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Novel high resolution high temperature GPC column

Introduction

Molecular weight is a critical characteristic of all polymers and strongly influences polymer properties. Most mechanical and rheological properties are a linear function of molecular weight. Molecular weight characterization is therefore essential for the development and manufacturing of polymeric materials.

Gel permeation chromatography (GPC), also known as Size Exclusion Chromatography (SEC), is a well-known technique for determining the molecular weight distribution of macromolecules. In GPC, the separation occurs on the basis of size. Compounds are retained for different periods of time based upon their access to the porous structure of the chromatographic packing. The smaller analyte molecules enter the pores more easily and therefore spend more time in these pores, resulting in increased retention time. Conversely, larger analyte molecules spend less time in the pores and are eluted quickly. Thus, chromatographic separation is based on hydrodynamic volume (size in solution).

During standardized GPC, sample components are dissolved in a suitable solvent, chromatographically separated based on molecular size, detected using a Refractive Index detector and compared to standards of known molecular weight. Absolute molecular weight determinations can also be performed by coupling light scattering and viscometry detection to a GPC separation.

In GPC the mobile phase serves to dissolve the sample and carry it through the column. In order to obtain a purely size based separation, a suitable combination of column stationary phase and mobile phase is necessary. Under ideal conditions, there is no interaction between the analyte molecules and the stationary phase. The separation mechanism is therefore expected to be entropically driven. Temperature affects the polymer solubility, mobile phase viscosity and therefore chromatographic performance. High temperature GPC provides a great advantage for high molecular weight and crystalline engineering polymers that requires elevated temperature for dissolution. High molecular weight polyolefines, such as polyethylene (PE) and polypropylene (PP) are in the crystalline state and insoluble in GPC solvents at room temperature. They need to be heated in the solvent to their melting point for dissolution. Typically, polyolefines are analyzed in 1,2,4-trichlorobenzene (TCB) or o-dichlorobenzene at 160 ^{o}C. High temperature GPC columns therefore should be able to be used with aggressive organic solvents at high temperatures without loss of resolution and column lifetime.

Jordi Labs has recently developed a novel packing material for high temperature GPC systems. This column packing is based on 100% divinylbenzene providing enhanced mechanical stability and utilizes a new synthetic process which results in a monodisperse polymer column packing. It is well known that broad particle size distributions in particle based columns produces variations in packing density, lowers column resolution, reduces the column permeability and generates high back pressure. New generation Jordi GPC columns prepared with monodisperse 100% divinylbenzene particles with precisely controlled particle diameter and finely controlled pore structure provide high efficiency, high separation capacity and low back pressure with greater bed stability. Scanning electron micrograph and particle size distribution of 13 µm macroporous column packing material with 10^3 A pore sizes are shown in **Figure 1**.

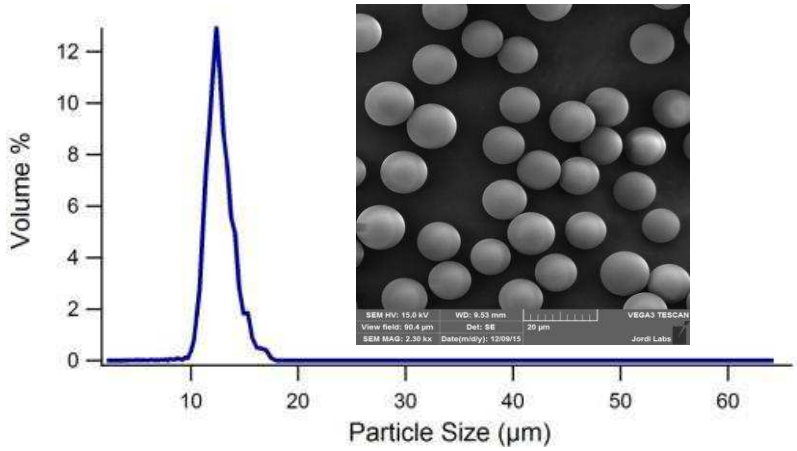

Figure 1. Scanning electron micrograph and particle size distribution of Jordi Resolve 13 µm column packing material with 10^3 Å pore size.

