



TOSOH

No.083

SEPARATION REPORT

Solvent-Compatible High Performance GPC Columns: TSKgel H_{HR} Series

— Contents —

	Page
1. Introduction	1
2. Features	1
3. Basic Characteristics	5
3-1. Resolution of grades for polymer analysis	5
3-2. Dependence of height equivalent to theoretical plate on flow rate	7
3-3. Solvent compatibility	9
3-4. Mechanical strength	11
3-5. Separation of ultra high molecular weight polymers	11
3-6. Mixed column (linear type)	17
3-7. Effect of adding salt to special solvents	23
4. Applications	27
5. Conclusion	34

1. Introduction

Gel permeation chromatography (GPC) is the dominant analytical procedure used to investigate the molecular properties of polymer substances, such as molecular weight and molecular weight distribution, and is widely used given the good repeatability of the procedure, as well as its relative simplicity and rapidity.

In 1983, Tosoh developed and produced the TSKgel H_{XL} series (hereafter H_{XL} series) of high performance GPC columns for use with organic solvent systems. Up to now, the performance of these columns has been extensively evaluated both inside and outside of the company.

Recently, high performance highly functional polymer materials such as engineering plastics have been developed and commercialized. Due the high performance and high functionality of these polymers, they are not readily soluble (or are insoluble) in solvents conventionally used in GPC such as tetrahydrofuran (THF) and chloroform. As a result, a variety of solvents are being proposed and used for GPC analysis of these polymers as replacements for THF and chloroform. Examples of these include: fluorinated alcohols such as 2,2,2-trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP),¹⁻⁴⁾ pentafluorophenol (PFP)/chloroform,⁵⁾ N-methylpyrrolidone (NMP), dimethylformamide (DMF) and dimethylsulfoxide (DMSO). For the most part, these solvents have stronger polarity and higher viscosity than THF and chloroform, and are difficult to use in conventional H_{XL} columns from the perspective of durability and stability. Moreover, conversion to these solvents from THF has been a problem, and usage conditions have been limited with conventional columns. Furthermore, using an unsuitable solvent during analysis (eluent conditions) can cause adhesion and repulsion, etc., to occur as a result of interactions between the packing material and the sample.

Thus, it has now become difficult to assure the repeatability, stability, and accuracy of GPC analyses of various types of polymers under conventional analysis conditions alone (for example, using a H_{XL} column with THF as the solvent).

The TSKgel H_{HR} series (hereafter H_{HR} series) is a series of GPC columns for use with organic solvent systems that is packed with a material designed and developed to solve all of these problems. This series of columns not only has the ability to withstand conversion between solvents, it also improves analysis stability under specialized conditions or with specialized solvents, in comparison to the H_{XL} series.

In this report, the features and basic characteristics of the TSKgel H_{HR} series will be introduced, and application examples are presented.

2. Features

The TSKgel H_{HR} series contains a highly cross-linked styrene-vinyl benzene copolymer that maintains the pore characteristics of the TSKgel H_{XL} series while at the same time is extremely robust, with virtually no swelling or shrinkage, and which, as a result, facilitates conversion between various solvents, and increases polymer-analysis grade performance.

Table 1 compares the performance characteristics of the H_{HR} and H_{XL} series. Grades used for polymer analysis (G5000 H_{HR} – G7000 H_{HR} and GMH_{HR}-M, and -H) use a 5-μm packing material, in contrast to the 10-μm size packing material of the conventional H_{XL} series. As a result, the guaranteed number of theoretical plates is increased from 14,000 TP/30 cm to 16,000 TP/30 cm, and performance is elevated. Moreover, the grades used for analyzing low molecular weight substances (G1000 H_{HR} - G4000 H_{HR} and GMH_{HR}-L) maintain the same performance levels as the H_{XL} series. In addition, an S-type grade has been prepared for high temperature analysis of ultra high molecular weight substances for use in separation of polymers.

Table 2 lists the solvents that the H_{HR} series can accommodate. As shown in this table, the TSKgel H_{HR} series can be converted to accommodate a variety of organic solvents, and has excellent stability with each of these solvents. In addition, this series of columns is shipped with THF preloaded as the solvent, making it possible to be directly converted to a variety of organic solvents.

Figures 1 to 8 show calibration curves of the TSKgel H_{HR} series produced when various standard samples were analyzed in a variety of solvents.

Table 1 Comparison of performance of TSKgel H_{HR} and H series

Column	H _{HR}		H <subxl< sub=""></subxl<>	
	Particle size (μm)	Guaranteed number of theoretical plates (TP/column)	Particle size (μm)	Guaranteed number of theoretical plates (TP/column)
G1000H	5	16000	5	16000
G2000H	5	16000	5	16000
G2500H	5	16000	5	16000
G3000H	5	16000	5	16000
G4000H	5	16000	5	16000
G5000H	5	16000	10	14000
G6000H	5	16000	10	14000
G7000H	5	16000	10	14000
G5000H (S)	13	8000	—	—
G6000H (S)	13	8000	—	—
G7000H (S)	13	8000	—	—
GMH-H	5	16000	—	—
GMH-M	5	16000	—	—
GMH-L	5	16000	5	16000
GMH	—	—	10	14000
GMH-H (S)	13	8000	—	—
GMH-M (S)	13	8000	—	—

Conditions for analyzing number of theoretical plates

Column size: 7.8 mm I.D. x 30 cm

Solvent: Tetrahydrofuran (THF)

Flow rate: 1.0 mL/min

Samples: Benzene: G1000H - G2500H

n-butylbenzene: G3000H, G4000H and GMH-L

Dicyclohexylphthalate: G5000H to G7000H, GMH-M, and GMH-H

Table 2 Solvents that can be used in TSKgel H_{HR} series

Solvent compatible solvents
Toluene, xylene, chloroform, benzene, dichloromethane, dichloroethane, dimethylformamide, dimethylsulfoxide, dioxane, N-methylpyrrolidone, m-cresol/chloroform, quinoline, methyl ethyl ketone (MEK), o-dichlorobenzene, trichlorobenzene, hexafluoroisopropanol (HFIP), HFIP/chloroform, o-chlorophenol/chloroform, pyridine, carbon tetrachloride, ethyl acetate, methanol/chloroform, THF/methanol, acetone, ethanol, dimethylacetamide, n-hexane, dodecane, 1-chloronaphthalene, FC-113, trichloroethane

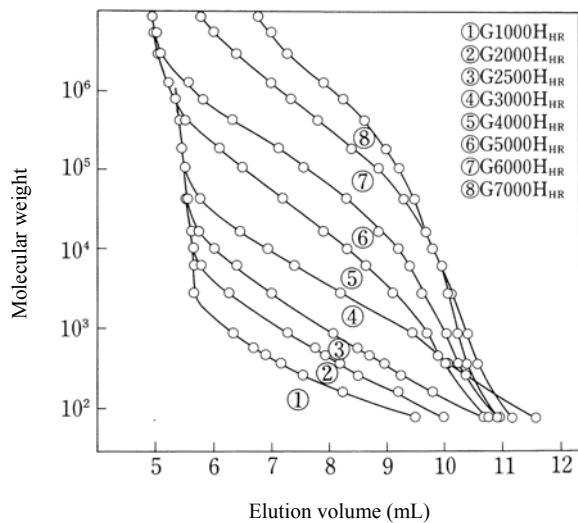


Fig. 1 Calibration curves produced by polystyrene in THF

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: Tetrahydrofuran (THF)

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

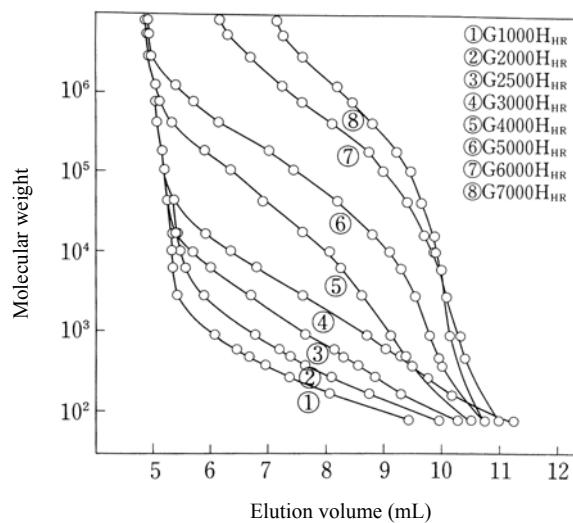


Fig. 3 Calibration curves produced by polystyrene in chloroform

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: Chloroform

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

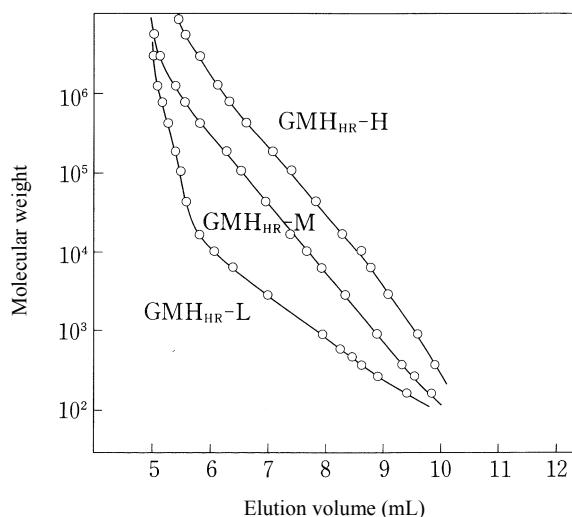


Fig. 2 Calibration curves produced by polystyrene in THF

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

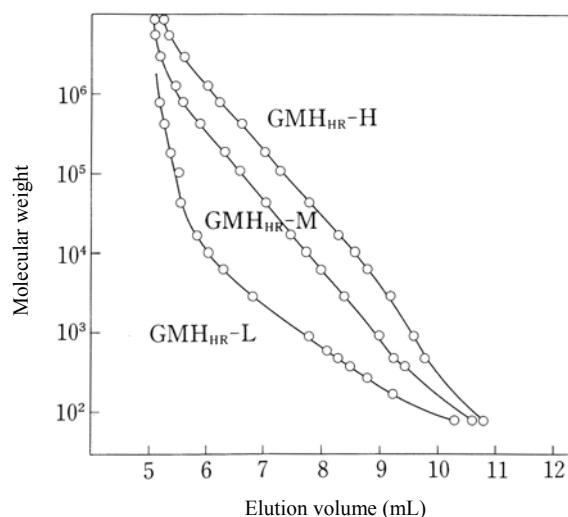


Fig. 4 Calibration curves produced by polystyrene in chloroform

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: Chloroform

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

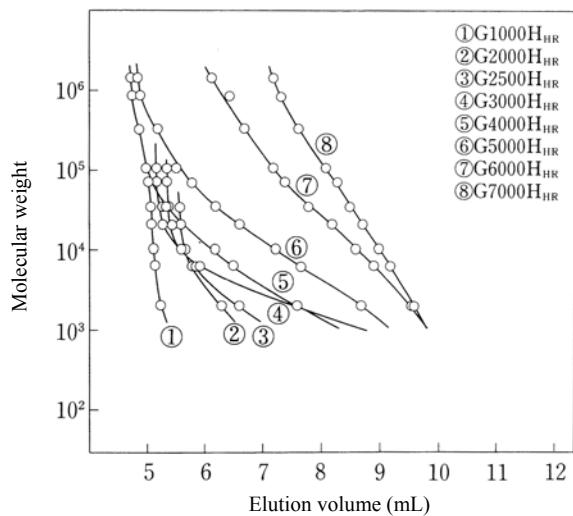


Fig. 5 Calibration curves produced by polymethylmethacrylate in HFIP

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: 5 mM sodium trifluoroacetate in HFIP

Flow rate: 1.0 mL/min

Temperature: 40 °C

Detection: UV (220 nm)

Sample: Standard polymethylmethacrylate

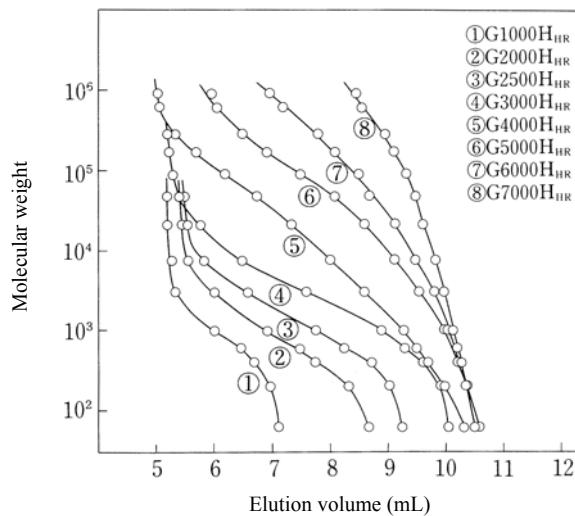


Fig. 7 Calibration curves produced by PEO and PEG in DMF

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: 10 mM lithium bromide in DMF

Flow rate: 10 mL/min

Temperature: 25 °C

Detection: RI

Samples: Standard polyethylene oxide and polyethylene glycol

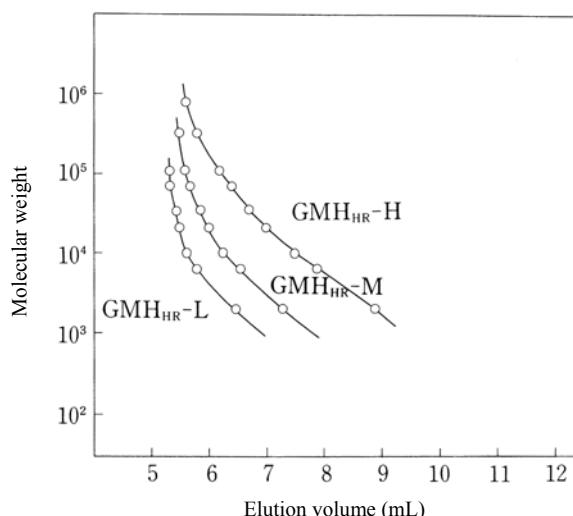


Fig. 6 Calibration curves produced by polymethylmethacrylate in HFIP

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: 5 mM sodium trifluoroacetate in HFIP

Flow rate: 1.0 mL/min

Temperature: 40 °C

Detection: UV (220 nm)

Sample: Standard polymethylmethacrylate

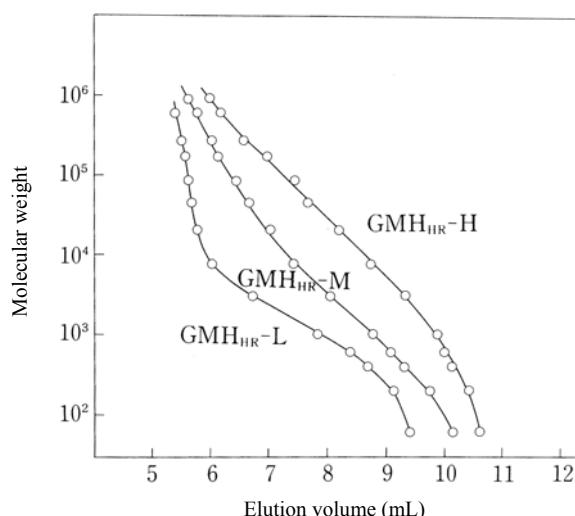


Fig. 8 Calibration curves produced by PEO and PEG in DMF

Columns: TSKgel H_{HR} series (7.8 mm I.D. x 30 cm)

Solvent: 10 mM lithium bromide in DMF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: RI

Samples: Standard polyethylene oxide and polyethylene glycol

3. Basic Characteristics

3-1. Resolution of grades for polymer analysis

Table 1 shows the grades used for polymer analysis: G5000H_{HR} - G7000H_{HR}, GMH_{HR}-M and GMH_{HR}-H. The particle size of the packing material has been decreased to 5 µm, realizing better resolution in comparison with the H_{XL} series.

