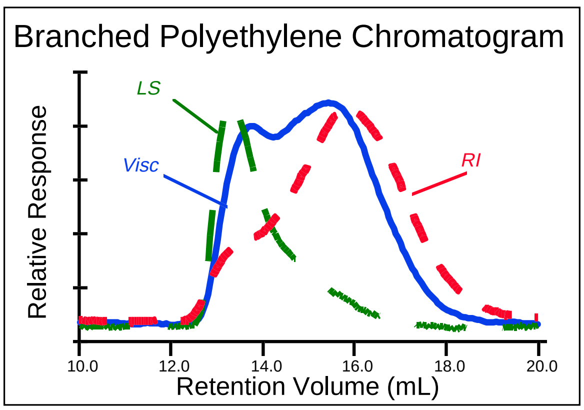
The Leader in Polymer Characterization

BRANCHED POLYETHYLENE

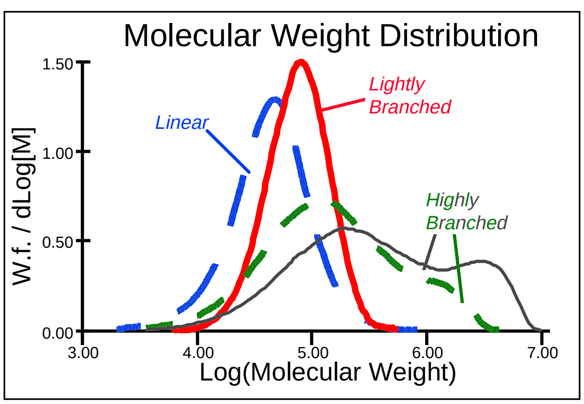
Triple Detector Application Note 2

Run Conditions
Solvent: TCB
Columns: 2 -10µ Linear Mixed Bed
Concentration: 1.4 mg/mL
Injection Volume: 210 µL
Flow Rate: 1 mL/min

Branching affects physical properties of polyolefins to a larger extent than molecular weight or intrinsic viscosity. Analysis cannot be done by conventional GPC techniques alone. Low angle light scattering measurements rely on the Universal Calibration Principle, yet molecular sizes often extend above the calibration curve, making extrapolation of properties difficult. The solution is the SEC^3 approach: molecular weight and intrinsic viscosity of polyolefins can be measured rapidly, with fewer columns.



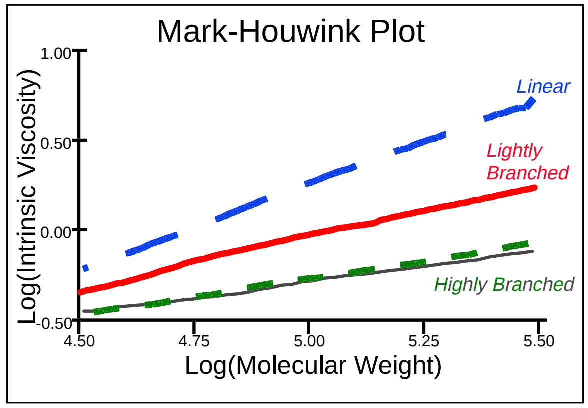
The characteristic rise in the light scattering peak with only a moderate viscosity rise compared to the refractive index peak indicates a higher ratio of molecular weight to intrinsic viscosity of the early-eluting species. Thus from the above chromatogram, one can conclude that the polyethylene's structure is more dense, meaning it is branched.



Similarly processed resins may have similar structures but different molecular weight distributions. This is clearly illustrated in the figure above, showing a polyethylene molecular weight distribution overlay.

Detectors
Viscotek Laser Refractometer
Viscotek Differential Viscometer
Laser Light Scattering Detector

The extent of polyethylene branching is determined by plotting molecular density as a function of molecular weight, a Mark-Houwink Plot as shown below.

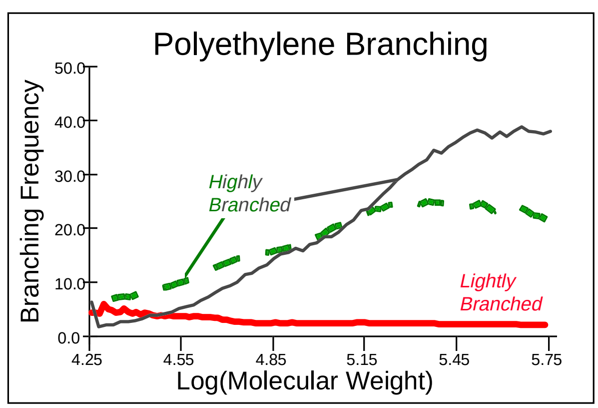


Polyethylene branching can be calculated according to the Zimm-Stockmayer equation for a randomly branched polymer:

$$g = \frac{6}{B_n}\left[\frac{1}{2}\left(\frac{2+B_n}{B_n}\right)^{\frac{1}{2}}\ln\left(\frac{(2+B_n)^{\frac{1}{2}}+B_n^{\frac{1}{2}}}{(2+B_n)^{\frac{1}{2}}-B_n^{\frac{1}{2}}}\right)-1\right]$$

where: B_n is the number of branches
$g = (IV_b / IV_l)^{1/\varepsilon}$
ε is a shape factor.

A branching frequency plot can also be generated for the polymer, as shown below.



The frequency is described as a function of molecular weight:

$$\lambda(M) = \frac{RB_n}{M}$$ where R is the repeat unit molecular weight.

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