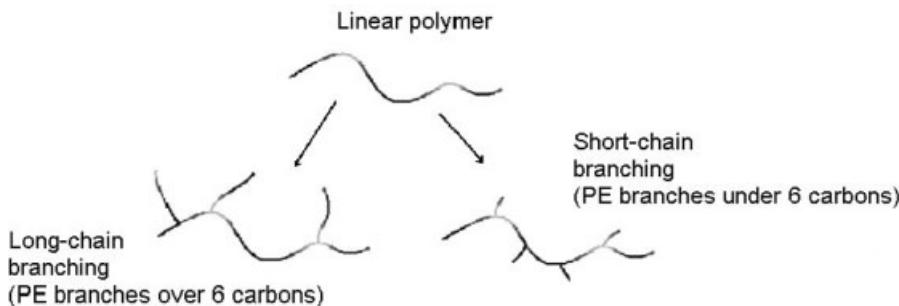
High Temperature GPC for Polyolefin Analysis

The PL-GPC 220 is a fully integrated high temperature GPC instrument capable of operating over the temperature range 30–220 °C. The oven compartment is fitted with an injection valve, GPC columns and a selection of detectors, including Differential Refractive Index (DRI), Light Scattering (LS) and Viscosity (Visc).

Connection to external devices is facilitated by a heated transfer line, which transfers the eluent stream from the columns to external heated flow cell. This arrangement is used to couple the GPC system with a heated FTIR flow cell, which is situated in an FTIR spectrometer.

Typical conditions for the GPC analysis of polyolefins are as follows:

- Eluent: TCB (stabilized with 250 ppm BHT)
- Columns: 3×PLgel 10 μm MIXED-B, 300 × 7.5 mm
- Flow Rate: 1.0 ml/min
- Inj Vol: 200 μl
- Sample Conc: Accurately at nominally 2 mg/ml
- Temp: 160 °C
- Chromatographic System: PL-GPC 220

**Figure 1.**

Long Chain and Short Chain Branching in Polyethylene.

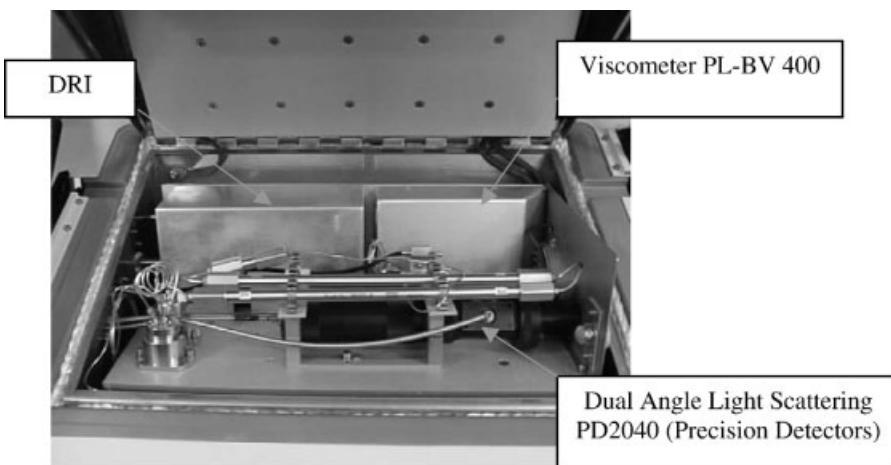
- Data Handling: Cirrus Multi Detector Software

The triple detector combination in the oven (RI, LS, Visc) was used to measure both molecular weight and molecular size information from which the level of long chain branching was derived as a function of molecular weight. The GPC-FTIR combination was used to determine short chain branching as a function of molecular weight.

Determination of Long Chain Branching

Long chain branching can be determined for polyolefins by comparing the behavior of a branched polymer to that of a linear-

chain analogue of the same chemistry (see Figure 4). Compared to a linear polymer, the branched polymer will be more compact at any given molecular weight. As a result, the branched molecule will have a smaller hydrodynamic volume and the branched polymer will have a smaller radius of gyration and a lower intrinsic viscosity. The degree of branching in a material can be modeled based on the difference in intrinsic viscosity (as determined by GPC/Viscometry) or the radius of gyration (as determined by GPC/Light Scattering) of a branched sample compared to a linear analogue. Plots of log intrinsic viscosity (Mark-Houwink plots) and log radius of gyration (Conformation plots) versus log molecular weight can be gener-

**Figure 2.**

PL-GPC 220 Oven Compartment fitted with Triple Detection.

