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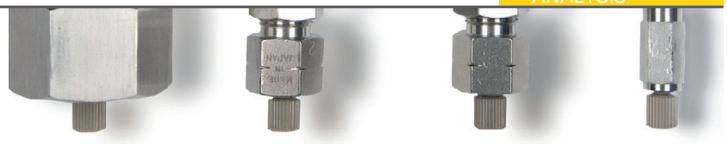

ANALYSIS OF WATER-SOLUBLE POLYMERS USING LINEAR SIZE EXCLUSION HPLC COLUMNS AND A SEMI-MICRO SEC SYSTEM

In recent years water-soluble polymers are gaining more and more interest in different applications. The molecular weight distribution of polymers is usually characterized by size exclusion chromatography (SEC) coupled with refractive index, viscometric or laser light scattering detection. Recent advances in SEC comprise semi-micro SEC and the design of linear columns providing wide molecular weight separation ranges and near-linear calibrations. We describe the separation of water-soluble polymers with a new generation of linear, polymer-based SEC columns using the compact EcoSEC SEC system.

INTRODUCTION

One of the most widely used water-soluble polymers is Polyvinylpyrrolidone (PVP). For more than 70 years it is applied in a variety of applications in medicine, pharmacy, cosmetics and industrial production. PVP binds to polar molecules exceptionally well. It supports the solubility of tablets in water, makes the glue stick adhesive and plays an essential role in the production of membranes. In ceramic, paper and dye applications, it produces visual effects such as gloss and brilliancy. As a food additive, PVP is a stabilizer (E1201). A characteristic feature of a certain polymer is its molecular weight distribution curve, which is usually obtained by SEC Analysis.

LINEAR SEC COLUMNS

The latest progress in size exclusion chromatography (SEC) column technology was the development of columns with an extended linear calibration range. A linear molecular weight calibration curve covering an extended molecular weight operation range can be obtained in different ways. The traditional and simplest way is to couple different columns, each containing particles with distinct pore size distributions. It is inevitable that the resulting calibration curve will deviate from linearity between each pore size range, resulting in irregularities in the chromatogram. Therefore mixed-bed columns were developed to overcome column mismatches. Mixed-bed columns are prepared by mixing batches of particles each containing a narrow pore size distribution. However, inflection points in chromatograms can still arise due to a mismatch of pore sizes. The latest development in SEC column design, the multi-pore particle synthesis technology can provide a real solution to avoid inflection points. Particles prepared by multi-pore technology contain a broad range of pore sizes in a single polymeric bead. This innovative approach essentially creates a linear calibration curve within each particle (Figure 1).

MULTI-PORE TECHNOLOGY

Strategies for wide range separation using Size Exclusion Chromatography

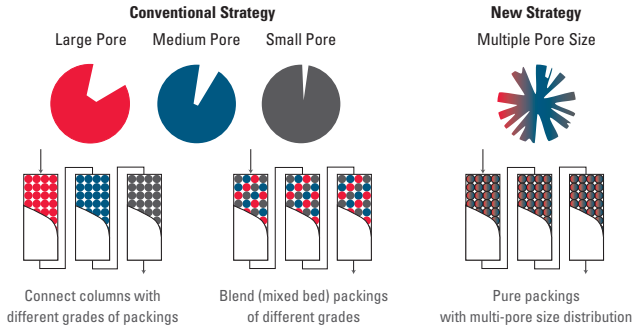

Figure 1

The multi-pore particle synthesis technology was used to design multi-pore particles of the polymethacrylate based TSKgel PW type packing for aqueous SEC. The new TSKgel SuperMultiporePW columns are packed with spherical mono-disperse polymethacrylate particles, each containing a wide range of pore sizes. Based on their small particle sizes it is possible to reach high theoretical plates at half of the length of a conventional SEC column of 30 cm length. The TSKgel SuperMultipore PW series comprises of three column types covering different molecular weight ranges (PW-N; PW-M, PW-H). They exhibit high resolution and good linearity of the calibration curves across a wide range of molecular mass of PEO and PEG standards in aqueous eluent as shown in Figure 2. With dimensions of 6 mm ID and 15 cm length they belong to the semi-micro type of SEC columns.

SEMI-MICRO SEC

Semi-micro column dimensions are advantageous in terms of shorter analysis time, lower solvent consumption and reduced solvent disposal cost. To fully exploit the advantages of semi-micro SEC columns the HPLC system needs to be optimized to minimize extra column peak broadening. This means first of all minimization of dead volume. Key components of the HPLC system with regard to dead volume reduction are the void volumes

of tubings, the detector cell volume and the void volume of the injection unit. EcoSEC is a compact, all-in-one SEC system that was designed to perform both, semi-micro and conventional SEC. Key features of the system are the low system dead volume, outstanding pump reproducibility and an extremely stable baseline of the dual flow refractive index (RI) detector. The RI detector is designed in a way that the pure mobile phase is permanently rinsing the reference site of the detector cell. The solvent in the sample site and the reference site of the cell has always the same quality and temperature. This leads to extremely stable baselines allowing a proper integration and processing of smallest peaks. The small size of the RI's detector cell (2.5 µl) minimizes peak broadening. The EcoSEC SEC system offers outstanding performance, high sensitivity and short analysis time when combined with TSKgel semi-micro SEC columns.

