590b An Alternative Method for Calibrating a Size-Exclusion Chromatograph (Sec) to Measure the Molar Mass Distribution of Polyethylenes

Ryan Krenz, Eric Cheluget, and Robert A. Heidemann

The molar mass distribution of a polymer is an important quantity because the distribution of molecules affects the physical properties of the sample. Absolute measurement techniques such as static light scattering (SLS) are assumed to be more accurate than size-exclusion chromatography (SEC) but measure only one of the average molar masses and not the details of the molar mass distribution. The average molar masses measured by SLS and SEC can differ by more than 50%.

The ASTM standard (1999) for using SEC to measure the molar mass distribution of polyethylenes involves calibration using polystyrene standards. The Mark-Houwink relationship was used to convert the molar mass of the polystyrene standards into polyethylene equivalents. Average molar masses for polyethylenes obtained using this technique usually do not compare well with those obtained by absolute methods at either low or high molar masses.

Two simple modifications are suggested to improve the accuracy when using SEC for measuring the molar mass distribution of polyethylenes. The first modification is to use a combination of heavy nalkane, polyethylene, and polystyrene standards for SEC calibration instead of solely polystyrene standards. The second modification is to use the complete distribution of the standards for calibration as opposed to only their peak heights. These two modifications are practical solutions that improve the agreement between the average molar masses of polyethylenes measured by SLS and SEC.

The paper reports on the detailed process for incorporating alkane and polyethylene standards in the SEC calibration process.