Fig. 9 compares chromatograms of the separation of a

mixed polystyrene sample produced using the G5000H_{HR} and G5000H_{XL}. Fig. 10 compares chromatograms of the separation of a mixed polystyrene sample produced using the GMH_{HR}-H and GMH_{XL} and GMH_{HR}-H (S). It is clear that in both grades better separation is achieved with the H_{HR} series than the conventional H_{XL} series.

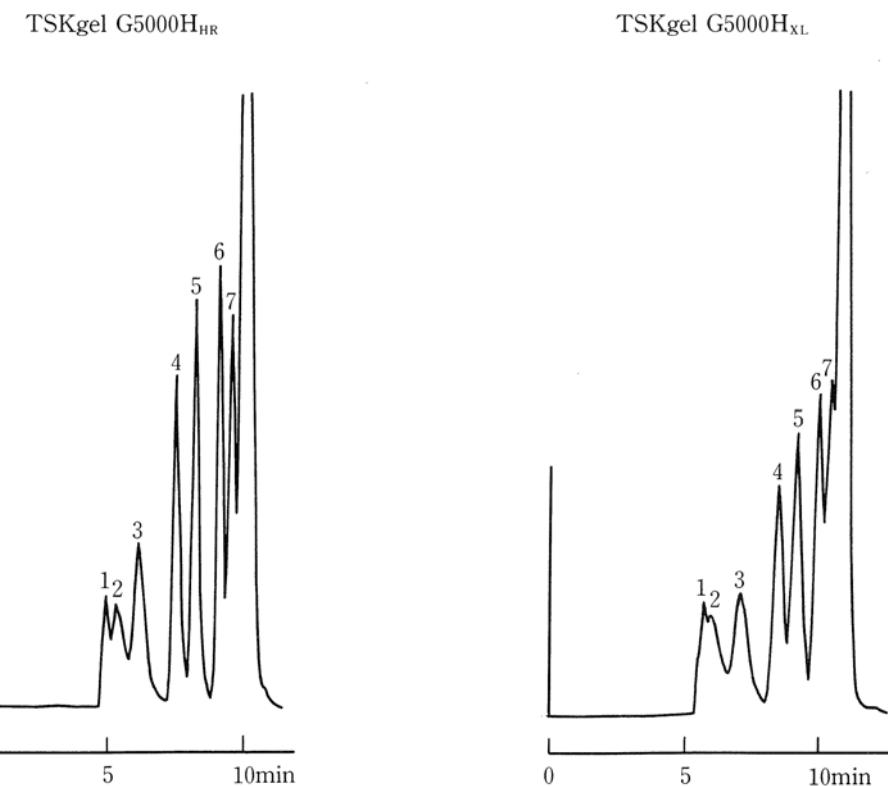


Fig. 9 Comparison of resolution of TSKgel G5000H_{HR} and TSKgel G5000H_{XL}

Columns: TSKgel G5000H_{HR} and TSKgel G5000H_{XL}
(both: 7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 2,890,000 2.MW 1,260,000

3.MW 422,000 4.MW 107,000

5.MW 42,800 6.MW 10,200

7.MW 2,800

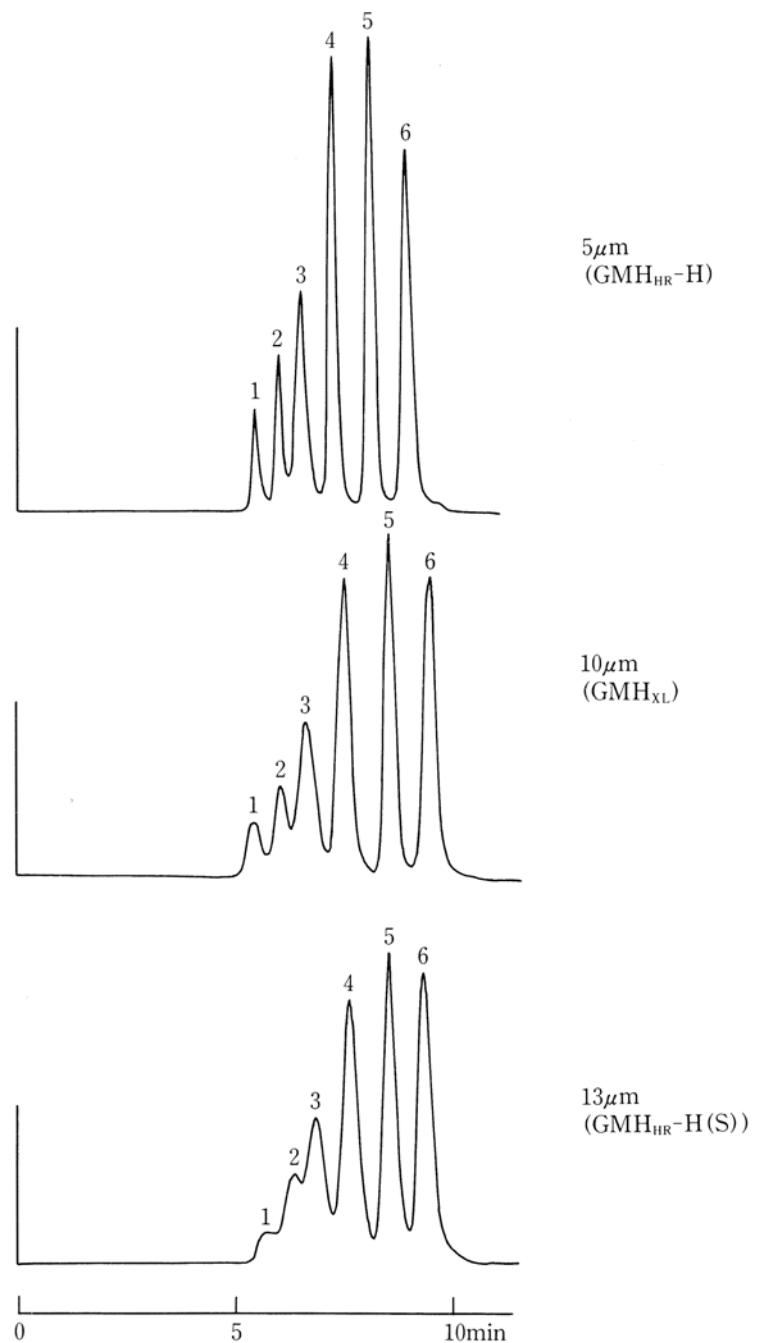


Fig. 10 Separations of polystyrene mixtures by TSKgel GMH

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{XL}, TSKgel GMH_{HR}-H (S)
(all 7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 8,420,000	2.MW 1,260,000
3.MW 422,000	4.MW 107,000
5.MW 16,700	6.MW 2,800

3-2. Dependence of height equivalent to theoretical plate on flow rate

Height equivalent to theoretical plate (HETP) depends greatly on the particle size of the packing material, the molecular size of the sample, and the viscosity of the solvent, etc. Fig. 11 shows a comparison of the flow rate dependency of HETP in the GMH_{HR}-H (5 μm) versus the GMH_{XL} (10 μm) and GMH_{HR}-H(S) (13 μm), using dicyclohexyl phthalate (DCHP) as the sample.

When separating DCHP, a low molecular weight sample, in the GMH_{HR}-H, there is little change in HETP, even when the flow rate is increased. On the other hand the GMH_{XL} and GMH_{HR}-H(S) are affected by flow rate, as HETP increases at high flow rates (1.5 mL/min or more).

Thus, with the GMH_{HR}-H, containing a packing material comprised of small-sized particles, HETP depends little on flow rate when a low molecular weight sample (DCHP) is analyzed. Therefore, analysis time can be reduced by using a high flow rate (1.5 to 2.0 mL/min).

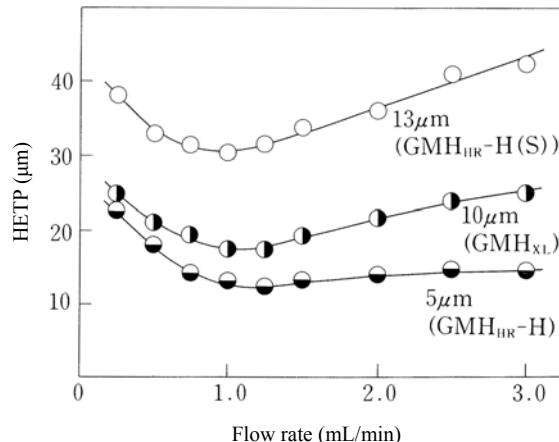


Fig. 11 Relationship between flow rate and HETP in TSKgel GMH

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{XL},
TSKgel GMH_{HR}-H (S)
(all 7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 0.25 mL/min to 3.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Dicyclohexyl phthalate (DCHP)

Fig. 12 shows the relationship between flow rate and resolution of polymer samples using GMH_{HR}-H, GMH_{HR}-H(S), and GMH_{XL}. Resolution was least dependent on flow rate in GMH_{HR}-H (5 μm), but regardless of the particle size of the packing material, resolution decreased as the flow rate increased. Consequently, a suitable flow rate should be 0.5 mL/min or less when analyzing particularly high molecular weight polymer samples.

Figures 13 to 15 show how the separation of a standard polyethylene mixture depends on flow rate, in the GMH_{HR}-H, GMH_{XL} and GMH_{HR}-H(S). The GMH_{HR}-H shows little flow rate dependence, and is able to perform analyses at high flow rates, even with a polymer sample with a molecular weight around 3,000,000. However, from the perspective of individual peak sharpness, with general samples including polymers, a flow rate between 0.5 and 1.0 mL/min is considered optimal.

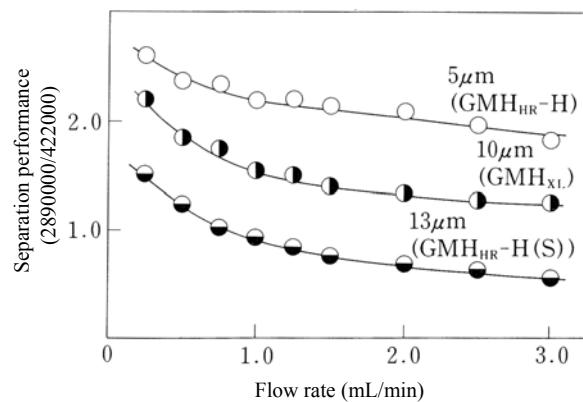


Fig. 12 Relationship between flow rate and resolution in TSKgel GMH

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{XL},
TSKgel GMH_{HR}-H (S)
(all 7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 0.25 mL/min to 3.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

MW 2,890,000 422,000

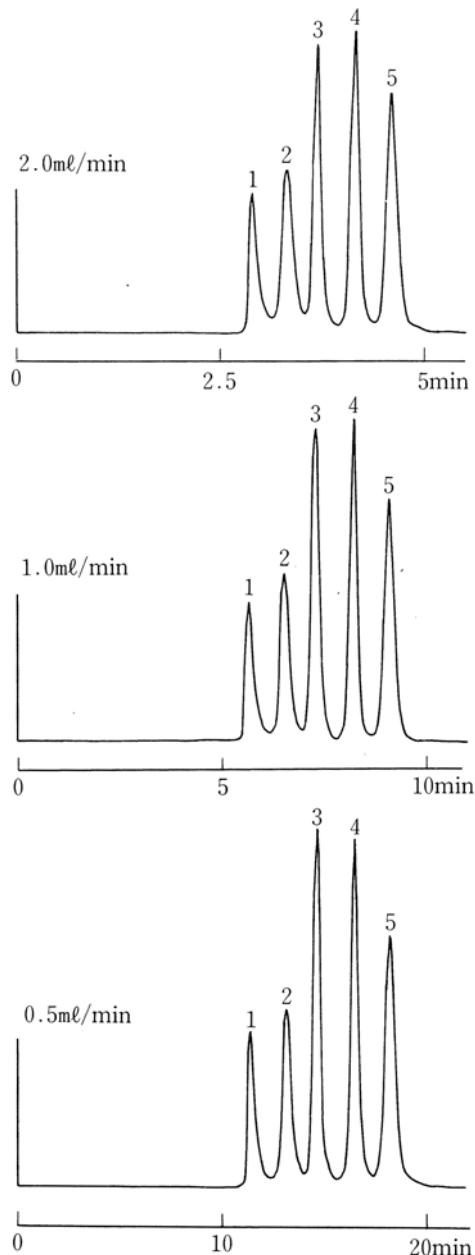


Fig. 13 Flow rate dependence of separation of standard polystyrenes by TSKgel GMH_{HR}-H

