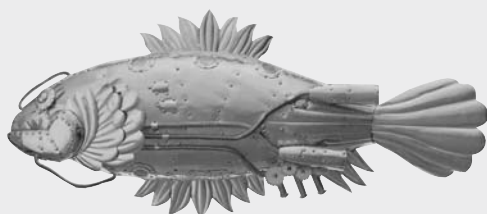
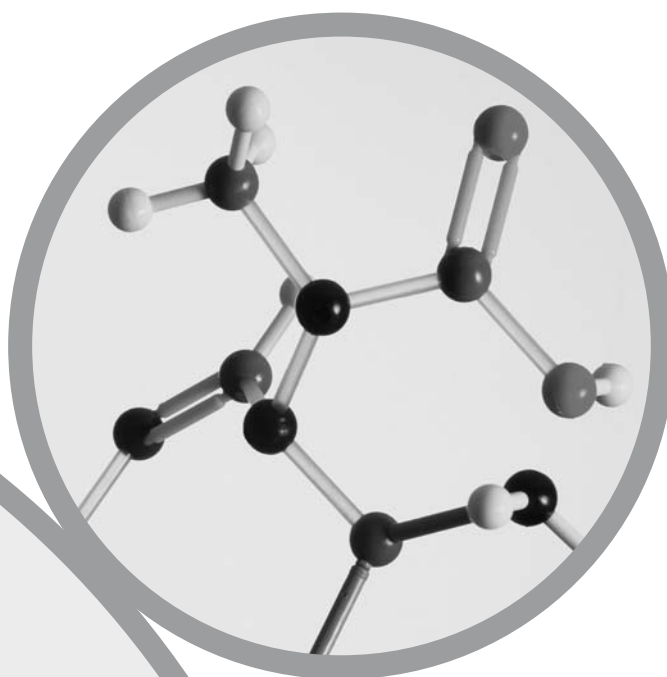




SHOWA
DENKO

Shodex[®] GPC LF Series Columns

Linear Calibration Curves over a Wide Molecular Weight Range



Shodex[®]

TECHNICAL NOTEBOOK

No. 1

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1. Introduction

Gel permeation chromatography (GPC) is a widely used technique for determining the molecular weight distributions of polymers. For the determination of the molecular weight distribution of a polymeric substance by GPC, it is common practice to use a number of serially connected columns of different pore sizes, or to use three to four serially connected units of a column packed with a mixed gel (mixture of gels having different pore sizes). These connections are diagramed in Figures 1-A and 1-B. When using these configurations, we have observed the following problems.

- I.) It was difficult to obtain a highly linear calibration curve even when columns with individual pore sizes were connected in series. (Fig. 1-A)
- II.) Even when a highly linear calibration curve was obtained using columns with mixed gel having different pore sizes (Fig1-B), there are cases that a true molecular weight distribution curve cannot be obtained due to abnormal or inflectional chromatograms with some samples.

To resolve these problems, we developed a new gel having a wide pore size distribution. The pore size distribution of this gel has been adjusted to obtain a linear calibration curve. Using a single kind of column packed with this gel, a wide range of molecular weights was covered and the above problems were resolved. This so-called 'multi-pore' gel is diagramed in Figure 1-C.

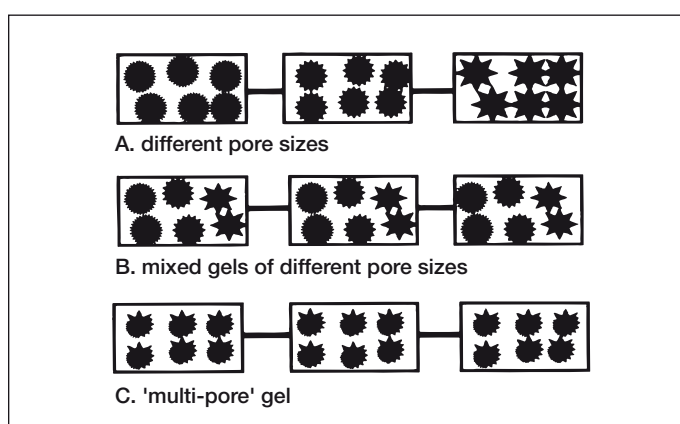


Figure 1. Model of three type of columns with different gels
 A. Columns with different pore sizes
 B. Columns with mixed gels of different pore sizes in the same column
 C. Columns with 'multi-pore' gel

2. Shodex GPC LF Series

2.1. Specifications

Two types of columns are available in the Shodex GPC LF Series; General-purpose columns with 8.0mm inside diameter and semi-micro analytical columns with 4.6mm and 6.0mm inside diameter. Table 1 shows the specifications of the LF-series columns. Figure 2 shows a comparison of chromatograms obtained by LF-804, LF-404 and LF-604.

