TB266: Branching Analysis of Polyethylenes with Cirrus Multi Detector Software

Keywords
GPC, PL-GPC 220, Cirrus Multi Detector Software, RI, Viscometry, PLgel, Polyethylenes, TCB, BHT

The presence of long chain branching (over 6 carbons in length) in polyolefins strongly influences physical properties such as melt viscosity and mechanical strength. The distribution chain branches 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 technical bulletin describes the analysis of three samples of polyethylene with the PL-GPC 220 by GPC/Viscometry. Two of the samples had been 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 PLgel 10µm MIXED-B columns in trichlorobenzene (TCB) with 0.015% butyrated hydroxytoluene (BHT) as a stabilizer.

Refractive index viscometry detectors were employed and the data were analysed using Cirrus Multi Detector software using the Universal Calibration approach. Polystyrene standards were used to generate the Universal Calibration and the unbranched sample was used as a linear model in the determination of branching.

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

Figure 2 (page two) shows the Mark Houwink plots of log intrinsic viscosity for the three samples. The upper most 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 E is a constant:

$$g = \left[\frac{\text{Intrinsic Viscosity (branched)}}{\text{Intrinsic Viscosity (linear)}} \right]^{\frac{1}{E}}$$

Figure 1 - Molecular weight distributions for the three polyethylene samples

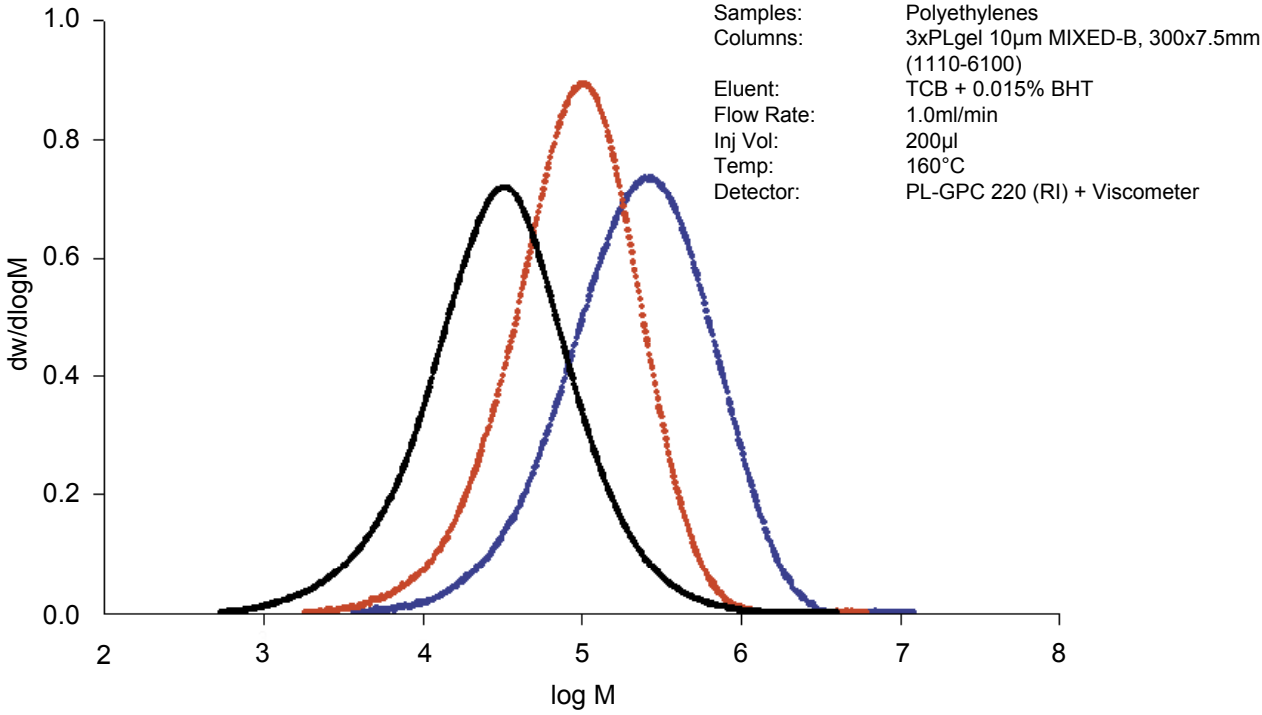

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Figure 2 - Mark Houwink plots for the three polyethylene samples. The black plot is for the unbranched sample.

