

SEC-MALS of Silicones

Polydimethylsiloxane is the world's most common silicone. Its applications range from contact lenses and medical devices to elastomers, caulking, lubricating oils and heat resistant tiles. For all of its applications, the weight-average molar mass (and its distribution) is directly associated with the performance of the product. A DAWN DSP multi-angle light scattering (MALS) detector coupled with a Size-Exclusion Chromatograph (SEC) provides the perfect tool for making molecular weight determinations without reference to standards or column calibration.

For this Note, a polydimethylsiloxane sample was analyzed by SEC in toluene, using Wyatt Technology's DAWN and an Optilab refractometer as the respective MALS and concentration detectors.

Figure 1 shows the chromatograms of polydimethylsiloxane with signals from the light scattering at 90° (top) and the RI (bottom) detectors. The RI signal is negative because the refractive index increment (dn/dc) of polydimethylsiloxane in toluene is negative. A positive signal can be obtained if the polarity of the signal output is reversed. Because the light scattering signal is proportional to dn/dc squared, its signal is positive.

By combining the DAWN and Optilab data, the absolute molar masses of this siloxane were calculated without making any assumptions about the polymer's conformation or elution time.

A polystyrene standard with a molar mass of 200kD was analyzed under the same conditions, as it is frequently used to calibrate columns for conventional chromatography. Both results are plotted in Figure 2. Even though polydimethylsiloxane is a linear polymer, just as is this polystyrene standard, the molar masses at the same elution time are *not identical* for the two polymers.

If polystyrenes had been used as calibration standards, the molar mass for polydimethylsiloxane would have been erroneous. The results once again demonstrate the power of MALS in determining *absolute* molar masses of polymers without any reference to calibration routines or polymer standards—even when those polymers appear to share the same conformation as the standards.

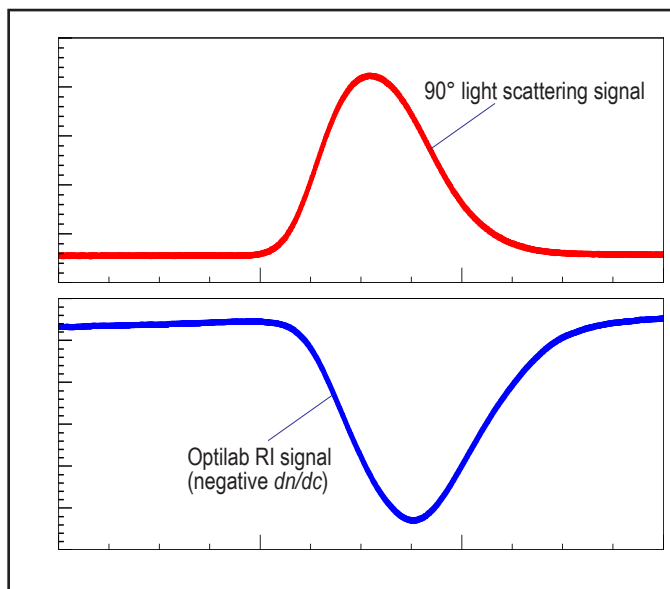


Figure 1. Chromatograms obtained by SEC of a PDMS sample with signals from the DAWN DSP (top) and the Optilab RI (bottom).

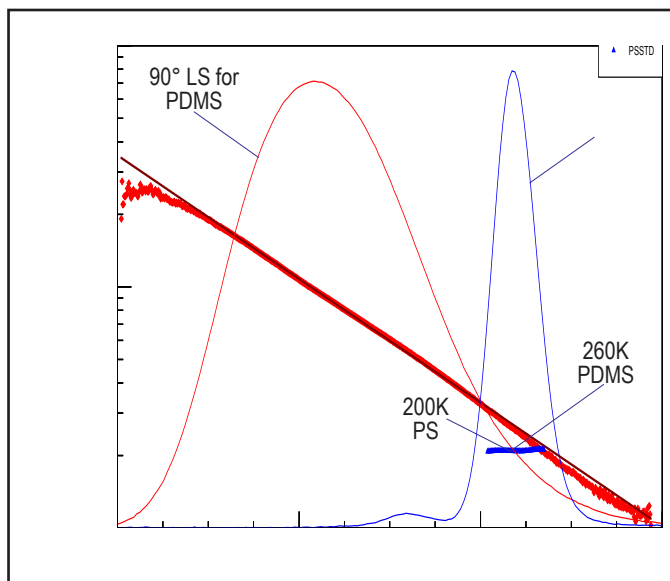


Figure 2. Plots of the molar mass versus elution time superimposed over the signals from the DAWN, for the PDMS sample and the polystyrene "standard" showing the large errors associated with conventional column calibration.



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