Characteristics of newly-developed, monodisperse, multi-pore organic GPC columns

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Abstract

In 2005, Tosoh introduced a novel GPC column containing spherical, monodisperse 4 micron particles exhibiting distinct multiple pore sizes for analyzing polymers up to $1x10^6$ MW. This column (TSKgel SuperMultiporeHZ-M, 4.6mmID x 15cm) provides us with fast and precise analyses of high MW polymers.

Now we developed an additional GPC column which has multipore type pores for analyzing polymers below 4 x 10^4 MW (TSKgel SuperMultiporeHZ-N). The fundamental properties of the new GPC support were determined using semi-micro column dimensions (4.6 mmID x 15cm). We compared the separation performance of various synthetic polymers with conventional columns in series (TSKgel H_{XL} and SuperHZ columns, packed in 7.8mmID x 30cm and 4.6mmID x 15cm, respectively).

The new packing material demonstrated good linearity of the calibration curve in the range from MW 5 x 102 to 3.8 x 104 for standard polystyrenes in THF eluent.

It was confirmed that the analyses were completed in half the time required for conventional columns with better resolution. As expected from the narrower column dimensions, solvent consumption was only 1/6th of that for conventional GPC columns. Peak shapes of various low molecular weight polymers and oligomers on the semi-micro column were found to be very smooth without any inflection point, although inflection points were observed in the chromatograms of other mixed-bed and single pore size columns.

Introduction

Gel Permeation Chromatography (GPC) is a powerful tool to analyze and determine molecular mass distribution and average molecular mass of organic polymers. GPC has an important role not only in new polymer research but also in the quality control of synthetic polymers in the chemical industry.

In the last decade, we introduced a novel concept GPC column which features a wide distribution of pores in the particle (TSKgel MultiporeH$_{XL}$ column, 7.8mmID x 30cm). Traditionally, two approaches have been available for measuring polymers over a wide MW range, (1) mixed-bed columns and, (2) connecting columns with differing exclusion limits in series. Mixed-bed columns are prepared by using particles that contain different pore sizes. This approach is often hampered by lot-to-lot variation and poor reproducibility of the position of the inflection point.

The new column featured in this poster was designed to improve the linearity of the calibration curve over a wide range of molecular weights and to remove inflection points in the calibration curve. The solution was provided by the use of particles having a wide distribution of pores in each particle. We developed a novel multi-pore column packed with spherical monodisperse 3 micron particles consisting of cross-linked polystyrene-divinylbenzene (PS-DVB). This column allows for fast analysis times and low solvent consumption per analysis.

In this poster, we report on the comparison of elution profiles of synthetic polymers on new multipore and commercially available mixed-bed column.

Experimental

Instrumentation

GPC was carried out using HLC-8220GPC and a modular LC system consisting of a DP-8020 pump, UV-8020 ultraviolet detector at 254nm and RI-8012 refractive index detector (TOSOH, Tokyo).

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 PS narrow-molecular-mass distribution standards were obtained from TOSOH (Tokyo, Japan).

GPC columns

- TSKgel SuperMultiporeHZ-N (4.6mm I.D. x 15cm)
- TSKgel SuperMultiporeHZ-M (4.6mm I.D. x 15cm)
- TSKgel Multipore H_{XL}-M (7.8mm I.D. x 30cm)
- TSKgel SuperHZ2000 and 2500, 3000 and 4000 (4.6mm I.D. x15cm)
- Detailed information is listed in Tables 1 and 2.