Table 1. Specification of Shodex GPC LF Series

Type (Solvent)	Exclusion Limit (PS)	TPN (per Column)	Particle Size (μm)	Pore Size (\AA)	Size ID x L(mm)	Purpose
GPC LF-804 (THF)	2,000,000	17,000	6	3000	8.0 x 300	general
GPC LF-404 (THF)	2,000,000	14,000	6	3000	4.6 x 250	high resolution
GPC LF-604 (THF)	2,000,000	9,000	6	3000	6.0 x 150	high speed
GPC LF-G (THF)	guard column	—	—	—	4.6 x 10	guard column

Working temperature is 20 to 60 °C (recommended temperature: 25 - 40 °C)

For solvent compatibility, please refer to article 4 "Replacement of In-column Solvent for LF Series".

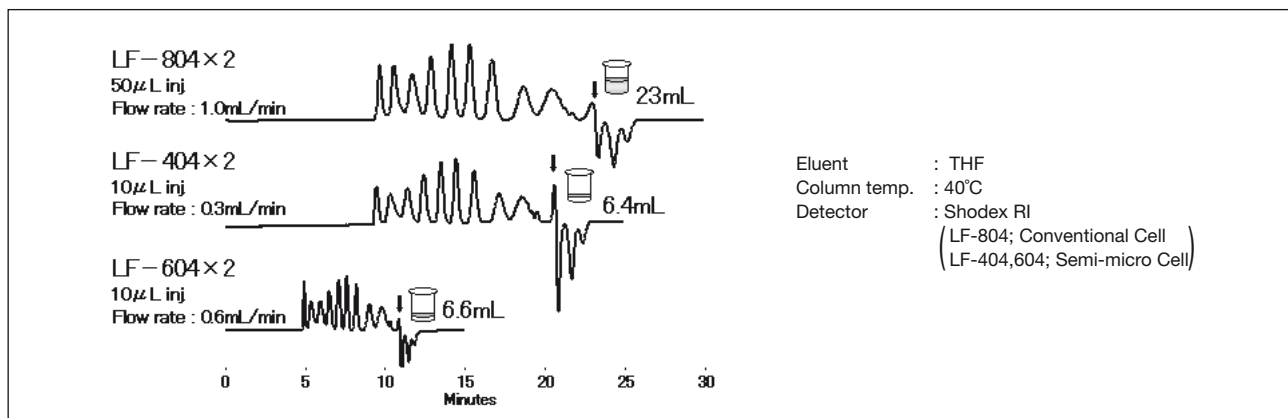


Figure 2. Comparison of Chromatograms obtained by LF-804, LF-404 and LF-604

2.2. Advantages of the GPC LF Series

(1) Covers a broad range of molecular weights with a column packed with a single gel

Figure 3 shows the calibration curve of LF-804. LF-804 is capable of determining a very broad range of molecular weights, from 100 to 2,000,000. The wide coverage is achieved by a single gel.

(2) Offers a highly linear calibration curve

As seen from the calibration curve in Figure 3, excellent linearity is obtained over the molecular weight range from 300 to 2,000,000.

(3) Avoids chromatogram anomalies due to connection of columns of different pore sizes

Figure 4 compares chromatograms of the EPON1009 epoxy resin analyzed using a combination of three columns of different pore sizes (KF-804+803+802), three units of a column packed with a mixed gel (KF-804L), and three units of a 'multi-pore' column (LF-804). The chromatogram from KF-804+803+802 shows a shoulder-like distortion close to the peak crest. The chromatogram from KF-804L shows a slight swelling on the high-molecular side.

