Evaluation of New SEC Columns for Aqueous Cationic Polymers

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Introduction

Size exclusion chromatography (SEC) is routinely utilized to determine the molecular weight and molecular weight distribution of hydrophilic and hydrophobic synthetic and natural polymers. In general, hydrophobic and hydrophilic polymers can be analyzed with SEC columns packed with hydrophobic polymer-based particles similar to polystyrene and hydrophilic polymer-based particles such as polyacrylate, respectively.

The analysis of cationic polymers requires a high salt concentration in the mobile phase to prevent adsorption of the polymers onto the particles in SEC columns. As a result, many polymer researchers encounter low recovery when analyzing cationic polymers, as well as poor reproducibility from run to run.

For the analysis of aqueous cationic polymers, Tosoh Corporation developed three new specialty SEC columns with unique exclusion limits, TSKgel G6000PW$_{XL}$-CP, TSKgel G5000PW$_{XL}$-CP and TSKgel G3000PW$_{XL}$-CP. These columns eliminate ionic adsorption onto the particle by incorporating a cationic functionality on the particle surface. This modification results in high recovery for cationic polymers from the first injection on a fresh column.

In this poster, we report the evaluation of the three new specialty TSK-GEL SEC columns for analyzing cationic polymers. A comparison of these columns with currently available SEC columns is also included.

Experimental Conditions

TSK-GEL Columns (Tosoh, Japan):

TSKgel G6000PW$_{XL}$-CP (7.8mm ID x 30cm)
TSKgel G5000PW$_{XL}$-CP (7.8mm ID x 30cm)
TSKgel G3000PW$_{XL}$-CP (7.8mm ID x 30cm)
TSKgel G5000PW$_{XL}$ and G6000PWxl (7.8mm ID x 30cm)

Commercially available aqueous SEC column:

Brand A (7.5mm ID x 30cm, Japan)

Eluent: **- H2O (for measurement of column efficiency)**
- 0.1mol/L $NaNO_3$ (aq.) (for calibration curves and analysis of cationic polymers)

Flow rate: **- 0.25~1.0mL/min (for measurement of column efficiency)**
- 1mL/min (for analysis)

Detection: **RI (Tosoh), MALLS (Wyatt)**

Temp.: **25ºC, except MALLS measurement (40ºC)**

Samples: **Polyethylene oxides (PEO) standards**
Polyethylene glycols (PEG) standards
Cationic polymers:
Polyallylamines (PAA)
Polyethyleneimines (PEI)
Polydiallyldimethylammonium chloride (PDADMA)

All samples were dissolved in the indicated eluent. Standard polyethylene oxides (Tosoh) and PEG (Kishida Chemicals, Japan) were employed for measuring calibration curves. Cationic polymers were purchased from Kishida Chemicals (Japan).

Part I: Basic Properties

	G3000PW$_{XL}$-CP	G5000PW$_{XL}$-CP	G6000PW$_{XL}$-CP
Base Material	Polymethacrylate	Polymethacrylate	Polymethacrylate
Particle size	7µm	10µm	13µm
Exclusion limit MW	100,000	1,000,000	20,000,000*
MW range for PEO	200~50,000	400~500,000	1,000~10,000,000
Theoretical plates (N/column)	16,000	10,000	7,000
Column size	7.8mm ID x 30cm	7.8mm ID x 30cm	7.8mm ID x 30cm
Guard column size	6.0mm ID x 4cm	6.0mm ID x 4cm	6.0mm ID x 4cm