Columns: TSKgel GMH_{HR}-H (7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 0.5, 1.0, and 2.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 2,890,000	2.MW 422,000
3.MW 107,000	4.MW 16,700
5.MW 2,800	

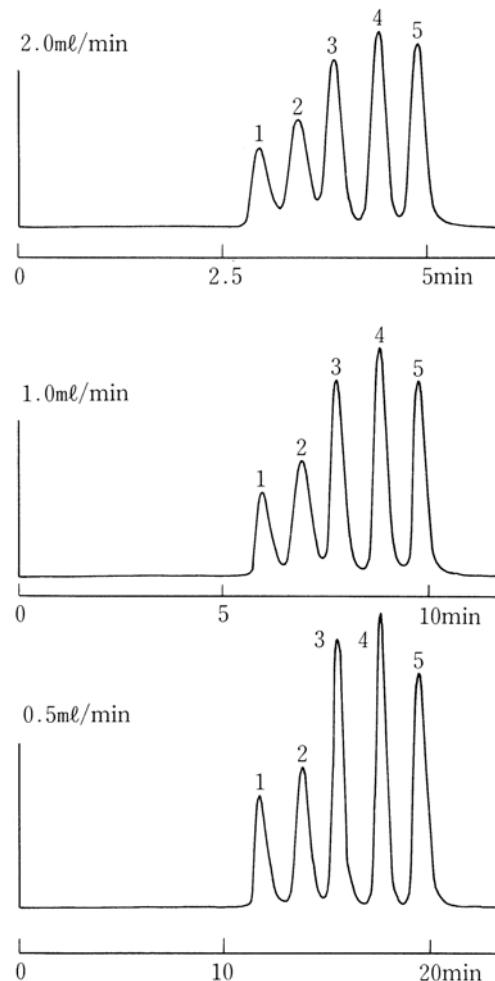


Fig. 14 Flow rate dependence of separation of standard polystyrenes by TSKgel GMH_{XL}

Columns: TSKgel GMH_{XL} (7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 0.5, 1.0, and 2.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 2,890,000	2.MW 422,000
3.MW 107,000	4.MW 16,700
5.MW 2,800	

3-3. Solvent compatibility

Table 3 compares the swelling and shrinkage properties of the packing materials in the G2000H_{HR} and G2000H_{XL} in various organic solvents. The packing materials in the H_{HR} series experience much less swelling and shrinkage in each of the solvents than those in the H_{XL} series. This logically suggests that with these columns it would be possible to replace THF, which is loaded in the column at the time of shipment, with a variety of other solvents.

Table 3 Comparison of swelling and shrinkage properties of TSKgel G2000H_{HR} and G2000H_{XL}

Solvent	Swelling/shrinkage	
	G2000H _{HR}	G2000H _{XL}
Toluene	1.01	1.06
Benzene	1.00	—
THF	1.00	1.00
DMF	0.99	0.86
Acetone	0.99	0.86
Methanol (MeOH)	0.98	0.67
THF/water = 1/1	0.98	—
MeOH/water = 1/1	0.93	—
Water	0.86	0.52

* Swelling or shrinkage with each solvent calculated based on 1.00 as the index for the swelling volume that occurs with THF.

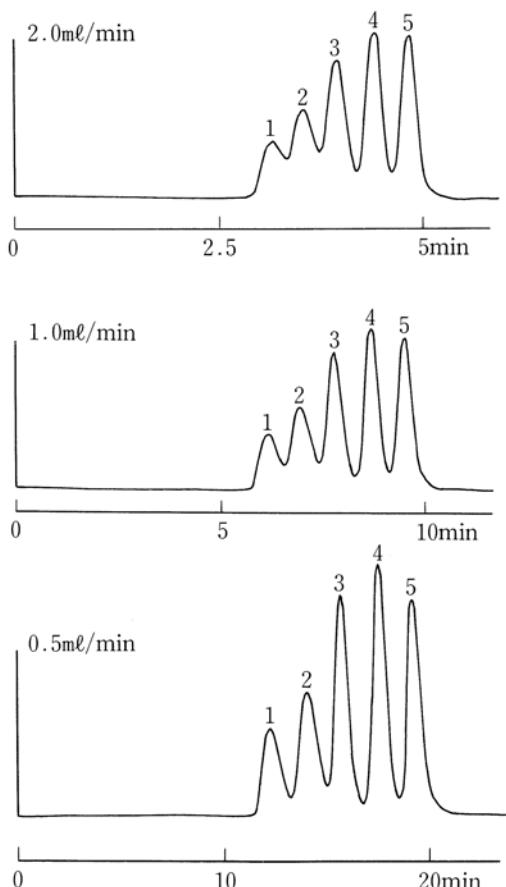


Fig. 15 Flow rate dependence of separation of standard polystyrenes by TSKgel GMH_{HR}-H(S)

Columns: TSKgel GMH_{HR}-H(S) (7.8 mm I.D. x 30)

Solvent: THF

Flow rate: 0.5, 1.0, and 2.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 2,890,000	2.MW 422,000
3.MW 107,000	4.MW 16,700
5.MW 2,800	

Tables 4 and 5 show the changes in the number of theoretical plates when the solvent in the column is directly converted from THF to other organic solvents. The following procedure for converting between solvents was followed: first, the solvent was directly converted from THF to an organic solvent, then after leaving this solvent in the column for 1 week, it was converted back to THF, and then converted again to another solvent. In other words, solvent conversion was performed in sets (THF → organic solvent) continuously run as the solvent was converted from THF to a different organic solvent and back again, while examining changes in the performance of the packing material under these conditions.

Table 4 shows that in the G2000H_{HR}, despite converting to 8 different organic solvents, the number of theoretical plates for benzene changed very little, and column performance remained stable even when repeatedly converting to different solvents.

Table 5 compares solvent compatibility in the G1000H and G2500H and the H_{HR} and H_{XL} series. In the H_{XL} series, the solvent could be converted to chloroform or DMF, but when it was converted to HFIP, a void appeared on the column inlet side, and the packing material contracted.

On the other hand, in the H_{HR} series, the solvent could be directly converted from THF to another solvent, even to HFIP, and could also withstand the continuous replacement of solvents thereafter up through ethanol. However, with G2500H_{HR}, after the solvent was converted to ethanol, the number of theoretical plates for benzene dropped noticeably below 16,000, the guaranteed number of plates.

Thus, the TSKgel H_{HR} series can be converted from a good solvent (THF, chloroform, etc.) to a poor solvent (DMF, HFIP, etc.), which is not possible with the conventional H_{XL} series. Moreover, solvent conversion can also be performed at the same flow rate as analysis (0.5 to 1.0 mL/min). Furthermore, conversion from a poor solvent to another poor solvent (for example, from DMSO to DMF, or from acetone to methanol, etc.) is also possible. In particular, when converting to a high

viscosity solvent, this can generally be accommodated by reducing the flow rate to 0.3 mL/min or less.

As a result, because a single H_{HR} column can be converted to accommodate various organic solvents, by using these columns, analyses can be conducted with a variety of organic solvents, which is expected to provide a great deal of information.

Table 4 Solvent compatibility of TSKgel G2000H_{HR}

Solvent	Column No. 1	Column No. 2
	Number of theoretical plates (TP/30 cm)	
THF	22200	20900
Chloroform		
THF	21400	20300
DMF		
THF	21800	23400
DMSO		
THF	24100	21200
Dioxane		
THF	223000	20700
ODCB		
THF	22300	21100
Acetone		
THF	22400	19800
HFIP		
THF	22000	19300
Quinoline		
THF	21700	19900

<Solvent conversion conditions>

Flow rate during conversion to test solvent: 1.0 mL/min
Temperature during conversion to test solvent: 25 °C
Duration of conversion from THF to test solvent: 16 hours
Time left in column with test solvent: 1 week
Flow rate during conversion from test solvent to THF: 1.0 mL/min
Duration of conversion from test solvent to THF: 1 hour

<Conditions for measuring number of theoretical plates>

Solvent: THF
Flow rate: 1.0 mL/min
Temperature: 25 °C
Detection: UV (254 nm)
Sample: Benzene, 20 µL

Table 5 Comparison of solvent compatibility of TSKgel H_{HR} and H_{XL} series

Solvent	H _{HR}		H _{XL}	
	G1000	G2500	G1000	G2000
Number of theoretical plates (TP/30 cm)				
THF	18700	20700	20300	20550
Chloroform				
THF	19000	17800	20400	20800
DMF				
THF	18700	18200	17200	21300
HFIP			Void*	Void*
THF	18200	16600		
Methyl cellosolve			Void*	Void*
THF	18500	17400		
DMSO				Void*
THF	16900	18200		
Carbon tetrachloride				
THF	19500	17200		
Methanol				Void*
THF	17200	15400		

<Solvent conversion conditions>

Flow rate during conversion to test solvent: 1.0 mL/min
Temperature during conversion to test solvent: 25 °C
Duration of conversion from THF to test solvent: 24 hours
Time left in column with test solvent: 1 week
Flow rate during conversion from test solvent to THF: 1.0 mL/min
Duration of conversion from test solvent to THF: 1 hour

<Conditions for measuring number of theoretical plates>

Solvent: THF
Flow rate: 1.0 mL/min
Temperature: 25 °C
Detection: UV (254 nm)
Sample: Benzene, 20 µL
*: Void occurred on the column inlet side.

3-4. Mechanical strength

Fig. 16 shows changes in column efficiency when a sample was passed through the G2000H_{HR}, G2500H_{HR}, G2000H_{XL} and G2500H_{XL} at a flow rate of 2.5 mL/min. In the H_{XL} series, at a high flow rate, the number of theoretical plates decreases as the running time increases. However, in the H_{HR} series, there is no change in the number of theoretical plates even after 400 hours, and it is clear that the H_{HR} series not only has the ability to withstand solvent conversion, but also has excellent mechanical strength.

3-5. Separation of ultra high molecular weight polymers

Reducing the particle size of the packing material to the microparticulate level, creating high performance columns, and concluding high level separation and analysis in a short amount of time are extremely important to sample analysis. However, to accurately measure the average molecular weight and mean molecular distribution of ultra high molecular weight polymers, it is vital to be aware of the following issues:

- (1) Solvent load (concentration, injection volume)
- (2) Overloading
- (3) Shear degradation
- (4) Column temperature

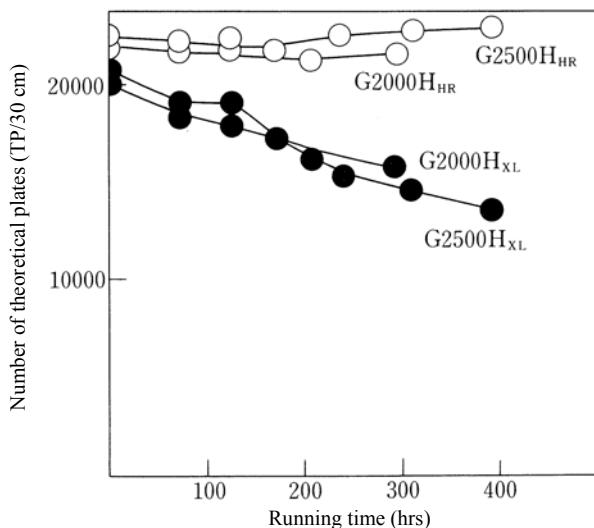


Fig. 16 Change in column efficiency of TSKgel H_{HR} and H_{XL} at high flow rate

Columns: TSKgel G2000H_{HR}, TSKgel G2500H_{HR},
TSKgel G2000H_{XL} and TSKgel G2500H_{XL}
(each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Benzene

Conditions for measuring number of theoretical plates as shown in Table 4.

3-5-1. Sample load

Sample load depends on the type and molecular weight of the sample, the mobile phase, and the particle size of the packing material. The sample load decreases as the molecular weight of the sample increases and the particle size of the packing material decreases. Moreover, in the case of polymer samples, known methods for increasing the sample load include reducing the sample concentration as much as possible (0.02% or below) and increasing the injection volume.^{6,7)}

Fig. 17 shows the relationship between sample injection volume and resolution of standard polystyrenes (MW: 2,890,000 and 422,000) using the GMH_{HR}-H, GMH_{XL}, and GMH_{HR}-H(S). The dependence of resolution on the sample injection volume increases as the particle size grade decreases. The maximum sample load that does not cause a decrease in resolution is considered to be 10 µL or less with the GMH_{HR}-H, about 20 µL with the GMH_{XL}, and around 100 µL with the GMH_{HR}-H(S). In addition, with the GMH_{HR}-H, when overloading does not appear, a comparatively high level of resolution is obtained even with a sample load around 50 µL. It is also clear that the large particle size TSKgel GMH_{HR}-H(S) would be superior when a larger injection volume than this is required.

3-5-2. Overloading

Similar to the problems seen with the sample load, overloading can also occur when the injection volume is increased when separating polymer samples. Figures 18 to 20 show the effects produced by sample injection volume in packing materials of different particle sizes. With the GMH_{HR}-H, as shown in Figure 18, when a MW 2,890,000 sample is analyzed at an injection volume of 20 µL and higher, or when a MW 422,000 sample is analyzed at an injection volume of 100 µL, overloading occurs, peak spreading appears, and peaks appear later than their normal elution positions. Figure 19 shows that similar results occur in the GMH_{XL} when a 100 µL sample is injected.

On the other hand, in the GMH_{HR}-H(S), which has a large particle size (13 µm), overloading does not appear, and as discussed above in 3-5-1, the GMH_{HR}-H(S) is optimal for use when there is a need to increase the injection volume of a polymer sample.