The chromatogram from LF-804 is smooth without distortion.

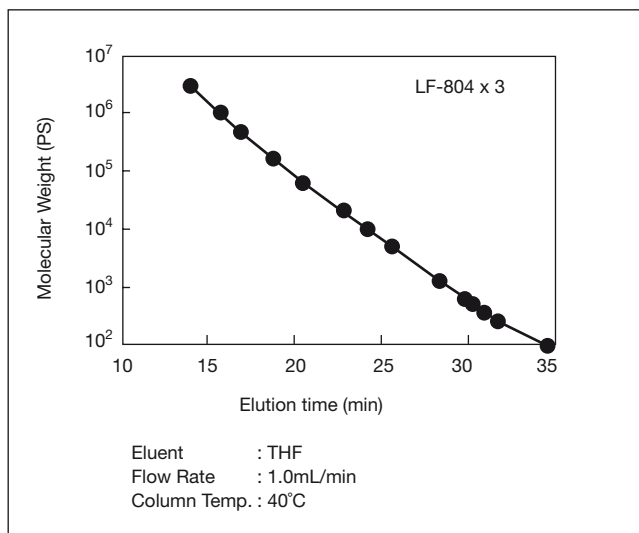


Figure 3. Calibration Curve of LF-804

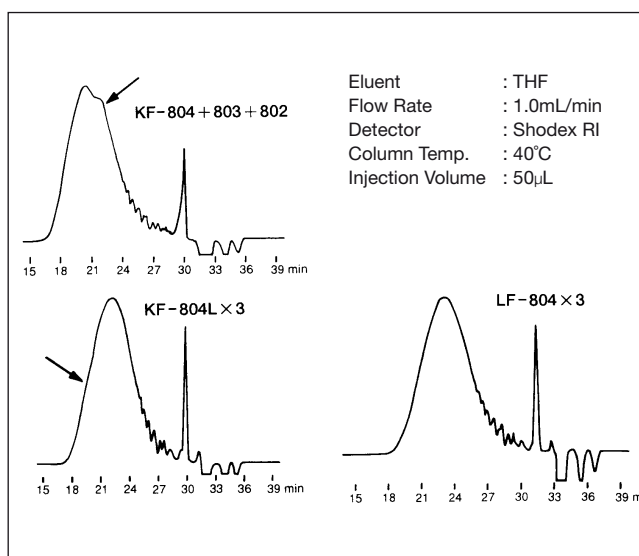


Figure 4. Chromatograms of Epoxy Resin EPON1009

(4) Offers large pore volume

Figure 5 shows chromatograms obtained by analyzing a standard mixture of polystyrenes using various columns. By comparison of these results, it was proven that LF-804 offered the largest volume (gel pore volume) from a molecular weight of 2,000,000 to ethyl benzene. Larger pore volume means greater resolution.

(5) Offers good resolution in the low-molecular range

As seen from Figure 5, LF-804 offers good resolution in the low-molecular range and also shows a high size exclusion limit of 2,000,000g/mol. A low-molecular polystyrene oligomer (average molecular weight: 580) was separated into individual peaks.