* Estimated value

Figure 1: Calibration Curves of TSK-GEL $PW_{XL}CP$-Type Columns

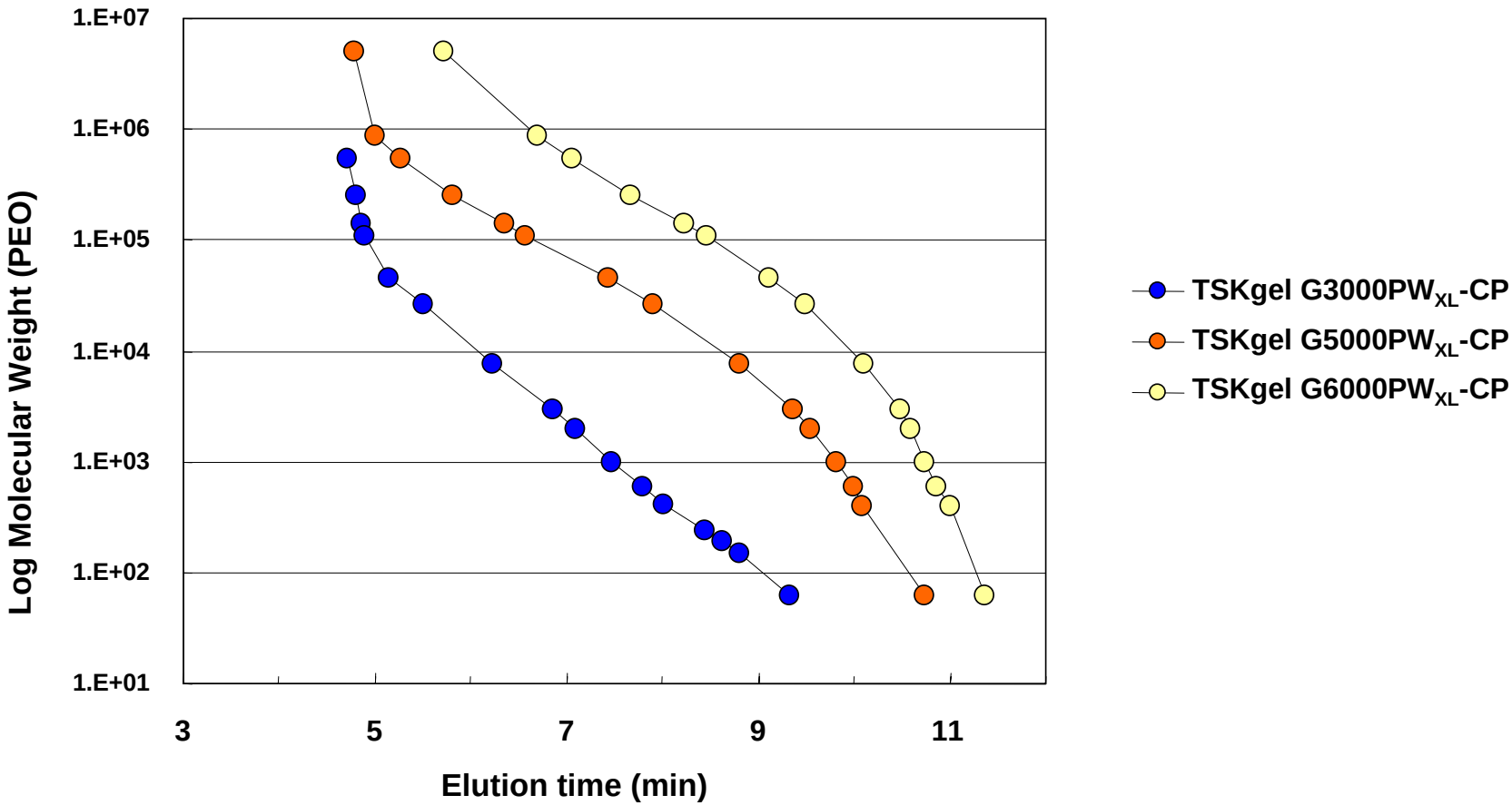
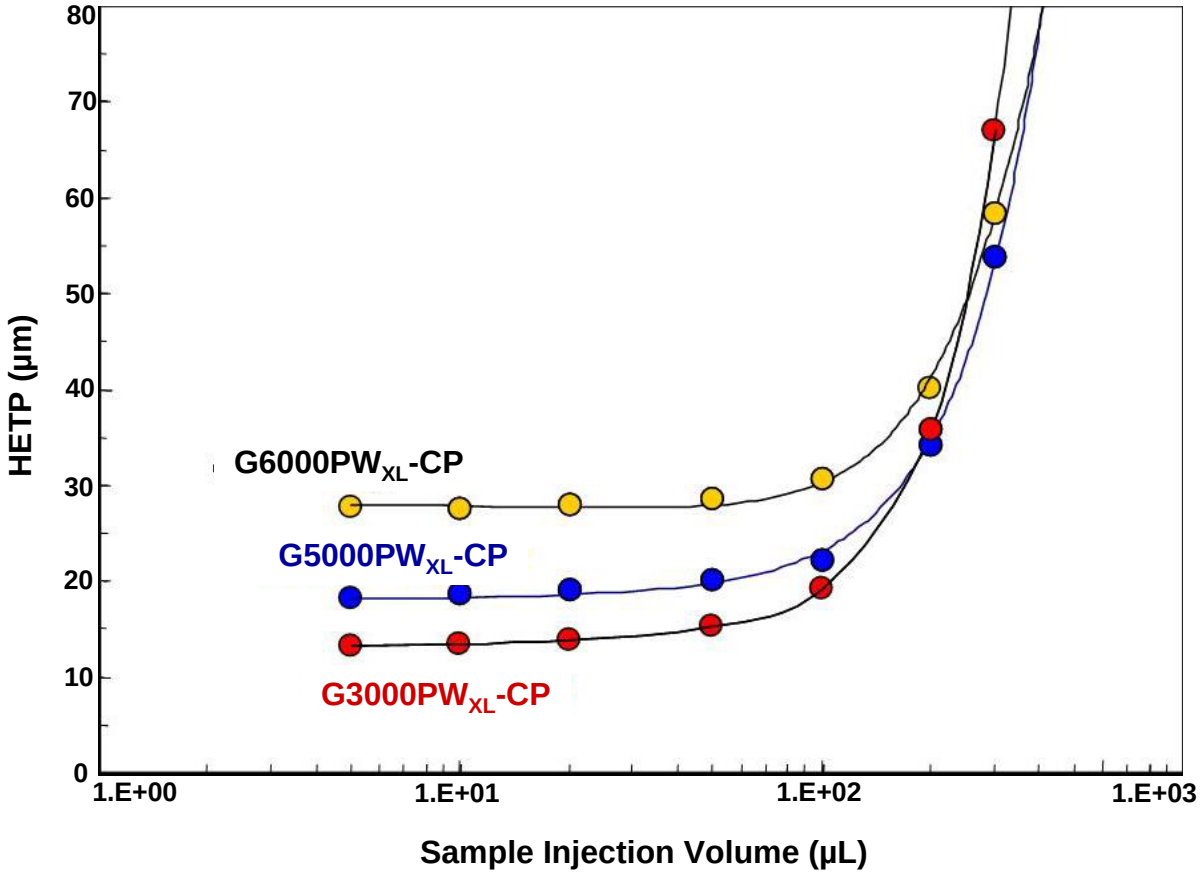
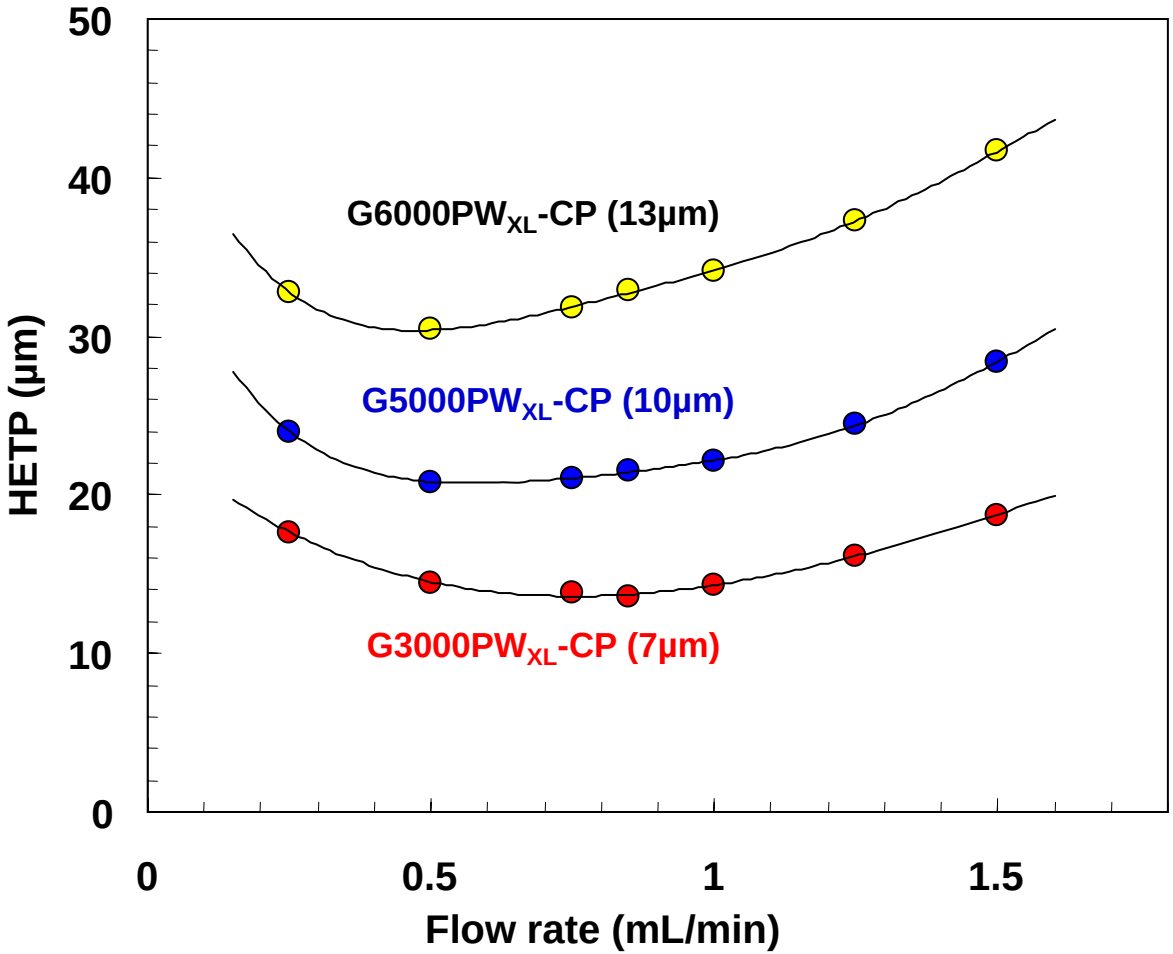


