



Characterization of Linear-type SEC Semi-micro Columns for Polymer Analysis

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Introduction

- Size exclusion chromatography (SEC) in an organic mobile phase, gel permeation chromatography (GPC), is a powerful tool for the analysis and determination of molecular mass distribution and the average molecular mass of organic polymers. GPC plays an important role in not only R&D, but also in the quality control of synthetic polymers in the chemical industry.
- In 1997, Tosoh Corporation introduced a novel GPC column which was packed with particles having a wide pore size distribution (TSK-GEL[®] MultiporeH_{XL}-M, 7.8mm ID x 30cm, 4-7 μ m). This column was designed for improving the linearity of the calibration curve over a wide range of molecular weights and removing inflections on chromatograms. These innovations resulted in better reproducibility for polymer analysis by GPC.
- Recently, Tosoh Corporation developed a series of novel multipore columns packed with spherical monodisperse, 3, 4 or 6 μ m particles consisting of cross-linked polystyrene/divinylbenzene copolymer (PS-DVB) for high speed and low solvent consumption analyses with precise results.
- In this poster, the basic properties and the comparison of elution profiles of synthetic polymer on these new monodisperse multipore columns and conventional columns is reported.



Experimental Conditions

GPC Columns:

- Multipore-type, monodisperse:
 - TSK-GEL SuperMultiporeHZ-N, -M and -H, 4.6mm ID x15cm, 3, 4 or 6 μ m
- Multipore type, polydisperse:
 - TSK-GEL MultiporeHxl-M, 7.8mm ID x30cm, 5 μ m
- Individual pore size type, multi-disperse:
 - TSK-GEL SuperHZ2000, 2500, 3000, and 4000, 4.6mm ID x 15cm, 3-5 μ m
 - TSK-GEL G2000, 2500, 3000, and 4000Hxl, 7.8mm ID x30cm, 5-8 μ m
- Mixed bed type, polydisperse:
 - TSK-GEL SuperHZM-M and -N, 4.6mm ID x15cm, 3-5 μ m

All TSK-GEL columns were manufactured by Tosoh Corporation, Japan



Experimental Conditions, Continued

Instrumentation

All-in-one GPC System: EcoSEC[®] HLC-8220GPC system

Chemicals and Materials

Stabilized tetrahydrofuran (analytical grade) was used as the eluent without further treatment (Wako, Osaka). Synthetic polymers and other reference standards were obtained from Wako and other resin suppliers. The narrow molecular mass distribution polystyrene standard kits (“PStQuick”) were obtained from Tosoh (Tokyo).

Preparation of sample solution

Synthetic polymers were dissolved in THF at concentrations of 0.0125-0.1mg/mL. Polystyrene standards were dissolved at concentrations of 0.2-1.0mg/mL. Polystyrene standards were gently stirred occasionally for a period of 12-24hrs prior to use.



Part 1: Physical Properties of TSK-GEL SuperMultiporeHZ Series Columns



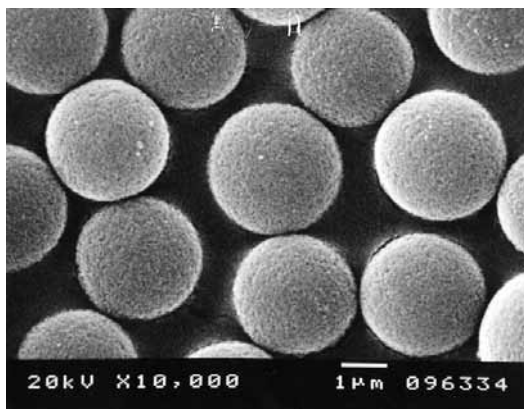
Physical Properties of TSK-GEL SuperMultiporeHZ Series Columns

	TSK-GEL SuperMultiporeHZ-N	TSK-GEL SuperMultiporeHZ-M	TSK-GEL SuperMultiporeHZ-H
Base material	Poly(styrene/divinylbenzene)	Poly(styrene/divinylbenzene)	Poly(styrene/divinylbenzene)
Particle size	3 μ m (monodisperse)	4 μ m	6 μ m
Max. exclusion limit MW	120,000	2,000,000	40,000,000(*)
Mean pore size	80Å	140Å	-----
Range of polystyrene sample	300-50,000	500-1,000,000	1,000-10,000,000
Theoretical plates/column	20,000	16,000	11,000
Column size (Analytical)	4.6mm ID x 15cm	4.6mm ID x 15cm	4.6mm ID x 15cm
Column Size (Guard column)	4.6mm ID x 2cm	4.6mm ID x 2cm	4.6mm ID x 2cm

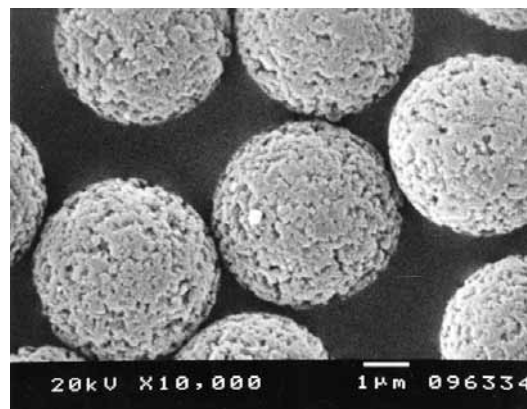


SEM Photographs of TSK-GEL SuperMultiporeHZ Series Particles Prepared by Multipore Synthesis Technology