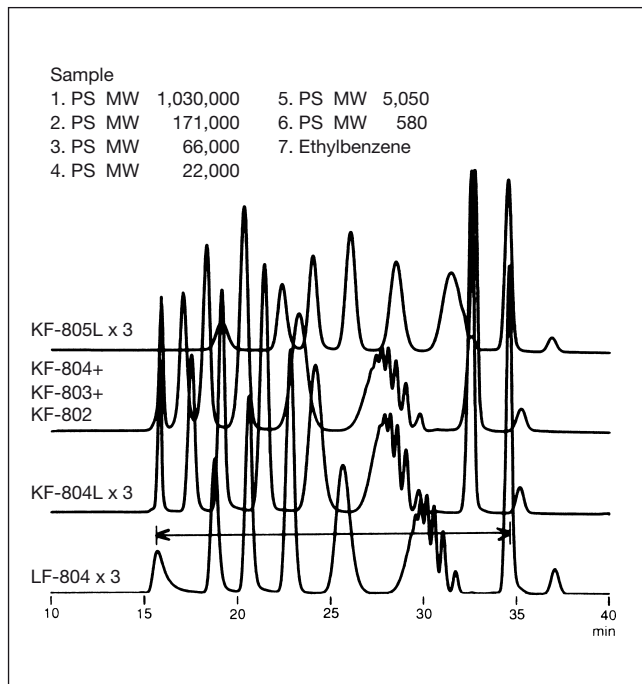


Figure 5. Separation of Standard Polystyrene Mixture

3. Application Data

3.1. GPC LF-804 Column Conventional GPC Columns

Figure 6 compares calibration curves obtained from measurements of a standard mixture of polystyrene, using a combination of KF-804+803+802, three units of KF-804L, and three units of LF-804. LF-804 produced a calibration curve of higher linearity over a broader range, than the other columns.

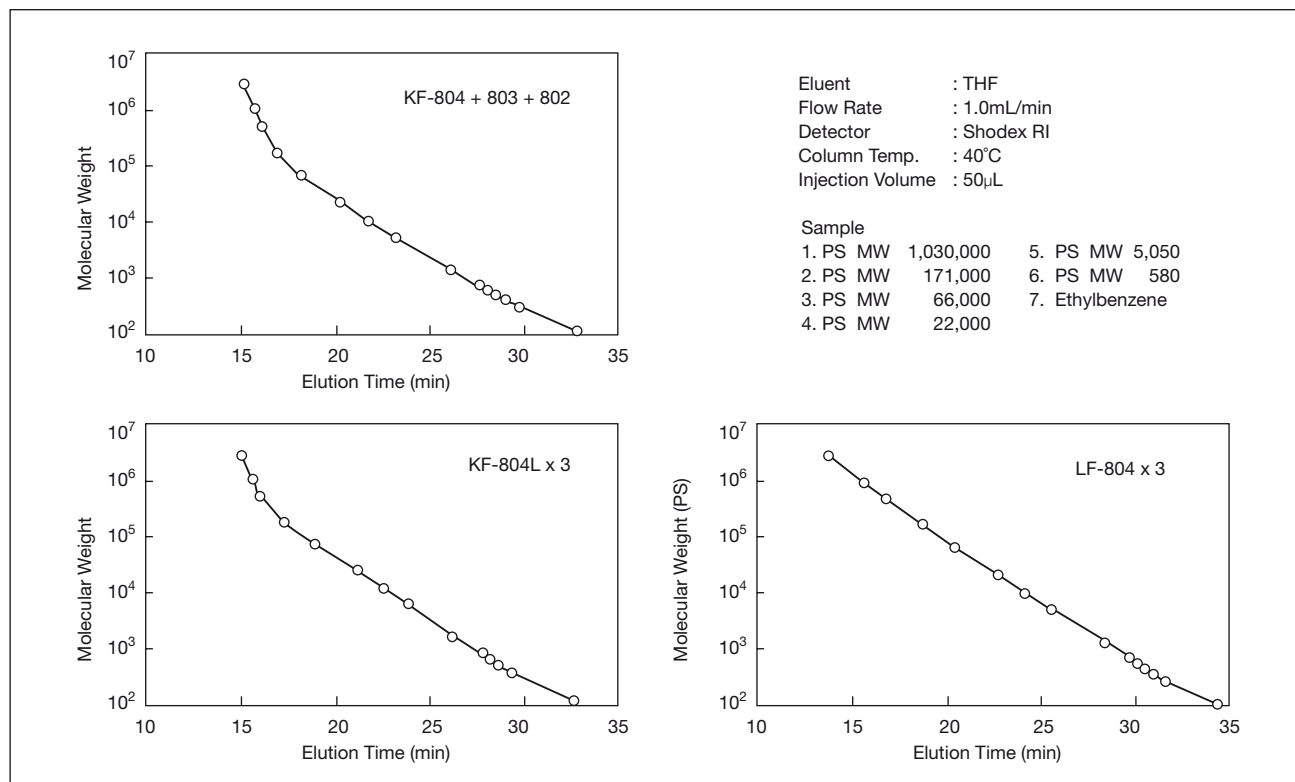


Figure 6. Comparison of Calibration Curves with Combination of Columns

Table 2 shows estimation errors of molecular weight compared to the actual value when the estimated value is calculated using calibration curves. We used three types of columns for this estimation. The 'multi-pore' type of LF-804, the mixed gel type of KF-804L and a combination of different pore sizes of KF-804+803+802. The approximation expressions were calculated using more than 10 points of actual results obtained by three kinds of column combination. The errors (R^2) were calculated with the first and the third degree of approximation expression.

