No.105
SEPARATION REPORT

TOSOH

Multipore type Semi-micro Columns for Size Exclusion Chromatography (SEC) in Organic Solvent Systems: TSKgel® SuperMultipore HZ Series

— Contents —

1. Introduction

Size exclusion chromatography (SEC) is widely used for determining the molecular weight and molar mass distribution of polymers.

SEC is a method for calculating molecular weight from a calibration curve created using molecular weight standards. However, when SEC is used to analyze polymers with a wide molar mass distribution, it is necessary to use either a method where multiple columns of different pore sizes are linked together, or a method where a mixed bed column is used in which the column is packed with materials of different pore sizes at an optimized mix ratio. Problems can occur with both of these methods, including distortion of the chromatogram or deviations between the actual calibration curve and the calibration curve approximated from data obtained from the molecular weight standards. To solve these problems Tosoh has developed a mulitpore packing material in which a wide range of pore sizes are contained within a single particle (TSKgel Multipore H_{XL}-M).[1)]

With this new product, while maintaining the properties of TSKgel Multipore H_{XL}-M, Tosoh has increased performance using a packing material composed of monodisperse microparticles, and reduced column size to the semi-micro level (4.6 mm ID x 15 cm) which cuts down on solvent consumption. In addition, we have developed new multipore packing materials both for use with low molecular weight samples and oligomers, as well as for use with polymers.

In this report, the features and basic characteristics of the TSKgel® SuperMultipore HZ Series are introduced, and application examples are presented.

2. Features

The TSKgel® SuperMultipore HZ series of semi-micro columns for size exclusion chromatography (SEC) for use with organic solvent systems are packed with a material comprised of monodisperse microparticles. While maintaining the features of the TSKgel Multipore H_{XL}-M, this series of columns is able to achieve the same level of separation as the TSKgel Multipore H_{XL}-M in half the time and 1/6 the solvent consumption.

The basic properties of the TSKgel® SuperMultipore HZ series are shown in Tables 1 and 2, and the features are summarized in Table 3.

Table 1 Physical properties of TSKgel® SuperMultipore HZ Series

	TSKgel SuperMultipore HZ-N	TSKgel SuperMultipore HZ-M	TSKgel SuperMultipore HZ-H
Packing material	Poly (Styrene/divinylbenzene)	Poly (Styrene/divinylbenzene)	Poly (Styrene/divinylbenzene)
Particle size	3 μm (monodisperse particles)	4 μm (monodisperse particles)	6 μm (monodisperse particles)
Molecular weight exclusion limit (PSt/THF)	120,000	2,000,000	40,000,000*
Central pore size	8 nm	14 nm	—
Molecular mass fractionation range (PSt/THF)	300 ~ 50,000	500 ~ 1,000,000	1,000 ~ 10,000,000
Theoretical number of plates	16,000 TP/15 cm	20,000 TP/15 cm	11,000 TP/15 cm
Column size	4.6 mm I.D. x 15 cm	4.6 mm I.D. x 15 cm	4.6 mm I.D. x 15 cm
Guard column size	4.6 mm I.D. x 2 cm	4.6 mm I.D. x 2 cm	4.6 mm I.D. x 2 cm

*Estimate

Table 2 Properties of Multipore SEC columns

Product name	Number of theoretical plates (TP/column)	Asymmetrical coefficient	Column size (mm ID x cm)	Particle size (μm)
TSKgel SuperMultipore HZ-N	20,000/15 cm	0.7 ~ 1.4	4.6 x 15	3.0
TSKgel SuperMultipore HZ-M	16,000/15 cm	0.7 ~ 1.4	4.6 x 15	4.0
TSKgel SuperMultipore HZ-H	11,000/15 cm	0.7 ~ 1.4	4.6 x 15	6.0
TSKgel Multipore H_{XL}-M	16,000/30 cm	0.7 ~ 1.4	7.8 x 30	6.0

Conditions

Eluent: THF
Flow rate: 0.35 mL/min (4.6 mm ID x 15 cm)
1.0 mL/min (7.8 mm ID x 30 cm)
Temperature: 25 ºC
Detection: UV 254 nm (UV-8020 microcell)
Sample: DCHP (0.5 %)
Inj. volume: 1 μL (4.6 mm ID x 15 cm)
20 μL (7.8 mm ID x 30 cm)

3. Basic Characteristics

3-1. Pore characteristics

As shown in Tables 1 and 2, the TSKgel® SuperMultipore HZ series consists of a total of 3 types of columns: one grade for low molecular weight samples, and two columns with different molecular mass fractionation ranges for polymers.

Fig. 1 shows calibration curves created with a standard polystyrene kit (PSt Quick) using THF as the solvent.

Samples within the following molecular mass fractionation ranges can be analyzed: TSKgel SuperMultipore HZ-N can analyze low molecular weight samples between approximately 50,000 to 500; the TSKgel SuperMultipore HZ-M, polymers between about 1,000,000 and 500; and the TSKgel SuperMultipore HZ-H, approximately 10,000,000 to 1,000. Linear calibration curves are produced within each of these molecular mass fractionation ranges.

Fig. 2 compares calibration curves produced with the TSKgel SuperMultipore HZ-N for low molecular weight samples, using a series of multiple connected columns of different pore sizes (TSKgel Super HZ 4000 + 3000 + 2500 + 2000). The slope of the calibration curve in the low molecular weight region is more gradual with the TSKgel SuperMultipore HZ-N than in the series of multiple connected columns from the TSKgel® Super HZ series.

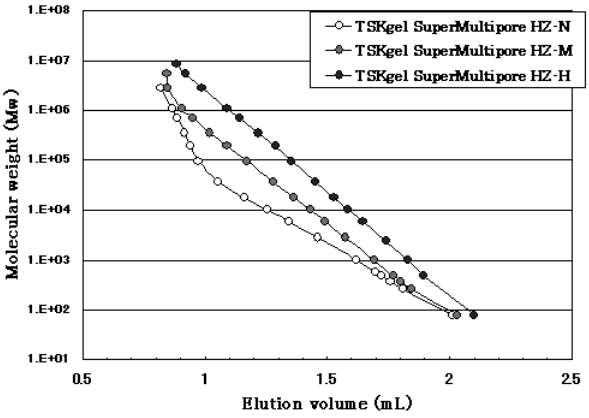

Fig. 1 Calibration curves for TSKgel® SuperMultipore HZ Series

Columns: TSKgel® SuperMultipore HZ Series (4.6mm ID x 15cm)
Solvent: THF
Flow rate: 0.35 mL/min
Temperture: 25 ºC
Sample: Standard polystyrene kit (PSt Quick kit-H) and benzene
Injection volume: 5 µL

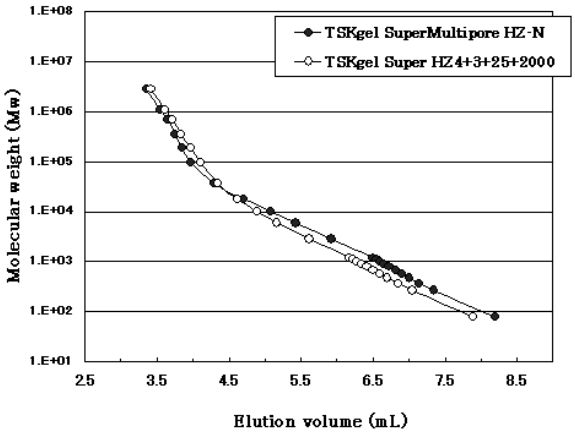

Fig. 2 Calibration curves with TSKgel SuperMultipore HZ-N and TSKgel® Super HZ Series

Columns: TSKgel SuperMultipore HZ-N
TSKgel Super HZ 4000+3000+2500+2000
(4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: 0.35 mL/min
Temperture: 25 ºC
Sample: Standard polystyrene kit (PSt Quick kit-H) and benzene
Injection volume: 5 µL

Table 3 Features of TSKgel® SuperMultipore HZ Series

Features	Advantages
1) Multipore packing material (Wide range of pores contained in single particle)	・ Calibration curves of superior linearity ・ No observable distortion on chromatograms of samples analyzed → Improved accuracy and repeatability of molecular weight data
2) Smaller particle size (monodisperse particles) packing material	・ Capable of rapid analysis with high separation performance → Capable of achieving the same separation performance as conventional columns (30 cm) in half the analysis time ・ No reduction in separation performance even in analysis at high flow rates ・ Improved robustness of column performance
3) Semi-micro column	・ Decreased solvent consumption → 1/6 the consumption of conventional (30 cm) columns
4) Can use low-adsorbent packing material	・ Can be used with a wide variety of samples

3-2. Separation performance

The TSKgel SuperMultipore HZ-N for low molecular weight samples uses a 3-μm particle size packing material, and has twice the number of theoretical plates per unit length as the general purpose TSKgel® H_{XL} series of columns for low molecular weight use. As shown in Fig. 3, the TSKgel SuperMultipore HZ-N achieves the same separation performance as the existing TSKgel® H_{XL} series in half the analysis time.