ANALYSIS OF WATER-SOLUBLE POLYMERS

Water-soluble synthetic polymers were analyzed using the EcoSEC SEC system with RI detection and the newly developed TSKgel SuperMultiporePW-M (5 µm particle size, 6 mm ID x 15 cm L) size exclusion column with 0.1 M $NaNO_3$ as mobile phase. Injection volume was 35 µl and flow rate 0.6 mL/min at 25 °C. Figure 3 shows the SEC analysis of a real sample - Polyvinylpyrrolidone (PVP) K-30 - on a series of conventional TSKgel G3000PW$_{XL}$ and G5000PW$_{XL}$ columns compared to the one obtained with a single TSKgel SuperMultiporePW-M semi-micro linear SEC column (MW range 600 000 – 1 500 000). When analyzed with a series of conventional SEC columns the Polyvinylpyrrolidone peak shows an inflection point, which does not appear on the SuperMultiporePW-M column. Due to its smaller particle size and the semi-micro column dimensions, analysis is much faster and more sensitive when applying the new multi-pore packing. Figure 4 shows the SEC elugrams of various water-soluble polymers obtained on a TSKgel SuperMultiporePW-M column.

CALIBRATION CURVES FOR TSKgel SuperMultiporePW

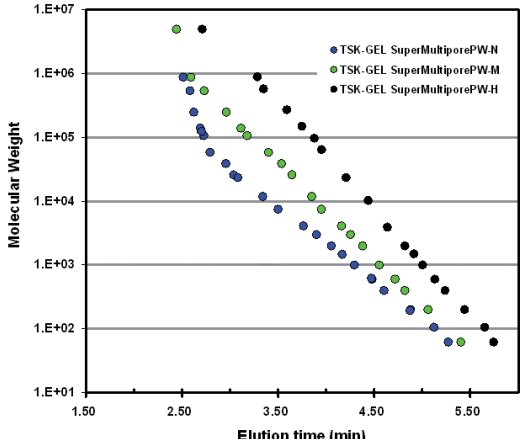

Figure 2

Mobile phase: H_2O, Flow rate: 0.6 mL/min, RI detection, 25°C,

CONCLUSION

Chromatograms obtained on TSKgel SuperMultiporePW columns show high resolution and smooth peak shapes without shoulders or inflection points, thus allowing better accuracy and reproducibility when determining the molecular mass distribution of water soluble polymers. Various polymers and oligomers were analyzed on the TSKgel SuperMultiporePW semi-micro columns. Compared with conventional SEC columns, the TSKgel SuperMultiporePW columns delivered superior results at shorter run times and lower solvent consumption. The results illustrate the advantages of these materials over traditional columns for aqueous SEC.

ANALYSIS OF POLYVINYLPYRROLIDONE

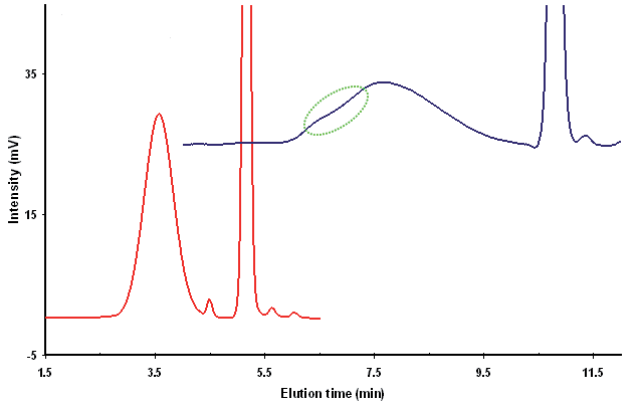

Figure 3

Columns: TSKgel SuperMultiporePW-M (6 mm ID x 15 cm L x 1) (red); TSKgel G3000PW$_{XL}$ & G5000PW$_{XL}$ (each 7.8 mm ID x 30 cm

ANALYSIS OF WATER-SOLUBLE POLYMERS

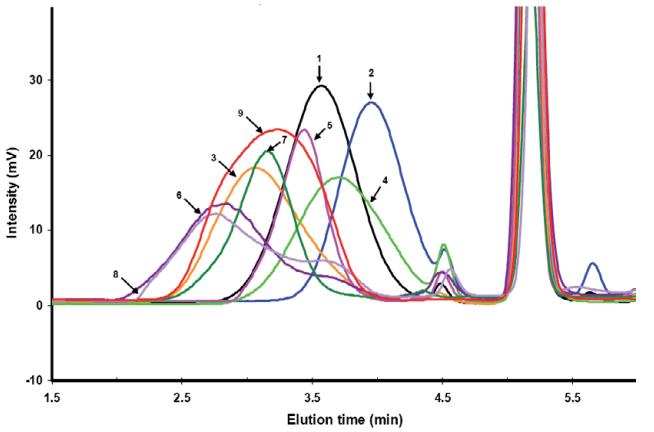

Figure 4

Column: TSKgel SuperMultiporePW-M (6 mm ID x 15 cm L), Samples: 1: polyvinylpyrrolidone (K-30), 2: polyvinylpyrrolidone (K-15), 3: hydroxypropylcellulose (200 K) 4: hydroxypropylcellulose (100 K), 5: chondroitin sulfate sodium salt, 6: carboxymethyl cellulose, 7: arabic gum, 8: poly(sulfopropyl methacrylate-co-acrylic acid), 9: dextran (200K)