The LF-804 column showed the best fit to the actual value with the third degree of approximation. Even with the first degree of approximation, the LF-804 column showed an equivalent or slightly better fit to the actual value, compared to the third degree of approximation for KF-804L. When columns of different pore sizes were connected (KF-804+803+802), a calibration curve of complex shape was obtained, and the error was considerable even with the third degree of approximation.

Table 2. Estimation Errors of Molecular Weight Compared to Actual Value with the First and the Third Degrees of Approximation Expression

Column Combination	MW RSD (%)	R^2	Degree	Points
LF-804 x 3	1.20	0.9999	3	11
	2.48	0.9997	1	11
KF-804L x 3	2.86	0.9998	3	10
	3.06	0.9998	1	10
KF-804+803+802	7.50	0.9994	3	12
	8.75	0.9980	1	10

$$\% \text{ Error in } M = 100 (M_{\text{FIT}} - M_{\text{STD}}) / M_{\text{STD}}$$

Figures 7 to 11 compare chromatograms obtained by analyzing phenol resin, phenoxy resin, polyvinylbutyral, polyvinylformal, and polycarbonate, respectively, using a single unit of KF-804+803+802, three units of KF-804L, and three units of LF-804. With the KF-804+803+802 combination, a hill and a valley appeared somewhere in each chromatogram. With the KF-804L x 3 combination, considerably better chromatogram shapes were obtained compared to KF-804+803+802, but slight distortions remained. In contrast, with the LF-804 x 3 combination, a smooth chromatogram of normal shape was obtained in all cases.

