



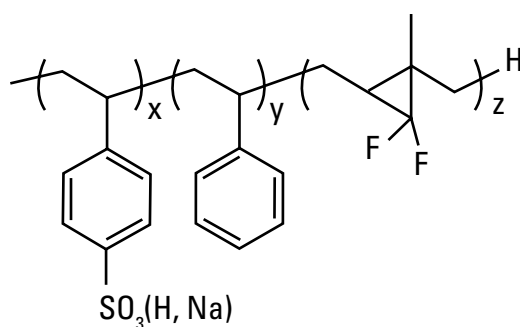
APPLICATIONS

ANALYSIS OF STYRENE AND ISOPRENE BLOCK COPOLYMERS BEFORE AND AFTER FLUORINATION

Dr. Jimmy Mays' group from the Department of Chemistry at the University of Tennessee, Knoxville, is synthesizing and characterizing the bulk morphology of fluorinated and sulfonated block copolymers. Well-defined block copolymers of sulfonated polystyrene-*b*-fluorinated polyisoprene (sPS-*b*-fPI), Figure 18, were synthesized by anionic polymerization followed by fluorination and sulfonation³.

The EcoSEC GPC System, equipped with TSKgel SuperMultipore® columns, was then used to determine the number-average molar mass, M_n , and the polydispersity index, PDI, of sPS-*b*-fPI, as well as that of the precursor polymer (PS-*b*-PI), Table 7. As seen in Figure 19, complete analysis of sPS-*b*-fPI was obtained in less than 10 minutes with excellent resolution using the EcoSEC GPC System.

➤ **FIGURE 18**



➤ **TABLE 7**

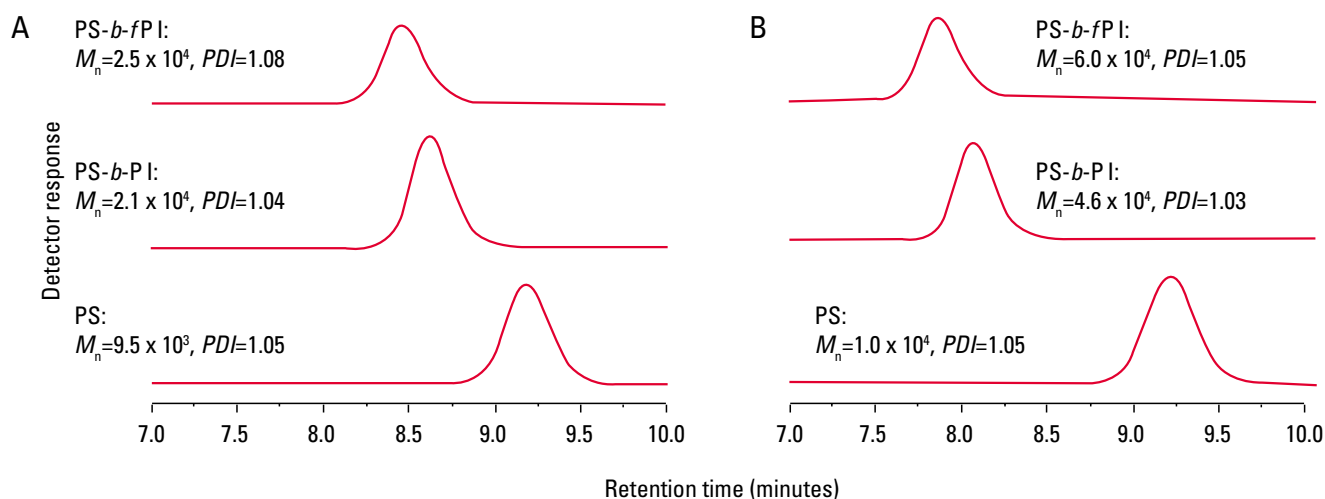
NUMBER-AVERAGE MOLAR MASS, M_n , AND THE POLYDISPERSITY INDEX (PDI) OF sPS-*b*-fPI AND THE PRECURSOR POLYMER (PS-*b*-PI)

Series ^a	PS- <i>b</i> -PI		sPS- <i>b</i> -fPI	
	M_n (SEC)	PDI	M_n (SEC)	PDI
1	2.1×10^4	1.04	2.5×10^4	1.08
2	4.6×10^4	1.03	6.0×10^4	1.05