Fig. 4 compares separation of a PTMEG (polytetramethylene ether glycol) 650 oligomer with the TSKgel SuperMultipore HZ-N versus the TSKgel® Super HZ series (TSKgel Super HZ 4000 + 3000 + 2500 + 2000 and TSKgel Super HZM-N). It is clear that the TSKgel SuperMultipore HZ-N has better separation performance than either multiple columns from the TSKgel® Super HZ Series linked together or the mixed bed type of column.

The TSKgel SuperMultipore HZ-M for polymers uses a 4-μm particle size packing material, and has twice the number of theoretical plates per unit length as the TSKgel Multipore H_{XL}-M. Fig. 5 compares elution curves for a standard polyethylene kit (PSt Quick) produced by both types of columns. The TSKgel SuperMultipore HZ-M provides separation equivalent to that of the TSKgel Multipore H_{XL}-M in half the analysis time.

Fig. 6 compares separation in the TSKgel SuperMultipore HZ-N versus the TSKgel SuperMultipore HZ-M in the low molecular weight region (standard polystyrene A-500). The calibration curve is not as steep, and better separation is provided in the low molecular weight region by the small particle size (higher number of theoretical plates) TSKgel SuperMultipore HZ-N column.

Fig. 7 is a chromatogram of an epoxy resin (Mw approximately 6,000) created using the TSKgel® SuperMultipore HZ series of columns.

The best separation performance is shown by the TSKgel SuperMultipore HZ-N, the grade used for low molecular weight samples, and it is clear that the TSKgel SuperMultipore HZ-H polymer grade column does not provide adequate separation performance.

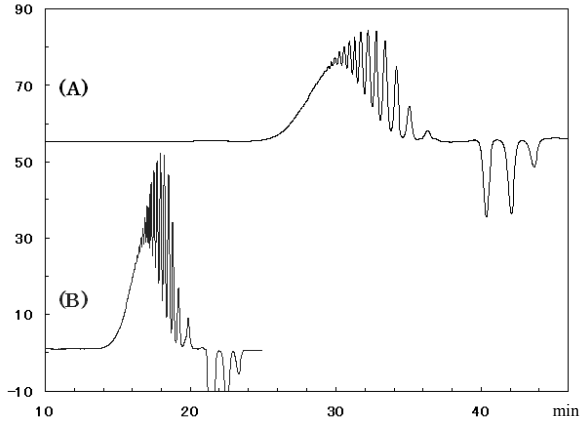

Fig. 3 Separation of PTMEG by TSKgel SuperMultipore HZ-N and TSKgel® H_{XL}

Columns: (A) TSKgel G 4000+3000+2500+2000 H_{XL} (7.8 mm ID x 30 cm) x 4
(B) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: (A) 1.0 mL/min
(B) 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: PTMEG 650 (10 g/L)
Injection volume: (A) 50 μL
(B) 10 μL

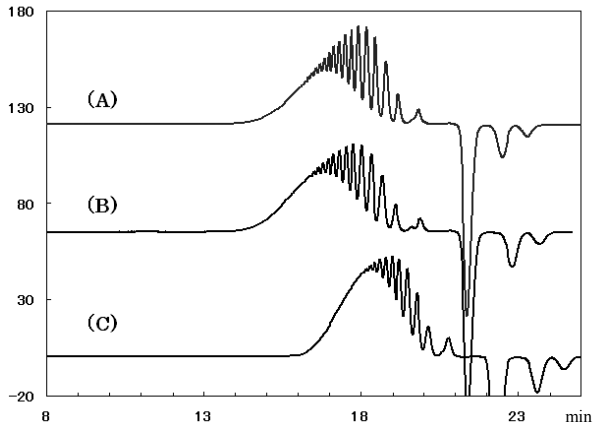

Fig. 4 Separation of PTMEG by TSKgel SuperMultipore HZ-N and TSKgel® Super HZ

Columns: (A) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 4
(B) TSKgel Super HZ 4000+3000+2500+2000 (4.6 mm ID x 15 cm) x 4
(C) TSKgel Super HZM-N (4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: PTMEG 650 (10 g/L)
Injection volume: 10 μL

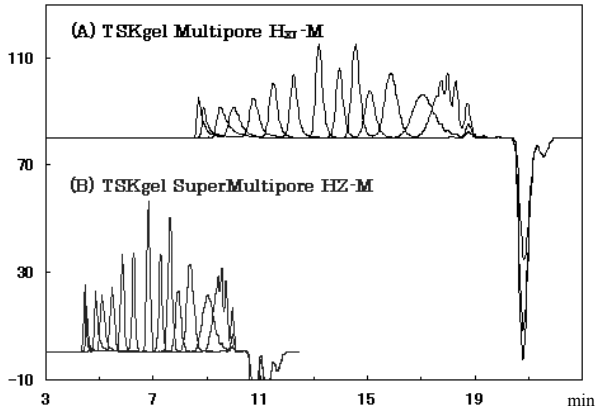

Fig. 5 Elution curves of standard polystyrene in TSKgel SuperMultipore HZ-M and TSKgel Multipore H_{XL}-M

Columns: (A) TSKgel Multipore H_{XL}-M
(7.8 mm ID x 30 cm) x 2
(B) TSKgel SuperMultipore HZ-M
(4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: (A) 1.0 mL/min
(B) 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene kit (PSt Quick kit-H)
Injection volume: (A) 50 µL
(B) 10 µL

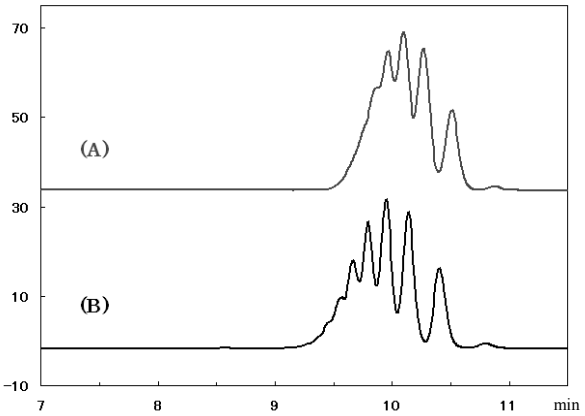

Fig. 6 Separation of standard polystyrene by the TSKgel SuperMultipore HZ-N and TSKgel SuperMultipore HZ-M

Columns: (A) TSKgel SuperMultipore HZ-M
(4.6 mm ID x 15 cm) x 2
(B) TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: UV 254 nm
Temperature: 25 ºC
Sample: Standard polystyrene oligomer (TSK standard polystyrene A-500) (5 g/L)
Injection volume: 5 µL

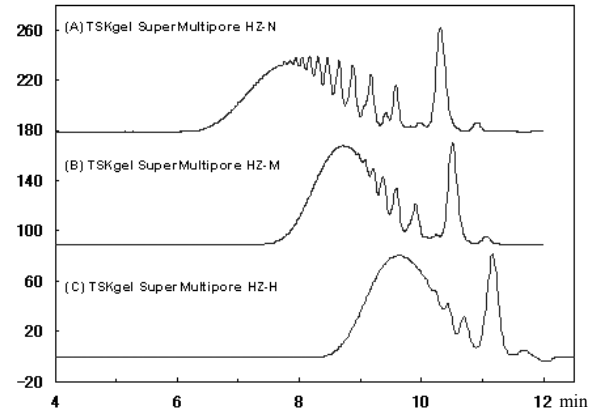

Fig. 7 Chromatograms of epoxy resin produced by the TSKgel® SuperMultipore HZ series