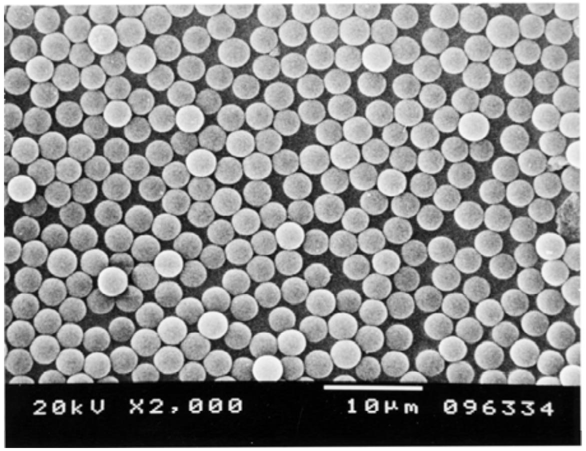
Preparation of sample solutions

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

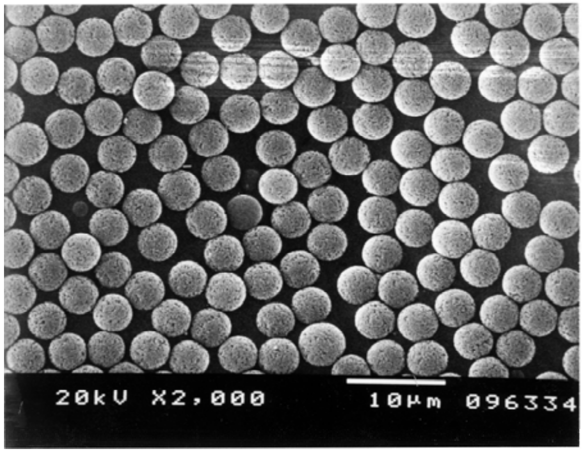
Table 1: Physical Properties of TSKgel SuperMultiporeHZ-N

	TSKgel SuperMultiporeHZ-N	TSKgel SuperMultiporeHZ-M
Base material	poly(styrene-divinylbenzene)	poly(styrene-divinylbenzene)
Particle size	3μm	4μm
Max. exclusion limit MW	120,000	2,000,000
Mean pore size	8 nm	14 nm
MW range of polystyrene sample	500 - 50,000	500 - 1,000,000
Theoretical plates/column	18,000	16,000
Column size (Analytical)	4.6mmID x 15cm	4.6mmID x 15cm
Column size (Guard)	4.6mmID x 2cm	4.6mmID x 2cm

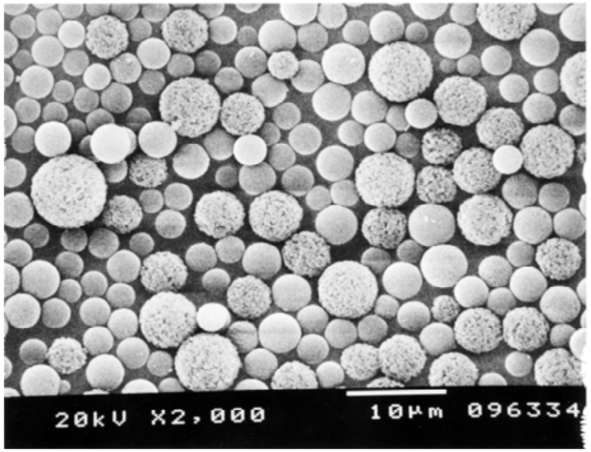
Figure 1: SEM Photographs of TSK-GEL SuperMultiporeHZ series and mixed-bed type columns



TSKgel SuperMultiporeHZ-N
(3 micron particles)

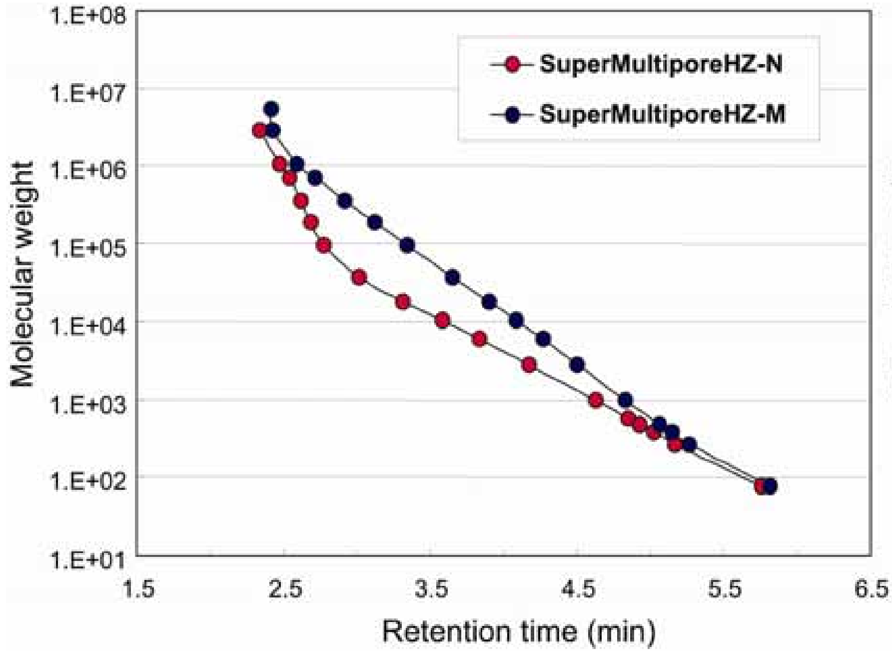


TSKgel SuperMultiporeHZ-M
(4 micron particles)



TSKgel SuperHZM-M (mixed-bed)
(4-7 micron particles)