^a series 1 in acid form; series 2 in Na form

STRUCTURE OF SULFONATED POLYSTYRENE-*b*-FLUORINATED POLYISOPRENE (sPS-*b*-fPI)

➤ **FIGURE 19**



SULFONATED POLYSTYRENE-*b*-FLUORINATED POLYISOPRENE PRECURSOR SAMPLES

TSKgel SuperMultiporeHZ-M, 4.6 mm ID x 15 cm x 1; Samples: A. series 1, table 3 B, series 2, table 3; Mobile Phase: THF; Flow rate: 0.35 mL/min; Detection: RI; Temperature: 35°C Inj. vol.: 20 μ L

³Wang, X.; Hong, K.; Baskaran, D.; Goswami, M.; Sumpter, B.; Mays, J. *Soft Matter*, 2011, 7, 7960



TSKgel COLUMNS AND STANDARDS

TSKgel GPC COLUMNS

SEMI-MICRO COLUMNS

Tosoh introduced its first line of GPC columns in 1971. Ever since, Tosoh scientists have made important contributions to advances in polymer analysis by developing state-of-the-art GPC columns for the most demanding applications.

Semi-micro columns are the TSKgel columns of choice for use with the EcoSEC GPC System. They are referred to as such since their dimensions are smaller than conventional columns in terms of internal diameter as well as in length: 4.6 mm or 6 mm ID x 15 cm vs. 7.8 mm ID x 30 cm.

GPC COLUMNS FOR POLYMERS SOLUBLE IN ORGANIC SOLVENTS

Semi-micro columns* (4.6 or 6.0 mm ID x 15 cm)

- TSKgel SuperMultiporeHZ columns
- TSKgel SuperHZ columns for ultra-low adsorption
- TSKgel SuperH columns for low adsorption



Conventional columns (7.8 mm ID x 30 cm)

- TSKgel H_{XL} columns for ultra-low adsorption
- TSKgel H_{HR} columns for low adsorption; max temp. 140°C

GPC COLUMNS FOR POLYMERS SOLUBLE IN POLAR ORGANIC SOLVENTS

Semi-micro columns* (6.0 mm ID x 15 cm)

- TSKgel SuperAW columns

Conventional columns (7.8 mm ID x 30 cm)

- TSKgel Alpha columns

*EcoSEC GPC System recommended columns

*EcoSEC GPC System recommended columns



GPC COLUMNS FOR POLYMERS SOLUBLE IN AQUEOUS SOLVENTS

Semi-micro columns* (6.0 mm ID x 15 cm)