The uniform size distribution and perfect spherical shapes are clearly seen. In addition, Resolve columns provide a long operating lifetime due to the highly crosslinked (100% DVB) structure and can be operated at 220^{o}C without column bed degradation. This new column has the added advantage of very low bleed of fine particulates rendering it especially useful for light scattering detection. Light scattering background (0.4 mV baseline thickness, equivalent to instrument background levels) was observed with negligible amounts of spiking after less than 24 hours of column introduction, enabling high signal to noise ratios. Comparison of the RALS background with that for a leading column manufacturer reveals that Resolve columns perform equally well in terms of baseline thickness and stability (**Figure 2**).

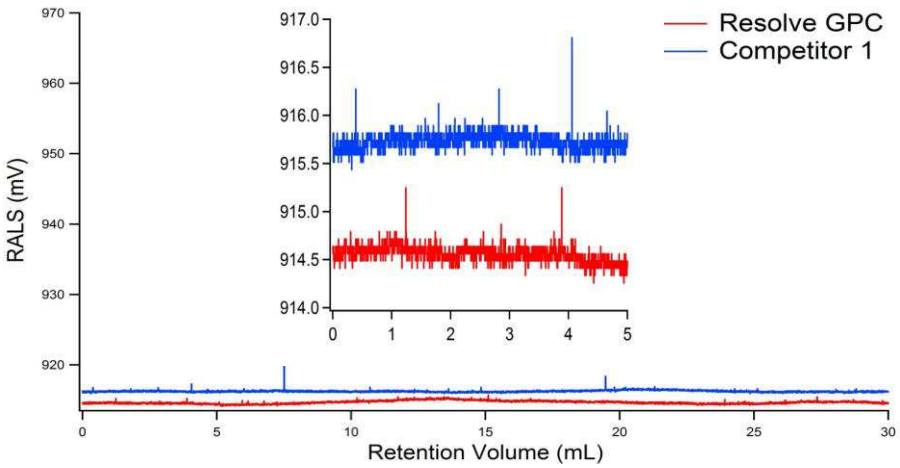

Figure 2. RALS background of Jordi Resolve13 µm (7.8 mm ID x 300 mm L) and competitor column. Mobile phase: TCB with 0.05% BHT, flow rate: 1.0 mL/min, temperature: 160 °C.

To maximize GPC resolution, the key is to use a column containing the maximum number of pores of the desired size to separate the molecular weight range of interest. New generation Jordi Resolve columns (7.8 mm ID x 300 mm L) are mixed bed columns that contain mixtures of a large number of different pore sizes in a single column allowing separation over the molecular weight range from 160 to 11,000,000 g/mol (PS equivalent), as shown in **Figure 3**, with a coefficient of determination (R^2) of 0.999 and an industry leading specification of 38,000 theoretical plates. Jordi Resolve columns yielded a better calibration curve with a higher R^2 value when compared to two leading competitor's columns of the same particle size and length (**Figure 3**).