Figure 2: HETP versus Sample Injection Volume



No significant increase of HETP was observed up to ca. 100µL injection on each column. An injection volume of 10µL to 50µL is recommended.
Sample: ethyleneglycol

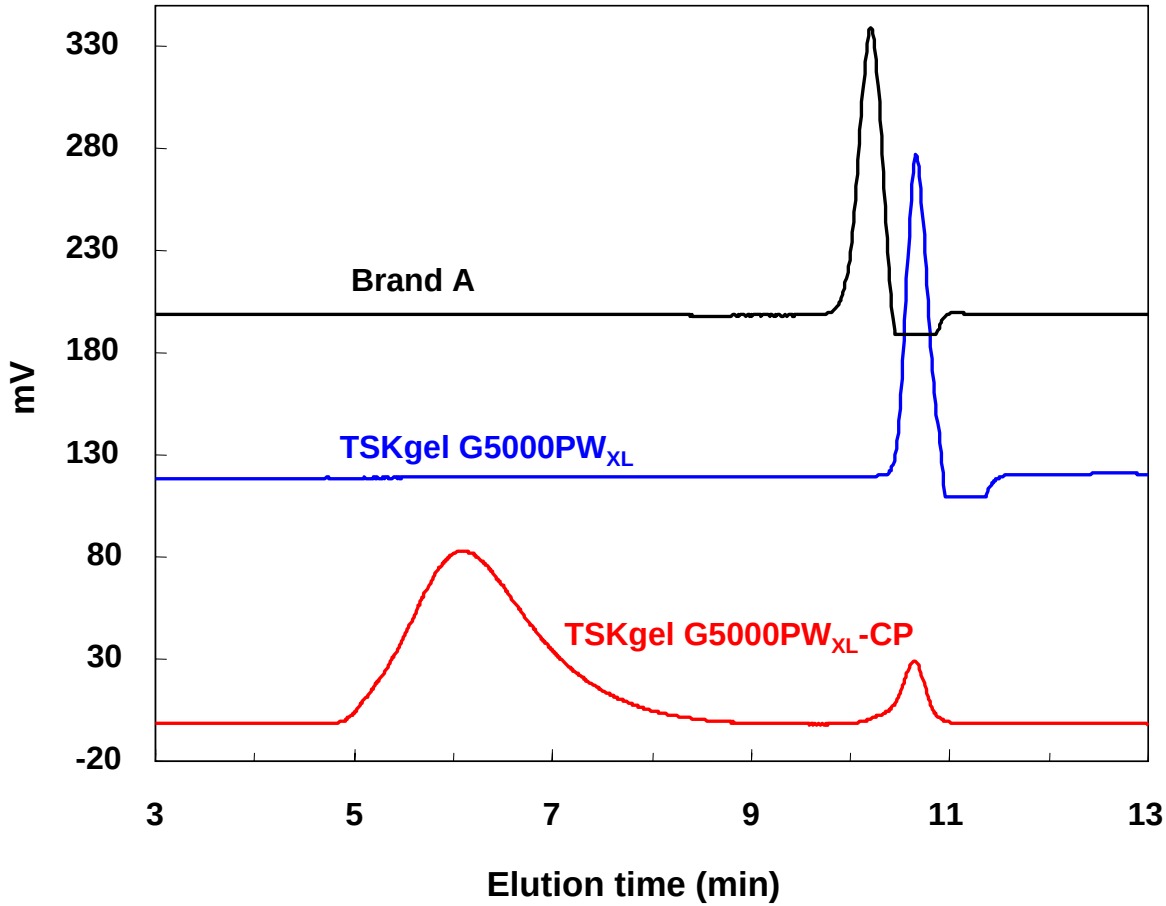
Figure 3: HETP versus Flow Rate



Optimal flow rates are 0.4-1.0mL/min.
Sample: ethylene glycol

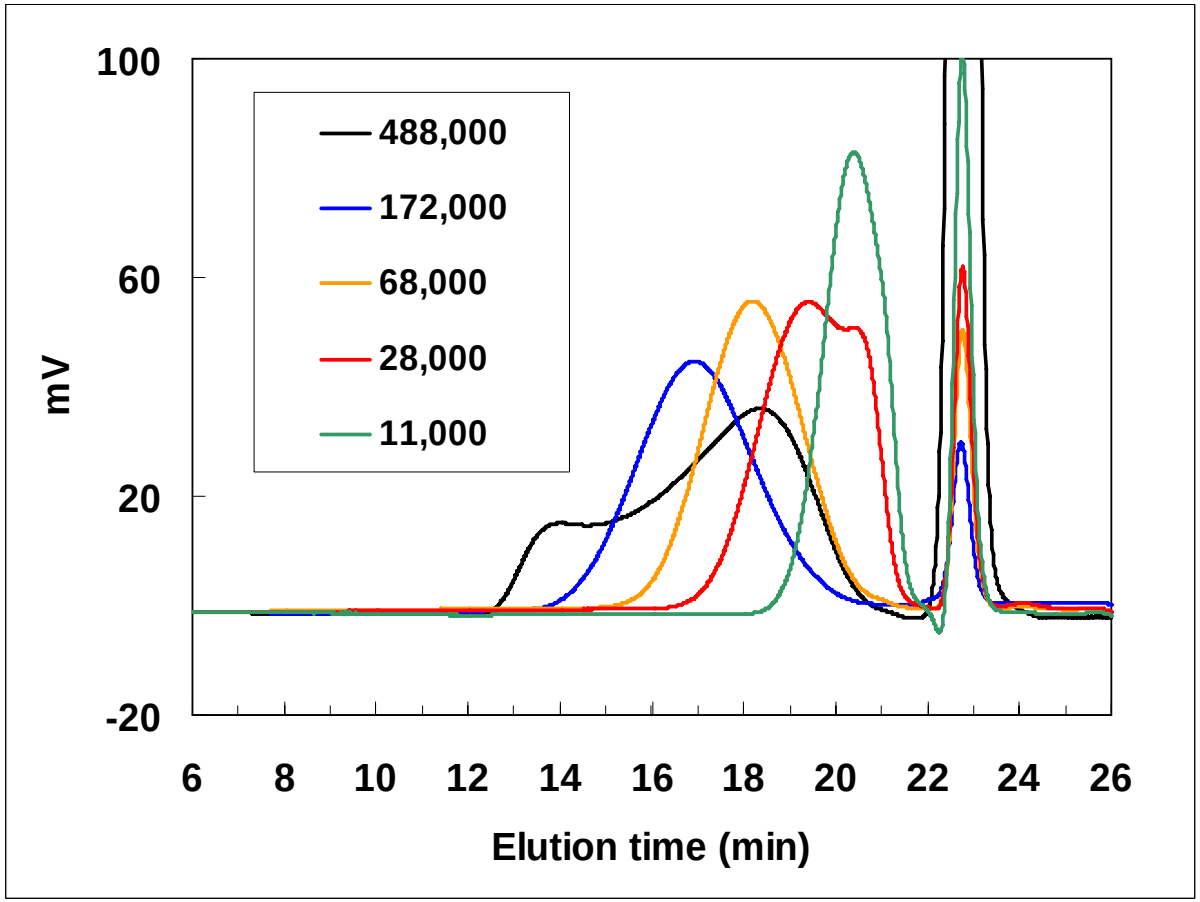
Part II: Elution Profile of Cationic Polymers

