Branching Analysis of Polyethylenes by GPC and Agilent Cirrus Multi Detector Software

Application Note

Materials Testing and Research

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Introduction

The presence of long chain branching (over six carbons in length) in polyolefins strongly influences their physical properties such as melt viscosity and mechanical strength. The distribution of chain branching in polyolefins is determined by the polymerization mechanism and there is significant interest in the production of materials with well-defined and characterized molecular weight and branching distributions for specific applications.

This note describes the analysis of three samples of polyethylene with the Agilent PL-GPC 220 instrument by gel permeation chromatography (GPC) and viscometry.

Polyethylene Resin Analysis

Two of the polyethylene samples were synthesized by a mechanism to promote branching while the third was a standard linear reference material NBS 1475. The analysis was carried out at 160 °C with three Agilent PLgel 10 µm MIXED-B columns in trichlorobenzene (TCB) with 0.015% butyrated hydroxytoluene (BHT) as a stabilizer.

Verified for Agilent
1260 Infinity
GPC/SEC System

Refractive index and viscometry detectors were employed and the data analyzed using Agilent's Cirrus Multi Detector software and the Universal Calibration approach. Polystyrene standards were used to generate the Universal Calibration and the un-branched sample was used as a linear model in the determination of branching.

Figure 1 shows the molecular weight distributions for the three samples. The black plot is for the un-branched sample. Although there was some overlap, the samples clearly had significantly different molecular weights.

Figure 2 shows the Mark-Houwink plots of log intrinsic viscosity for the three samples. The uppermost sample is the unbranched material. The other two samples have lower intrinsic viscosities at any given molecular weight, with the unbranched polymer indicating the presence of branching. This can be expressed in terms of g, the branching ratio, defined as follows, where ε is a constant:

$$g' = g^{\frac{1}{\varepsilon}}$$

$$g' = \left(\frac{branched\ intrinsic\ viscosity}{linear\ intrimsic\ viscosity}\right)^{\varepsilon}$$

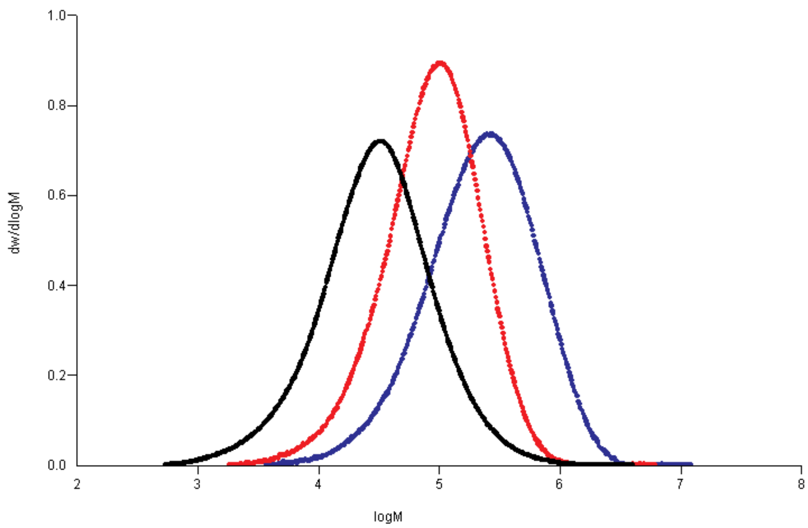

Figure 1. *Molecular weight distributions for three polyethylene samples on Agilent PLgel 10 µm MIXED-B columns.*

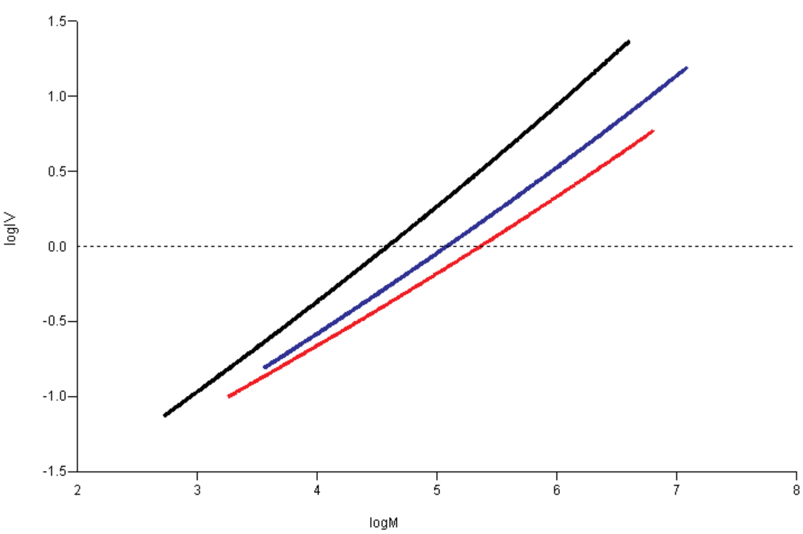

Figure 2. *Mark-Houwink plots for three polyethylenes. The black plot is for the un-branched sample.*