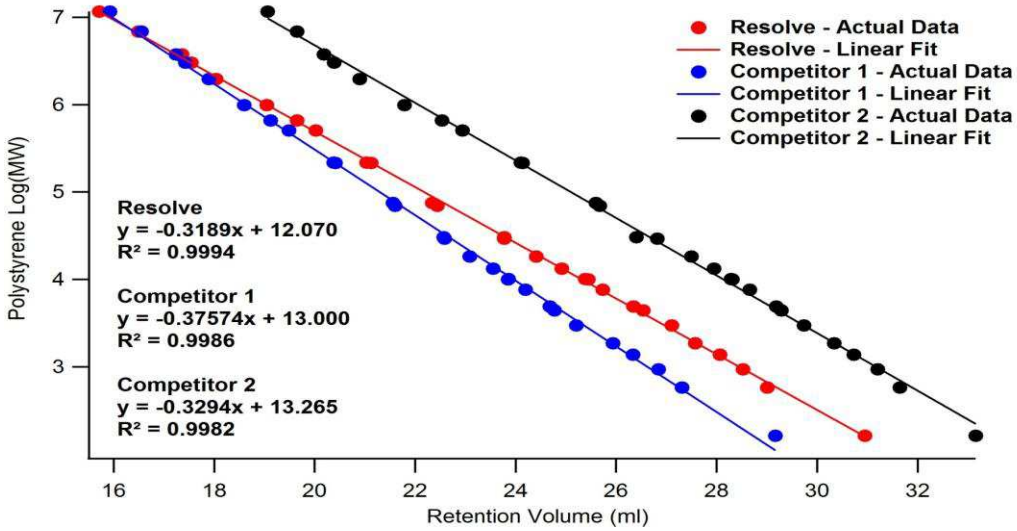

Figure 3. Comparison of the calibration curves of a three column set of Jordi Resolve 13 µm column and two competitor column sets of equal dimensions for polystyrene standards. Mobile phase: tetrahydrofuran, flow rate: 1.0 mL/min, injection volume: 100 µL.

In addition, the high pore volume of Jordi Resolve columns provides increased resolution compared to the competitor columns (**Figure 4**).

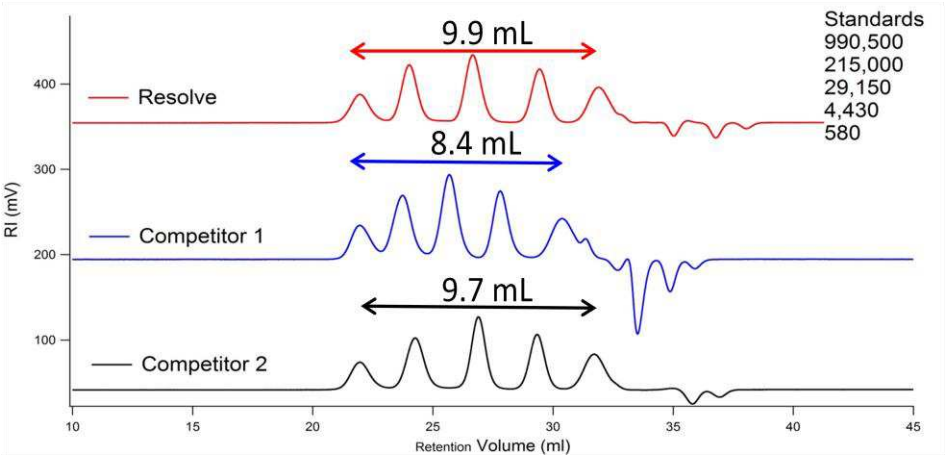

Figure 4. Overlay of chromatograms of 5 polystyrene standards obtained with three column set of Jordi Resolve (7.8 mm ID x 300 mm L) and competitor column sets of equal dimensions. Mobile phase: tetrahydrafuran , flow rate: 1.0 mL/min, injection volume: 100 µL.

Accurate blending of a large number of individual pore size gels results in a wide linear molecular weight range and smooth peak shapes. Analyses of broad distribution polymers obtained using Jordi Resolve column, as illustrated in **Figure 5**, show high resolution without any dislocations or shoulders.