Figure 2: TSK-GEL SuperMultiporeHZ series

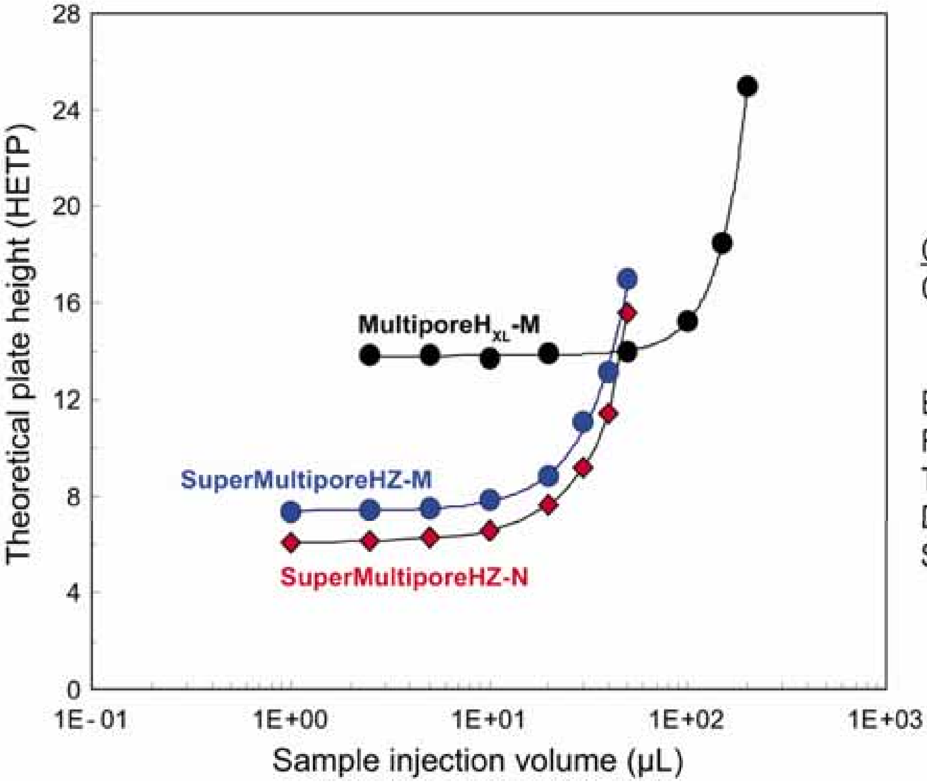


<u>Conditions</u>

Column size: 4.6mmID x 15cm
Eluent: THF
Flow rate: 0.35mL/min
Temperature: 25°C
Detection: UV@254nm (UV-8020 microcell)
Sample: Standard polystyrene

Column	Linearity	Slope	Max. Exclusion Limit	Porosity (%)	Pore Size (nm)
SuperMultiporeHZ-N	0.9996	-2.8131	125,000	70.3	8.2
SuperMultiporeHZ-M	0.9998	-3.8211	1,810,000	72.6	13.9

Figure 3: Relationship between injection volume and HETP



Conditions

Column: SuperMultiporeHZ-N (4.6mmID x 15cm x 2)
SuperMultiporeHZ-M (4.6mmID x 15cm x 2)
MultiporeH$_{XL}$-M (7.8mmID x 30cm x 2)

Eluent: THF

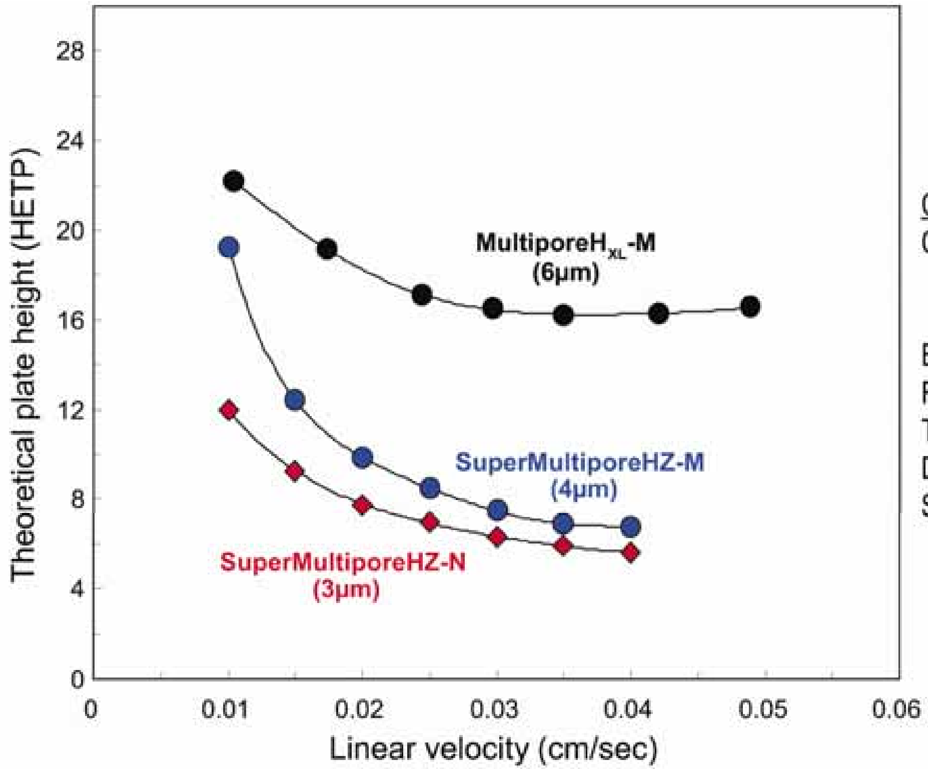
Flow rate: 0.35mL/min (4.6mmID); 1.0mL/min (7.8mmID)

