Star-Branched Polymers

Star-branched polymers are materials with many fascinating properties. Their compact structure enhances their mechanical properties and decreases solution viscosities, which can lead to attractive applications in the paint industry, for example. These polymers are the products of specialized polymerization reactions, which contain the branched polymer as well as the remaining linear polymer. Their properties are derived from the following:

- the ratio of linear to branched polymers
- the true molar mass distribution of both linear and branched polymers
- the degree of branching of the branched polymer. These important characteristics can be obtained readily by a single SEC-MALS measurement, as demonstrated in this application note.

Chromatograms of a mixture of linear and star-branched polymers obtained from the light-scattering and refractive index detectors are depicted in Figure 1. Both linear and branched polymers can be separated by SEC and characterized by a MALS detector, such as Wyatt Technology's DAWN EOS or miniDAWN. The ratio of linear to branched molecules and their molar mass distributions can be read from the cumulative distribution curve shown in Figure 2.

The degree of branching of the branched polymers is best characterized by branching ratio, $g_M$. It is defined as the ratio of the mean square (MS) radius, $<r^2>$, of branched polymer (br) to that of linear polymer (lin) at the same molar mass:

$$g_M = \frac{<r^2>_{br}}{<r^2>_{lin}}$$

The calculation of branching ratio of a polydisperse branched polymer requires MS radii of the same moment. A branching ratio of 0.12 was obtained for the branched polymer, which confirms the very compact structure of this polymer.

Information about branching cannot be obtained by conventional SEC. In addition, calibration with linear standards underestimates the molar mass of branched polymers significantly.

Figure 1: Chromatograms of the mixture of linear and branched polymers obtained from light scattering and DRI detectors.

Figure 2: Cumulative distribution for the same mixture of linear and branched molecules. Ratio of linear to branched molecules: 75% to 25%.