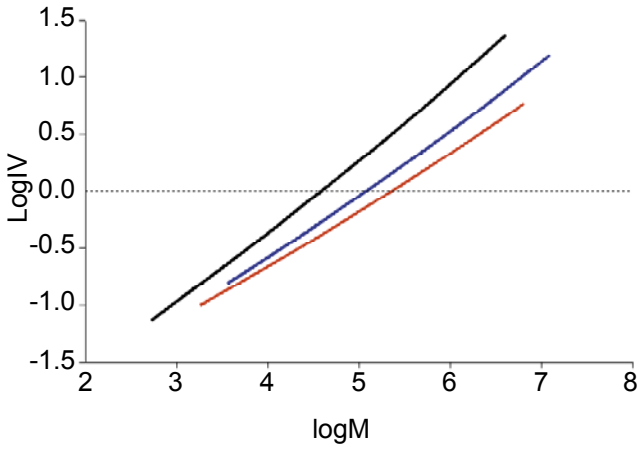


Figure 3 - Branching ratio g plots for the three polyethylene samples. The black plot is the unbranched sample.

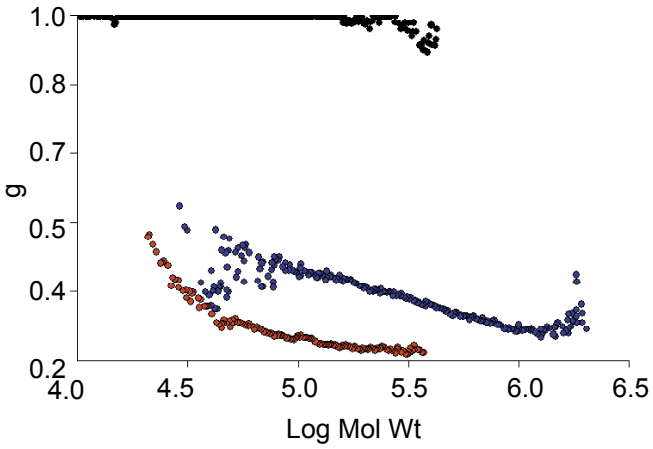
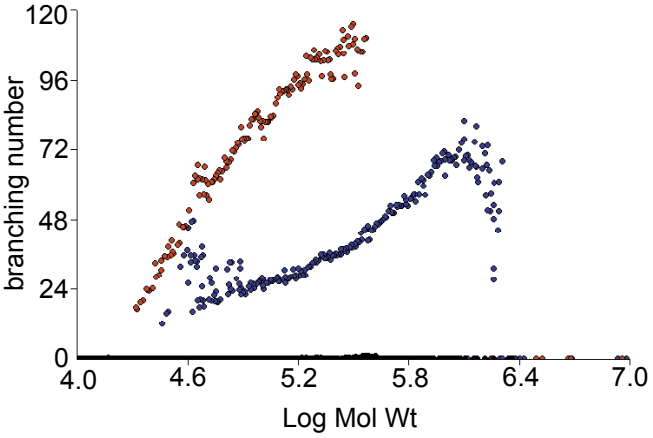


Figure 3 opposite shows a plot of g as a function of molecular weight for the three samples. The unbranched sample was used as the linear model and so gives a g value of unity (except at high molecular weight due to scatter in the data). The other two samples both exhibit a decrease in g as a function of molecular weight, indicating that as molecular weight increases the number of branches increase. 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 and the Cirrus Multi Detector software offers a selection of branching models which can be employed in this approach. In this case a model was used which calculates a number-average branching number assuming a random distribution of branches on the polymer.

Figure 4 below shows the calculated branching numbers as a function of molecular weight for the three samples. The black plot is the unbranched sample.



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.

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