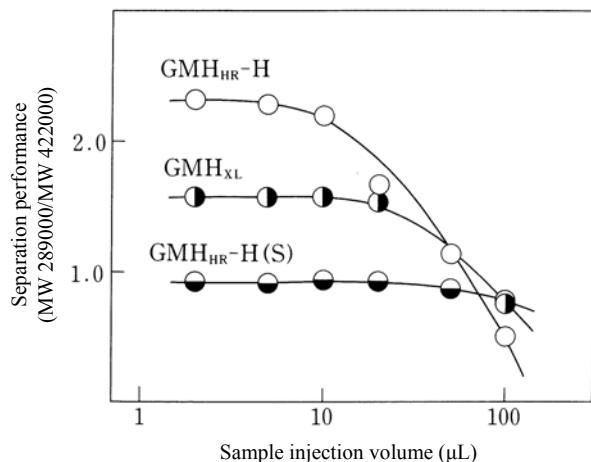


Fig. 17 Relationship between resolution and sample injection volume in TSKgel GMH

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{XL},
TSKgel GMH_{HR}-H(S) (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Samples: Standard polystyrene (MW: 2,890,000, 422,000)

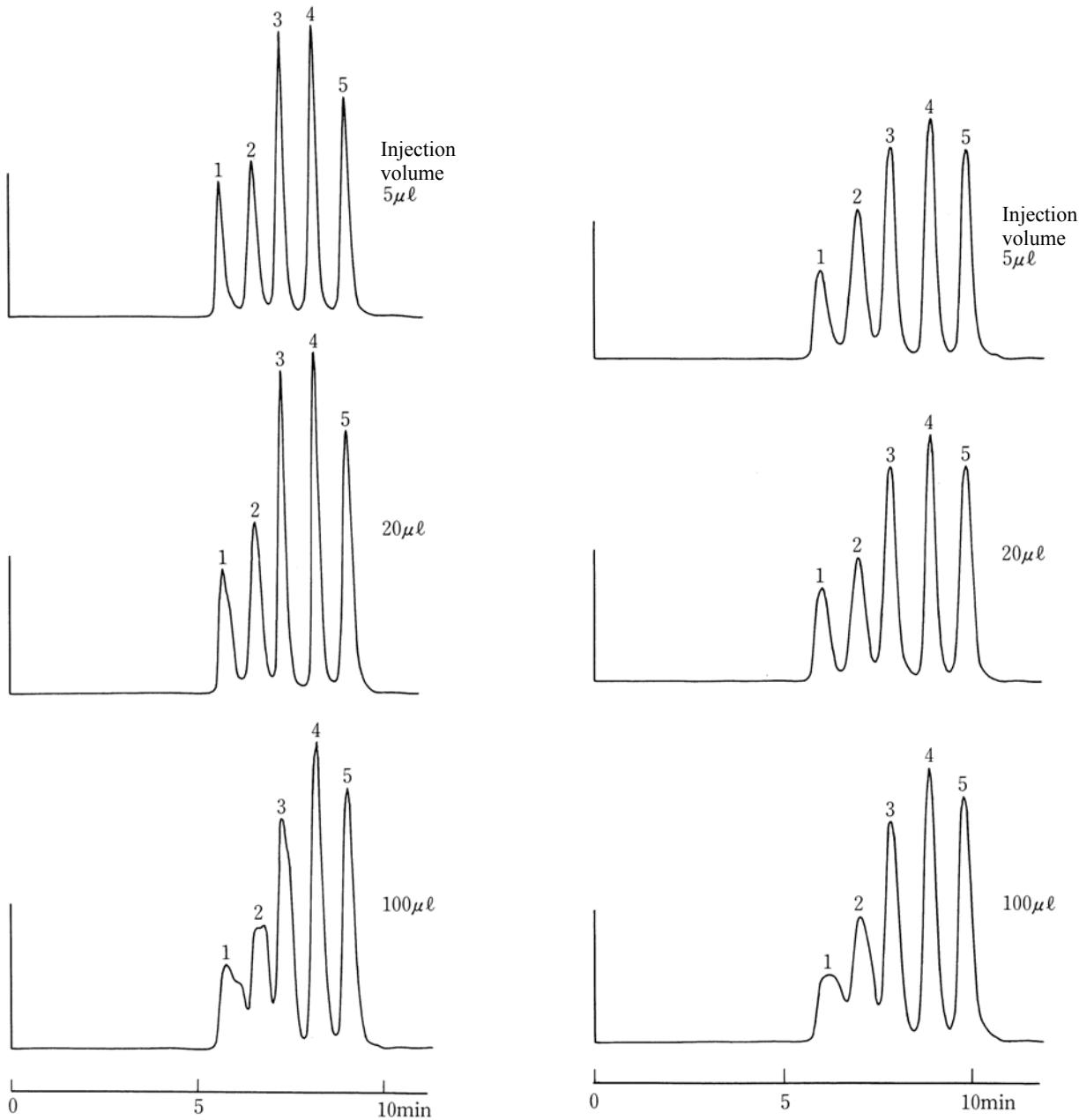


Fig. 18 Effect of sample load on separation of polystyrenes by TSKgel GMH_{HR}-H

Column: TSKgel GMH_{HR}-H (7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Samples: Standard polystyrenes (5 μL, 20 μL, 100 μL)

1.MW 2,890,000 (0.5 mg/mL)

2.MW 422,000 (0.7 mg/mL)

3.MW 107,000 (1.0 mg/mL)

4.MW 16,700 (1.0 mg/mL)

5.MW 2,800 (1.0 mg/mL)

Fig. 19 Effect of sample load on separation of polystyrenes by TSKgel GMH_{XL}

Column: TSKgel GMH_{XL} (7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Samples: Standard polystyrenes (5 μL, 20 μL, 100 μL)

1.MW 2,890,000 (0.5 mg/mL)

2.MW 422,000 (0.7 mg/mL)

3.MW 107,000 (1.0 mg/mL)

4.MW 16,700 (1.0 mg/mL)

5.MW 2,800 (1.0 mg/mL)

3-5-3. Shear degradation

This phenomenon is observed especially when ultra high molecular weight samples are analyzed. Shear degradation tends to occur when analysis is performed at high flow rates using a microparticle size packing material.

Fig. 21 shows the relationship between shear degradation and particle size of the packing material, when TSKgel GMH columns were used. When the flow rate is 1.0 mL/min, normal elution of an ultra high molecular weight sample (MW: 20,600,000) is only possible with the TSKgel BMH_{HR}-H(S), which has a large particle size. With the TSKgel GMH_{XL} and GMH_{HR}-H, shear degradation occurs and new peaks appear on the low molecular weight side.

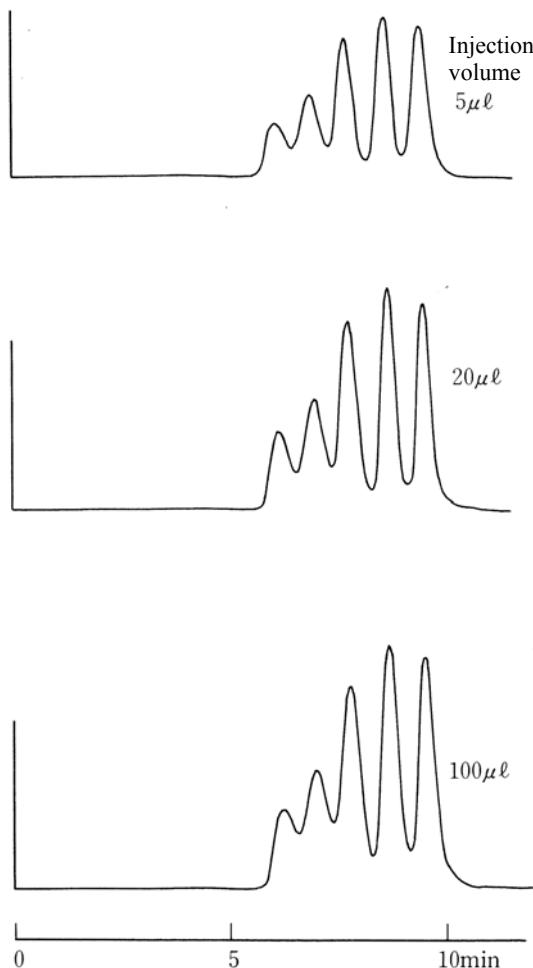


Fig. 20 Effect of sample load on separation of polystyrenes by TSKgel GMH_{HR}-H(S)

Column: TSKgel GMH_{HR}-H(S) (7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Samples: Standard polystyrenes (5 μL, 20 μL, 100 μL)

1.MW 2,890,000 (0.5 mg/mL)

2.MW 422,000 (0.7 mg/mL)

3.MW 107,000 (1.0 mg/mL)

4.MW 16,700 (1.0 mg/mL)

5.MW 2,800 (1.0 mg/mL)

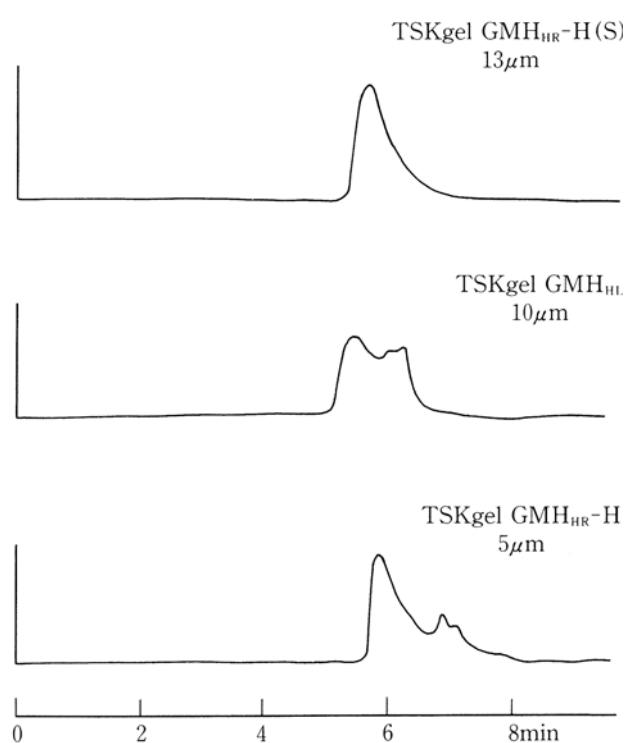


Fig. 21 Dependence of shear degradation of polymer samples on particle size in TSKgel GMH columns

Columns: TSKgel GMH_{HR}, TSKgel GMH_{XL},

TSKgel GMH_{HR}-H(S) (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene F-2000 (MW 20,600,000),

20 μL (0.025%)

Fig. 22 shows the dependence of shear degradation on flow rate. In the GMH_{XL}, shear degradation can be suppressed by reducing the flow rate to 0.6 mL/min or less. However, in the GMH_{HR}-H, shear degradation cannot be suppressed, even at a

flow rate of 0.4 mL/min. Consequently, when analyzing ultra high molecular weight samples with the H_{HR} series, it is more effective to use the (S) type column.

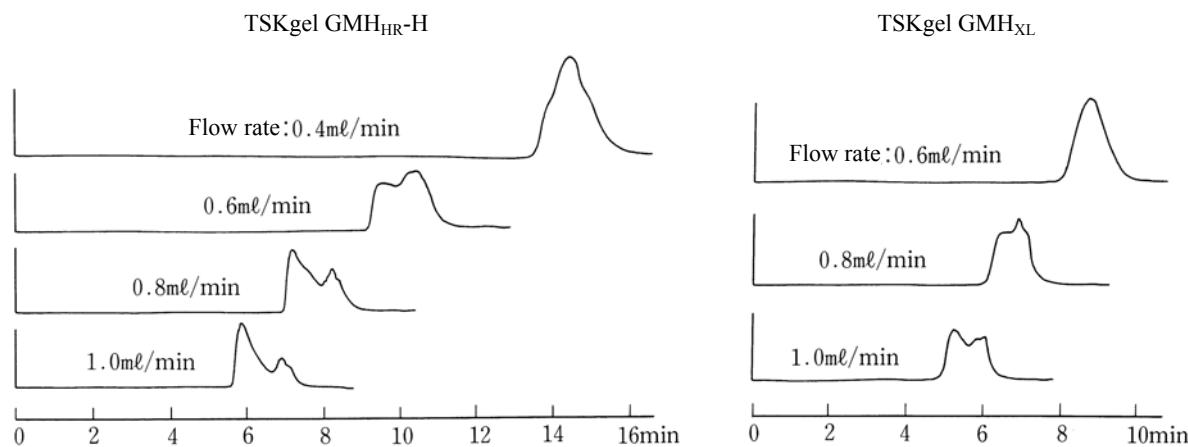


Fig. 22 Flow-rate dependence of shear degradation of samples in the TSKgel GMH_{HR}-H and TSKgel GMH_{XL}

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{XL}
(both 7.8 mm I.D. x 30 cm)
Solvent: THF
Flow rate: 0.4 to 1.0 mL/min
Temperature: 25 °C
Detection: UV (254 nm)
Sample: Standard polystyrene F-2000 (MW 20,600,000),
20 µL (0.025%)

3-5-4. Column temperature

In general, as the column temperature rises, sample elution occurs more rapidly due to changes in the distribution coefficient (K_d).⁸⁾ Fig. 23 shows the temperature dependence of calibration curves of standard polystyrenes produced using the GMH_{HR}-H.