Columns: (A) TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
(B) TSKgel SuperMultipore HZ-M
(4.6 mm ID x 15 cm) x 2
(C) TSKgel SuperMultipore HZ-H
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: UV 254 nm
Temperature: 25 ºC
Sample: Epoxy resin (3 g/L)
Injection volume: 10 µL

3-3. Dependence of height equivalent to theoretical plate on flow rate

Fig. 8 shows the relationship between height equivalent to theoretical plate (HETP) and flow rate in the TSKgel Multipore H_{XL}-M (particle size: 6 μm) and TSKgel SuperMultipore HZ-N, M and H (particle size: 3 μm, 4 μm, and 6 μm) columns using a low molecular weight sample [dichlorohexyl phthalate (DCHP)]. The minimum HETP in the TSKgel Multipore H_{XL}-M (particle size: 6 μm) occurs when the flow rate is around 0.035 cm/sec. At higher linear velocities, HETP increases and column efficiency declines. On the other hand, in the TSKgel® SuperMultipore HZ series in which the packing is made up of monodisperse microparticles, the optimal linear velocity is higher than that of the TSKgel Multipore H_{XL}-M, making high-speed analysis possible.

Fig. 9 shows the relationship between HETP and flow rate with the TSKgel SuperMultipore HZ-H column when high molecular weight samples [standard polystyrene F-128 (Mw: 1,090,000), F-20 (Mw: 190,000), F-2 (Mw: 18,100)] and low molecular weight samples [dichlorohexyl phthalate (DCHP)] are used. With a low molecular weight sample (D), column efficiency is maintained even at a high flow rate, but as the molecular weight increases, the appropriate flow rate decreases. In general, samples with an average molecular weight of 10,000 or less can be analyzed at high flow rates, but polymer samples with a molecular weight of 50,000 or more should be analyzed at a low flow rate.

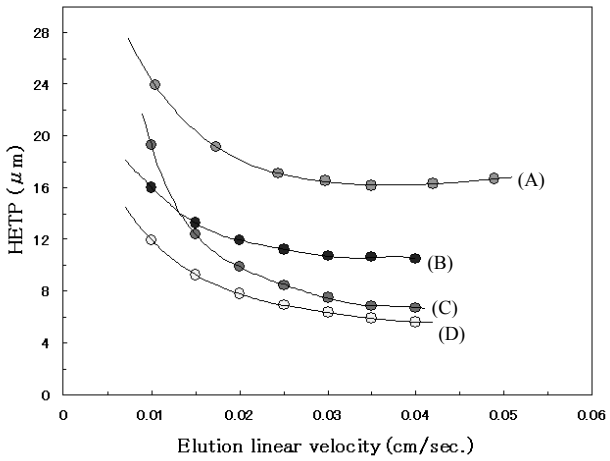

Fig. 8 Relationship between HETP and flow rate in TSKgel® SuperMultipore HZ series and TSKgel Multipore H_{XL}-M

Columns: (A) TSKgel Multipore H_{XL}-M (7.8 mm ID x 30 cm)
(B) TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm)
(C) TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm)
(D) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm)
Solvent: THF
Flow rate: 0.10 to 1.40 mL/min
Detection: UV 254 nm
Temperature: 25 ºC
Sample: Dicyclohexyl phthalate (DCHP) (5 g/L)
Injection volume: (A) 20 μL
(B), (C) and (D) 1 μL

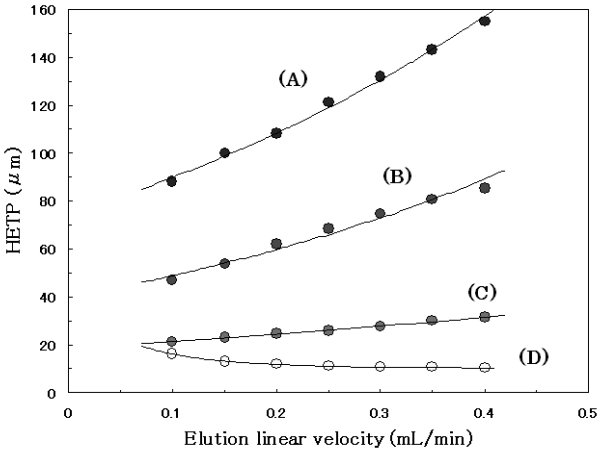

Fig. 9 Relationship between HETP and flow rate in TSKgel SuperMultipore HZ-H

Columns: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm)
Solvent: THF
Flow rate: 0.10 to 0.40 mL/min
Detection: UV 254 nm
Temperature: 25 ºC
Samples: (A) Standard polystyrene (Mw: 1,090,000) (0.25 g/L)
(B) Standard polystyrene (Mw: 190,000) (0.40 g/L)
(C) Standard polystyrene (Mw: 18,100) (0.50 g/L)
(D) DCHP (5 g/L)
Injection volume: (A), (B), (C) 5 μL
(D) 1 μL

3-4. Dependence of calibration curve on flow rate

Fig. 10 shows calibration curves obtained using standard polystyrene when the elution flow rate was varied from 0.1 mL/min to 0.35 mL/min, using the TSKgel® SuperMultipore HZ series of columns. Within the confirmed range of flow rates, no problems for SEC analysis were observed, such as overloading or shear degradation.

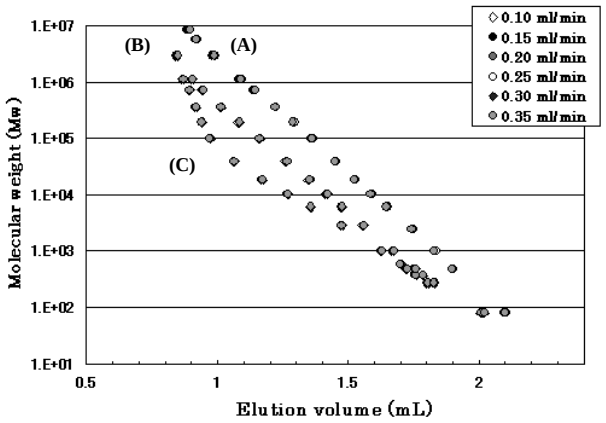

Fig. 10 Dependence of TSKgel® SuperMultipore HZ calibration curves on flow rate

Columns: (A) TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm)
(B) TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm)
(C) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm)

Solvent: THF
Flow rate: 0.10 to 0.35 mL/min
Temperature: 25 ºC
Sample: Standard polystyrene kit (PSt Quick MP-H, MP-M, and MP-N)
Injection volume: 5 µL

3-5. Effect of sample injection volume

It is well known that sample injection volume affects separation performance and molar mass distribution data. In general, the maximum sample injection volume decreases as the column size and particle size of the packing material decrease.

Fig. 11 shows the relationship between sample injection volume and HETP when a low molecular weight sample (DCHP) is used in the TSKgel® SuperMultipore HZ series. In the TSKgel Multipore H_{XL}-M, the maximum sample injection volume is about 50 µL, but in the TSKgel® SuperMultipore HZ series of columns which are packed with microparticles, the maximum sample injection volume is 5 µL.

Figures 12 and 13 show chromatograms and the separation performance of a standard polystyrene dimer/trimer, when a low molecular weight standard polystyrene (A-500) was analyzed at various injection volumes, using the TSKgel SuperMultipore HZ-N. The results shown here also indicate a maximum sample injection volume of around 5 µL.

