Waters® Alliance® GPC/V 2000 System:
Branching Determination in Polyolefins

Performance PerSPECtives

Introduction: GPC is a chromatographic technique that, when combined with the appropriate detector(s), provides an accurate molecular weight distribution of a polymer, as well as important information on branching. The molecular weight distribution may be used to predict physical properties and processing parameters. The branching distribution of a polymer is equally important for properties such as tensile strength, tear strength of films, elongation, and crystallinity. Polymer chemists use the level of branching in their polymers to help make these property predictions.

Branching in Polyolefins: The RI / Viscometer detector combination allows one to determine the intrinsic viscosity, $[\eta]$ of a polymer at each molecular weight increment (i.e. slice) in the distribution. For a linear polymer, the intrinsic viscosity increases linearly with molecular weight. For branched polymers, this relationship is nonlinear and the deviation from linearity is a measure of the amount of branching in the polymer. The plot of log $[\eta]$ vs. log MW is called the viscosity law plot, and can provide a wealth of information to the polymer chemist about the structure of the sample. The slope of this plot is called alpha, (α), and the intercept is defined as log K, (where K and alpha are the Mark-Houwink constants). The ratio of the branched plot to the linear plot $([\eta]/[\eta]_{lin})$, is called the branching index, (g'). The branching index may be used to calculate the branching frequency, the number of branches per 1000 carbon atoms and the branching probability, (λ), the number of branch points per unit molecular weight. Figure 1 shows the molecular weight distribution, (MWD), the intrinsic viscosity, $[\eta]$ and branching index, g' for a branched polyethylene broad standard, NIST 1476.

Fig. 1. MWD and Viscosity Law Plots for NIST 1476

$$g' = [\eta]/[\eta]_{lin}$$

$[\eta]_{lin}$

$[\eta]$

$M_w = 93,700$
$M_n = 28,100$
IV = 0.91

Log [η]

Log M

g'

TCB, 1 mL/min, 145°C
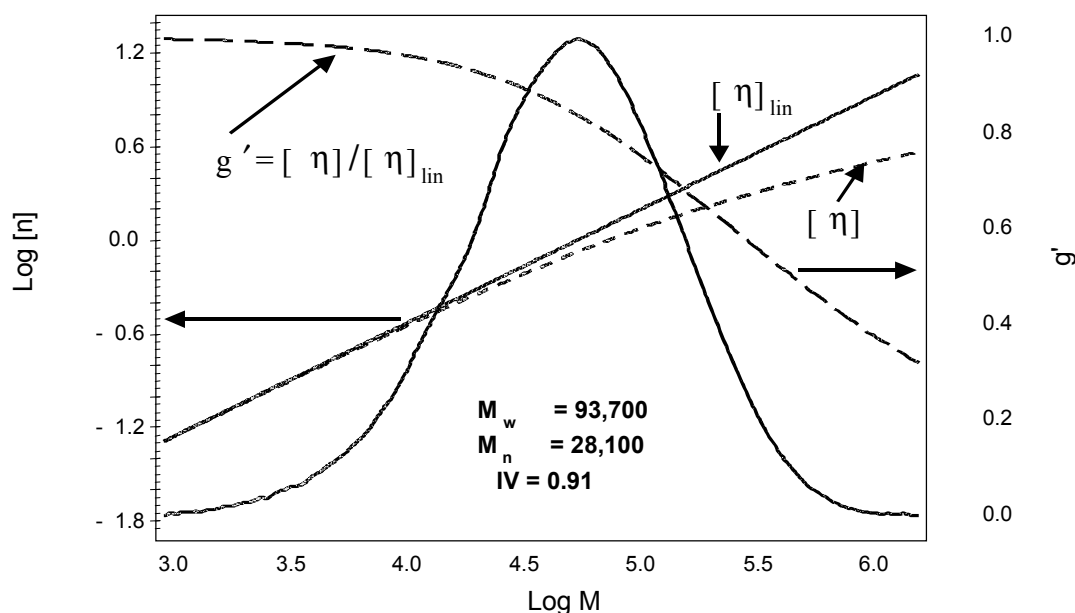
Waters

Importance of Chromatography Data: Waters Millennium[32] GPC/V software augments the performance of the Alliance GPC/V 2000 by providing real time GPC/V data reduction. Using the Universal Calibration technique, accurate molecular weights, branching distributions, and intrinsic viscosity of polymers can be obtained. The powerful Millennium[32] GPCV software allows determination (at each molecular weight) of the intrinsic viscosity, the branching index, K and alpha, as well as the branching probability, λ, (number of branch points per unit molecular weight), and the branching frequency, (number of branches per 1,000 carbon atoms).

Analysis of Metallocene Catalyzed LDPE: With single-site metallocene catalyst technology being introduced several years ago, synthetic polymer chemists have been able to better control the molecular weight and branching distributions of polymers. Figure 2 shows the molecular weight distribution and viscosity law plots for a highly branched metallocene catalyzed low density polyethylene with a broad polydispersity. Analysis of polymers having molecular weight slices in excess of 1,000,000 is facilitated by using very low concentrations, (0.02% in this case).

Fig. 2. MWD and Viscosity Law Plots for LDPE with Metallocene Catalyst
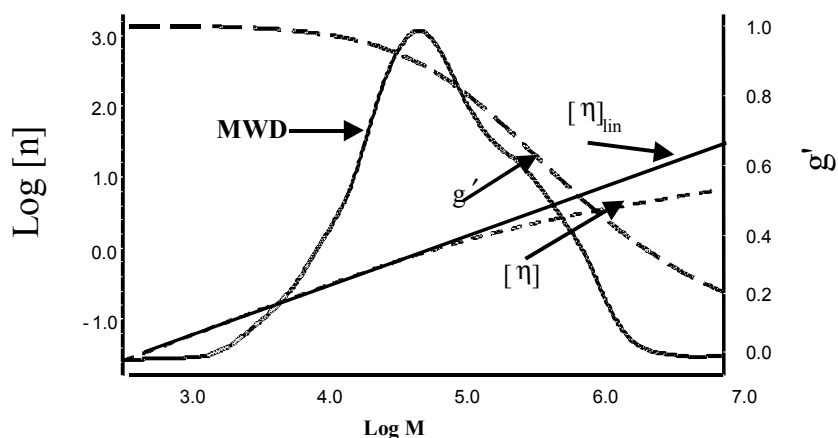
	Sample	M_n	M_w	M_z	g'	K	α	λ
	LDPE	25937	162658	624498	0.571	0.000370	0.725	0.0000313

	Branching Frequency
	1.406

TCB, 150°C, (3) HT Styragel ® Columns, 1 mL/min, Conc.: 0.2 mg/ml

Summary:

• Waters Alliance GPC/V 2000 System, in combination with a selection of detectors and with Millennium[32] software, provides invaluable MW and branching information to the polymer chemist and plastics engineer.