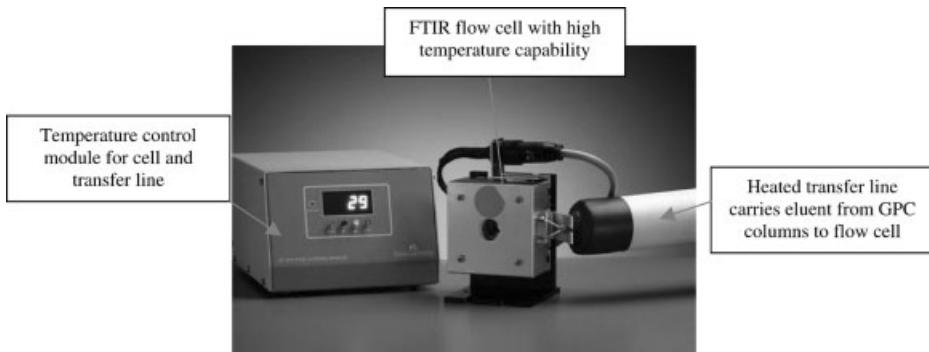


Figure 3.
PL HTGPC-FTIR Interface.

ated for the branched sample and linear analogue. The difference between the behaviour of the two polymers can be used to calculate values of g , the contraction factor. The value g can then be input into various structural models to estimate the degree of branching. The degree of branching is normally expressed as a branching number, B_n , defined as the number of branches per 1000 carbons.

Typical multi-detector data for a poly-olefin is shown in Figure 5 with chromatograms from differential refractive index, viscometry and 15° and 90° light scattering detection.

The LS detector (measuring response at two angles, 15° and 90°) is particularly

sensitive to small amounts of high molecular weight, branched polymer as evidenced by the early eluting pre-peak in the raw data chromatogram. Branching can be assessed from both GPC-LS and GPC-Visc independently via a conformation plot ($\log R_g$ versus $\log M$) or a Mark Houwink plot ($\log IV$ versus $\log M$) respectively. Figure 6 illustrates these two approaches for the analysis of the NIST 1476 branched polyethylene standard sample. The ability to measure R_g by LS below around 20 nm (equivalent to a M_w of around 100,000 g/mol) diminishes as the angular dependence of the scattered light intensity becomes negligible. However, the measurement of IV is reliable down to relatively low

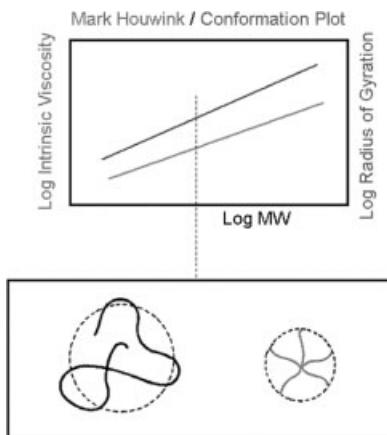


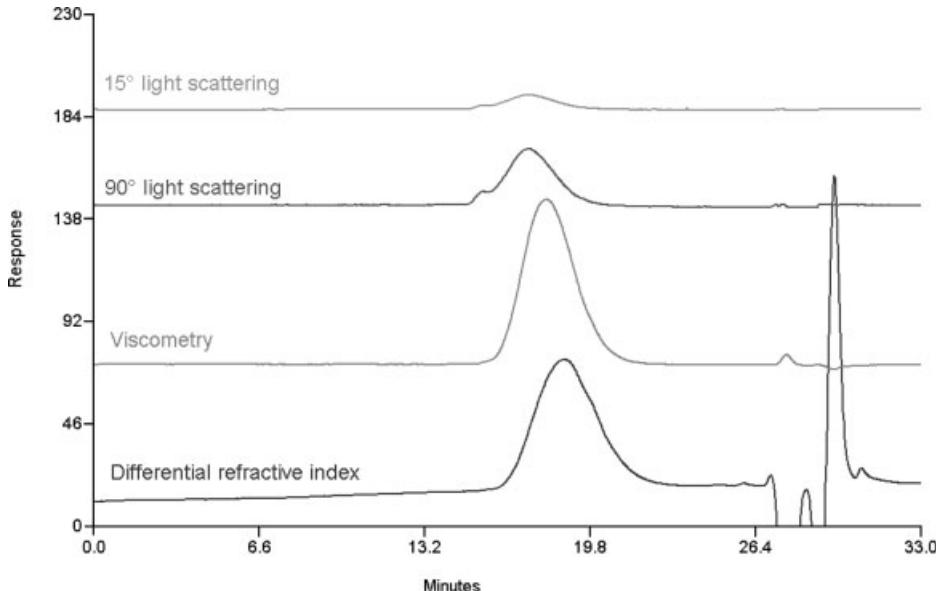
Figure 4.
Principle of LCB Determination by GPC with Viscosity or Light Scattering Detection.