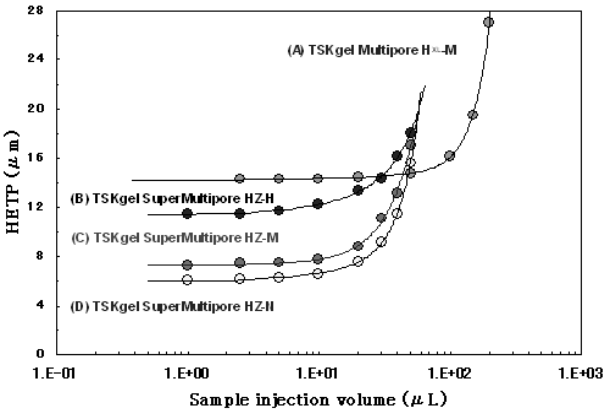

Fig. 11 Relationship between HETP and sample injection volume in TSKgel® SuperMultipore HZ series and TSKgel Multipore H_{XL}-M columns

Columns: (A) TSKgel Multipore H_{XL}-M (7.8 mm ID x 30 cm) x 2
(B) TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 2
(C) TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 2
(D) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: (A) 1.0 mL/min (B), (C) & (D) 0.35 mL/min
Detection: UV 254 nm
Temperature: Room temperature
Sample: DCHP (5 µg/L)
Injection volume: 1 to 200 µL

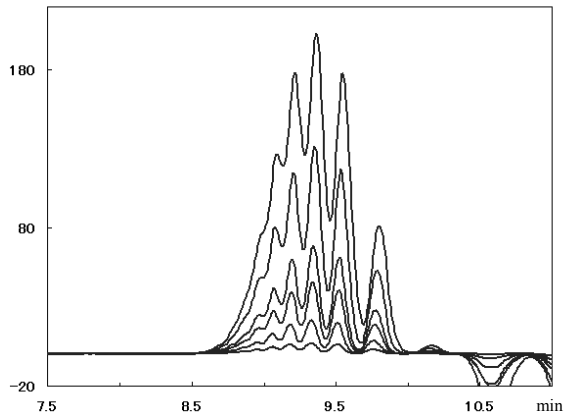

Fig. 12 Injection-volume dependence of chromatograms of standard polystyrene oligomer with TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultiporeHZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene oligomer (TSK standard polystyrene A-500)
Injection volumes: 2, 5, 10, 15, 30, and 50 µL

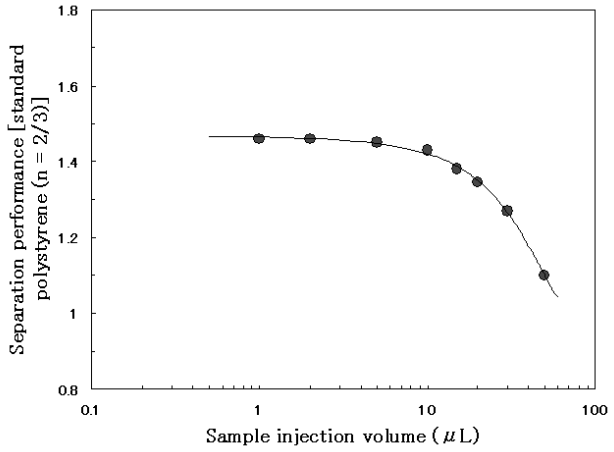

Fig. 13 Injection-volume dependence of separation performance of standard polystyrene oligomer (dimer and trimer) with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene oligomer (TSK standard polystyrene A-500)
Injection volumes: 1, 2, 5, 10, 15, 20, 30, and 50 µL

3-6. Effect of sample concentration

Changes in the sample concentration are linked to differences in mean molecular weight analysis results as well as fluctuations in separation performance. The smaller the particle size of the packing material and the greater the molecular weight of the sample, the more readily these analysis results tend to be affected. In addition, with polymers, it has been observed that hydrodynamic volume decreases and elution is delayed as the sample concentration increases.

Figures 14 and 15 show chromatograms and dimer/trimer separation performance, with standard polystyrene (A-500) samples of varying concentration, with the TSKgel SuperMultipore HZ-N. The results shown here indicate that stable and good separation performance can be obtained if the sample concentration is 10 g/L or less.

Figures 16 to 19 show mean molecular weights and chromatograms obtained of a phenol resin and an epoxy resin with analysis performed using different sample concentrations. These figures show that stable mean molecular weight values could be obtained up to a sample concentration of 20 g/L.

Figures 20 to 23 show mean molecular weight data and chromatograms obtained when an epoxy resin and polystyrene (NIST SRM706) were analyzed using the TSKgel SuperMultipore HZ-M with different sample concentrations. When an epoxy resin with a mean molecular weight (*Mw*) of approximately 20,000 was analyzed, results depended very little on sample concentration up to 4 g/L, and there were no problems with analysis. However, when polystyrene with a mean molecular weight (*Mw*) of approximately 250,000 was analyzed, delayed elution and decreased mean molecular weight were observed at sample concentrations greater than 2 g/L.

Figures 24 and 25 show how the chromatograms and mean molecular weight data vary depending on the sample concentration when an acrylic resin [mean molecular weight (*Mw*) approximately 600,000] is analyzed using the polymer grade TSKgel SuperMultipore HZ-H column. Even with the polymer grade column, a suitable concentration for a high molecular weight sample should be no more than 2 g/L.

Thus, the appropriate sample concentration will vary depending on the molecular weight of the sample, a crucial factor in optimizing the sample concentration.

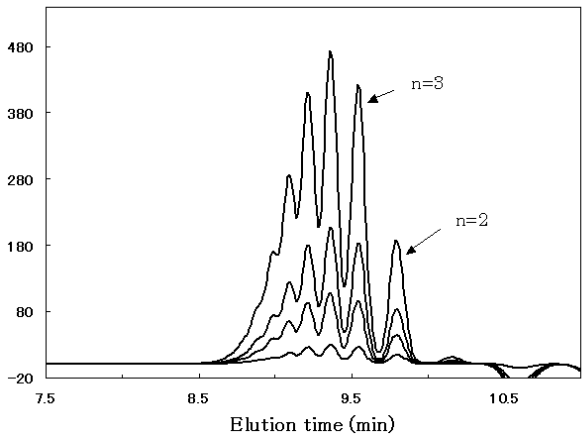

Fig. 14 Concentration dependence of chromatogram of standard polystyrene oligomer with TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene oligomer (TSK standard polystyrene A-500)
Injection volume: 15 µL
Sample concentrations: 1.2, 5, 10 and 20 g/L

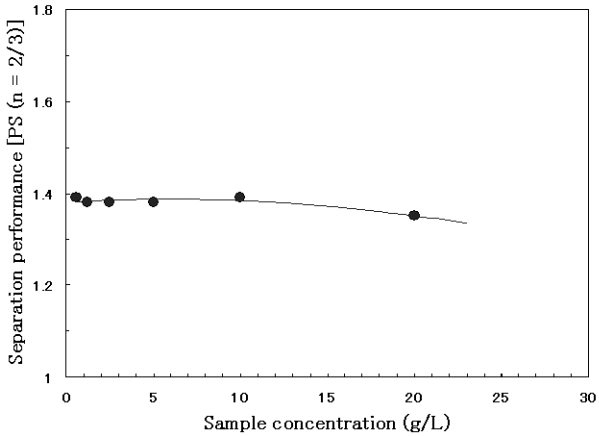

Fig. 15 Concentration dependence of separation performance of standard polystyrene oligomer with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene oligomer (TSK standard polystyrene A-500)
Injection volume: 15 µL
Sample concentrations: 0.6, 1.2, 2.5, 5, 10 and 20 g/L

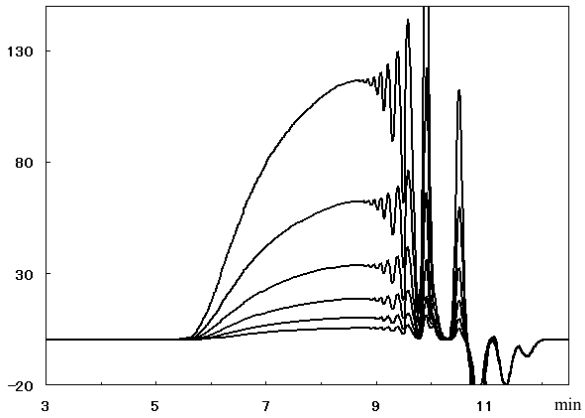

Fig. 16 Concentration dependence of phenol resin chromatogram with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (Mw: approximately 5,000)
Injection volume: 15 µL
Sample concentrations: 0.6, 1.2, 2.5, 5, 10 and 20 g/L