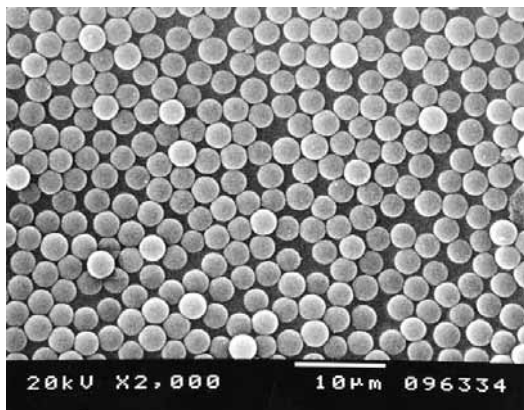
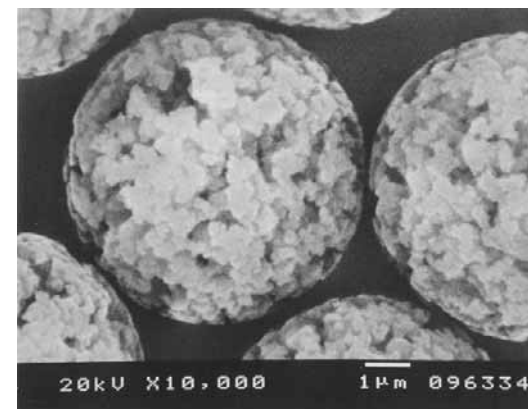
TSKgel SuperMultiporeHZ-N