Temperature: 25°C

Detection: UV@254nm (UV-8020 microcell)

Sample: DCHP (0.5%) 1~200µL

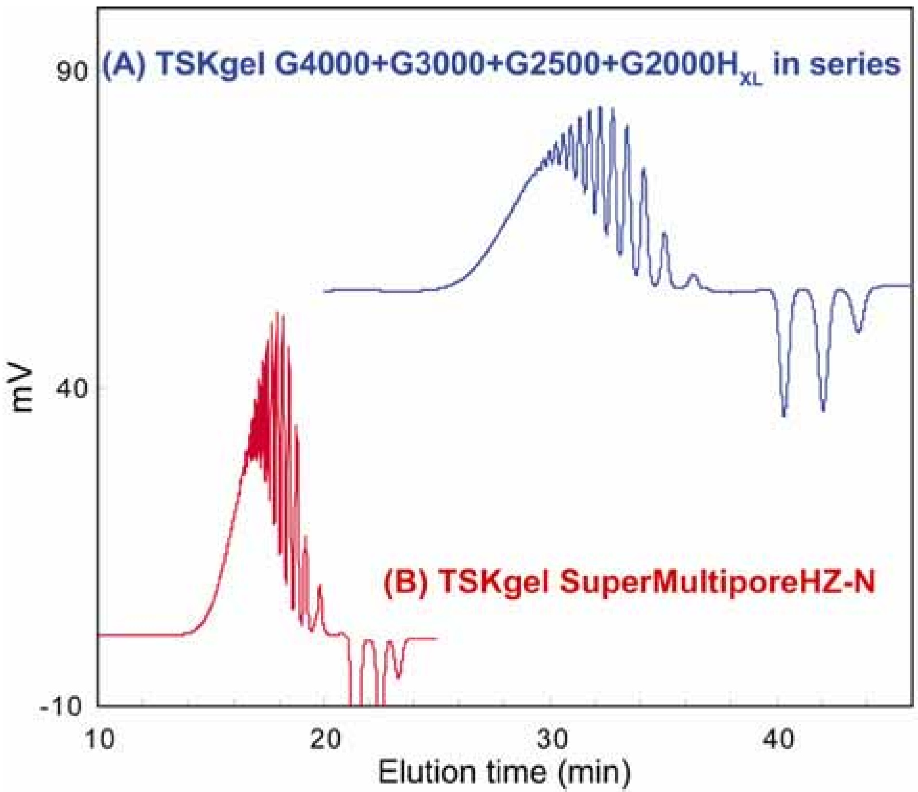
Figure 4: Relationship between linear velocity and HETP



<u>Conditions</u>

Column:	SuperMultiporeHZ-N (4.6mmID x 15cm)
	SuperMultiporeHZ-M (4.6mmID x 15cm)
	MultiporeH$_{XL}$-M (7.8mmID x 30cm)
Eluent:	THF
Flow rate:	0.10 ~ 1.4mL
Temperature:	25°C
Detection:	UV@254nm (UV-8020 microcell)
Sample:	DCHP (0.5%) 1μL & 20μL