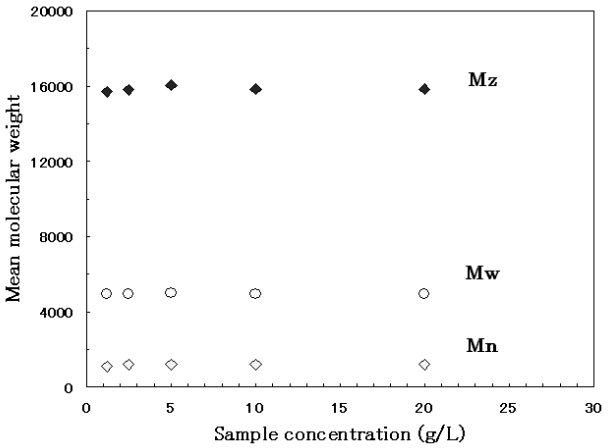

Fig. 17 Concentration dependence of molecular weight of phenol resin with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (Mw: approximately 5,000)
Injection volume: 15 µL
Sample concentrations: 0.6, 1.2, 2.5, 5, 10 and 20 g/L

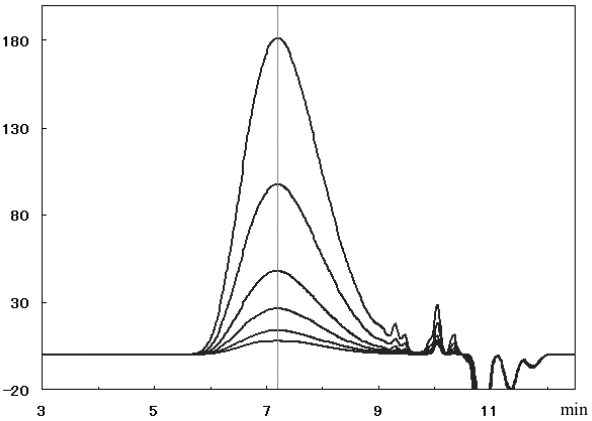

Fig. 18 Concentration dependence of epoxy resin chromatograms with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Epoxy resin (Mw: approximately 8,000)
Injection volume: 15 µL
Sample concentrations: 0.6, 1.2, 2.5, 5, 10 and 20 g/L

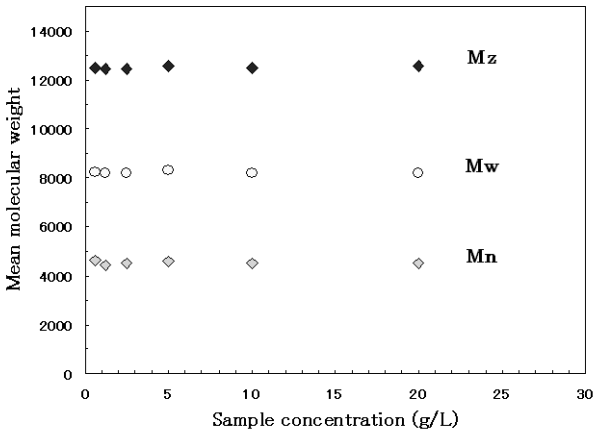

Fig. 19 Concentration dependence of molecular weight of epoxy resin using the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Epoxy resin (Mw: approximately 8,000)
Injection volume: 15 µL
Sample concentrations: 0.6, 1.2, 2.5, 5, 10 and 20 g/L

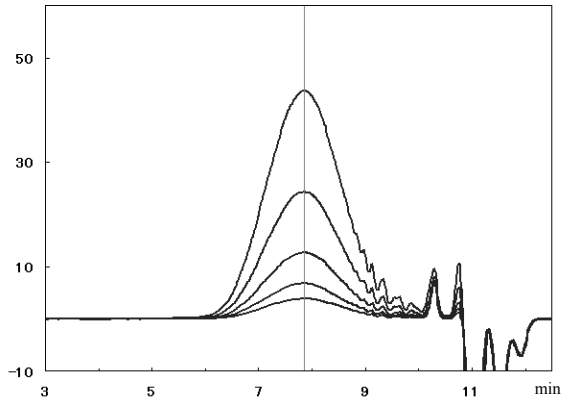

Fig. 20 Concentration dependence of epoxy resin chromatograms with the TSKgel SuperMultipore HZ-M

Column: TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Epoxy resin (Mw: approximately 20,000)
Injection volume: 15 µL
Sample concentrations: 0.5, 1, 1.5, 3, and 5 g/L

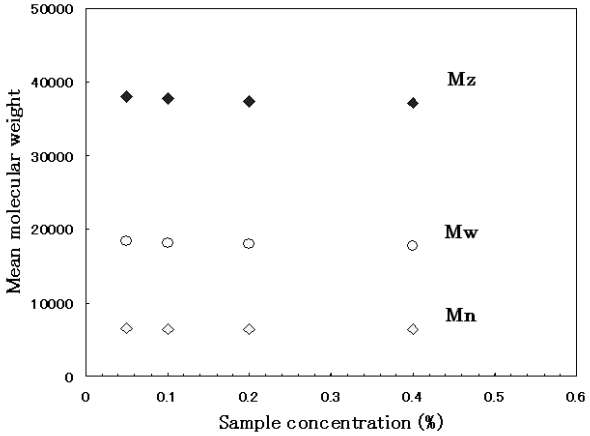

Fig. 21 Concentration dependence of molecular weight of epoxy resin using the TSKgel SuperMultipore HZ-M

Column: TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Epoxy resin (Mw: approximately 20,000)
Injection volume: 15 µL
Sample concentrations: 0.5, 1, 2 and 4 g/L

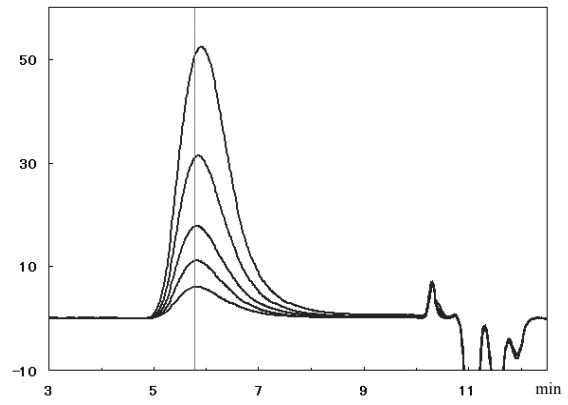

Fig. 22 Concentration dependence of polystyrene chromatograms with the TSKgel SuperMultipore HZ-M

Column: TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene (NIST SRM 706; Mw: approximately 258,000)
Injection volume: 15 µL
Sample concentrations: 0.5, 1, 2, 3 and 5 g/L

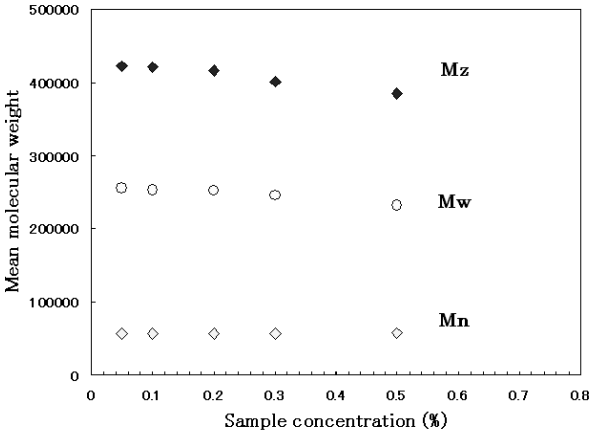

Fig. 23 Concentration dependence of molecular weight of polystyrene using the TSKgel SuperMultipore HZ-M

Column: TSKgel SuperMultipore HZ-M (4.6 mm ID x 15cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Standard polystyrene (NIST SRM 706; Mw: approximately 258,000)
Injection volume: 15 µL
Sample concentrations: 0.5, 1, 2, 3 and 5 g/L