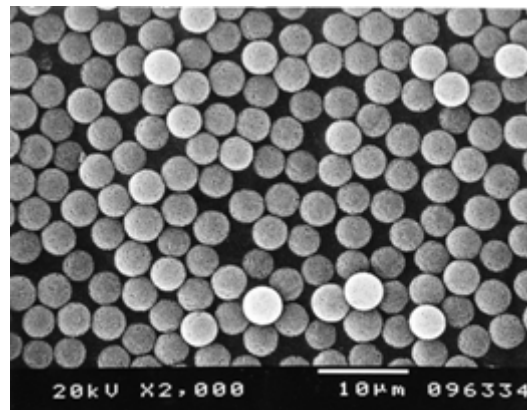
TSKgel SuperMultiporeHZ-M



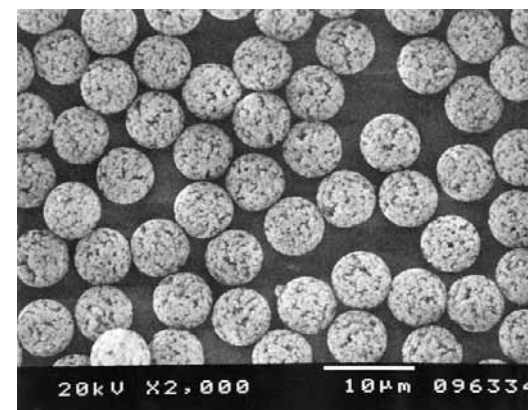
TSKgel SuperMultiporeHZ-H



3μm



4μm

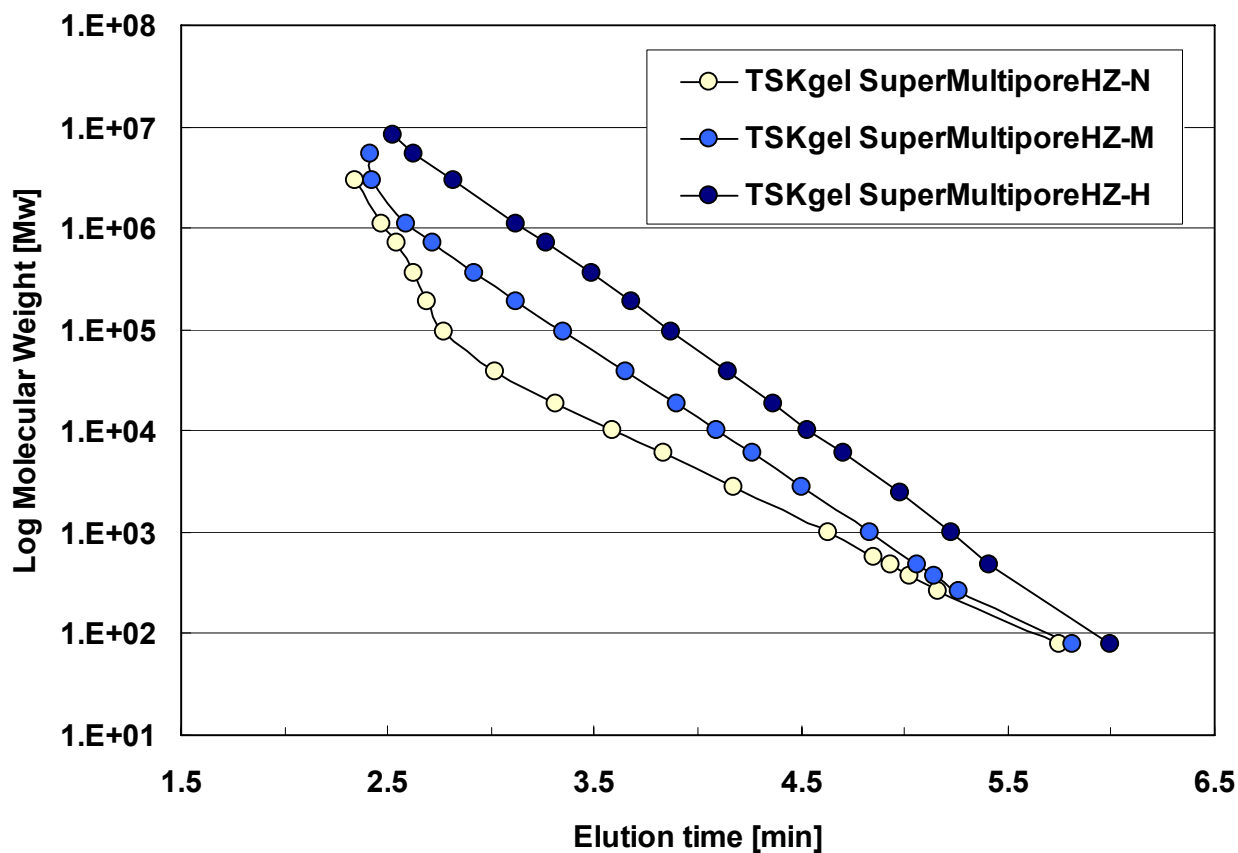


6μm

Part 2: Evaluation of calibration curve and resolution



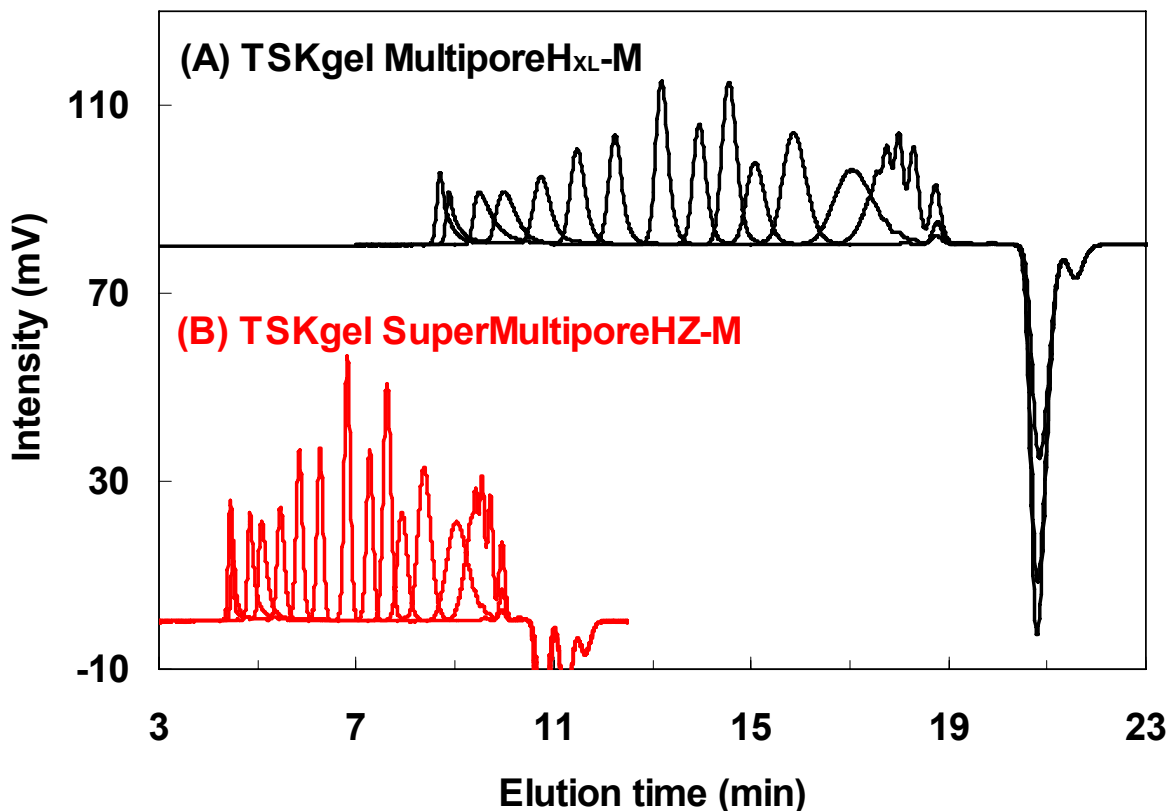
Calibration Curves of TSK-GEL SuperMultiporeHZ Series Columns



Columns: TSK-GEL SuperMultiporeHZ series (4.6mm ID x 15cm)
Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: UV@254nm
Sample: PStQuick (polystyrene standards)
Inj. vol.: 10µL



Comparison of Resolution: TSKgel SuperMultiporeHZ Column & Conventional Multipore Column



Resolution (Rs)		
MW	(A)	(B)
2,890,000/355,000	3.90	4.47
355,000/96,400	2.58	3.13
96,400/18,100	3.37	4.09
18,100/5,970	1.84	2.02
5,970/1,000	1.71	1.80

Columns: (A) TSKgel MultiporeH_{XL}-M (7.8mm ID x 30cm) x 2
 (B) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm) x 2