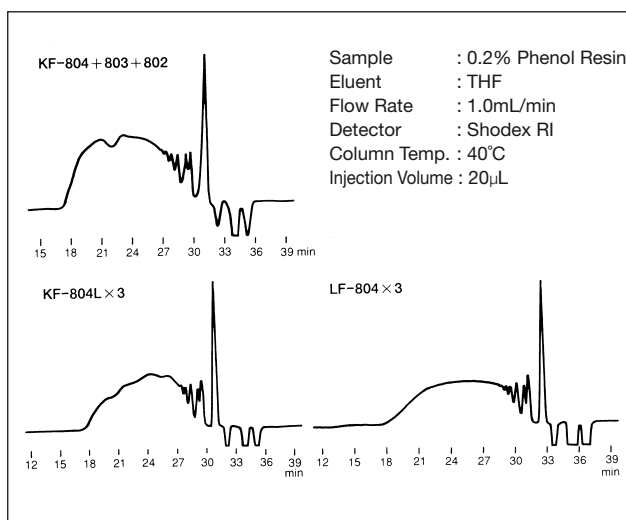


Figure 7. Phenol Resin

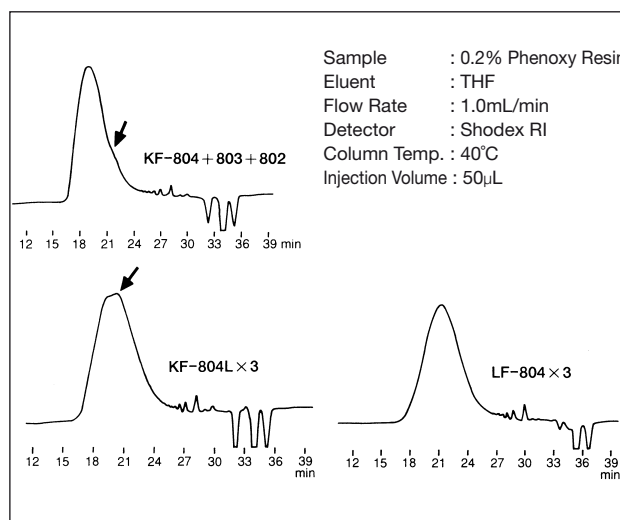


Figure 8. Phenoxy Resin

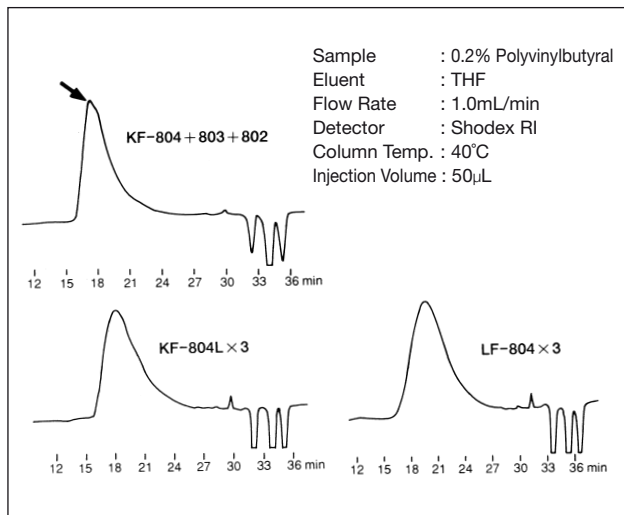


Figure 9. Polyvinylbutyral

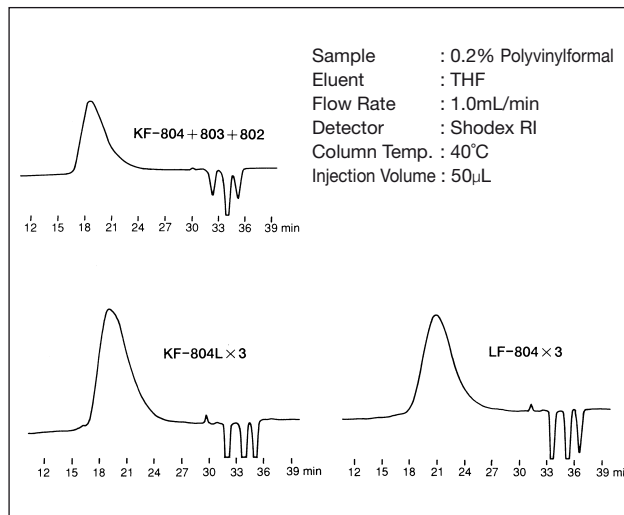


Figure 10. Polyvinylformal

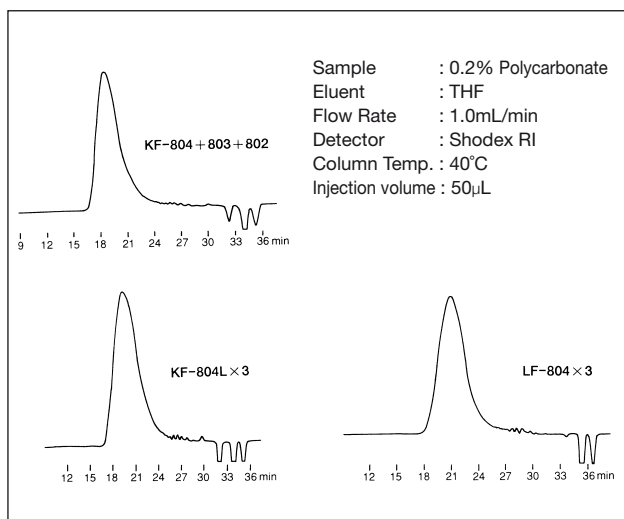


Figure 11. Polycarbonate

3.2. The LF-404 and LF-604 Semi-micro Analytical GPC Columns

LF-404 and LF-604 are semi-micro analytical columns containing the same gel as LF-804.

LF-404 was designed for high resolution analysis and LF-604 was designed for high speed analysis. They offer the following advantages:

(1) Highly linear calibration curves

Figure 12 shows calibration curves of LF-404 and LF-604. Both types show highly linear calibration curves, similar to that of LF-804. These columns had nearly the same capacity, the total capacity of two units of each column was about 6 mL.