Conditions

Columns	3 × Agilent PLgel 10 µm MIXED-B, 7.5 × 300 mm (p/n PL1110-6100)
Eluent	TCB + 0.015% BHT
Flow rate	1.0 mL/min
Inj vol	200 µL
Temp	160 °C
Detector	PL-GPC 220 (RI) + Viscometer

Figure 3 shows a plot of g as a function of molecular weight for the three samples. The un-branched sample was used as the linear model and gives a g value of unity (except at high molecular weight due to scatter in the data). The other two samples exhibit a decrease in g as a function of molecular weight, indicating that, as molecular weight increases, the number of branches increases. Based on these calculated g values, a branching number or number of branches per 1000 carbon atoms can be generated. This is achieved by fitting the data into a model. The Cirrus Multi Detector software offers a selection of branching models that can be employed in this approach. In this case, a model was used that calculates a number-average branching number assuming a random distribution of branches on the polymer.

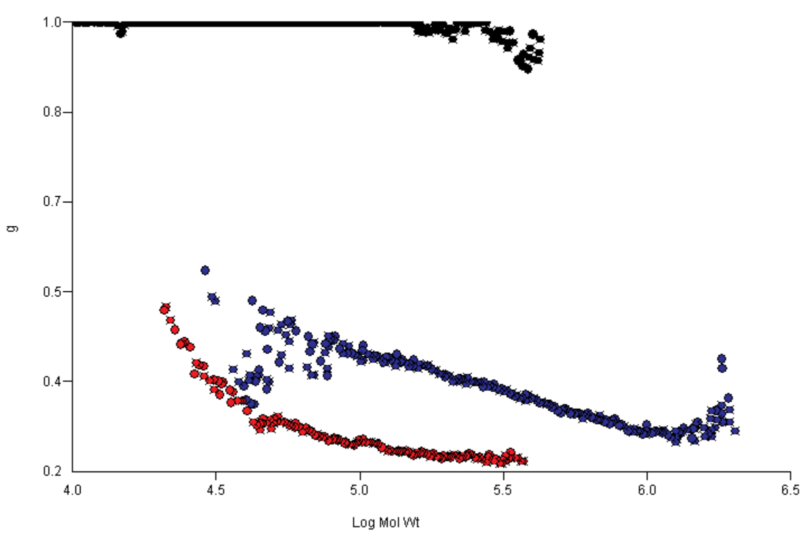

Figure 3. Branching ratio g plots for the three polyethylene samples. The black plot is the un-branched sample.

Figure 4 shows the calculated branching numbers as a function of molecular weight for the three samples.

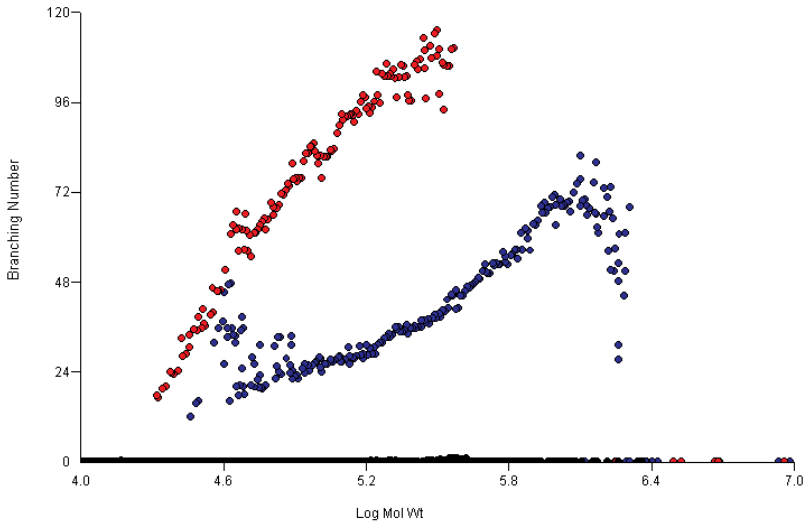

Figure 4. *Calculated branching numbers as a function of molecular weight for three polyethylene samples. The black plot is the unbranched sample.*

Conclusions

The results show that of the two branched samples, the trend in molecular weight distribution does not follow the trend in branching distribution. The sample showing the most branching at any given molecular weight has a lower molecular weight than the second sample. Clearly, understanding both the molecular weight and branching distributions will give an insight into the processibility of the two materials. High temperature gel permeation chromatography with Agilent Cirrus Multi Detector Software is ideal for assessment of polyethylene branching.

For More Information

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Printed in the USA
April 30, 2015
5990-8420EN

Agilent Technologies