Eluent: THF

Flow rate: (A) 1.0mL/min (B) 0.35mL/min

Temp.: 40°C

Detection: RI

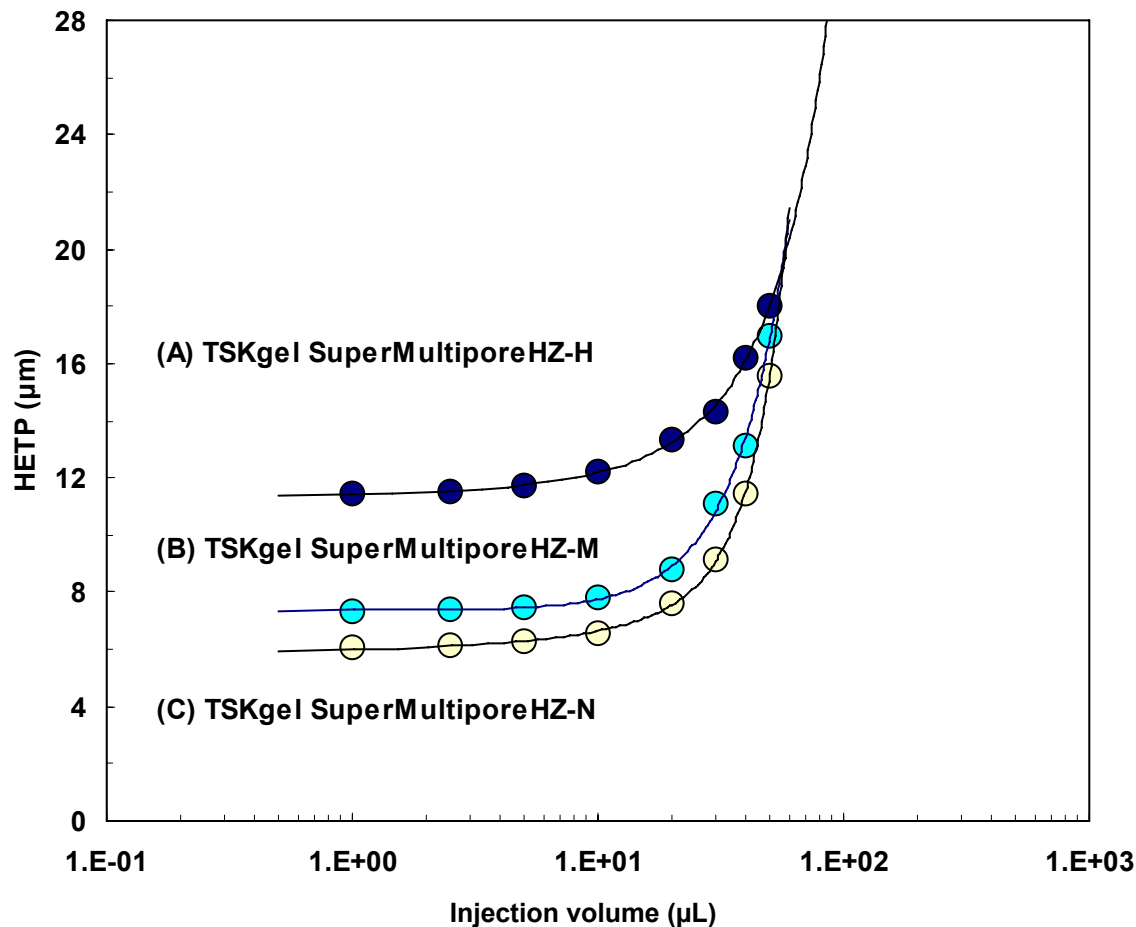
Sample: PStQuick (polystyrene standards)

Inj. vol.: (A) 50µL (B) 10µL

Part 3: Chromatographic Properties of TSK-GEL SuperMultiporeHZ Series Columns



Relationship between Injection Volume & HETP for TSK-GEL SuperMultiporeHZ Series Columns