- TSKgel SuperMultiporePW columns

*EcoSEC GPC System recommended columns



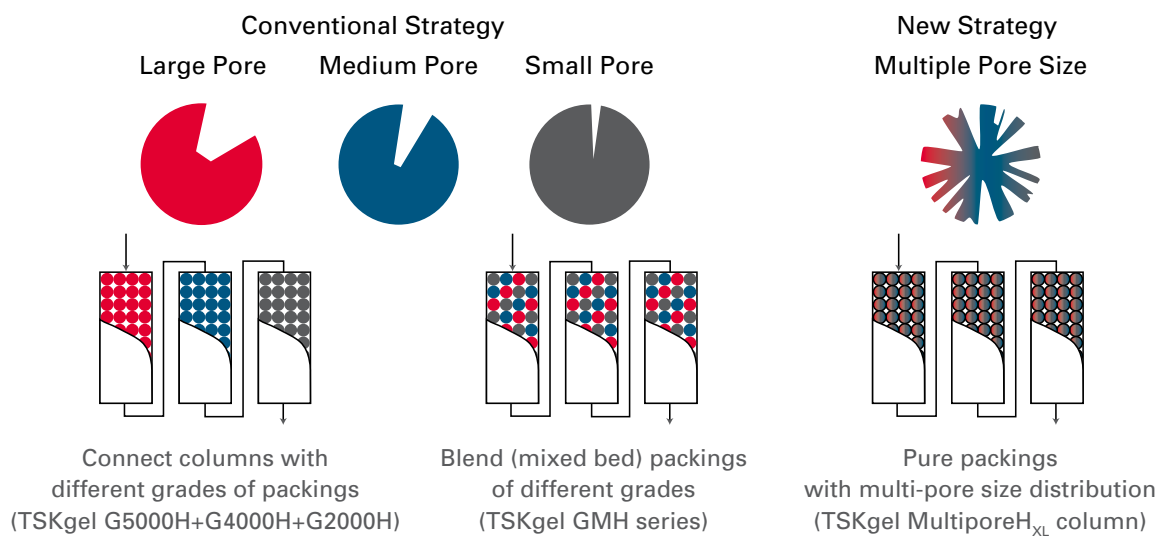
TSKgel COLUMNS AND STANDARDS

MULTI-PORE TECHNOLOGY

Prior to the introduction of TSKgel SuperMultiporeHZ columns, scientists separating polymers with a wide range of molar masses were left with two options. One option is to use multiple columns of different pore sizes linked together in series. A second is to use a column packed with a mixed-bed resin of different pore sizes at an optimized mix ratio. However, problems can occur with both of these methods, which include distortion of the chromatogram or deviations between the actual calibration curve and the calibration curve approximated from data obtained from the molar mass standards.

As is shown in Figure 20, a novel approach to solve this problem was developed by Tosoh scientists and is incorporated in TSKgel SuperMultiporeHZ columns. These columns are packed with small particles of uniform size synthesized with a broad distribution of pore sizes. This novel approach creates a linear calibration curve within each particle. Therefore, columns with an extended linear calibration curve can now be prepared without mixing particles of different pore sizes. Their small ID (4.6 mm ID) and length (15 cm) reduces solvent consumption, results in quick run times, and offers high throughput capabilities.