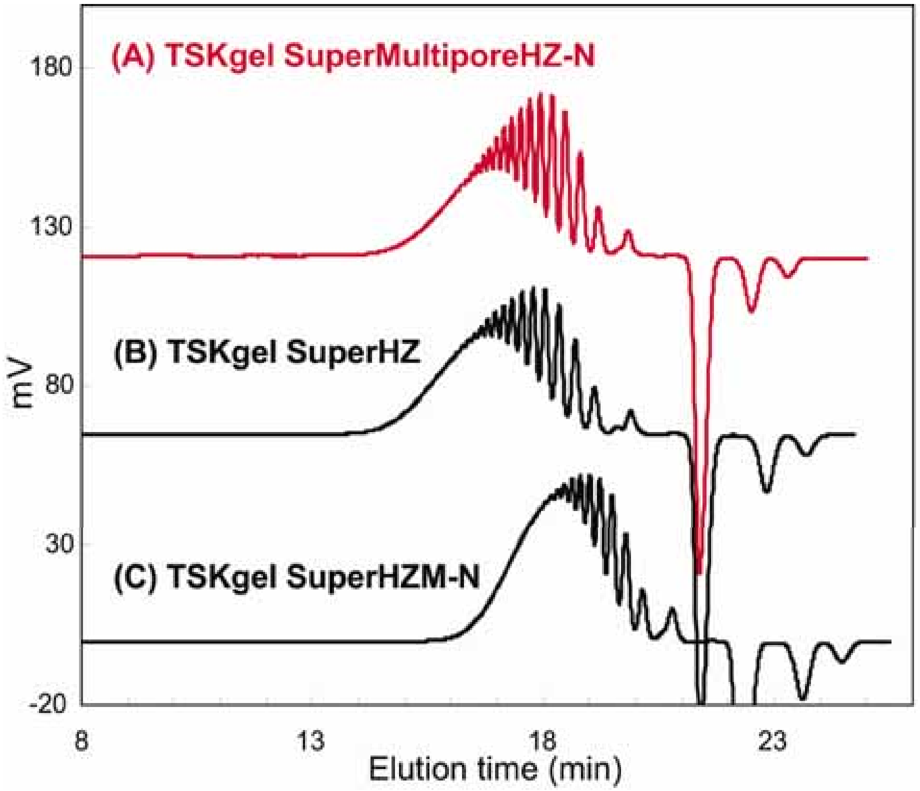
Figure 5: Comparison of elution profiles of PTMEG 650 on TSKgel SuperMultiporeHZ-N and H_{XL}



<u>Conditions</u>

Column:	(A) TSKgel G4000+3000+2500+2000H_{XL} (7.8mmID x 30cm x 4)
	(B) TSKgel SuperMultiporeHZ-N (4.6mmID x 15cm x 4)
Eluent:	THF
Flow rate:	(A) 1.0mL/min (B) 0.35mL/min
Temperature:	40°C
Detection:	RI
Sample:	PTMEG 650 (polytetramethylene ether glycol, 1.0%) (A) 60μL (B) 10μL

Figure 6: Comparison of elution profiles of PTMEG 650 on TSKgel SuperMultiporeHZ-N and SuperHZ



<u>Conditions</u>

Column: (A) TSKgel SuperMultiporeHZ-N (4.6mmID x 15cm x 4)
(B) TSKgel SuperHZ4000+3000+2500+2000H_{XL} (4.6mmID x 15cm x 4)
(C) TSKgel SuperHZM-N (4.6mmID x 15cm x 4)