Figure 4: Chromatograms of PAA Polymer on Several Aqueous SEC Columns



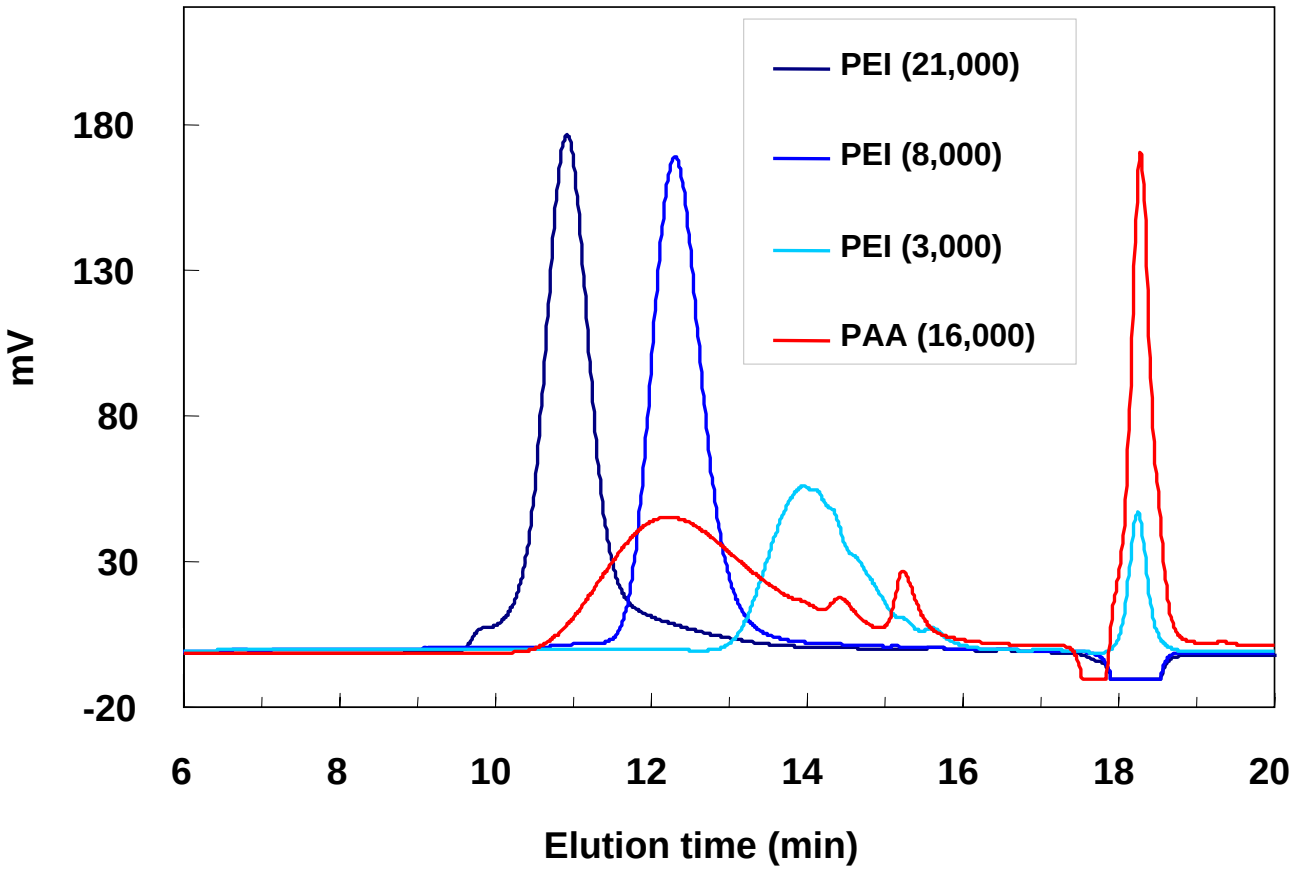
The cationic polymer was irreversibly adsorbed on both Brand A and TSKgel G5000PW$_{XL}$ columns, whereas it was eluted from TSKgel G5000PW$_{XL}$-CP column.

Figure 5: Overlaid Chromatograms of PAA Samples on TSKgel G6000PWXL-CP



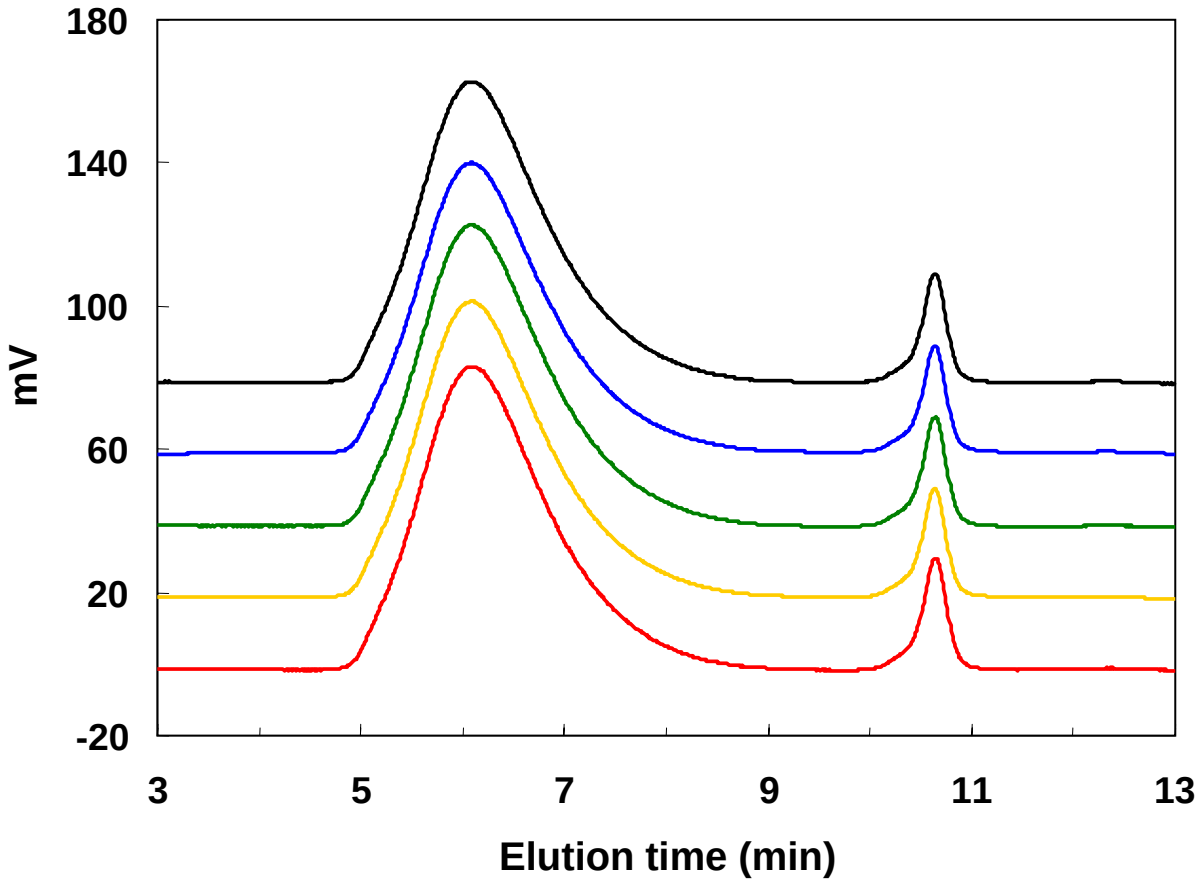
PAA samples of various molecular weights (11,000~488,000) were injected on two TSK-GEL G6000PWxl-CP columns in series. All samples were eluted at the 1st injection.