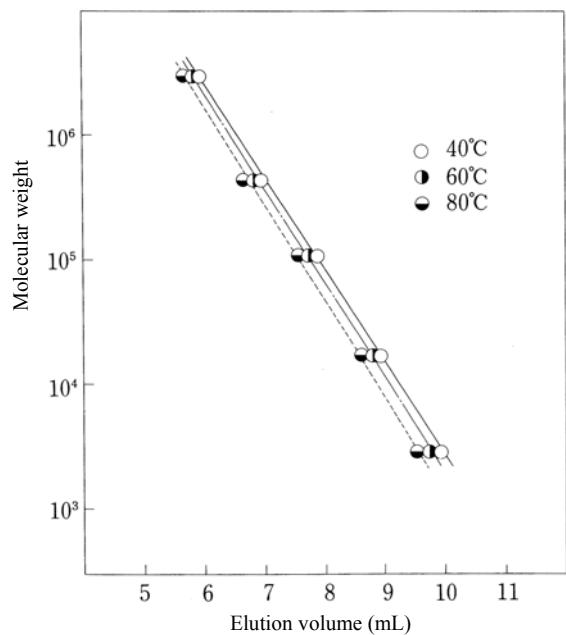


Fig. 23 Temperature dependence of calibration curve in TSKgel GMH_{HR}-H

Column: TSKgel GMH_{HR}-H (7.8 mm I.D. x 30 cm)

Solvent: DMF

Flow rate: 1.0 mL/min

Temperature: 40 °C to 80 °C

Detection: RI

Sample: Standard polystyrene

3-6. Mixed column (linear type)

In the TSKgel H_{HR} series, a linear type of mixed column is available in three grades. The GMH_{HR}-H maintains calibration curve linearity in a molecular weight separation range of 10³ to 10⁷, and the GMH_{HR}-M within a separation range of 500 to 10⁶. The GMH_{HR}-L was designed for analyzing oligomers and low molecular weight samples with a molecular weight of 10⁴ or below, and is optimal for pattern analysis, in which the oligomer region is well separated, while maintaining separation in the polymer region as well. Moreover, the GMH_{HR}-H(S) and GMH_{HR}-M(S) are used for analyzing ultra high molecular weight substances.

Fig. 2 shows calibration curves produced when THF is used as the solvent and standard polystyrene as the sample. Figures 4, 6 and 8 show calibration curves produced when chloroform, HFIP and DMF are used as the solvent.

Figures 24 to 27 compare chromatograms of the separation of a standard polystyrene mixture with GMH_{HR} series columns.

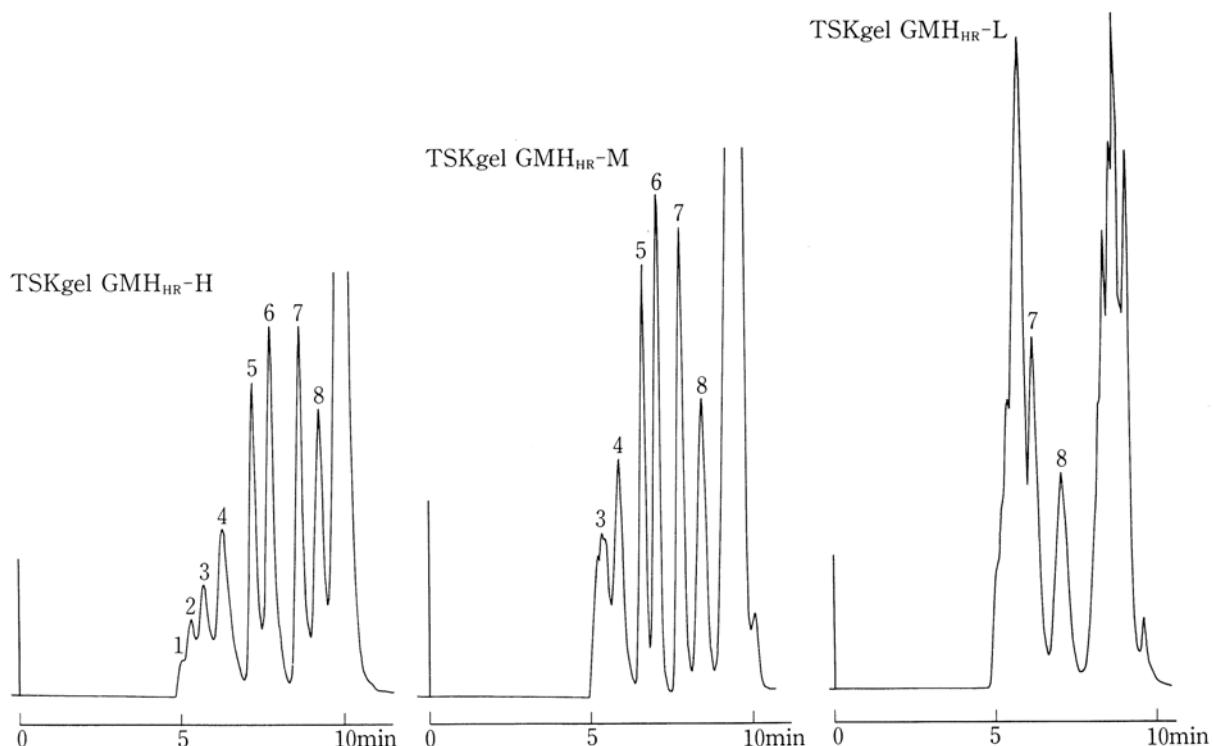


Fig. 24 Comparison of separation of standard polystyrene using the TSKgel GMH_{HR} series (1)

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 8,420,000 2.MW 2,890,000

3.MW 1,260,000 4.MW 422,000

5.MW 107,000 6.MW 42,800

7.MW 10,200 8.MW 2,800

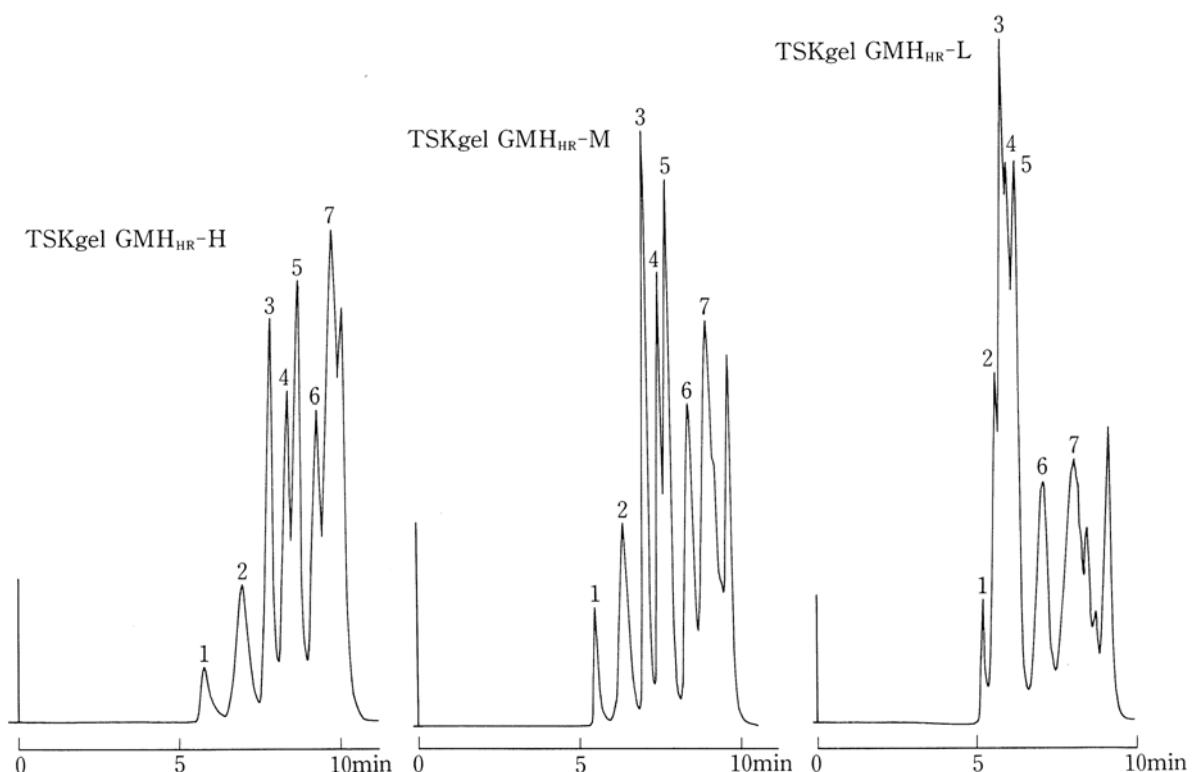


Fig. 25 Comparison of separation of standard polystyrene using the TSKgel GMH_{HR} series (2)

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 1,260,000 2.MW 186,000

3.MW 42,800 4.MW 16,700

5.MW 10,200 6.MW 2,800 7.A-1000

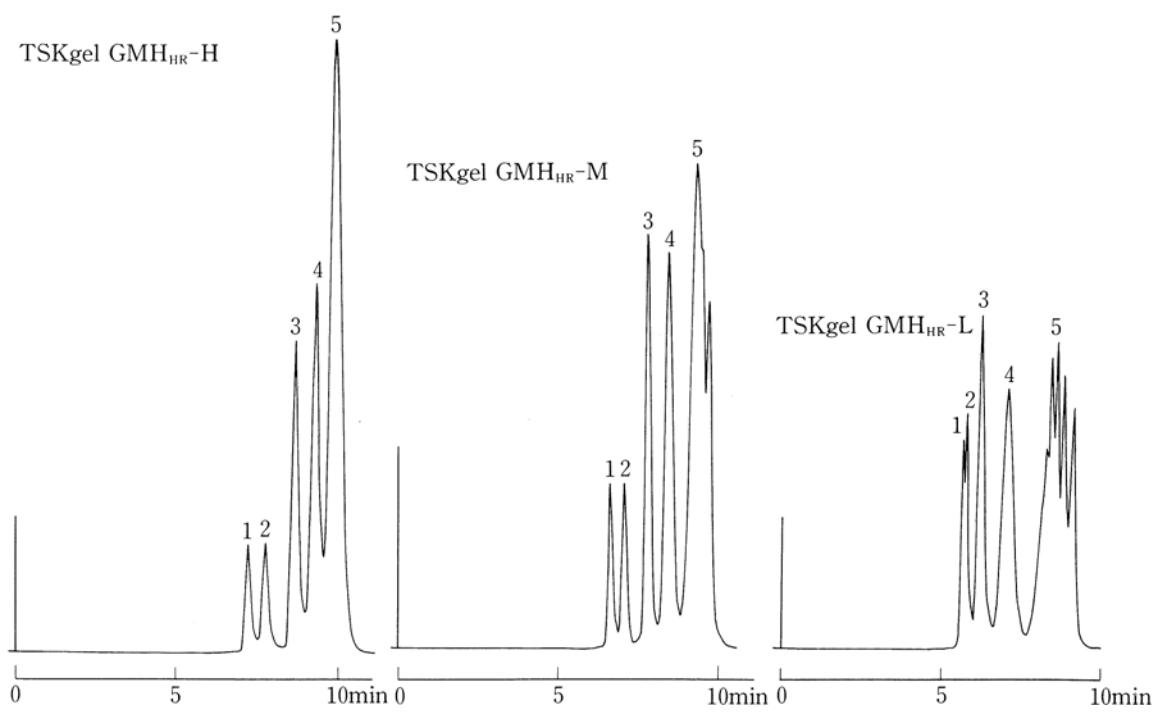


Fig. 26 Comparison of separation of standard polystyrene using the TSKgel GMH_{HR} series (3)

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 107,000 2.MW 42,800

3.MW 10,200 4.MW 2,800

5.MW A-500

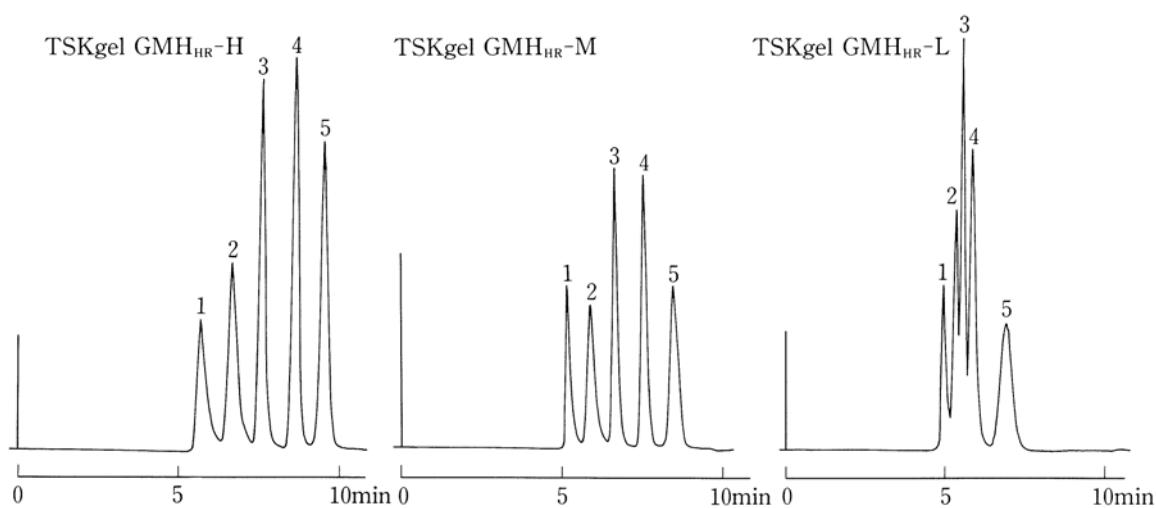


Fig. 27 Comparison of separation of standard polystyrene using the TSKgel GMH_{HR} series (4)

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Standard polystyrene

1.MW 2,890,000 2.MW 422,000

3.MW 107,000 4.MW 16,700

5.MW 2,800

Fig. 28 compares chromatograms of separation of an epoxy resin (Epikote 1001).