Eluent: THF

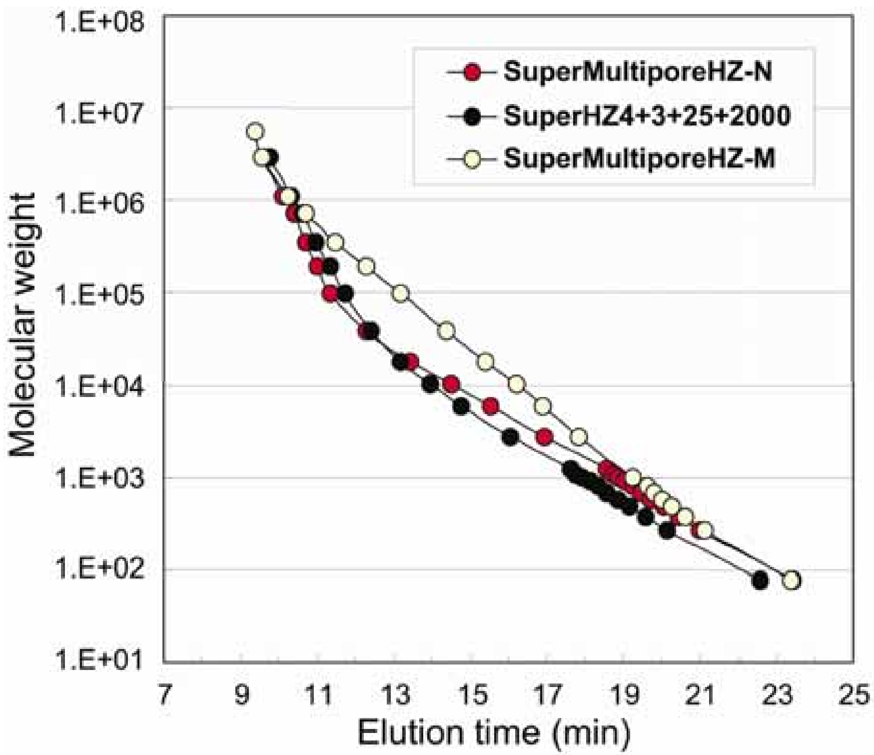
Flow rate: 0.35mL/min

Temperature: 40°C

Detection: RI

Sample: PTMEG 650 (polytetramethylene ether glycol, 1.0%), 10μL

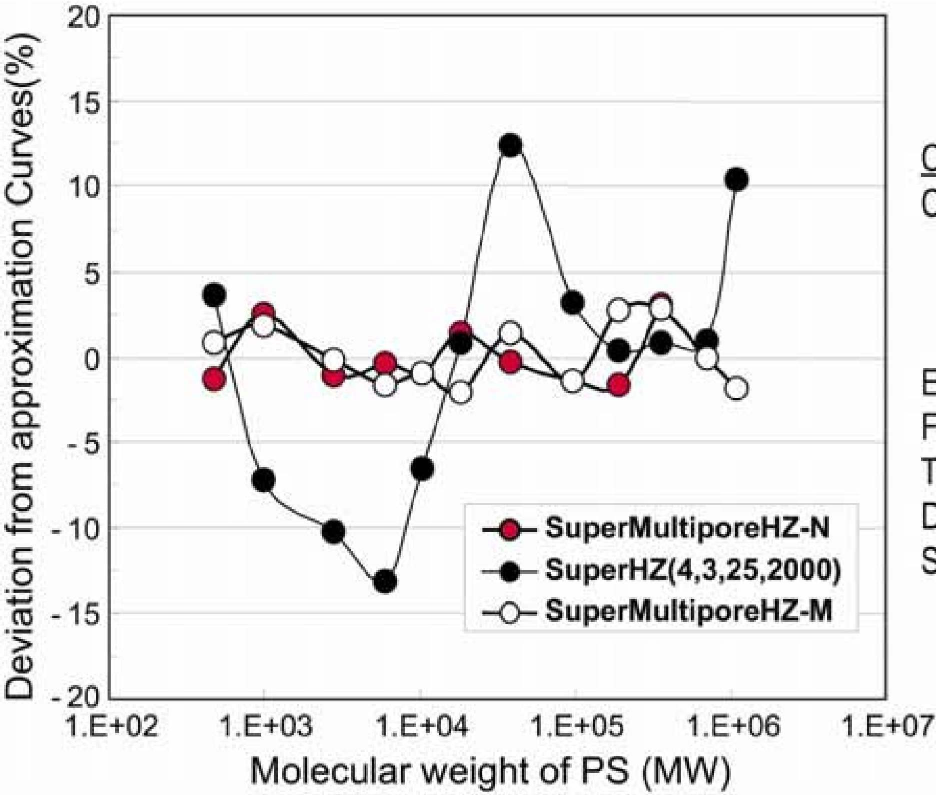
Figure 7: Calibration curves of TSK-GEL SuperMultiporeHZ series



<u>Conditions</u>

Column size:	4.6mmID x 15cm x 4
	SuperMultiporeHZ-N
	SuperHZ4000+3000+2500+2000
	SuperMultiporeHZ-M
Eluent:	THF
Flow rate:	0.35mL/min
Temperature:	25°C
Detection:	UV@254nm (UV-8020 microcell)
Sample:	Standard polystyrene, 10μL