FIGURE 20

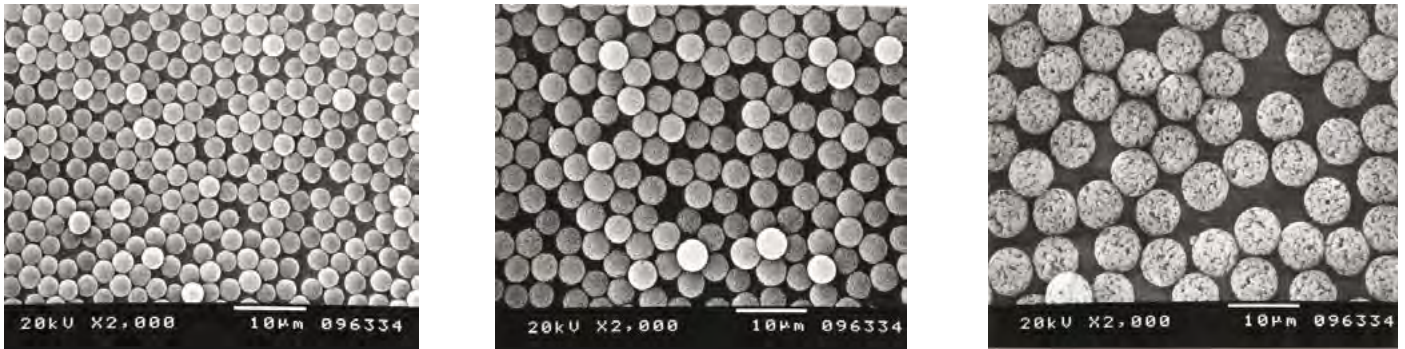


GRAPHICAL REPRESENTATIONS ILLUSTRATE THE MULTI-PORE PARTICLE SYNTHESIS TECHNOLOGY

TSKgel COLUMNS AND STANDARDS



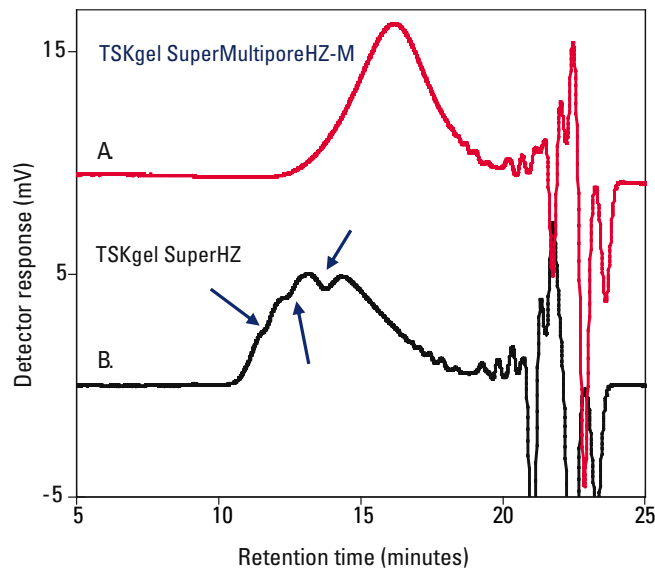
➤ **FIGURE 21**



TSKgel SuperMultiporeHZ COLUMNS PACKED WITH MONODISPERSE PARTICLES

Figure 21 shows the monodispersity of the particle size distribution of TSKgel SuperMultiporeHZ columns compared to a conventional mixed-bed column.

➤ **FIGURE 22**



COMPARISON OF TSKgel SuperMultiporeHZ-M AND TSKgel SuperHZ COLUMNS FOR THE SEPARATION OF ACRYLIC RESIN

Figure 22 demonstrates that inflection points are no longer observed with columns packed from particles prepared by multi-pore technology.



TSKgel COLUMNS AND STANDARDS

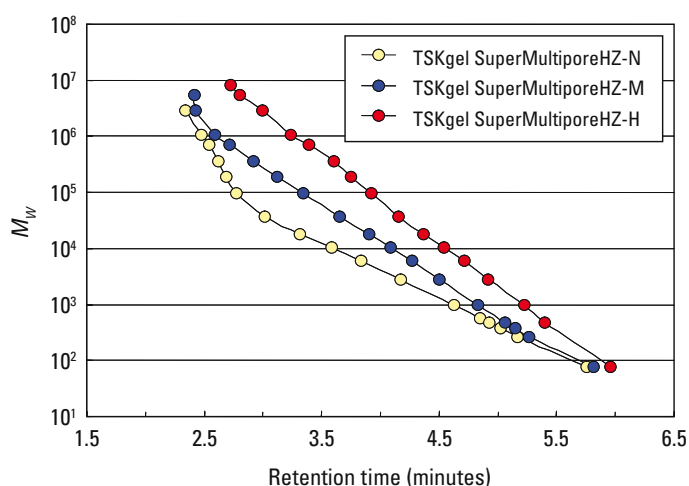
TSKgel SuperMultiporeHZ COLUMNS

TSKgel SuperMultiporeHZ columns combine ultra high performance GPC columns with low dead volume (4.6 mm ID x 15 cm) and feature multi-pore particles with a wide pore size distribution. The use of the multi-pore technology ensures that the calibration curves have excellent linearity. There are three columns available within the TSKgel SuperMultiporeHZ columns, each with a different particle size, separation range, and exclusion limit. These columns can separate and characterize polymers within a wide molar mass range.

As demonstrated in Figure 23, the TSKgel SuperMultiporeHZ columns have a highly linear calibration curve with a shallow slope, which indicates excellent reproducibility across various average molar mass values.

The TSKgel SuperMultiporeHZ-N columns provide the same or higher resolution at a much shorter analysis time than multiple columns linked together, as shown in Figure 5.

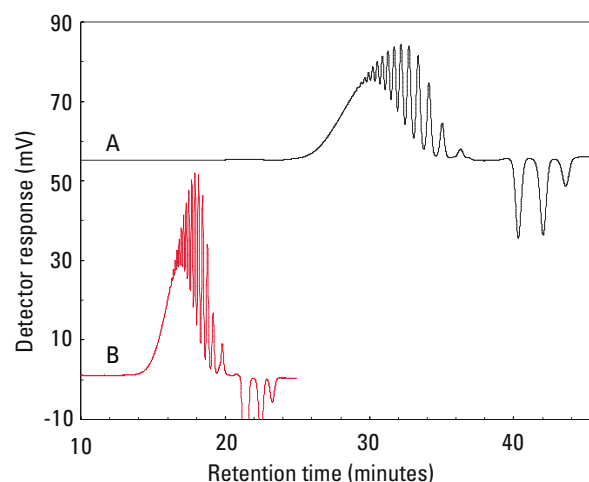
FIGURE 23



CALIBRATION CURVES OF TSKgel SuperMultiporeHZ-M, H AND N COLUMNS

Columns: TSKgel SuperMultiporeHZ-N, 3 μm , 4.6 mm ID x 15 cm; TSKgel SuperMultiporeHZ-M, 4 μm , 4.6 mm ID x 15 cm; TSKgel SuperMultiporeHZ-H, 6 μm , 4.6 mm ID x 15 cm; Samples: PStQuick polystyrene standards; Mobile phase: THF; Flow rate: 0.35 mL/min; Detection: UV@254nm; Temperature: 25°C