Figure 6: Elution Profiles of PAA and PEI Polymers on TSKgel G3000PWxl-CP



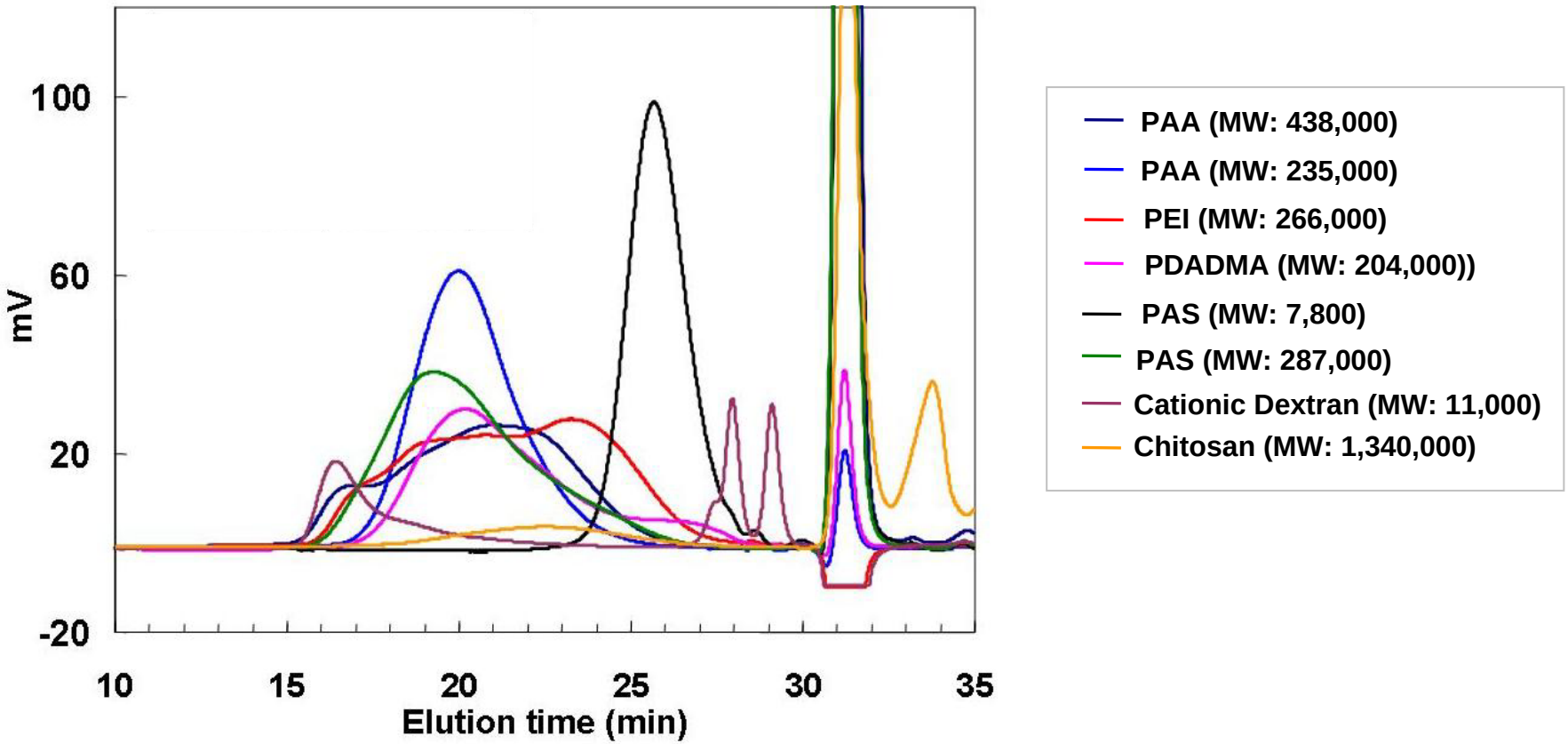
Small MW cationic polymers were analyzed on two TSK-GEL G3000PWxl-CP columns in series. The cationic polymers eluted in order of their molecular weights.

Figure 7: Reproducibility of Cationic Polymer on TSKgel G5000PW$_{XL}$-CP



PAA was injected on a TSKgel G5000PW$_{XL}$-CP column. All chromatograms (from 1st injection, red, to 5th, black) showed similar elution profiles without evidence of adsorption.

Fig.8 Elution Profiles of Various Cationic Polymers on TSKgel PW_{XL}-CP Type Columns



Various cationic polymers with different functional groups and molecular weights were injected on TSK-GEL PW_{XL}-CP type columns (TSKgel G6000PW_{XL}-CP, G5000PW_{XL}-CP and G3000PW_{XL}-CP, in series). This chromatogram demonstrates that the new SEC columns can be utilized for the analysis of a wide variety of cationic polymers.