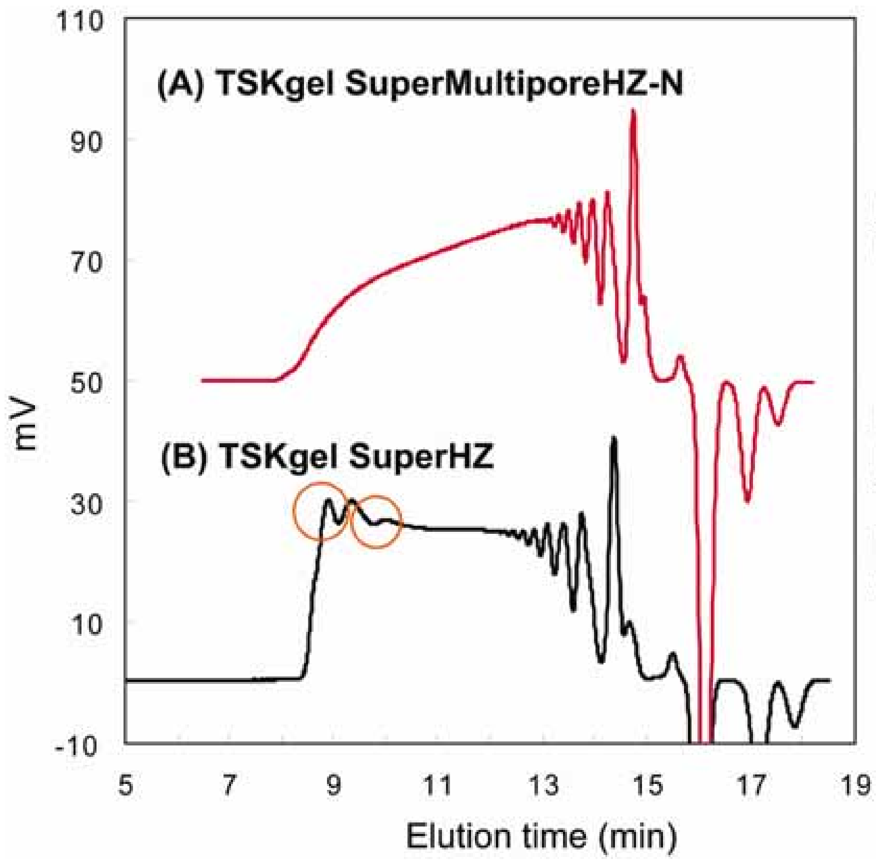
Figure 8: Comparison of deviation between calibration curve and approximation curve on SuperMultiporeHZ



Conditions

Column size:	4.6mmID x 15cm x 4 SuperMultiporeHZ-N SuperHZ4000+3000+2500+2000 SuperMultiporeHZ-M
Eluent:	THF
Flow rate:	0.35mL/min
Temperature:	25°C
Detection:	UV@254nm (UV-8020 microcell)
Sample:	Standard polystyrene, 10μL

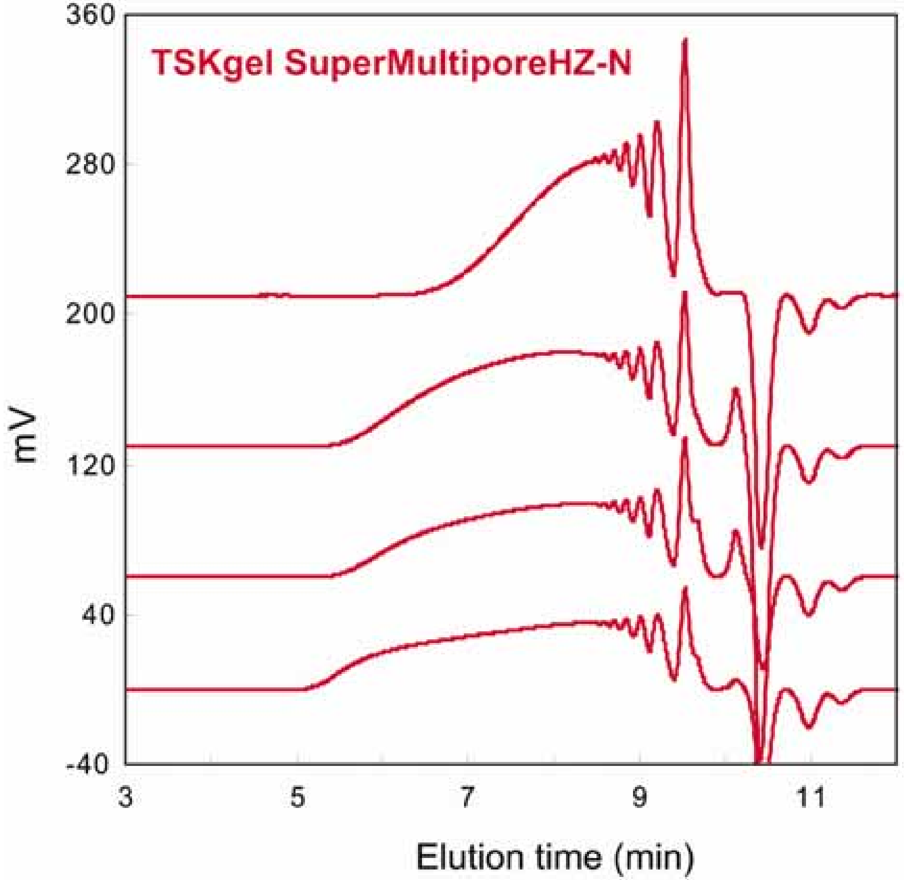
Figure 9: Chromatograms of Phenolic resin on TSKgel SuperMultiporeHZ-N and SuperHZ