FIGURE 24



COMPARING SEMI-MICRO AND CONVENTIONAL GPC COLUMNS

Columns: A. Conventional columns, 7.8 mm ID x 30 cm x 4; B. TSKgel SuperMultiporeHZ-N, 4.6 mm ID x 15 cm x 4; Sample: poly(teramethylene ether glycol); (PTMEG 650), 10 $\mu\text{g}/\mu\text{L}$; Mobile phase: THF; Flow rate: A. 1.0 mL/min B. 0.35 mL/min; Detection: RI; Temperature: 40°C; Injection vol.: A. 50 μL B. 10 μL ;

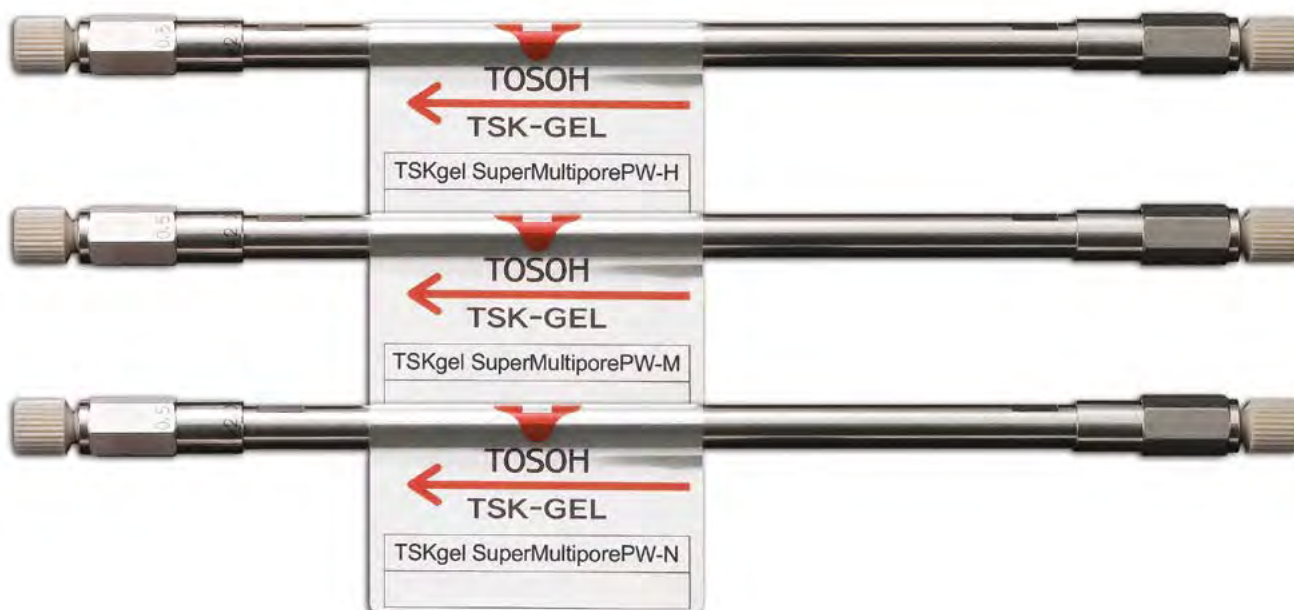
TSKgel COLUMNS AND STANDARDS



TABLE 8

ORDERING INFORMATION

Part #	Description	Particle size (µm)	Exclusion limit (polystyrene)	Theoretical plates/15 cm	Column dimensions
21815	TSKgel SuperMultiporeHZ-N	3	1.2 x 10 ⁵ Da	>20,000	4.6 mm ID x 15 cm
21488	TSKgel SuperMultiporeHZ-M	4	2 x 10 ⁴ Da	>16,000	4.6 mm ID x 15 cm
21885	TSKgel SuperMultiporeHZ-H	6	4 x 10 ³ Da	>11,000	4.6 mm ID x 15 cm
21886	TSKgel SuperMultiporeHZ-H Guardcolumn	6	N/A	N/A	4.6 mm ID x 2 cm
21489	TSKgel SuperMultiporeHZ-M Guardcolumn	4	N/A	N/A	4.6 mm ID x 2 cm
21816	TSKgel SuperMultiporeHZ-N Guardcolumn	3	N/A	N/A	4.6 mm ID x 2 cm