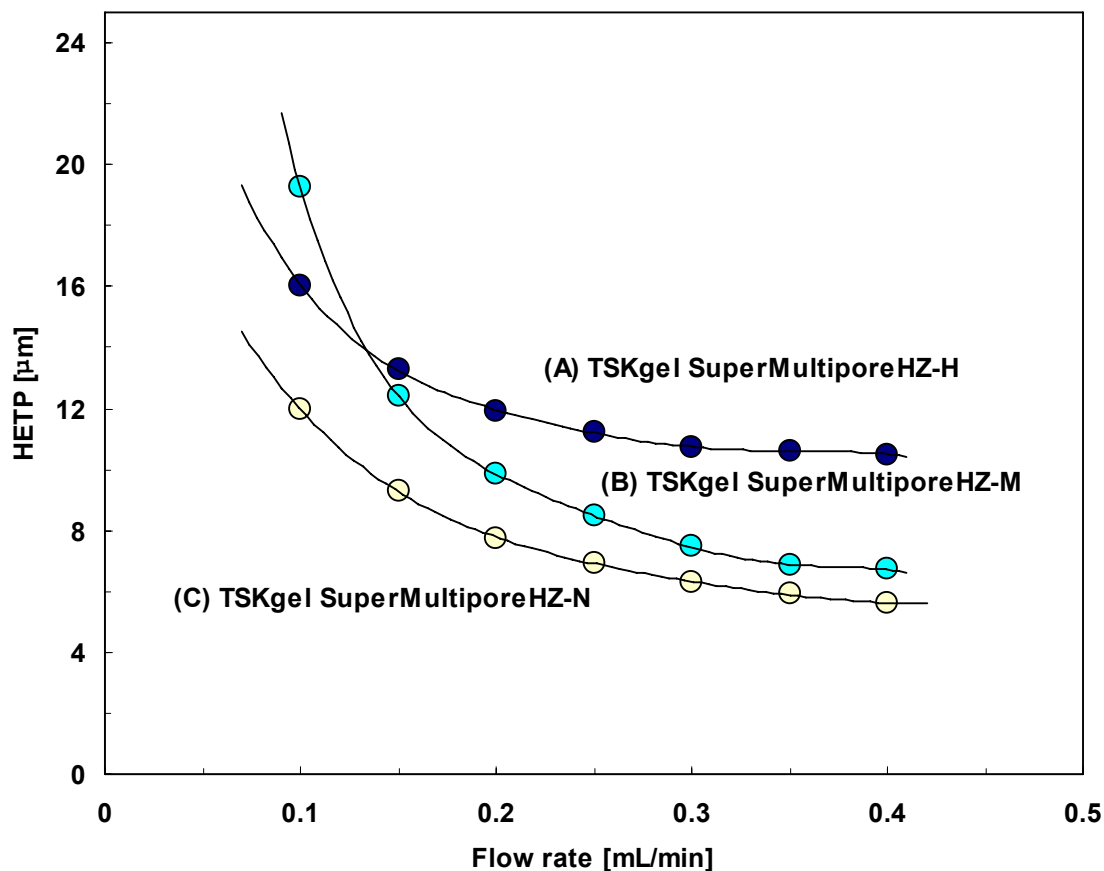


Columns: (A) TSKgel SuperMultiporeHZ-H (4.6mm ID x 15cm) x 2
(B) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm) x 2
(C) TSKgel SuperMultiporeHZ-N (4.6mm ID x 15cm) x 2

Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: UV@254nm
Sample: Dicyclohexylphtarate (DCHP), 0.3%
Inj. vol.: 1 – 200µL



Relationship between Flow Rate & HETP for TSK-GEL SuperMultiporeHZ Series Columns

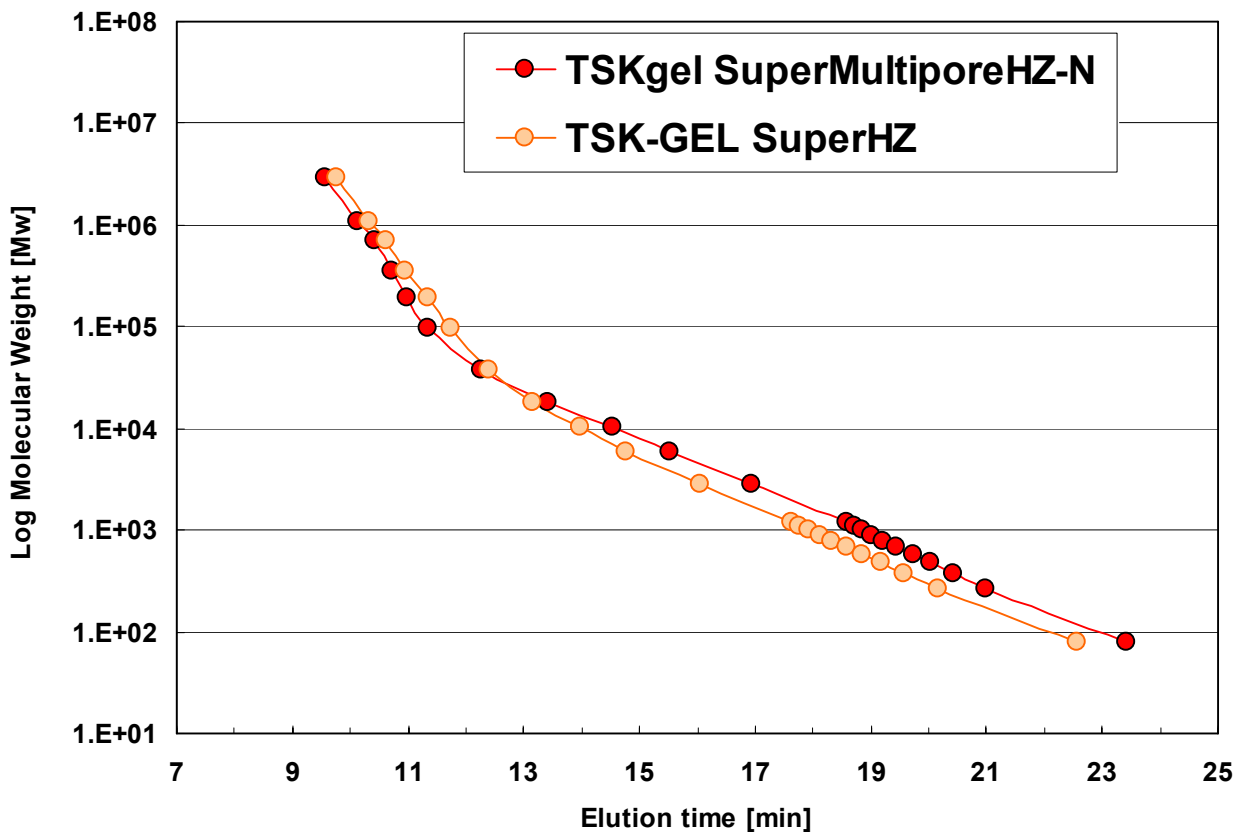


Columns: (A) TSKgel SuperMultiporeHZ-H (4.6mm ID x 15cm)
(B) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm)
(C) TSKgel SuperMultiporeHZ-N (4.6mm ID x 15cm)

Eluent: THF
Flow rate: 0.10 – 0.40mL/min
Temp.: 25°C
Detection: UV@254nm
Sample: Dicyclohexylphtarate (DCHP) , 0.3%
Inj. vol.: 1μL