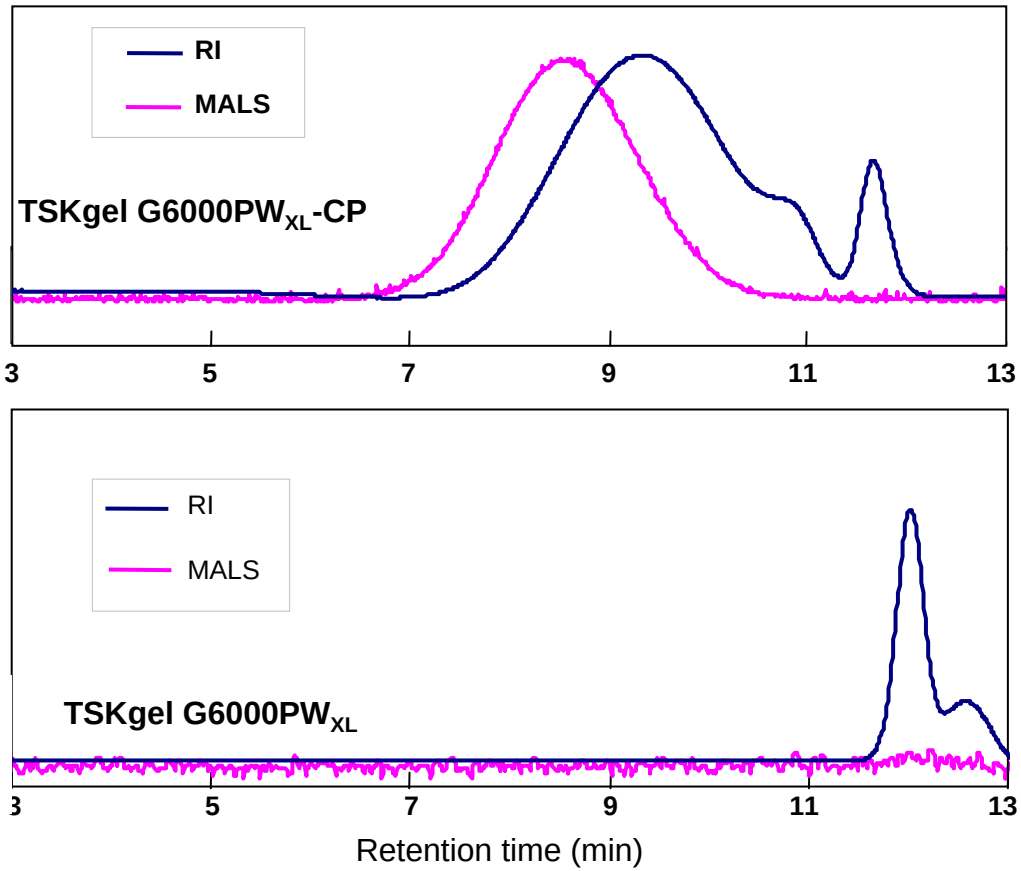
Table 2: Recovery of PAA Polymer on TSK-GEL PW_{XL}-CP Type Columns

Column	Recovery
G3000PW_{XL}-CP	**100.20%**
G5000PW_{XL}-CP	**98.80%**
G6000PW_{XL}-CP	**97.40%**

The recoveries of a PAA polymer on TSK-GEL PW_{XL}-CP type columns were measured. High recoveries (over 95%) were obtained on each column.
Sample: PAA (MW 438,000), Eluent: 0.1mol/L $NaNO_3$

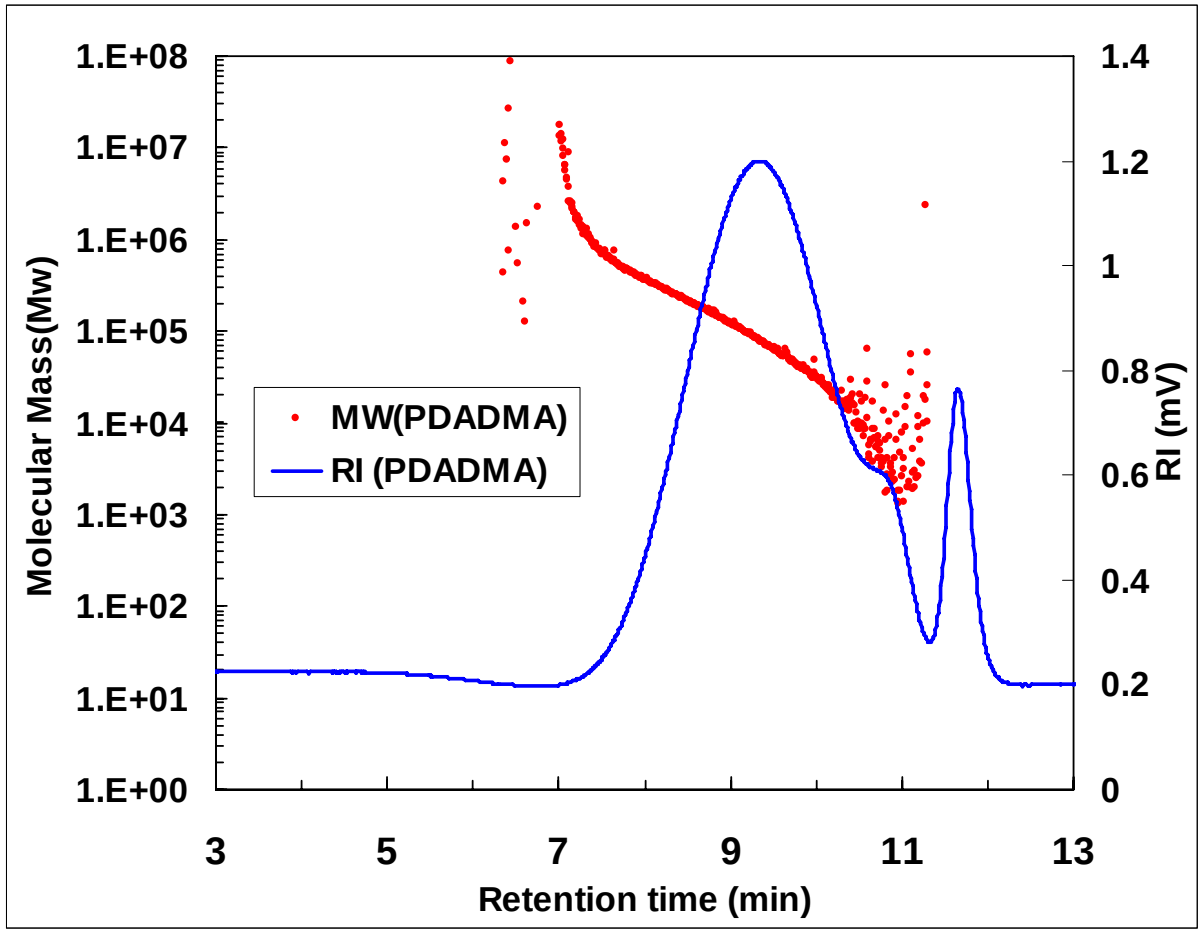
Part III: MALLS Detection of Cationic Polymer