$$g = \left(\frac{R_g \text{ branched}}{R_g \text{ linear}} \right)$$

or

$$g = \left(\frac{IV \text{ branched}}{IV \text{ linear}} \right)^{1/E}$$

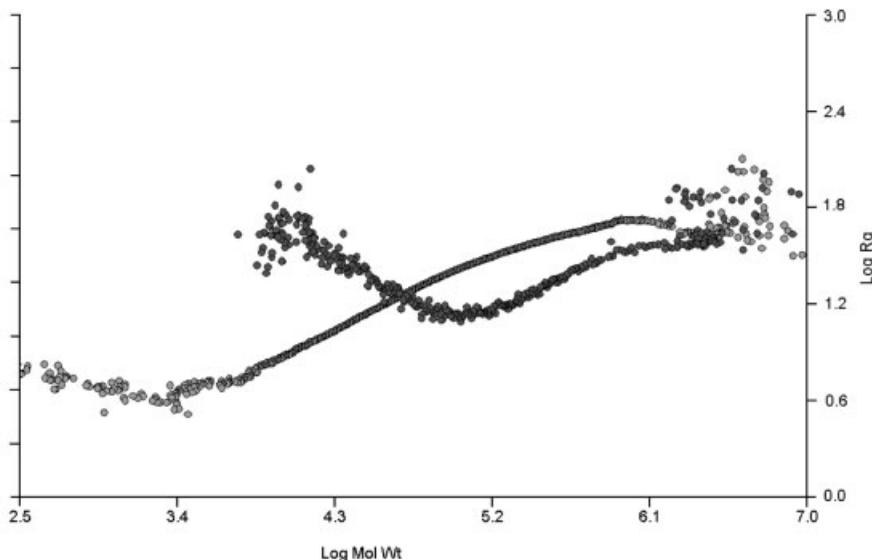
Different statistical models are used to determine branching from g and g' , based on assumptions about the distribution of branches on the polymer backbone

**Figure 5.**

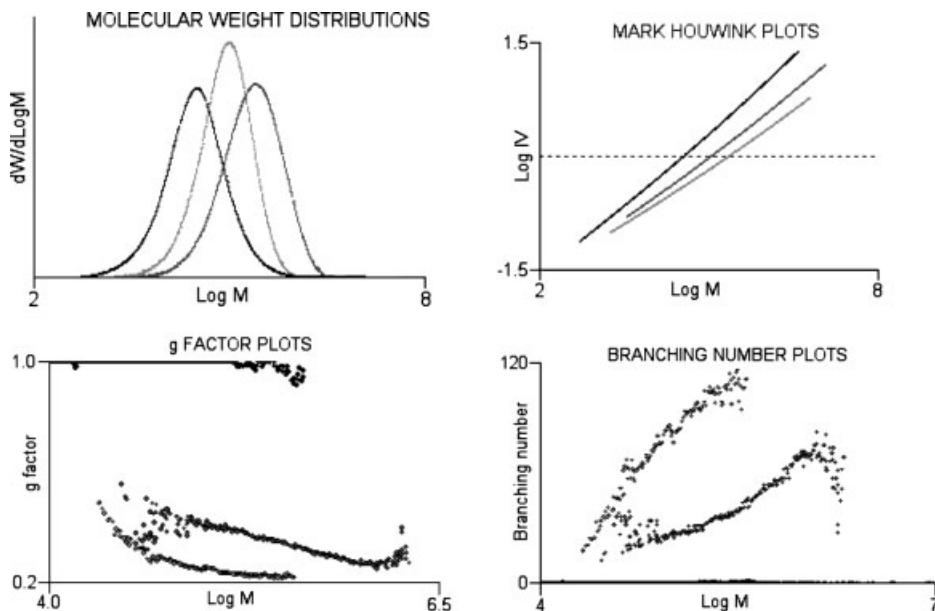
Typical Polyolefin Differential Refractive Index, Viscometry and 15° and 90° Light Scattering Detection.