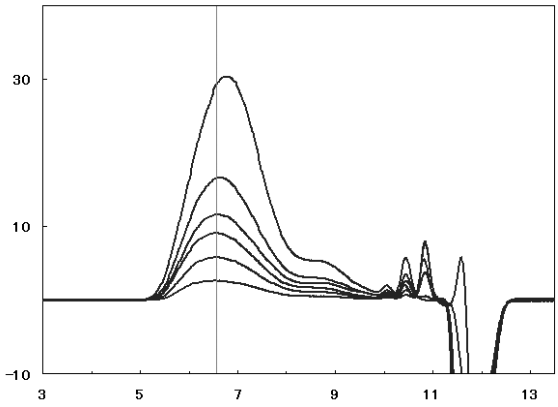

Fig. 24 Concentration dependence of acrylic resin chromatograms with the TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Acrylic resin (Mw: approximately 600,000)
Injection volume: 15 µL
Sample concentrations: 0.3, 0.6, 1.2, 2, 3, and 5 g/L

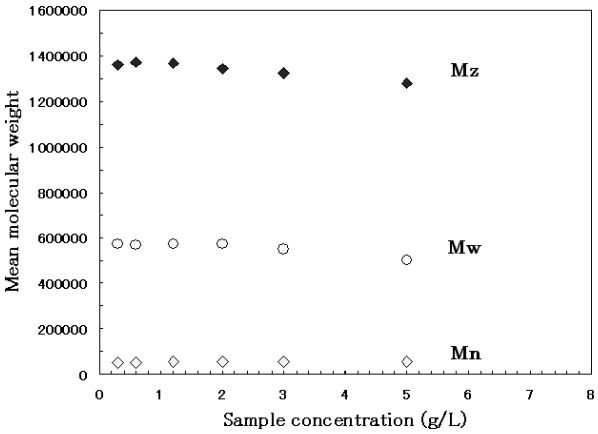

Fig. 25 Concentration dependence of molecular weight of acrylic resin with the TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H
(4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Detection: RI
Sample: Acrylic resin (Mw: approximately 600,000)
Injection volume: 15 µL
Sample concentrations: 0.3, 0.6, 1.2, 2, 3, and 5 g/L

3-7. Unevenness of chromatogram

The most important feature of multipore SEC columns is that their pore characteristics (pore structure) eliminate the unevenness that is observed in chromatograms produced by a connected series of multiple columns of varying pore sizes, or by a mixed bed type of column in which packing material of different pore sizes is used.

3-7-1. TSKgel SuperMultipore HZ-N

Fig. 26 shows chromatograms of phenol resin produced with the TSKgel SuperMultipore HZ-N, and with the TSKgel Super HZ (3000 + 2500 + 2000) series. Distortion appears on the chromatogram produced with the TSKgel® Super HZ Series (B), which does not appear with the TSKgel SuperMultipore HZ-N (A).

Figures 27 and 28 show chromatograms of various phenol resins produced with the TSKgel SuperMultipore HZ-N and the TSKgel Super HZ (3000 + 2000). In Fig. 28, which was created using the TSKgel Super HZ (3000 + 2000), distortions are seen on the chromatogram at a specific elution time with each sample at various molecular weights. On the other hand, with the TSKgel SuperMultipore HZ-N (Fig. 27), no distortion is observed on the chromatogram with any of the samples.

Table 4 shows mean molecular weight and polydispersity data when various silicone resins are analyzed with the TSKgel SuperMultipore HZ-N as well as with commercially available columns (4000 and 2000-grade columns linked together), using packing materials from different lots (2000 grade for the commercially available columns). As is clear from the table, there is less difference in the mean molecular weight data resulting from using packing material of different lots with the TSKgel SuperMultipore HZ-N, a multipore type of column, than occurs with the commercially available columns. Moreover, Fig. 29 shows chromatograms of silicone resin produced using the TSKgel SuperMultipore HZ-N. No marked differences between the chromatograms are apparent, and it is clear that there is very little difference between lots.

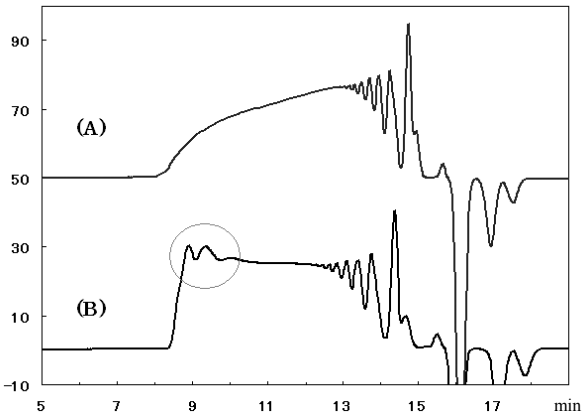

Fig. 26 Chromatograms of phenol resins created with the TSKgel SuperMultipore HZ-N and TSKgel® Super HZ Series

Column: (A) TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 3
(B) TSKgel SuperHZ 3000+2500+2000 (4.6 mm ID x 15 cm) x 3
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

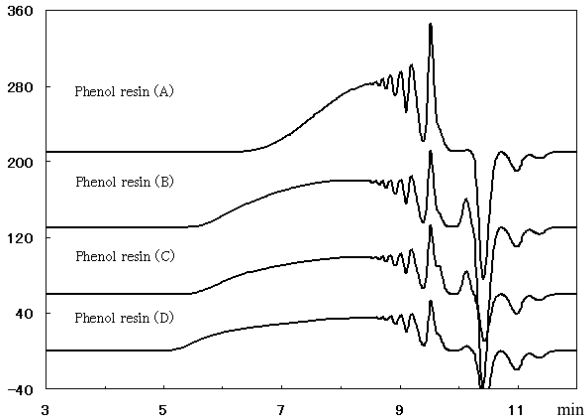

Fig. 27 Chromatograms of various phenol resins created with the TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

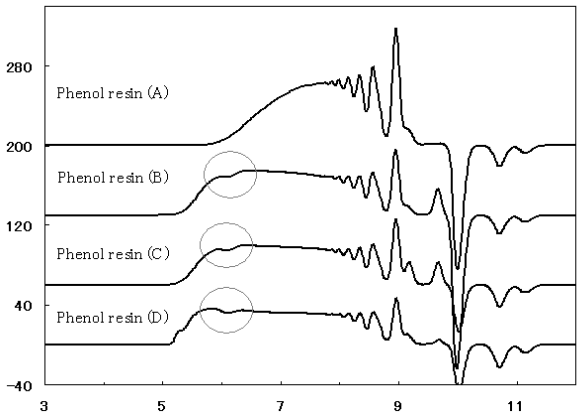

Fig. 28 Chromatograms of various phenol resins with TSKgel® Super HZ columns

Column: TSKgel Super HZ3000+2000 (4.6 mm ID×15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

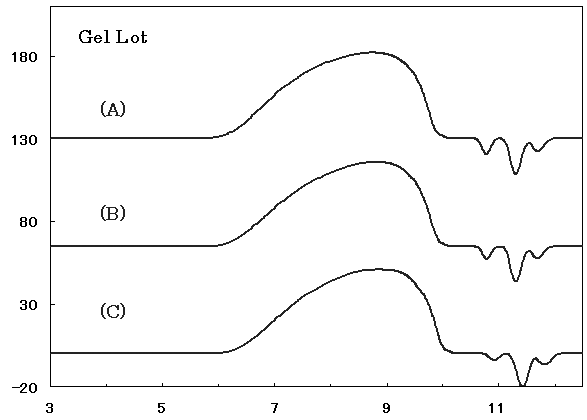

Fig. 29 Chromatograms of silicone resins created with TSKgel SuperMultipore HZ-N

Column: TSKgel SuperMultipore HZ-N (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Silicone resin (3 g/L)
Injection volume: 10 µL

Table 4 Mean molecular weight of silicone resin analyzed by TSKgel SuperMultipore HZ-N and commercially available columns using different lots

Column (Gel Lot)	Mean molecular weight			Polydispersity	
	Mw	Mn	Mz	Mz/Mw	Mw/Mn
TSKgel SuperMultipore HZ-N (A)	3,410	1,340	7,750	2.27	2.54
TSKgel SuperMultipore HZ-N (B)	3,400	1,340	7,740	2.28	2.54
TSKgel SuperMultipore HZ-N (C)	3,430	1,350	7,850	2.29	2.54
Ave. (RSD)	3,410 (0.37%)	1,340 (0.35%)	7,780 (0.64%)	2.28 (0.36%)	2.54 (0.00%)
Commercially available column (4000 + 2000 grade) (A)	3,430	1,330	7,640	2.23	2.58
Commercially available column (4000 + 2000 grade) (B)	3,480	1,310	7,990	2.3	2.66
Commercially available column (4000 + 2000 grade) (C)	3,370	1,270	7,850	2.33	2.65
Commercially available column (4000 + 2000 grade) (D)	3,540	1,320	7,710	2.18	2.68
Ave. (RSD)	3,455 (1.81%)	1,310 (1.74%)	7,800 (1.72%)	2.26 (2.60%)	2.64 (1.43%)

Column: (4.6 mm I.D. x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI (HLC-8220 GPC)
Temperature: 40 ºC
Sample: Silicone resin (3 g/L) 10 µL

3-8-2. TSKgel SuperMultipore HZ-M

Figures 30 and 31 show chromatograms of phenol resin produced with the TSKgel SuperMultipore HZ-M in comparison with the TSKgel G (4000 + 3000 + 2500 + 2000) H_{XL} and the TSKgel Super HZ (4000 + 3000 + 2500 + 2000) series. Distortion appears on the chromatograms produced with the TSKgel® H_{XL} and SuperHZ series, which does not appear with the TSKgel SuperMultipore HZ-M.