Figure 9: Comparison of PDADMA Polymer Profile on TSK-GEL G6000PW$_{XL}$CP and G6000PW$_{XL}$ Columns



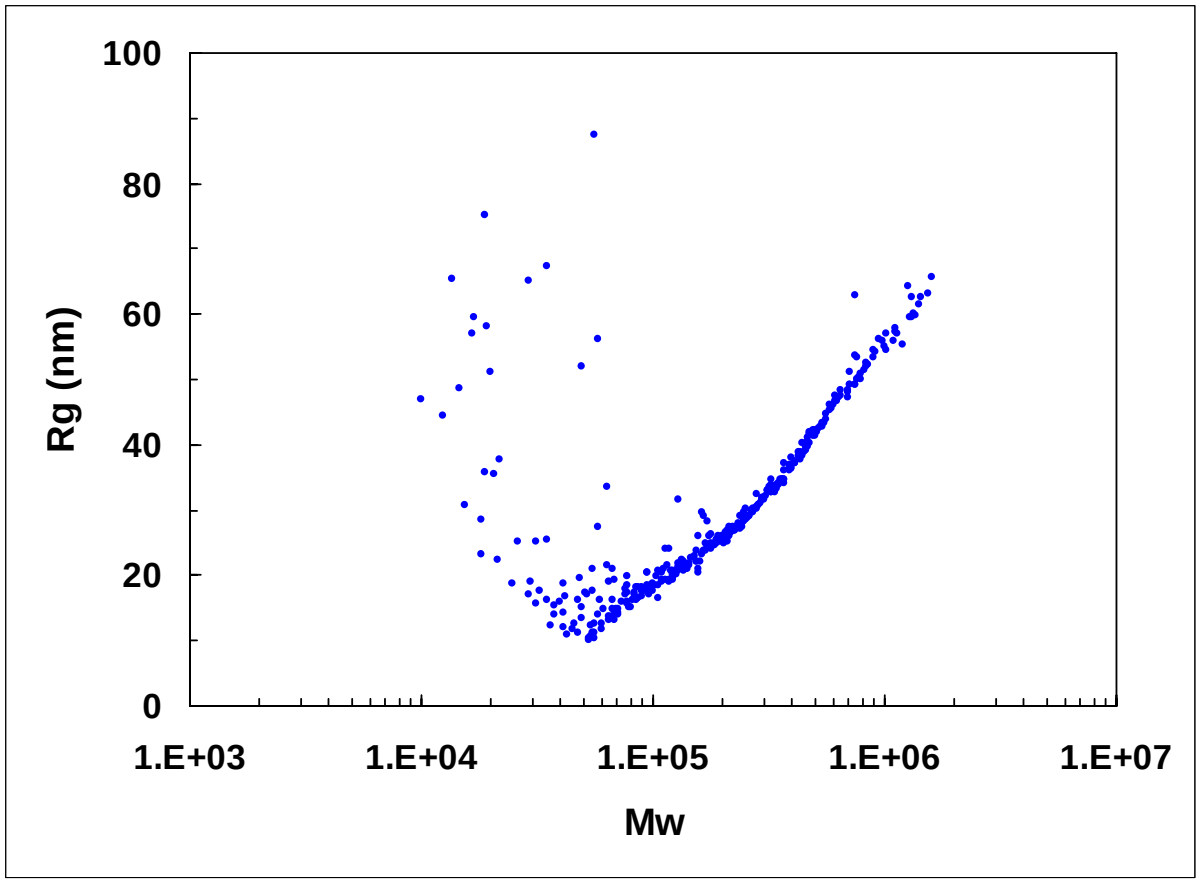
The cationic polymers (PDADMA) were measured with RI and MALLS detectors in series. No peaks except a solvent peak were observed on a TSKgel G6000PW$_{XL}$ column. On the other hand, the MALLS detection indicates that the cationic polymer eluted normally without adsorption on TSKgel G6000PW$_{XL}$-CP column.

Figure 10: Elution Profiles of PDADMA Polymer on TSKgel G6000PW$_{XL}$-CP



The profile of the molecular mass (in red) of PDADMA polymer indicates that the polymer samples eluted in order of their molecular sizes.

Fig.11 Relationship Between Radius of Giration and MW of PDADMA on TSKgel G6000PW$_{XL}$-CP



This figure shows good correlation between the radius of gyration (Rg) and molecular weight of the PDADM polymers analyzed on a TSKgel G6000PW$_{XL}$-CP column.
The measurements shown in Figs. 9-11 were completed at 40ºC and 0.1mol/L $NaNO_3$ was used as an eluent.

Conclusions

Three new TSK-GEL columns developed for the analysis of cationic polymers by size exclusion chromatography were evaluated. According to the calibration curves, the pore size distributions of each of these columns were similar to those of the commercially available TSK-GEL PW_{XL}-type SEC columns. These columns have the ability to analyze polymers having from 1 x 10 exp(4) to 1x10 exp(7) Daltons.

The optimal injection volume and flow rate were similar to those for current TSK-GEL PW_{XL}-type columns. Thus, the new columns can be operated under the same conditions.

TSK-GEL PW_{XL}-type columns, as well as another commercially available column, exhibited cationic polymer adsorption. On the other hand, the SEC columns described in this study exhibited excellent reproducibility using cationic polymers, including an absence of adsorption from the first injection on.

Recovery of the cationic polymers was excellent on the new columns for each grade, thus demonstrating that these columns will be valuable to both QC and polymer research laboratories.

The RI and MALLS detection of cationic polymers clearly demonstrate that the new SEC columns did not exhibit adsorption and ionic interaction.