Application Notes

Branching of PMMA

The degree of branching and its distribution in a polymer affects its physical and chemical properties. Characterization with a DAWN or miniDAWN coupled to a chromatograph provides the only direct method of determining the branching ratio, g_M, and, from a knowledge of the branching functionality, the branching frequency as a function of molecular weight. Other techniques are indirect at best, and are based on numerous assumptions.

In order to apply the column calibration approach for traditional GPC/SEC, a set of standards must be used which possess the *same* composition *and* conformation as the unknown sample. If the standards vary from the unknown in *any* respect, the calibration curve made from those standards will yield erroneous results. Thus, a compact, more spherical molecule will elute at a later time than a molecule with a random coil conformation of the same molecular weight.

Because light scattering is absolute, the branching parameters can be determined without assumptions. The branching ratio is defined simply as the ratio of the mean square radius of the branched polymer to that of the linear polymer, at the same molecular weight,

$$g_M = (\langle r^2 \rangle_b \,/\, \langle r^2 \rangle_l)$$

The molecular size and mass determined by a DAWN reflect the branching ratio directly; the greater the degree of branching relative to the corresponding linear molecule for the same molecular weight, the smaller the branching ratio.

The DAWN DSP and miniDAWN permit the measurement of the molecular weights *and* mean square radii for *both* branched and linear polymers, when used with GPC/SEC. WTC's ASTRA program calculates the g_M for polymers of different branching functionalities. ASTRA also permits g_M to be plotted as a function of molecular weight, calculates the number of branches per molecule (B_w) as well as the long chain branching frequency (λ), assuming tri- or tetra-functional branching.

One branched and one linear polymer (PMMA) were measured using a DAWN. Figure 1 shows a plot of the rms radius vs. molecular weight for both the branched and the linear polymer. Note that even though the samples cover the *same* molecular weights, they have significantly different sizes. Figure 2 shows g_M as a function of molecular weight.

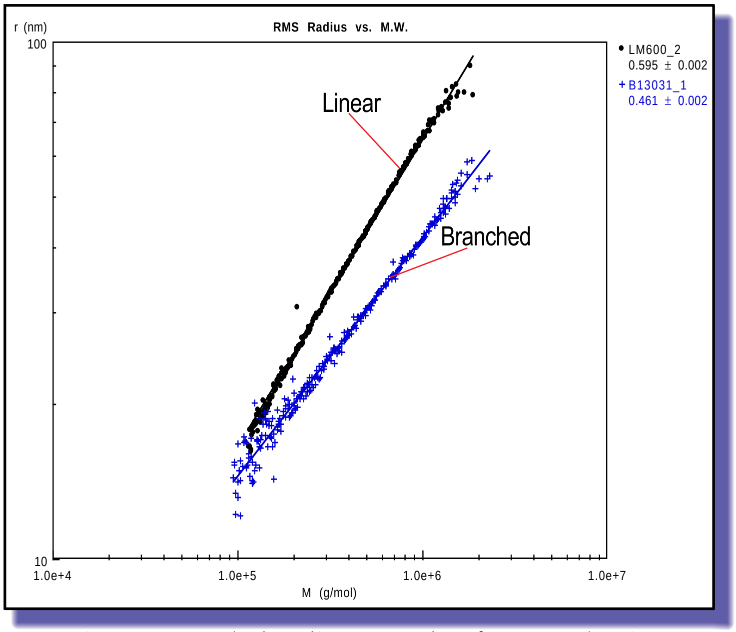

Figure 1. Branched vs. linear samples of PMMA showing identical molecular weight distributions but very different radii.

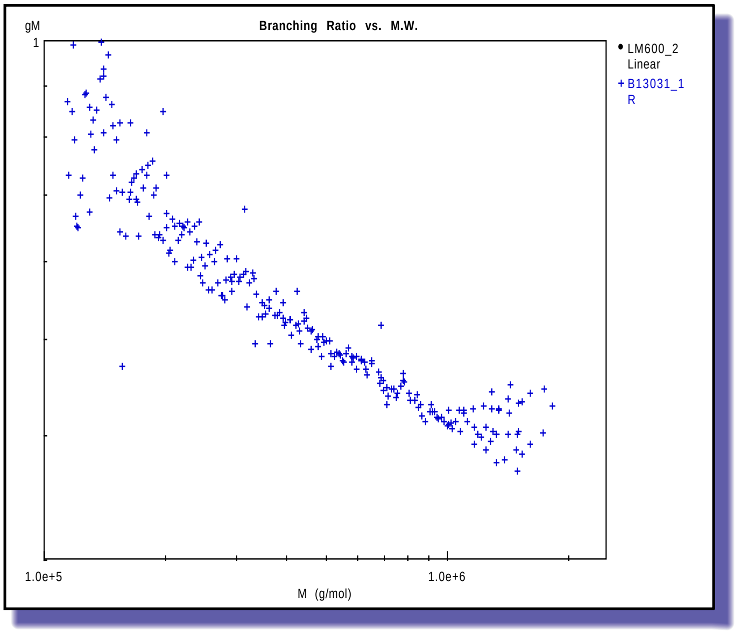

Figure 2. The branching ratio, g_m, as a function of molecular weight.

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