Calibration curves of TSKgel SuperMultiporeHZ-N & TSKgel SuperHZ columns

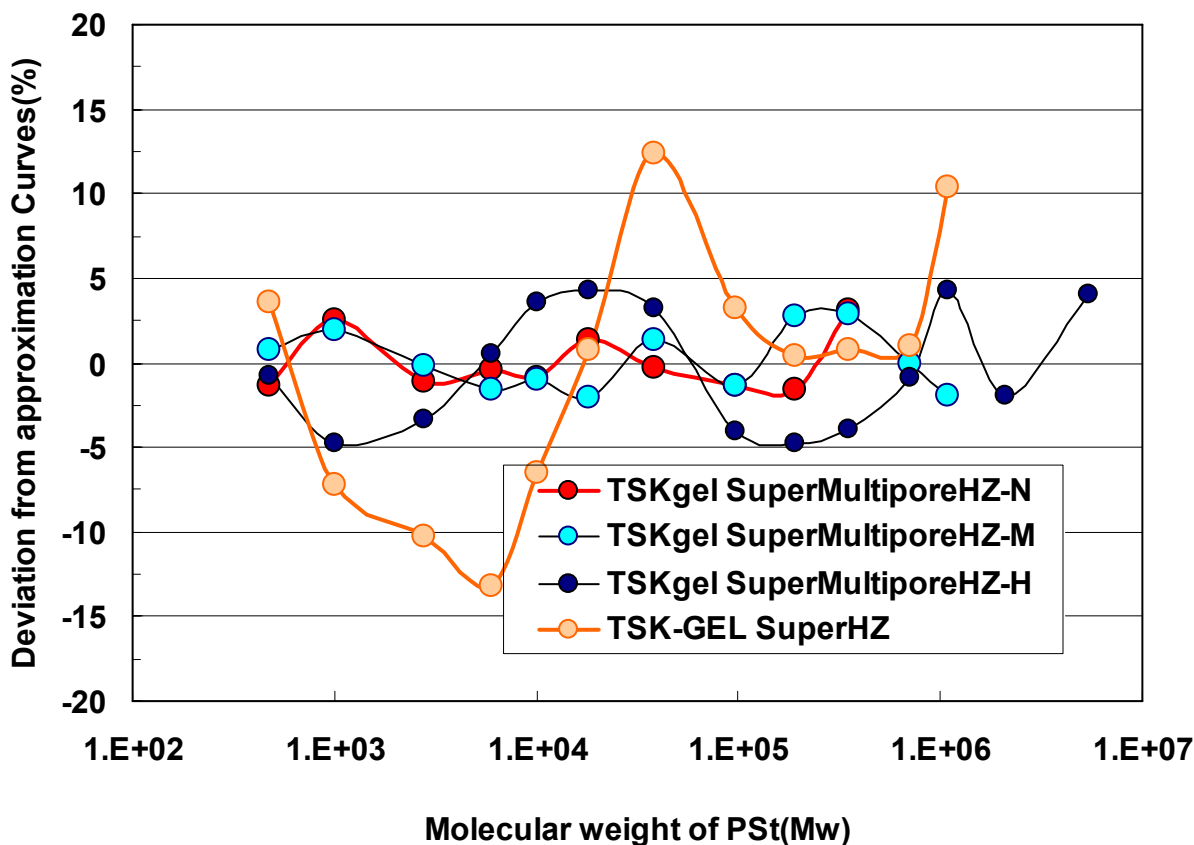


Columns: (A) TSKgel SuperMultiporeHZ-N (4.6mm ID x 15cm) x 4
(B) TSKgel SuperHZ 4000 + 3000 + 2500 + 2000 (4.6mm ID x 15cm) x 4

Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: UV@254nm
Sample: PStQuick (polystyrene standards)
Inj. vol.: 5µL



Deviation Between Calibration Curve and Approximation Curve on TSK-GEL SuperMultiporeHZ and TSK-GEL SuperHZ Columns