molecular weight values (around 1000 g/mol) and generally GPC-Visc, or a combination of GPC-LS-Visc, has a wider applicability for branching studies than GPC-LS alone.

Figure 7 shows a summary of typical data obtained from high temperature GPC with triple detection for a set of three commercial polyethylenes. Polymer MWD and long chain branching distribution were derived

**Figure 6.**

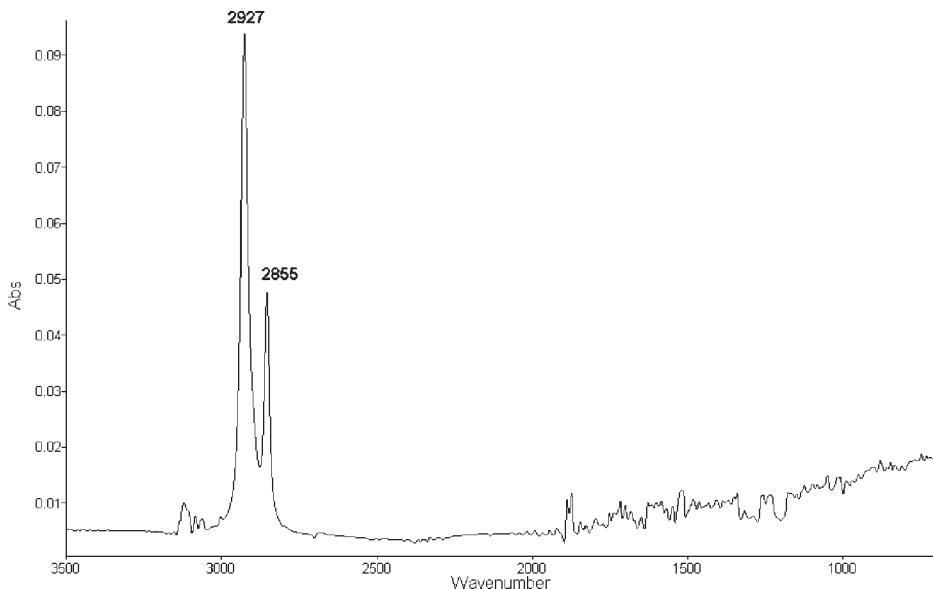
Mark Houwink Plot and Conformation Plot from GPC-Visc and GPC-LS for NIST 1476-Branched Polyethylene Standard.

**Figure 7.**

Summary of Results for the Analysis of Three Commercial Polyethylenes by Triple Detector GPC.

from GPC-LS-Visc measurements. The results indicated that the samples had varying molecular weight although similar and fairly narrow molecular weight dis-

tributions. The g factor plots were derived by comparing the MH relationship for each sample with that of a reference linear polyethylene (NIST 1475), and using an

**Figure 8.**

Typical FTIR Spectrum of Polyethylene after Solvent Subtraction.

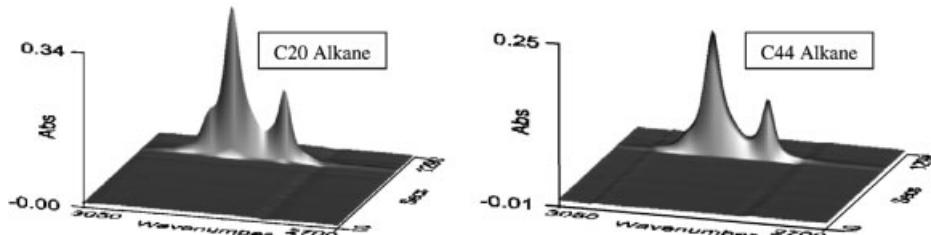


Figure 9.

3D Plots of Time-Resolved Spectra for GPC Analysis of a C20 and a C44 Alkane.

appropriate branching model, the degree of long chain branching as a function of molecular weight was determined.