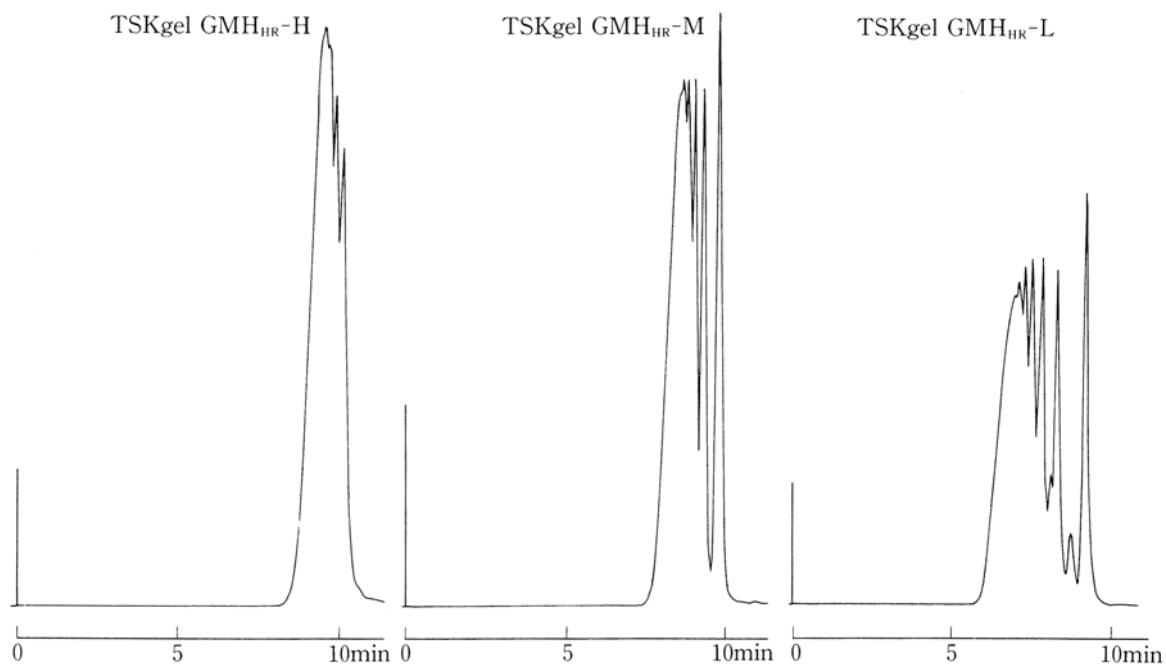


Fig. 28 Comparison of separation of an epoxy resin (Epikote 1001) using the TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Epoxy resin (Epikote 1001)

Figure 29 compares chromatograms of separation of phenol resin.

As is clear from these figures, the optimal fractionation range (range in which there is a high level of separation) will differ with each grade.

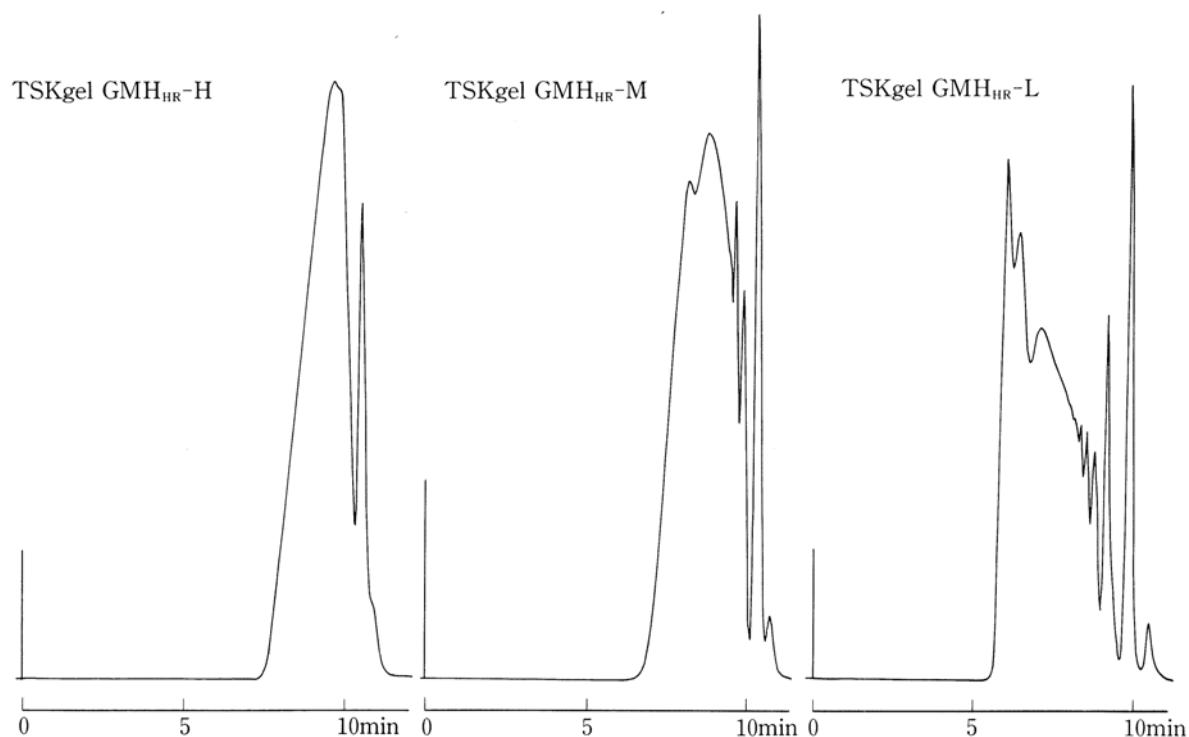


Fig. 29 Comparison of separation of phenol resin using the TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M, TSKgel GMH_{HR}-L
(each 7.8 mm x 30 cm)

Solvent: THF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Phenol resin

3-7. Effect of adding salt to special solvents

When a DMF solvent is used to analyze a sample containing a dissociable ionic group such as a sulfonate group or carboxyl group within the polymer molecule or at the terminus, the elution position of the sample can appear very early. Various explanations have been offered for the cause: expansion of the polymer coil due to electrostatic effects, swelling of the polymer structure due to intramolecular assembly, bipolar interactions between a polar group and DMF, and ionic repulsion between the packing material and a dissociable group in the sample. Adding a lithium salt (LiBr or LiCl) to the DMF solvent has been proposed as a method for suppressing this phenomenon.⁹⁻¹¹⁾

A similar phenomenon is also observed with phenol resins,¹²⁾ urea-formaldehyde resins,¹³⁾ and polymers that have a carboxyl group.¹⁴⁻¹⁷⁾ Moreover, Hann et al.¹⁸⁾ has noted that adsorption can occur with a quaternized polyurethane.

Accordingly, the elution behavior of alkyd resins, phenol resins, and polyetherimide was investigated using the TSKgel H_{HR} series of columns, in systems prepared by adding a salt (LiBr, sodium trifluoroacetate) to a DMF solvent, a THF/methanol mixed solvent, and a HFIP solvent.

Using the G3000H_{HR}, Fig. 30 shows the elution behavior of alkyd resin and phenol resin analyzed using a DMF solvent, as well as the effects of using a system containing added LiBr.

With the DMF solvent, both resins were eluted abnormally early due to a static electric interaction. However, by adding LiBr to the DMF solvent, a normal chromatogram is obtained. Normal analysis of alkyd resins is possible when the concentration of the added salt is about 30 mM, and with phenol resins, when the concentration of the added salt is around 10 mM.

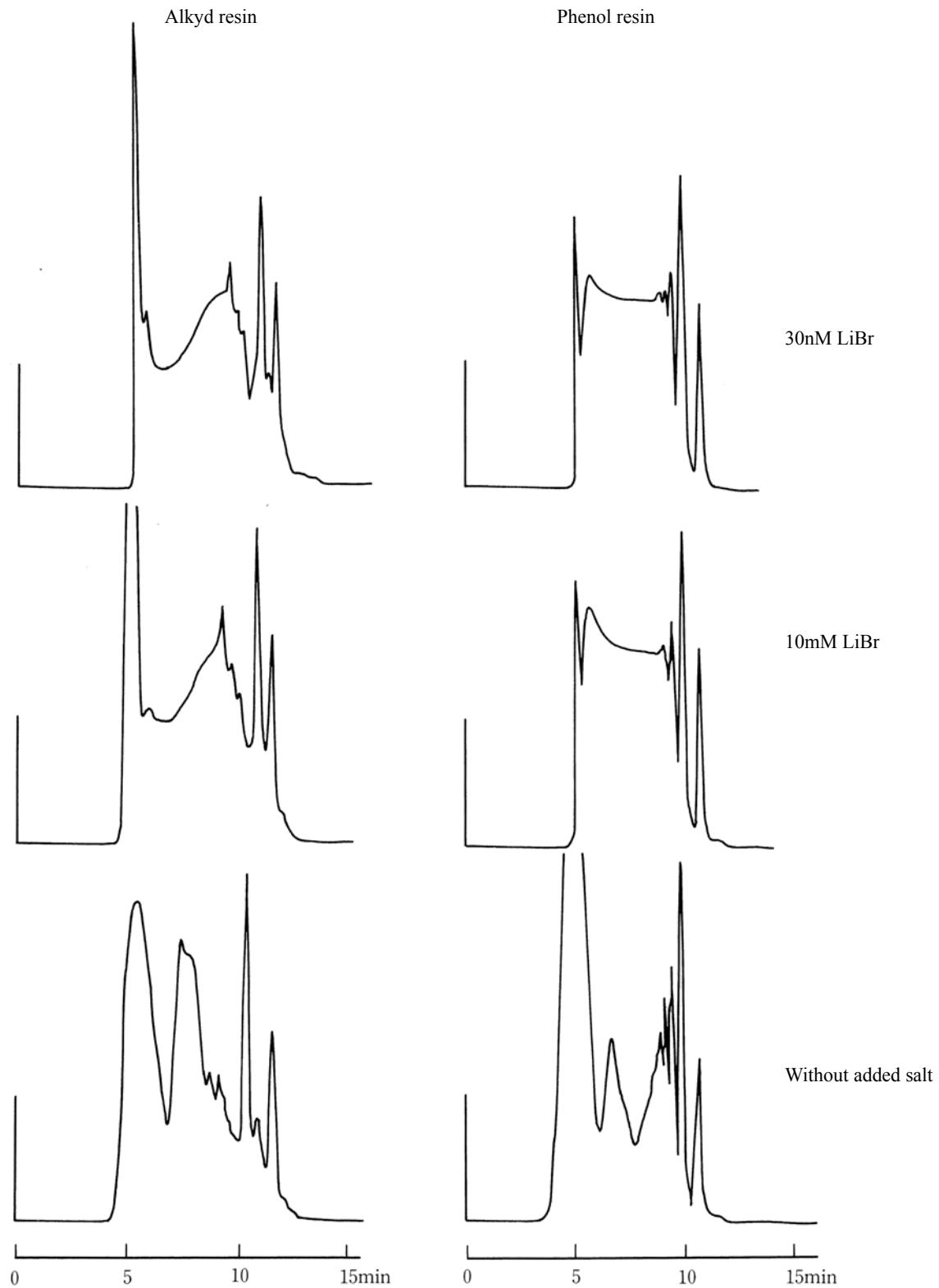


Fig. 30 Separation of alkyd resin and phenol resin by TSKgel G3000H_{HR}

Column: TSKgel G3000H_{HR} (7.8 mm I.D. x 30 cm)

Solvent: DMF (containing LiBr)

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Alkyd resin, phenol resin

Using the G3000H_{HR}, Fig. 31 shows the elution behavior of alkyd resin and phenol resin in a THF/methanol = 6/4 mixed solvent, as well as the effects of using a system prepared by adding 20 mM LiBr. With the THF/methanol = 6/4 mixed solvent, as in the DMF solvent, both resins were eluted abnormally early due to a static electric interaction, but by adding 20 mM LiBr to the THF/methanol = 6/4 mixed solvent, a normal chromatogram was obtained.

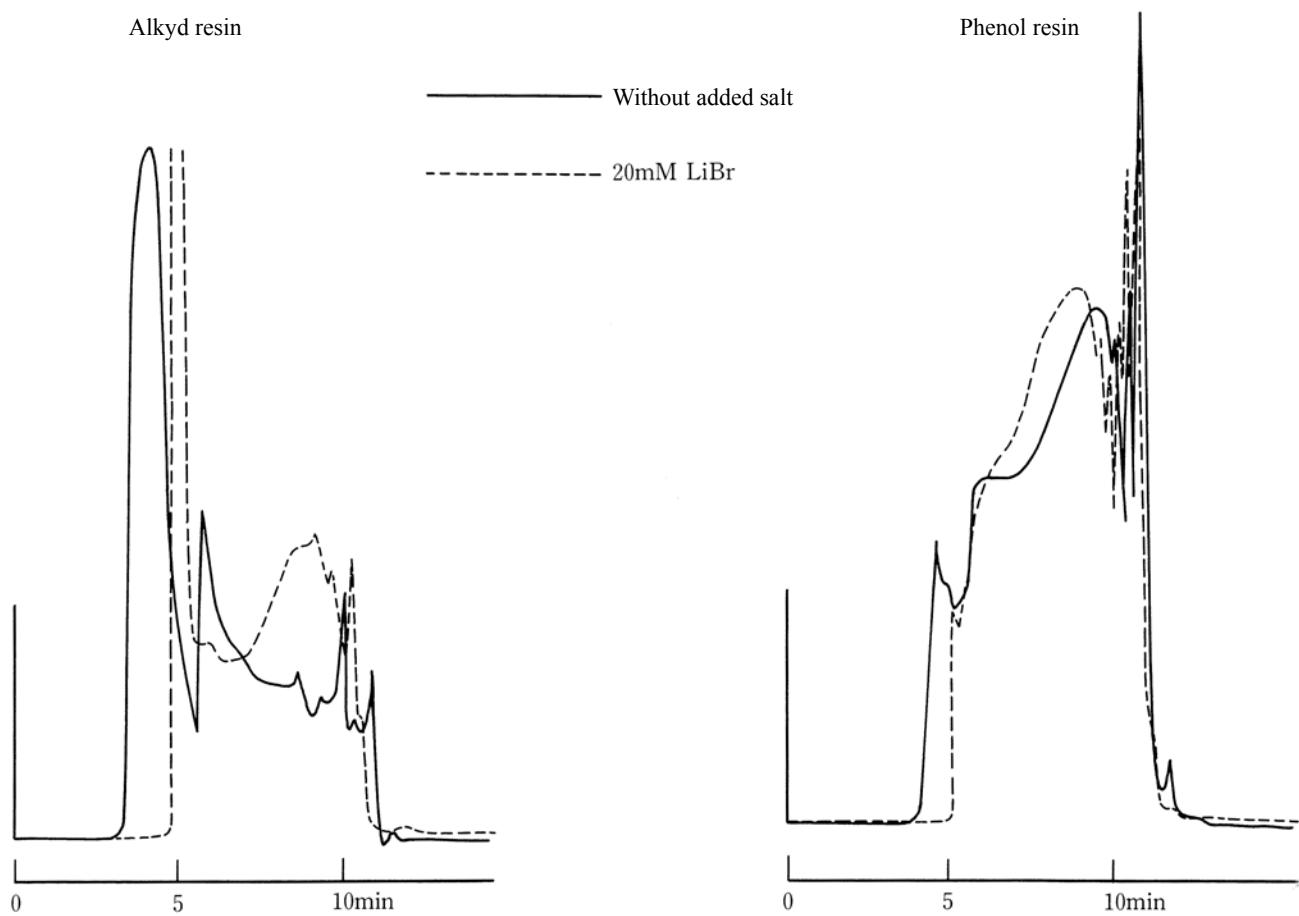


Fig. 31 Separation of alkyd resin and phenol resin by TSKgel G3000H_{HR}

Column: TSKgel G3000H_{HR} (7.8 mm I.D. x 30 cm)

Solvent: THF/methanol = 6/4 (containing LiBr)

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

Sample: Alkyd resin and phenol resin

Using the G4000H_{HR} and G5000H_{HR}, Fig. 32 shows the elution behavior of polyetherimide in a HFIP solvent, as well as the effects of using a system prepared by adding 10 mM sodium trifluoroacetate. A different effect appeared from what was observed with the DMF solvent and THF/methanol = 6/4 mixed solvent as shown in Figures 30 and 31. In the system without the added salt, adsorption was observed, while normal GPC analysis could be conducted by adding 10 mM sodium trifluoroacetate to the HFIP solvent.