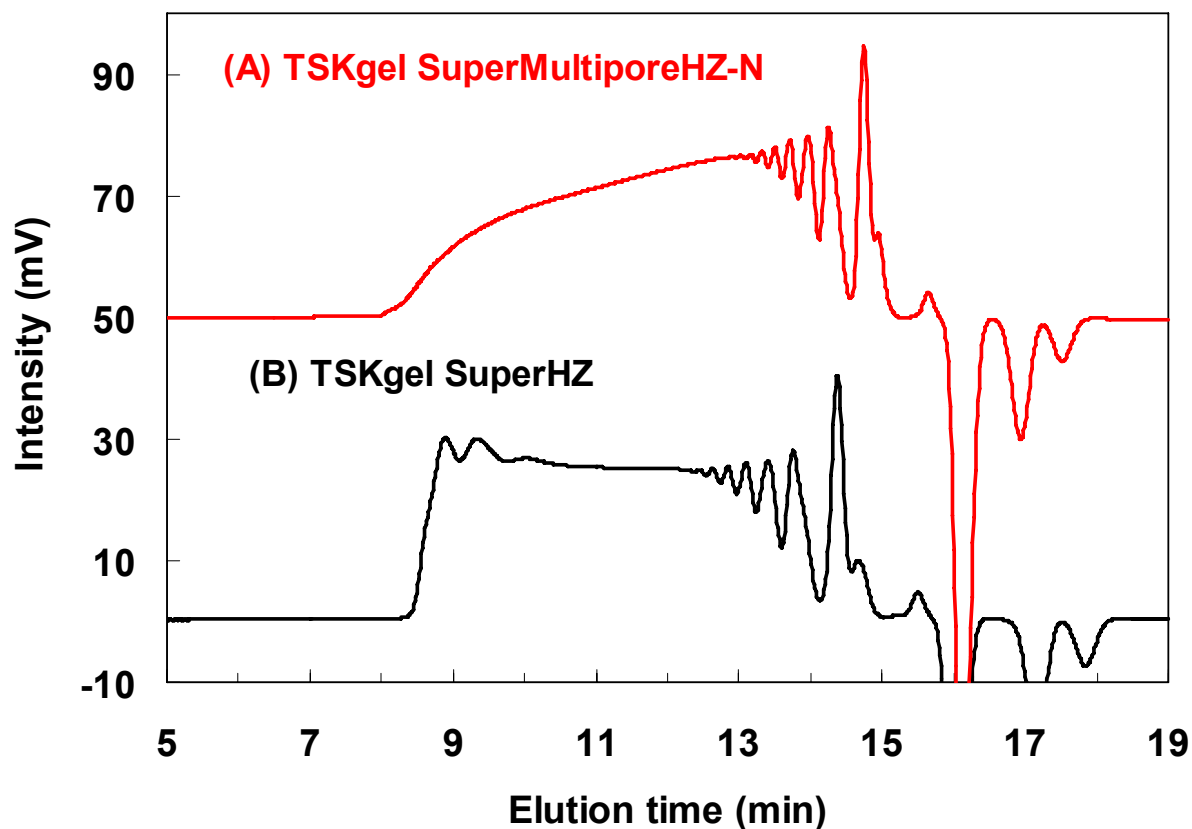
Columns: (A) TSKgel SuperMultiporeHZ-H (4.6mm ID x 15cm)
(B) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm)
(C) TSKgel SuperMultiporeHZ-N (4.6mm ID x 15cm)
(D) TSKgel SuperHZ 4000 + 3000 + 2500 + 2000 (4.6mm ID x 15cm) x 4

Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: UV@254nm
Sample: PStQuick (polystyrene standards)
Inj. vol.: 5µL

Part 4: Elution Profiles of Various Polymers on TSK-GEL SuperMultiporeHZ Series Columns



Analysis of Phenolic Resins using TSKgel SuperMultiporeHZ-M and TSK-GEL SuperHZ Columns

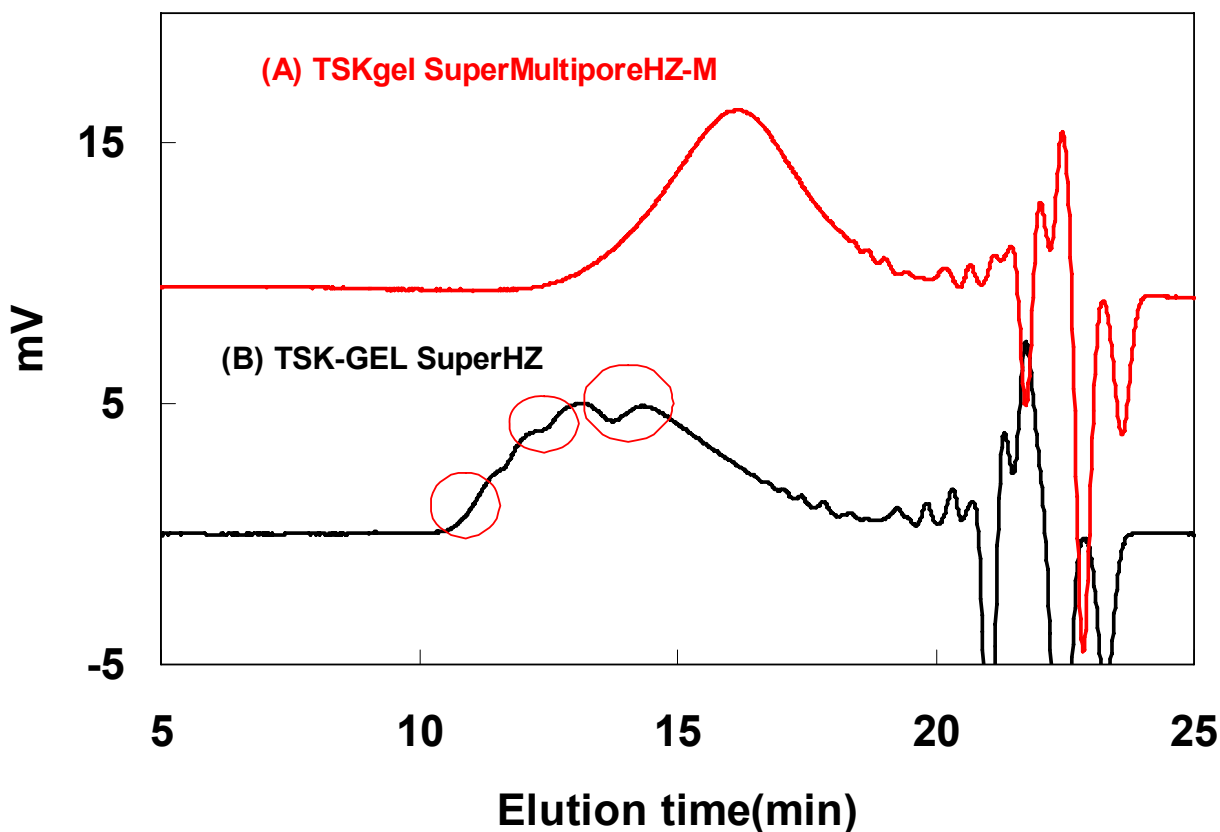


Columns: (A) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm) x 4
(B) TSKgel SuperHZ 4000 + 3000 + 2500 + 2000 (4.6mm ID x 15cm) x 4

Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: RI
Sample conc.: 0.3%
Inj. vol.: 10µL



Analysis of Acrylic Resins using TSKgel SuperMultiporeHZ-M and TSK-GEL SuperHZ Columns

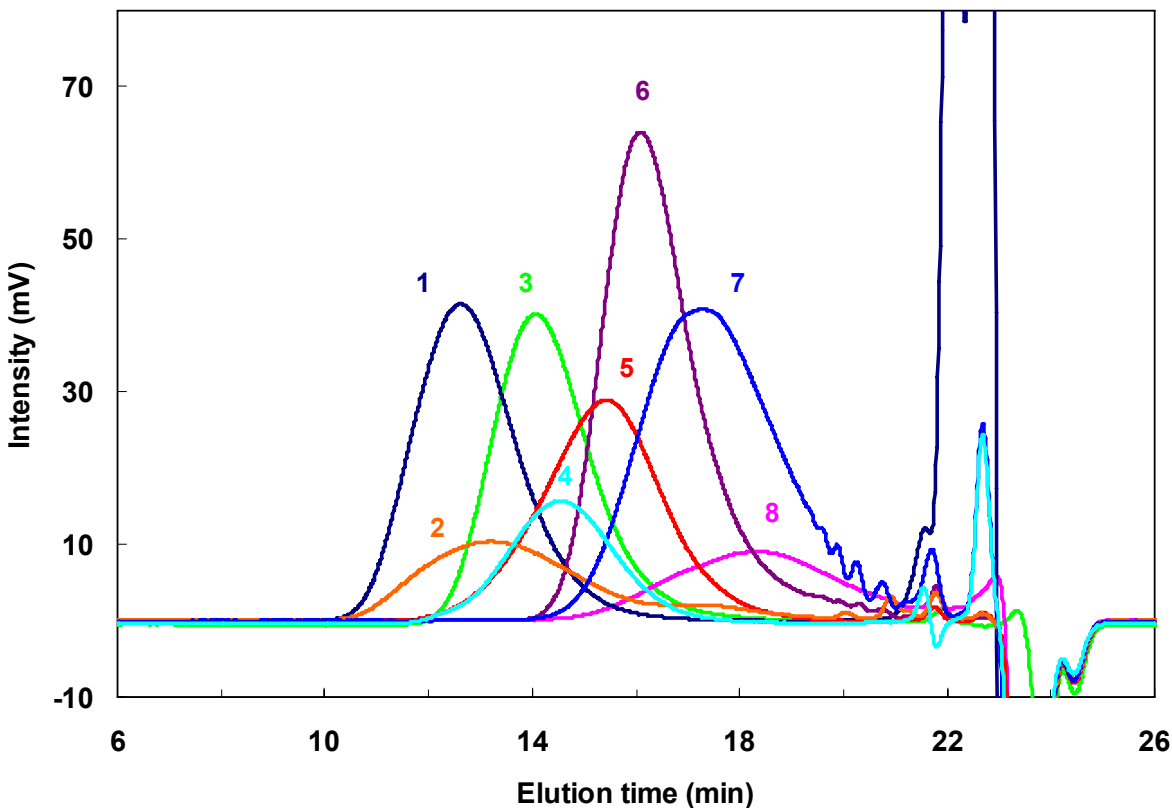


Columns: (A) TSKgel SuperMultiporeHZ-M (4.6mm ID x 15cm) x 4
(B) TSKgel SuperHZ 4000 + 3000 + 2500 + 2000 (4.6mm ID x 15cm) x 4

Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: RI
Sample conc.: 0.3%
Inj. vol.: 10µL



Analysis of Various Polymers using TSKgel SuperMultiporeHZ-M Column



Polymer	MW
(1) polyisobutylene	925,000
(2) acrylic resin (1)	635,000
(3) Polystyrene (SRM706)	258,000
(4) polybutadiene	215,000
(5) polyvinyl butyral	125,000
(6) polycarbonate	45,000
(7) epoxyresin	18,000
(8) acrylic resin (2)	12,000

Column: TSKgel SuperMultiporeHZ-M
(4.6mm ID x 15cm) x 4
Eluent: THF
Flow rate: 0.35mL/min
Temp.: 25°C
Detection: RI
Sample conc.: 0.3%
Inj. vol.: 10µL



Summary

- TSK-GEL SuperMultiporeHZ GPC semi-micro columns, packed with spherical monodisperse PS-DVB particles, each containing a wide range of pore sizes, was developed by Tosoh Corporation.
- TSK-GEL SuperMultiporeHZ series columns exhibited high resolution and good linearity of the calibration curves across a wide range of molecular mass of polystyrene standards in THF.
- Various polymers were analyzed on the TSK-GEL SuperMultiporeHZ series columns, and when compared with conventional GPC columns, the semi-micro columns separated the polymers in half the run time and with 1/6th the solvent consumption. Chromatograms obtained on TSK-GEL SuperMultiporeHZ columns did not show inflection points, thus allowing better accuracy and reproducibility when determining the molecular mass distribution of polymers.