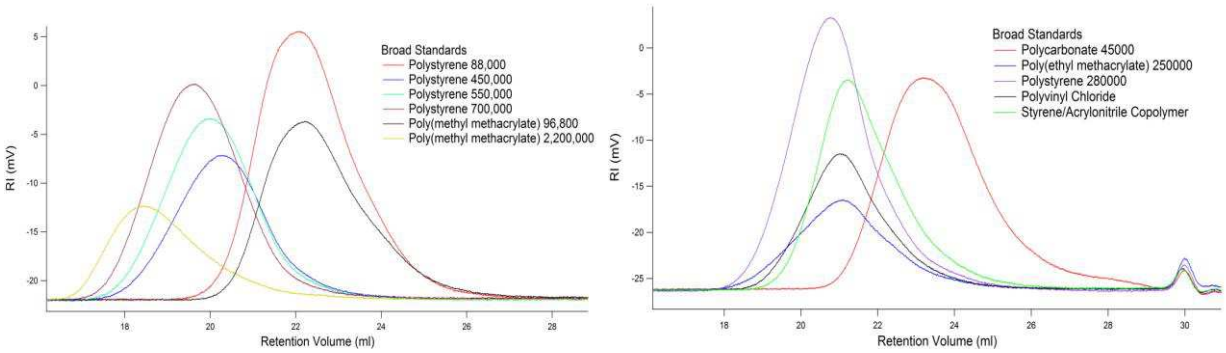

Figure 5. Analyses of broad distribution polymers. Columns: 3x Jordi Resolve 13 µm (7.8 mm ID x 300 mm L), mobile phase: TCB with 0.05% BHT, flow rate: 1.0 mL/min, injection volume: 100 µL, temperature: 160 ^{o}C.

Jordi Resolve 13 µm columns have been used to analyze a range of polyolefins including polyethylene and polypropylene in high temperature GPC.

Experimental

Analyses were performed on a Malvern GPC system equipped with differential refractive index and light scattering detectors. Three Jordi Resolve 13 µm (7.8 mm ID x 300 mm L) columns were used for chromatographic separation. The samples were dissolved in trichlorobenzene (TCB) stabilized with 300 ppm of BHT. Typical chromatographic conditions was 160 ^{o}C, 1 mL/min flow rate with a sample injection volume of 100 µL.

Results

Polyolefins often have broad molecular weight ranges characterized by high polydispersity values. Jordi Resolve 13 um mixed bed columns were designed especially for these high molecular weight, broad distribution samples. Analysis of NIST polyethylene standards including NIST 2887, 1475a and 1476a along with industry samples of polypropylene, polyethylene and polystyrene have been performed to demonstrate column performance at elevated temperatures (160^{o}C) and the related chromatograms are shown in **Figure 6**. The broad peak shape reveals the high resolution of the column and bimodal samples can be readily differentiated.

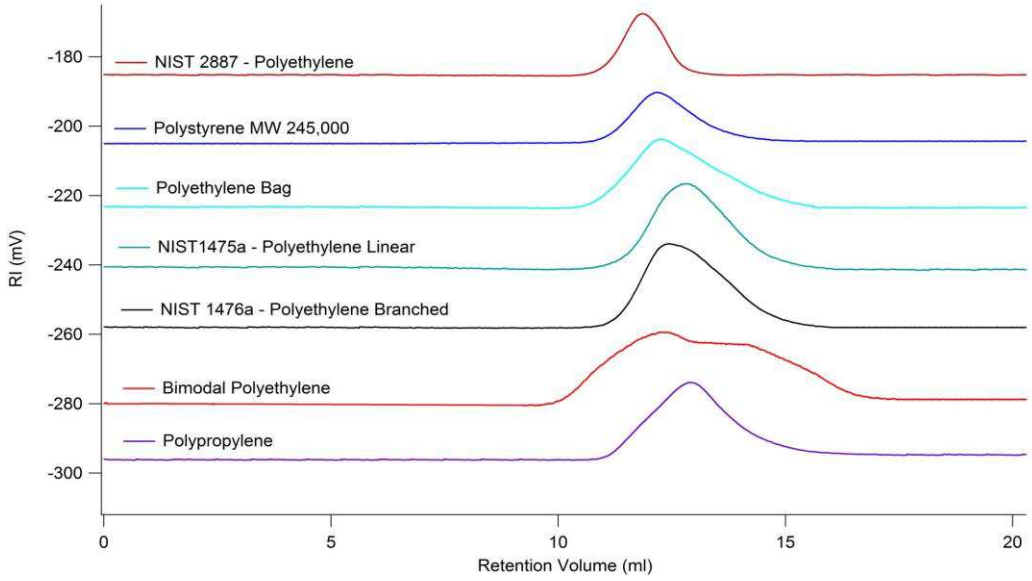

Figure 6. Analyses of NIST polyethylene standards including NIST 2887, 1475a and 1476a along with industry samples of polypropylene, polyethylene and polystyrene. Columns: 3x Jordi Resolve13 µm (7.8 mm ID x 300 mm L), mobile phase: TCB with 0.05% BHT, flow rate: 1.0 mL/min, injection volume: 100 µL, temperature: 160 ^{o}C.