<u>Conditions</u>

Column:	(A) TSKgel SuperMultiporeHZ-N (4.6mmID x 15cm x 3)
	(B) TSKgel SuperHZ3000+2500+2000H_{XL} (4.6mmID x 15cm x 3)
Eluent:	THF
Flow rate:	0.35mL/min
Temperature:	40°C
Detection:	RI
Sample:	Phenolic resin (G-C) 0.3%, 10μL

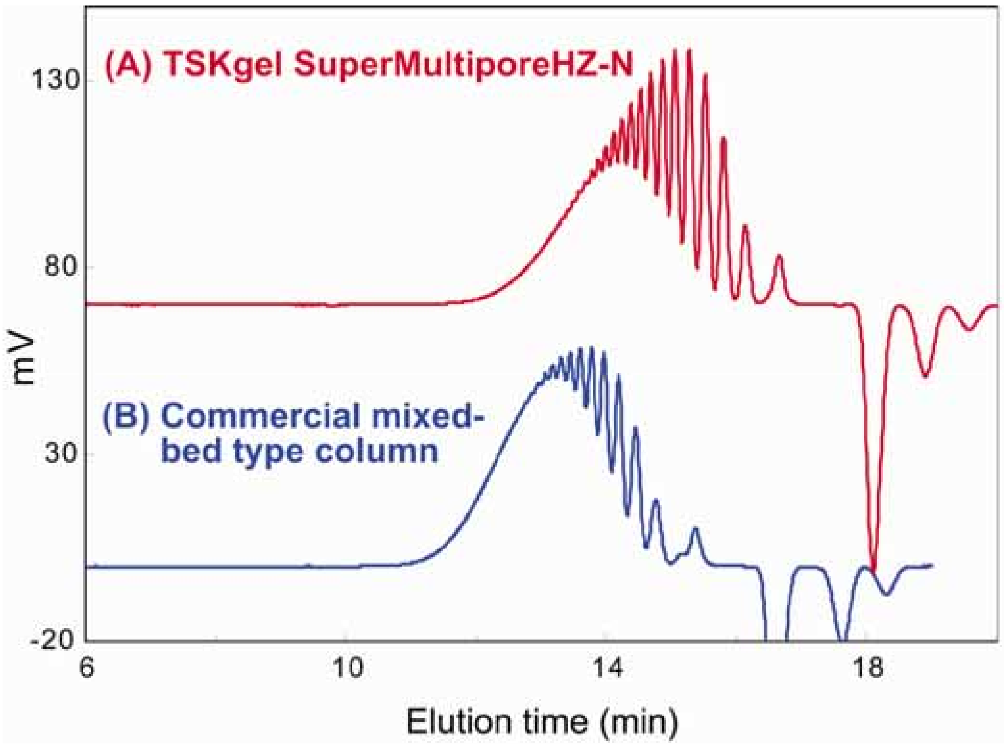
Figure 10: Chromatograms of various Phenolic resins on TSKgel SuperMultiporeHZ-N



<u>Conditions</u>

Column:	TSKgel SuperMultiporeHZ-N (4.6mmID x 15cm x 2)
Eluent:	THF
Flow rate:	0.35mL/min
Temperature:	40°C
Detection:	RI
Sample:	Phenolic resin 0.3%, 10μL

Figure 11: Comparison of PTMEG profile on SuperMultiporeHZ-N and Commercial mixed-bed column



Conditions

Column:	(A) TSKgel SuperMultiporeHZ-N (4.6mmID x 25cm x 2)
	(B) Commercial Mixed-bed column (4.6mmID x 25cm x 2)
Eluent:	THF
Flow rate:	0.35mL/min
Temperature:	40°C
Detection:	RI
Sample:	PTMEG 650 (1.0%), 10μL

Conclusions

- We developed a novel GPC semi-micro column, SuperMultiporeHZ-N packed with spherical monodisperse 3 micron PS-DVB particles, each containing distinct multiple size pores.
- SuperMultiporeHZ-N demonstrated good linearity of the calibration curve ranging from MW 5×10^2 to 3.8×10^4 for standard polystyrenes in THF eluent.
- Various polymers were analyzed on the SuperMultiporeHZ-N columns. It was confirmed that chromatograms were obtained in half the time required for conventional columns and with better resolution.
- The solvent consumption was only 1/6th of that for conventional GPC columns (7.8mm ID columns).
- Chromatograms of various polymers which have broad molecular weight distribution on SuperMultiporeHZ-N were found to be very smooth without any inflection points.
- This new column provides faster and more precise MW measurement of synthetic polymers.