Determination of Short Chain Branching

TCB can be used for flow through FTIR detection as it has an absorption window between *ca.* 3500–2700 cm^{−1}, which corresponds to the >C-H stretching region, the region of interest for polyolefins. Figure 8 shows a typical spectrum of polyethylene.

Focusing on the >C-H stretching region, differences in the proportions of >CH₂ and –CH₃ groups can be seen in the relative intensities of the absorption bands. Figure 9 shows two 3D plots of time-resolved spectra from GPC runs of two alkanes, a C20 and a C44. Relatively speaking the C20 alkane has over twice the number of –CH₃ groups to >CH₂ groups per unit mass compared to the C44 alkane, and this can be seen by the presence of shoulders on absorption bands.

This dependence of the infra-red spectra on the presence of –CH₃ and >CH₂ groups can be used to measure the level of short chain branching (SCB) in polyethylene. These are branches of less than six carbons long that cannot be detected by traditional multi-detector GPC experiments, as they do not affect the viscosity of the polymer. However, they do have a strong effect on crystallinity, density and stress crack resistance. By measuring the spectra of polyethylene containing SCB,

the relative intensities of the stretching vibrations due to –CH₃ and >CH₂ groups can be measured and providing that the monomers used to introduce SCB are known, the level of SCB can be determined. Coupling the detector to a GPC system allows the SCB as a function of molecular weight to be assessed. Figure 10 shows a correlation between the level of SCB calculated using FTIR and the values determined by a traditional NMR approach^[1].

Cirrus GPC-FTIR SCB software can be used to perform the experiments, calculating SCB based on a rigorous chemometrics approach^[1]. Figure 11 shows an example of an overlay molecular weight and SCB

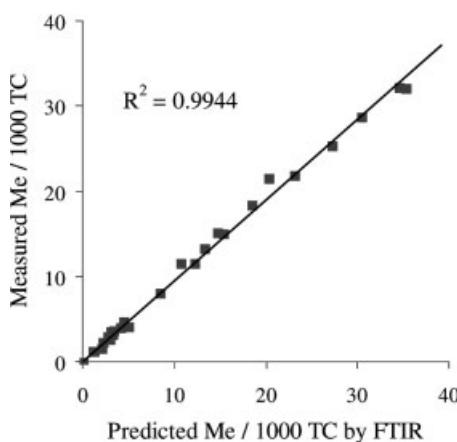


Figure 10.

Correlation Between SCB Results from GPC-FTIR and NMR.

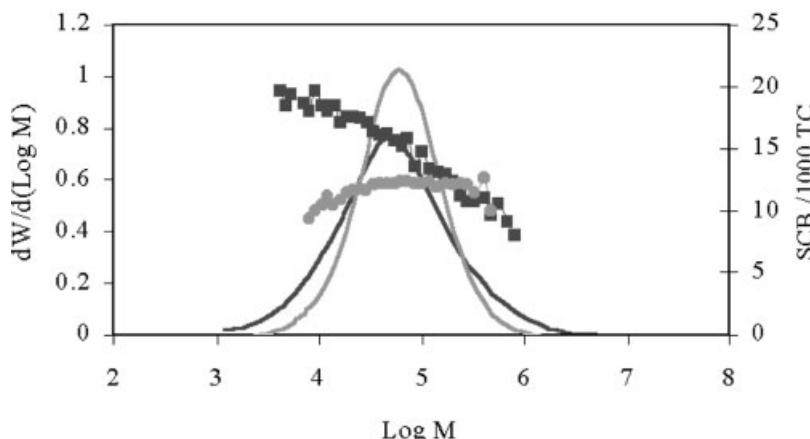


Figure 11.

An Example of Overlaid Molecular Weight and SCB Distributions for Two Samples of Polyethylene.

distributions of two samples of polyethylene determined by GPC with FTIR detection.

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acknowledge the permission of Dr Paul DesLauriers for the use of Figures 10 and 11.

[1] *Polymer*, 43 (2002) pp. 159–170; Quantifying Short Chain Branching Microstructures in Ethylene-1-Olefin Copolymers using Size Exclusion Chromatography and Fourier Transform Infrared Spectroscopy (SEC-FTIR), P.J. DesLauriers, D.C. Rohlfing, E.T. Shieh