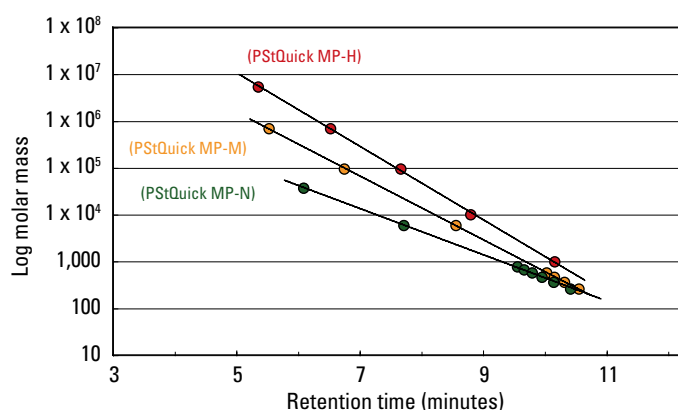
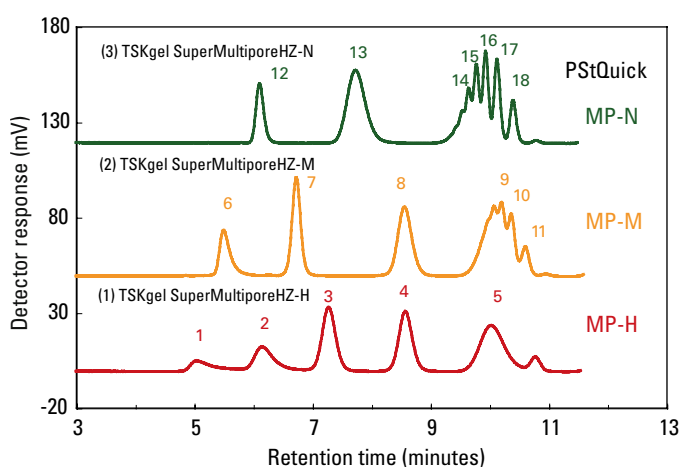
TSKgel COLUMNS AND STANDARDS

PStQuick GPC POLYSTYRENE CALIBRATION STANDARDS

PStQuick polystyrene calibration standards contain pre-mixed quantities of polystyrene polymers in autosampler vials for the calibration of GPC columns. Addition of solvent is all that is required for easy preparation and analysis.

12 different kits containing polystyrene polymers of various molar masses are available. Of the 12 kits, 9 are individual kits, each containing 3 to 5 polystyrene polymers. The remaining 3 are composite kits containing 2 or 3 of the individual kits.

FIGURE 25



(PStQuick MP-H)	(PStQuick MP-M)	(PStQuick MP-N)
1.Mw 5480000(Lot No.TS- 30)	6.Mw 706000(Lot No.TS-201)	12.Mw 37900(Lot No.TS-202)
2.Mw 706000(Lot No.TS-201)	7.Mw 96400(Lot No.TS-144)	13.Mw 5970(Lot No.TS-503)
3.Mw 96400(Lot No.TS-144)	8.Mw 5970(Lot No.TS-503)	14.Mw 682(Lot No.TS-505)
4.Mw 10200(Lot No.TS-508)	9.Mw 474(Lot No.TS-505)	15.Mw 578(Lot No.TS-505)
5.Mw 1010(Lot No.TS-507)	10.Mw 370(Lot No.TS-505)	16.Mw 474(Lot No.TS-505)
	11.Mw 266(Lot No.TS-505)	17.Mw 370(Lot No.TS-505)
		18.Mw 266(Lot No.TS-505)

CHROMATOGRAMS AND CALIBRATION CURVES OBTAINED USING THE PStQuickMP SERIES

Columns: SuperMultiporeHZ-H, 4.6 mm ID x 15 cm x 2; SuperMultiporeHZ-M, 4.6 mm ID x 15 cm L x 2; SuperMultiporeHZ-N, 4.6 mm ID x 15 cm x 2; Sample: PStQuick MPseries; Mobile phase: THF; Flow rate: 0.35 mL/min; Injection volume: 10 µL; Temperature: 25°C; Detection: UV@254nm (UV-8020 microcell)