Fig. 32 shows chromatograms of both grades using acrylic resin as the sample. With the acrylic resin, as with the phenol resin sample, distortion appears on the chromatogram produced with the conventional product that is not observed with the TSKgel SuperMultipore HZ-M.

Fig. 33 shows chromatograms of phenol resin produced with the TSKgel Super HZM-M, a mixed bed column in which packing materials of different pore sizes are combined in an optimized mixing ratio, and the TSKgel SuperMultipore HZ-M, a multipore type of column. Even in a mixed bed column, in which the pore characteristics have been improved by optimizing the packing material mixture, the same type of distortion appears on the chromatogram.

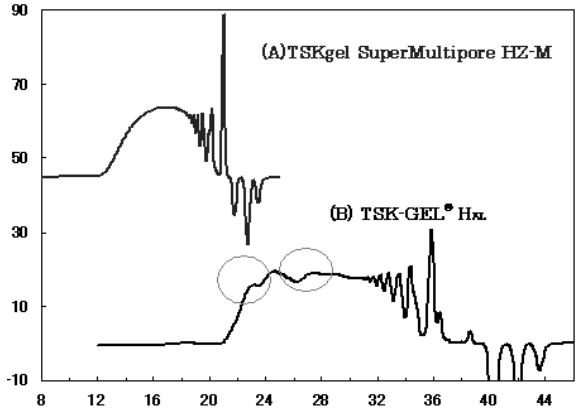

Fig. 30 Chromatograms of phenol resin created with TSKgel SuperMultipore HZ-M and TSKgel® H_{XL} Series

Columns: (A) TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 4
(B) TSKgel G 4000+3000+2500+2000H_{XL} (7.8 mm ID x 30 cm) x 4
Solvent: THF
Flow rate: (A) 0.35 mL/min
(B) 1.0 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: (A) 10 µL
(B) 50 µL

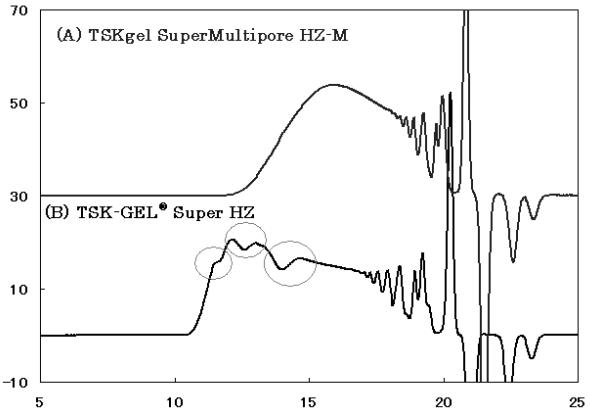

Fig. 31 Chromatograms of phenol resin created with TSKgel SuperMultipore HZ-M and TSKgel® Super HZ Series

Columns: (A) TSKgel SuperMultipore HZ-M (4.6 mm ID x 15 cm) x 4
(B) TSKgel Super HZ 4000+3000+2500+2000 (4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

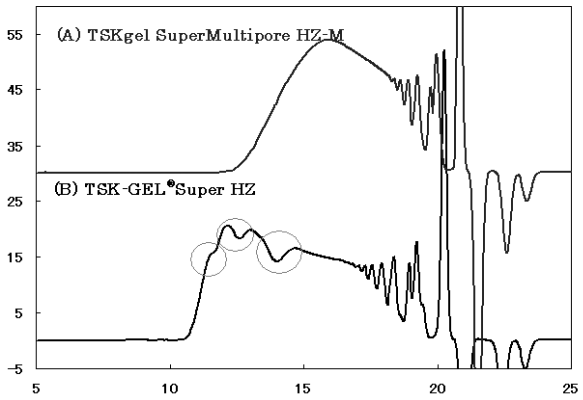

Fig. 32 Chromatograms of acrylic resin created with TSKgel SuperMultipore HZ-M and TSKgel® Super HZ Series

Columns: (A) TSKgel SuperMultipore HZ-M
(4.6 mm ID x 15 cm) x 4
(B) TSKgel Super HZ 4000+3000+2500+2000
(4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Acrylic resin (3 g/L)
Injection volume: 10 µL

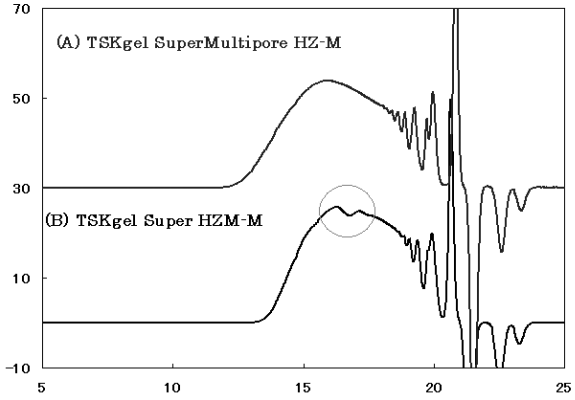

Fig. 33 Chromatograms of phenol resin created with TSKgel SuperMultipore HZ-M and TSKgel Super HZM-M

Columns: (A) TSKgel SuperMultipore HZ-M
(4.6 mm ID x 15 cm) x 4
(B) TSKgel Super HZM-M
(4.6 mm ID x 15 cm) x 4
Solvent: THF
Flow rate: 0.35 mL/min
Detection: RI
Temperature: 40 ºC
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

3-8-3. TSKgel SuperMultipore HZ-H

Fig. 34 shows chromatograms of a styrene-acrylic resin copolymer created using the TSKgel Super HZM-H, a mixed bed type of column in which packing materials of different pore sizes are combined at an optimized mixing ratio, and the TSKgel SuperMultipore HZ-H, a multipore type of column for use with polymers.

Even in the TSKgel Super HZM-H, a mixed bed column in which the pore characteristics have been improved by optimizing the packing material mixture, distortion of the chromatogram is confirmed, similar to what was observed with the TSKgel Super HZM-M.

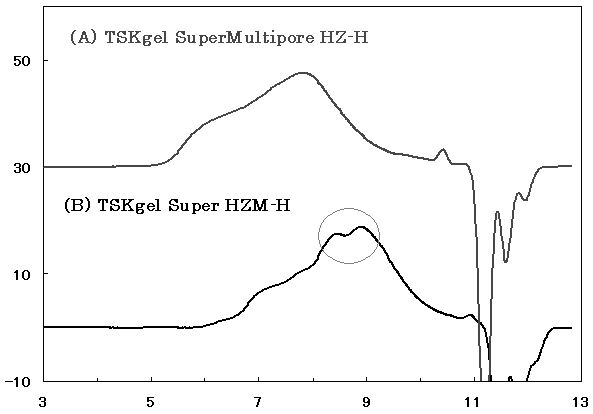

Fig. 34 Chromatograms of a styrene-acrylic resin copolymer produced with TSKgel SuperMultipore HZ-H and TSKgel Super HZM-H

Columns: (A) TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 2
(B) TSKgel Super HZM-H (4.6 mm ID x 15 cm) x 2
Solvent: THF
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Detection: RI
Sample: Styrene-acrylic resin copolymer(3 g/L)
Injection volume: 10 µL

3-8-4. Comparison to products of other companies

Fig. 35 shows chromatograms of phenol resin created with the TSKgel SuperMultipore HZ-M and with a mixed bed column of another company which is the same type as the TSKgel Super HZM-M.