Thus as described above, elution behavior of samples can become abnormal when conducting analyses using special solvent systems, but in some cases a normal chromatogram can be obtained by adding a salt to the solvent.

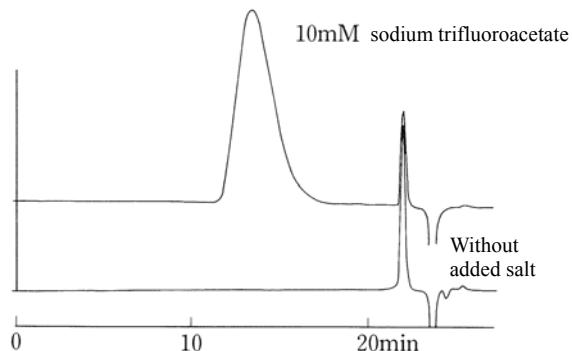


Fig. 32 Separation of polyetherimide by TSKgel H_{HR}

Columns: TSKgel G5000H_{HR} + TSKgel G4000H_{HR}

(7.8 mm I.D. x 30 cm x 2)

Solvent: HFIP (containing sodium trifluoroacetate)

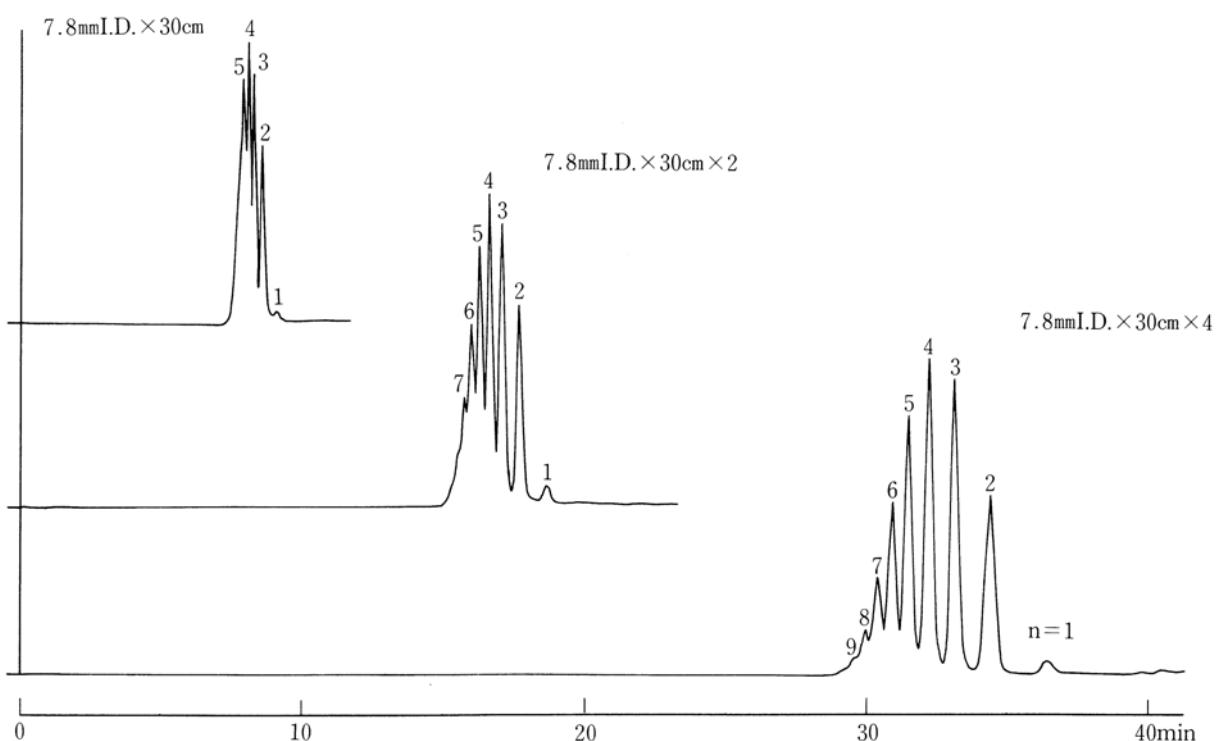
Flow rate: 1.0 mL/min

Temperature: 40 °C

Detection: RI

4. Applications

Fig. 33 compares chromatograms produced with multiple columns linked together.



**Fig. 33 Separation of standard polyethylene A-500 by
TSKgel G2500H_{HR}**

Columns: TSKgel G2500H_{HR}
(7.8 mm I.D. x 30 cm - 7.8 mm I.D. x 30 cm x 4)
Solvent: THF
Flow rate: 1.0 mL/min
Temperature: 25 °C
Detection: UV (254 nm)

Figures 34 to 43 show examples of analyses conducted using various resins and polymers in a variety of organic solvents.

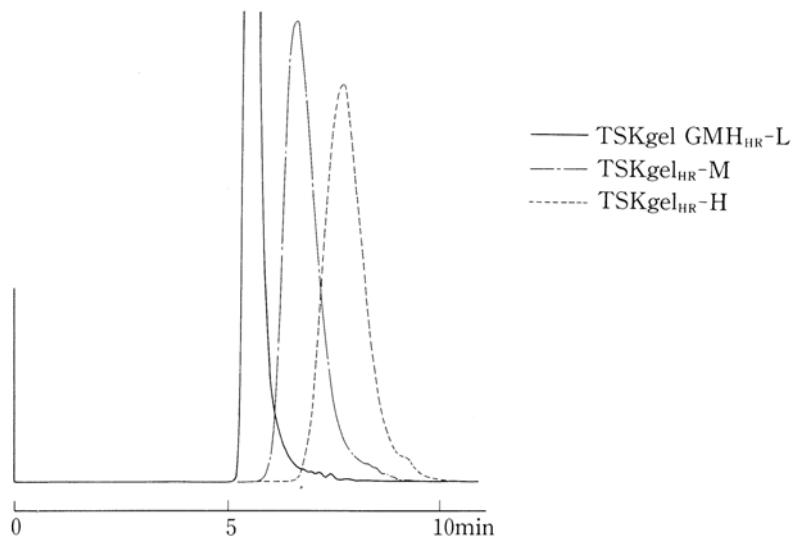


Fig. 34 Separation of polycarbonate using the TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm)

Solvent: Chloroform

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (254 nm)

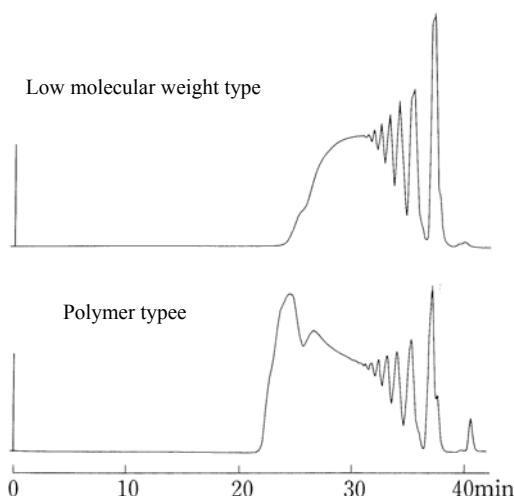


Fig. 35 Separation of phenol resin (novolak type) by TSKgel H_{HR}

Columns: TSKgel G4000H_{HR} + TSKgel G3000H_{HR}
+ TSKgel G2000H_{HR} x 2 (7.8 mm I.D. x 30 cm x 4)

Solvent: 10 mM LiBr in DMF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (270 nm)

Samples: Low molecular weight type and polymer type
phenol resins (novolak type)

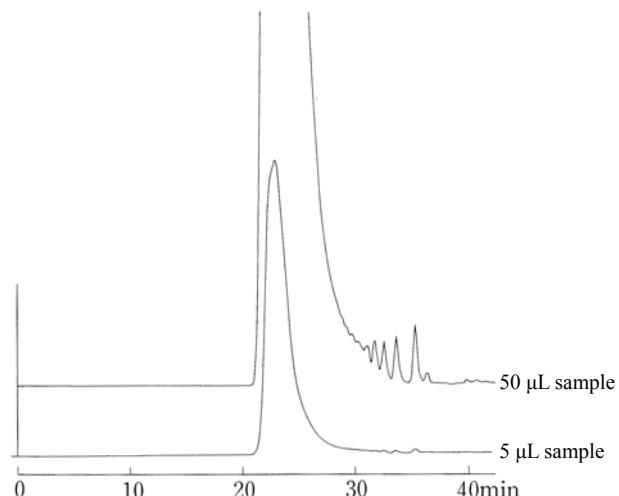


Fig. 36 Separation of polyethersulfone by TSKgel H_{HR}

Columns: TSKgel G4000H_{HR} + TSKgel G3000H_{HR}
+ TSKgel G2000H_{HR} x 2 (7.8 mm I.D. x 30 cm x 4)

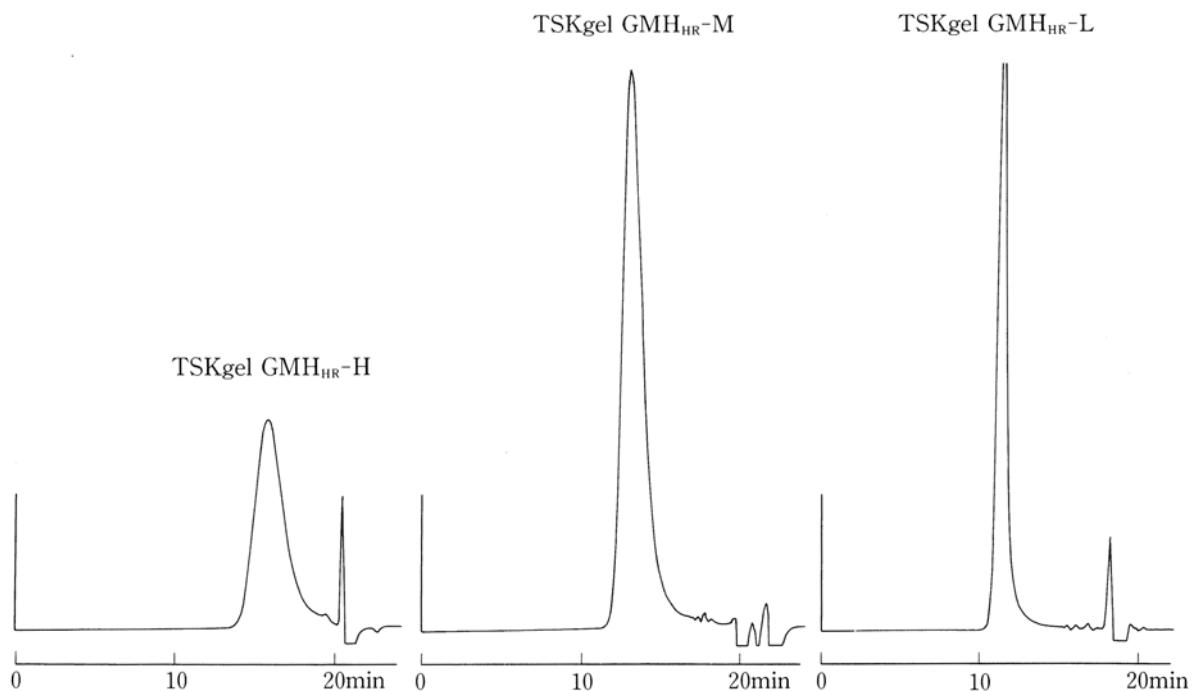
Solvent: 10 mM LiBr in DMF

Flow rate: 1.0 mL/min

Temperature: 25 °C

Detection: UV (270 nm)

Sample: Polyethersulfone



**Fig. 37 Separation of polyethersulfone using the
TSKgel GMH_{HR} series**

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm x 2)