TSKgel COLUMNS AND STANDARDS



TABLE 9

ORDERING INFORMATION FOR PStQuick POLYSTYRENE CALIBRATION STANDARDS

To calibrate TSKgel SuperMultiporeHZ Columns

Part #	Description	Remarks	Calibration range	Contents	Vials
21912	PStQuick MP-N	For SuperMultiporeHZ-N	5.3×10^2 to 4.4×10^4	A-500, A-5000, F-4	60
21913	PStQuick MP-M	For SuperMultiporeHZ-M	5.3×10^2 to 8.0×10^5	A-500, A-5000, F-10, F-80	60
21914	PStQuick MP-H	For SuperMultiporeHZ-H	9.5×10^2 to 5.5×10^6	A-1000, F-1, F-10, F-80, F-550	60

To calibrate TSKgel H-type Mixed-Bed Columns

Part #	Description	Remarks	Calibration range	Contents	Vials
21915	PStQuick Kit-L	for H-type – N Grade	5.3×10^2 to 4.2×10^5	PStQuick E, F	40**
21916	PStQuick Kit-M	for H-type – M Grade	5.3×10^2 to 2.9×10^6	PStQuick C, D	40**
21917	PStQuick Kit-H	for H-type – H Grade	5.3×10^2 to 8.4×10^6	PStQuick A, B, C	60*

*20 of each type x 3, **20 of each type x 2

To calibrate TSKgel GPC Columns

Part #	Description	Remarks	Calibration range	Contents	Vials
21911	PStQuick A	for other GPC columns	2.8×10^3 to 8.4×10^6	A-2500, F-2, F-20, F-128, F-850	20
21910	PStQuick B	for other GPC columns	9.5×10^2 to 5.5×10^6	A-1000, F-1, F-10, F-80, F-550	20
21909	PStQuick C	for other GPC columns	5.3×10^2 to 2.9×10^6	A-500, A-5000, F-4, F-40, F-288	20
21908	PStQuick D	for other GPC columns	2.8×10^3 to 1.3×10^6	A-2500, F-2, F-20, F-128	20
21907	PStQuick E	for other GPC columns	9.5×10^2 to 4.2×10^5	A-1000, A-5000, F-4, F-40	20
21906	PStQuick F	for other GPC columns	5.3×10^2 to 1.9×10^5	A-500, A-2500, F-2, F-20	20



TSKgel COLUMNS AND STANDARDS

TSKgel POLYSTYRENE CALIBRATION STANDARDS

TSKgel polystyrene bulk calibration standards are used to calibrate size exclusion columns for subsequent analysis of unknown samples. The standards range from 400 to 21,000,000 Da.



TABLE 10

ORDERING INFORMATION FOR TSKgel POLYSTYRENE CALIBRATION STANDARDS

Part #	Description	Weight
05202	A-300, 400 MW	10 g
05203	A-500, 530 MW	10 g
05204	A-1000, 950 MW	10 g
05205	A-2500, 2800 MW	5 g
05206	A-5000, 6200 MW	5 g
05207	F-1, 1.0×10^4 MW	5 g
05208	F-2, 1.7×10^4 MW	5 g
05209	F-4, 4.4×10^4 MW	5 g
05210	F-10, 1.0×10^5 MW	5 g
05211	F-20, 1.9×10^5 MW	5 g
05212	F-40, 4.2×10^5 MW	5 g
05213	F-80, 7.8×10^5 MW	5 g
05214	F-128, 1.3×10^6 MW	1 g
05215	F-288, 2.9×10^6 MW	1 g
05216	F-380, 3.8×10^6 MW	1 g
05217	F-450, 4.5×10^6 MW	1 g
05218	F-550, 5.5×10^6 MW	1 g
05219	F-700, 6.8×10^6 MW	1 g
05220	F-850, 8.4×10^6 MW	1 g
05221	F-2000, 2.1×10^7 MW	1 g
06476	Oligomer Kit, A-500 thru F-128	12 x 1 g
06477	High MW Kit, F-10 thru F-2000	12 x 1 g