The same type of distortion seen in Fig. 33 can also be observed here with this mixed bed type of column.

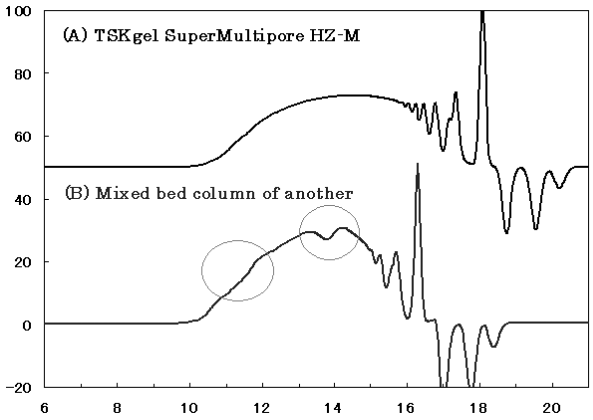

Fig. 35 Chromatograms of phenol resin produced with TSKgel SuperMultipore HZ-M and a mixed bed column of another company

Columns: (A) TSKgel SuperMultipore HZ-M (4.6 mm ID x 25 cm)
(B) Mixed bed column of another company (4.6 mm ID x 25 cm)
Solvent: THF
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Detection: RI
Sample: Phenol resin (3 g/L)
Injection volume: 10 µL

4. Application examples

Figures 36 to 43 show chromatograms of various polymers analyzed using the TSKgel SuperMultipore HZ-H.

Smooth chromatograms with no distortion are obtained for each of these polymers.

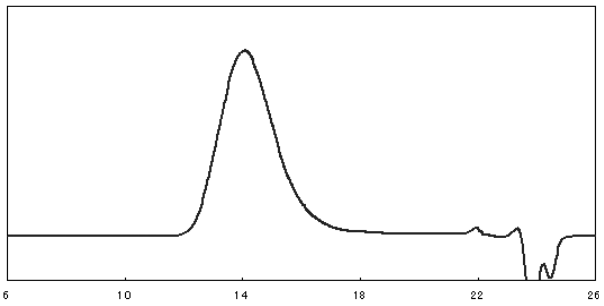

Fig. 36 Separation of polyisobutylene with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

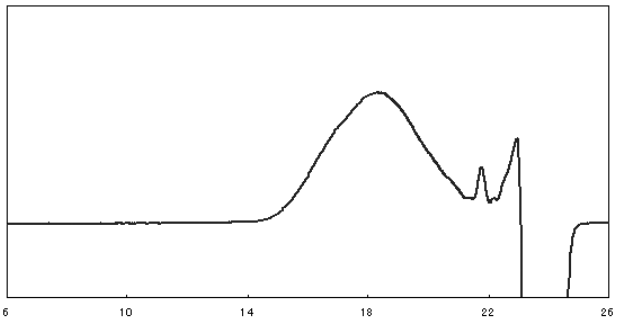

Fig. 37 Separation of acrylic resin (1) with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

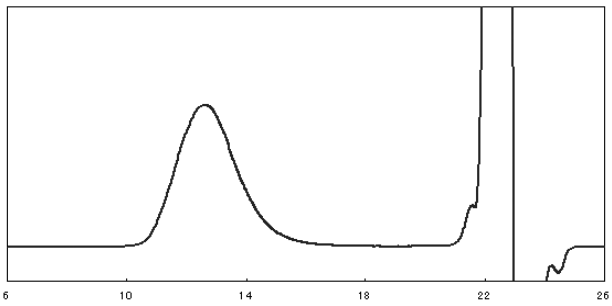

Fig. 38 Separation of polystyrene (NIST SRM 706) with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

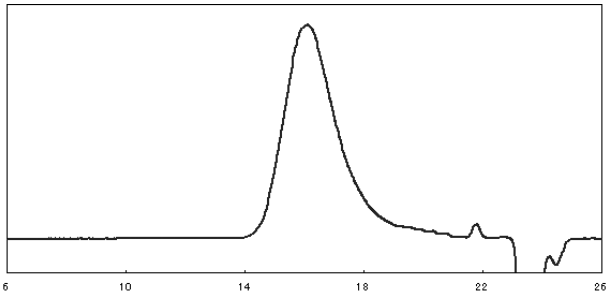

Fig. 39 Separation of polybutadiene with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

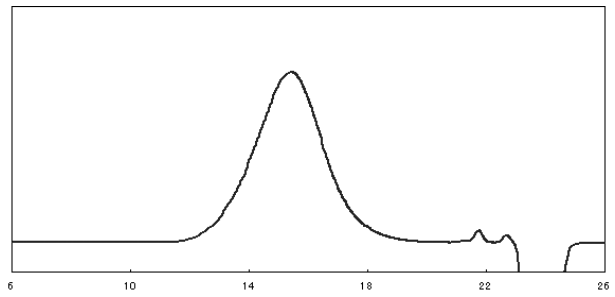

Fig. 40 Separation of polyvinylbutyral with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

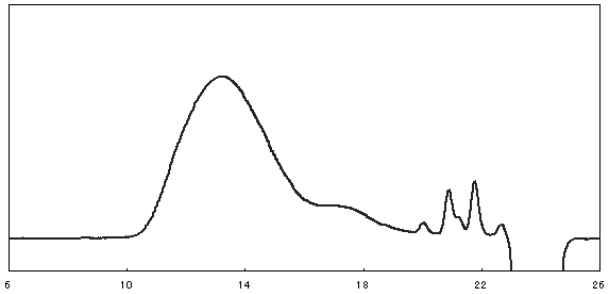

Fig. 41 Separation of polycarbonate with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

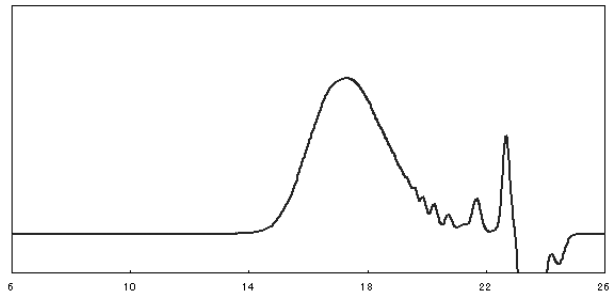

Fig. 42 Separation of epoxy resin with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

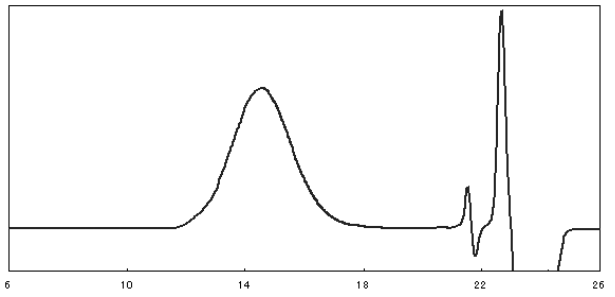

Fig. 43 Separation of acrylic resin (2) with TSKgel SuperMultipore HZ-H

Column: TSKgel SuperMultipore HZ-H (4.6 mm ID x 15 cm) x 4
Solvent: THF
Detection: RI
Flow rate: 0.35 mL/min
Temperature: 40 ºC
Injection volume: 3 g/L, 10 µL

5. Conclusion

The TSKgel® SuperMultipore HZ is a series of semi-micro multipore columns for SEC use with organic solvent systems that is capable of producing ideal chromatograms. In addition to maintaining the features of the TSKgel Multipore H_{XL}-M, this new series of columns is capable of high-speed analysis through the application of packing material composed of monodisperse microparticles, while at the same time cutting down on solvent consumption by reducing column dimensions to a semi-micro level. For high repeatability, it is recommended that these columns be used in combination with the HLC-8120 GPC, a high speed GPC instrument that is compatible with semi-micro columns.

Reference

1) M. Nagata, T. Kato, H. Furutani, J. Liq. Chrom & Rel.Technol.,21 (10) 1471-1484 (1998)