Solvent: 10 mM LiBr in DMF

Flow rate: 1.0 mL/min

Temperature: 80 °C

Detection: RI

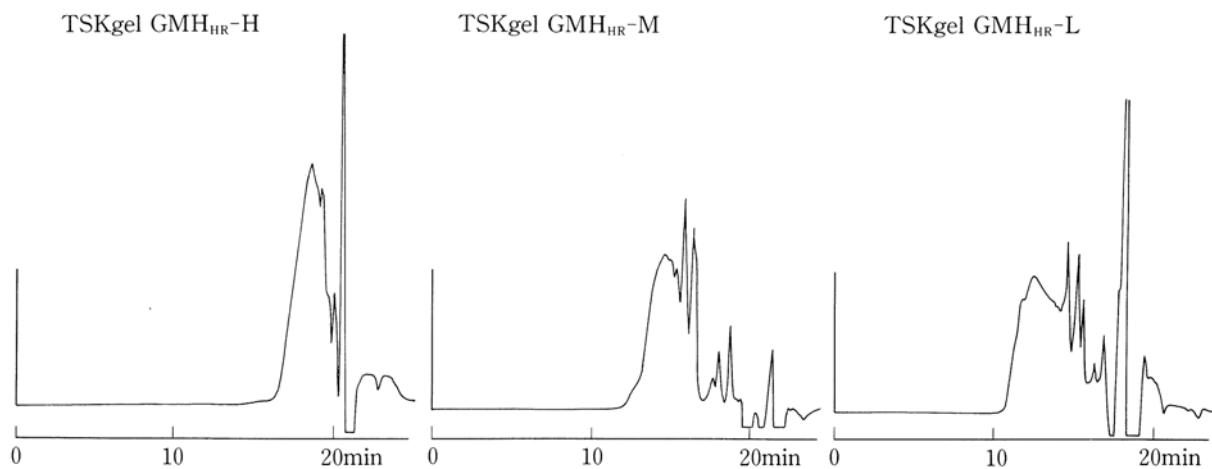


Fig. 38 Separation of phenol resin (resol type) by TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm x 2)
Solvent: 10 mM LiBr in DMF
Flow rate: 1.0 mL/min
Temperature: 80 °C
Detection: RI

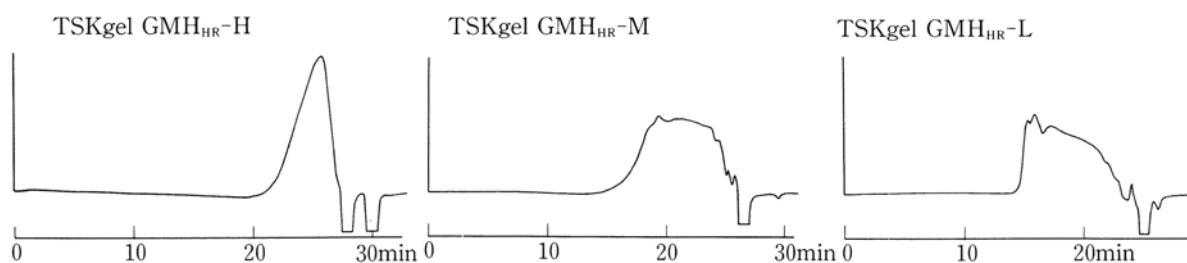


Fig. 39 Separation of melamine resin by TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M,
TSKgel GMH_{HR}-L (each 7.8 mm I.D. x 30 cm x 2)
Solvent: 10 mM LiBr in DMSO
Flow rate: 0.75 mL/min
Temperature: 80 °C
Detection: RI

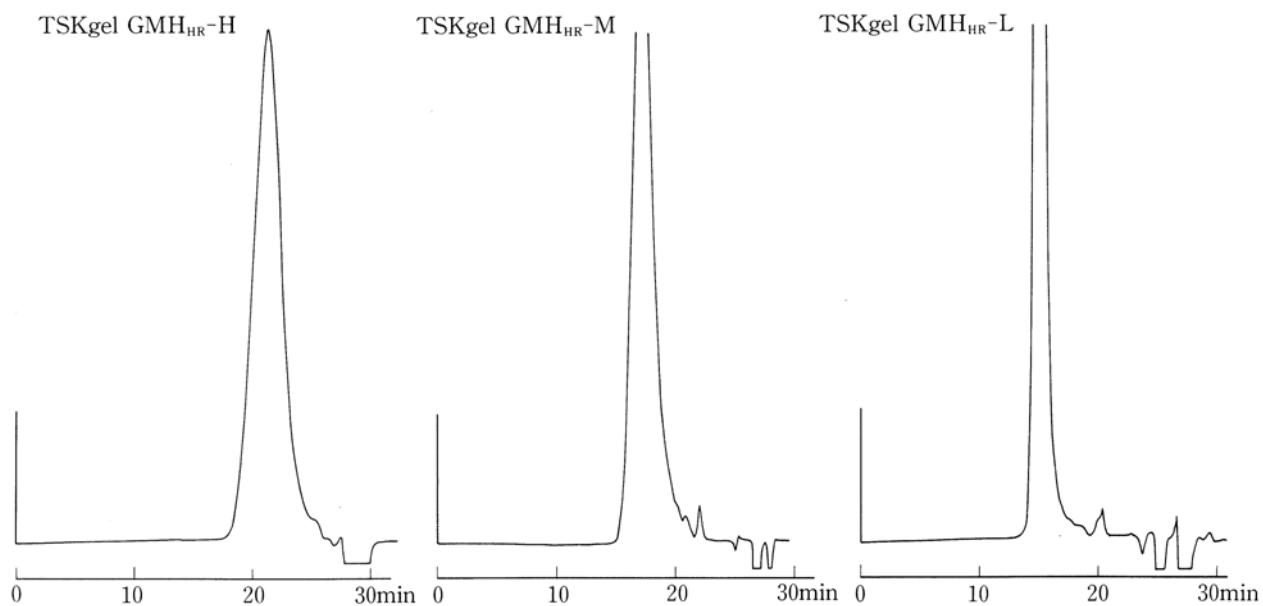


Fig. 40 Separation of polyetherimide by TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M, TSKgel GMH_{HR}-L

(each 7.8 mm I.D. x 30 cm)

Solvent: 10 mM LiBr in N-methylpyrrolidone

Flow rate: 0.75 mL/min

Temperature: 80 °C

Detection: RI

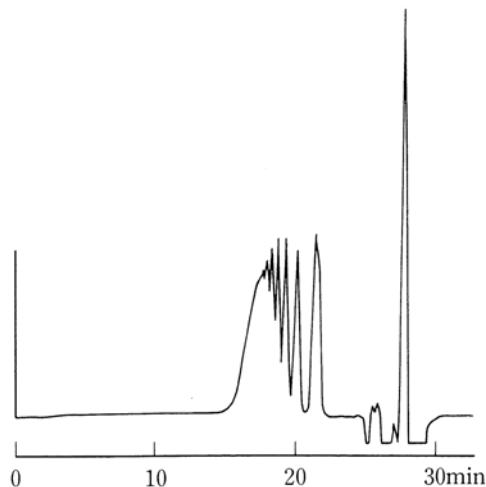


Fig. 41 Separation of Dextran T-40 hydrolysate by TSKgel H_{HR}

Columns: TSKgel GM3000H_{HR} + TSKgel G2500H_{HR}

(7.8 mm I.D. x 30 cm x 2)

Solvent: 10 mM LiBr in N-methylpyrrolidone

Flow rate: 0.75 mL/min

Temperature: 80 °C

Detection: RI

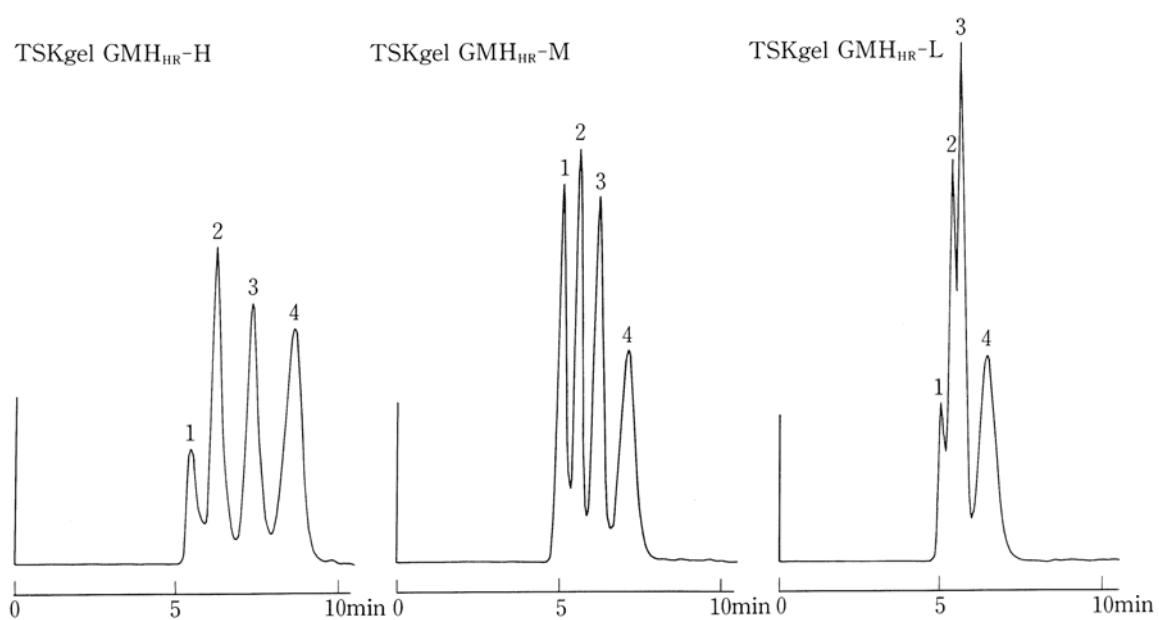


Fig. 42 Separation of polymethylmethacrylate mixture by TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M, TSKgel GMH_{HR}-L
(each 7.8 mm I.D. x 30 cm)

Solvent: 5 mM sodium trifluoroacetate in HFIP

Flow rate: 1.0 mL/min

Temperature: 40 °C

Detection: UV (220 nm)

Sample: Polymethylmethacrylate

1.MW 820,000 2.MW 67,000

3.MW 10,200 4.MW 1,950

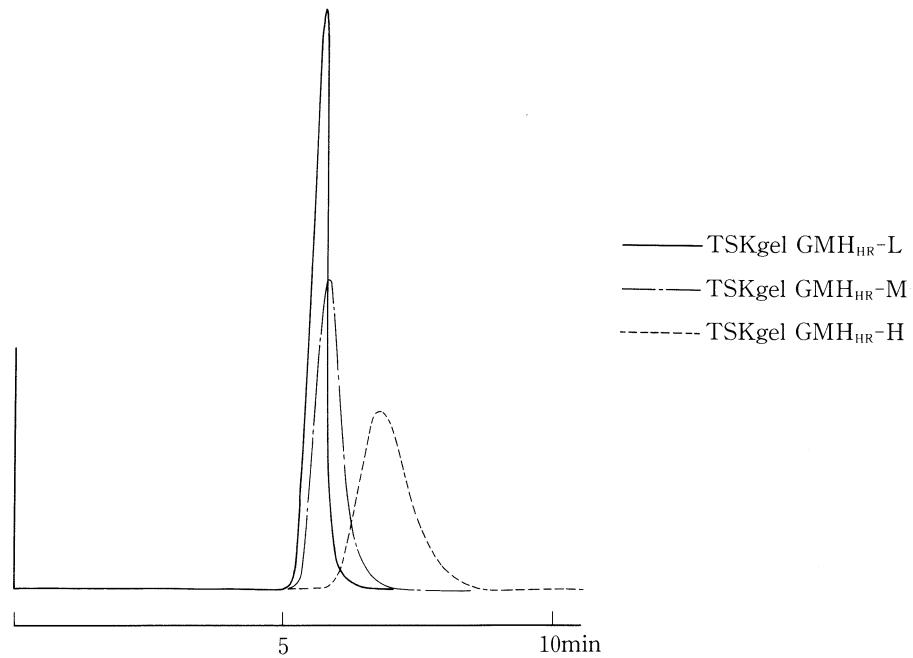


Fig. 43 Separation of Nylon 66 by TSKgel GMH_{HR} series

Columns: TSKgel GMH_{HR}-H, TSKgel GMH_{HR}-M, TSKgel GMH_{HR}-L

(each 7.8 mm I.D. x 30 cm)

Solvent: 5 mM sodium trifluoroacetate in HFIP

Flow rate: 1.0 mL/min

Temperature: 40 °C

Detection: RI

Sample: Nylon 66

5. Conclusion

By greatly increasing the strength of the packing material, the TSKgel H_{HR} series of columns significantly expands performance over what could be achieved with the conventional H_{XL} series of columns, improving the ability of the column to accommodate solvent conversion, increasing durability when used with specialized solvents, and improving the stability of analysis conducted at high flow rates.

It is widely anticipated that by using the H_{HR} series of columns, analysis under special conditions and analysis with solvents that were impossible in the past will now become possible, providing a great deal of new information.

References

- 1) P. J. Wang, R. J. Rivard, *J. Liq. Chromatogr.*, 10, 3059 (1987)
- 2) C. A. Veith, R. E. Cohen, *Polymer*, 30, 942 (1989)
- 3) S. Mori, *Anal. Chem.*, 61, 1321 (1989)
- 4) T. Ogawa, M. Sasaki, W. Ishitobi, *J. Polym. Sci., Polym. Chem. Ed.*, 24, 109 (1985)
- 5) A. Kinugawa, IUPAC 32nd International Symposium on Macromolecules Preprints, 489 (1988)
- 6) S. Mori, *J. Appl. Polym. Sci.*, 20, 2157 (1976)
- 7) S. Mori, "Steric Exclusion Liquid Chromatography of Polymers", by J. Janca, Marcel Dekker, N.Y. (1984), Chapter 4.
- 8) S. Mori, *Anal. Chem.*, 52, 1625 (1980)
- 9) C. Y. Cha, *J. Polym. Sci.*, B7, 343 (1969)
- 10) G. Coppola et al., *Appl. Polym. Sci.*, 16, 2829 (1972)
- 11) A. S. Kenyon et al., *Appl. Polym. Symp.*, 25, 57 (1974)
- 12) B. Riedl et al, *Holzforshung*, 42, 315 (1988)
- 13) P. R. Ludlam et al., *J. Appl. Polym. Sci.*, 29, 3863 (1984)
- 14) D. R. Sheuing, *J. Appl. Polym. Sci.*, 29, 2819 (1984)
- 15) P. P. Nefedr et al., *J. Chromatogr.*, 170, 11 (1979)
- 16) L. Z. Vilenchik et al., *Chromatographia*, 24633 (1987)
- 17) C. C. Walker, *J. Polym. Sci., Polym. Chem.*, 26, 1649 (1988)
- 18) N. D. Hann. *J. Polym. Sci., Polym. Chem.*, 15, 1331 (1977)