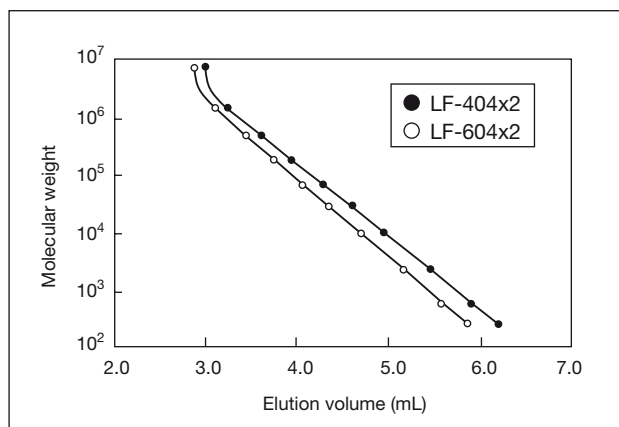


Figure 12. Calibration Curves of LF-404 and LF-604

(2) Highspeed, High-resolution Separation

Figure 13 shows the advantages of LF-604 and LF-404. LF-604 shows a good advantage in highspeed analysis. Even with two units of LF-604, the nine components of the standard polystyrene mixture were separated within 13 minutes.

LF-404 shows a good advantage in high resolution analysis. The nine components of the standard polystyrene mixture were nearly baseline resolved with three units of LF-404. Furthermore, the peaks of individual ingredients of the polystyrene oligomer (peak No. 9, Mw 580) can be observed.

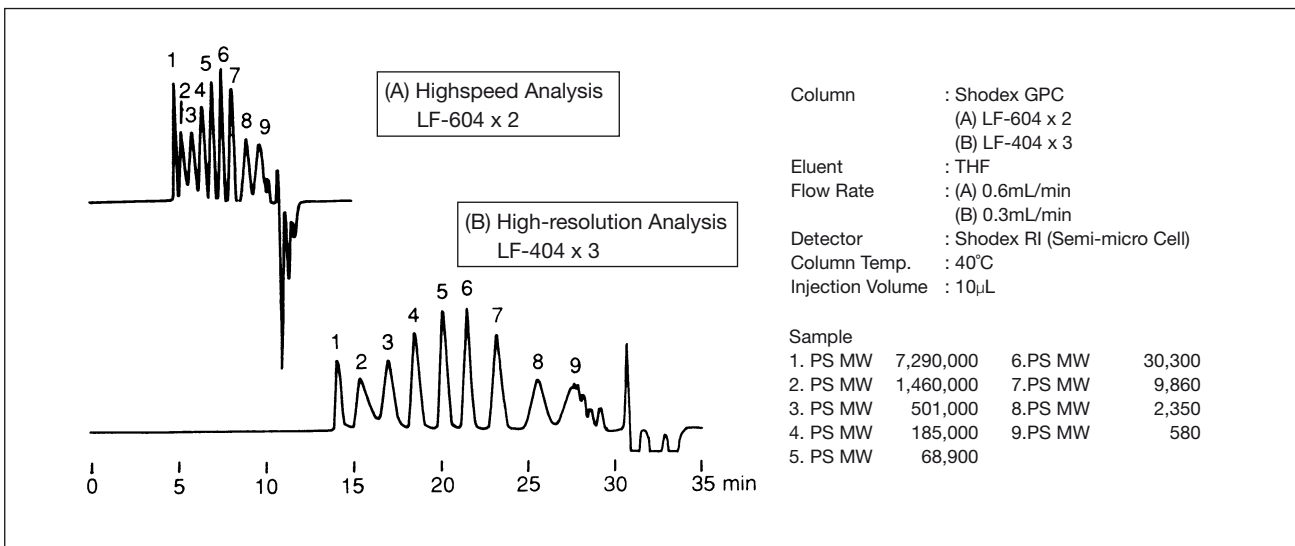


Figure 13. Highspeed Analysis with LF-604 and High-resolution Analysis with LF-404

(3) Improvement of Detection Sensitivity

Absolute detection sensitivity was improved by reducing the column diameter. Figure 14 shows the comparison of the peak heights of chromatograms using two units of LF-804 and two units of LF-404. Both samples were 10mL of a polystyrene standard having a molecular weight of 185,000 (0.05% solution). The detection sensitivity was improved, and the peak height with LF-404 was nearly 4 times as high as that with LF-804.

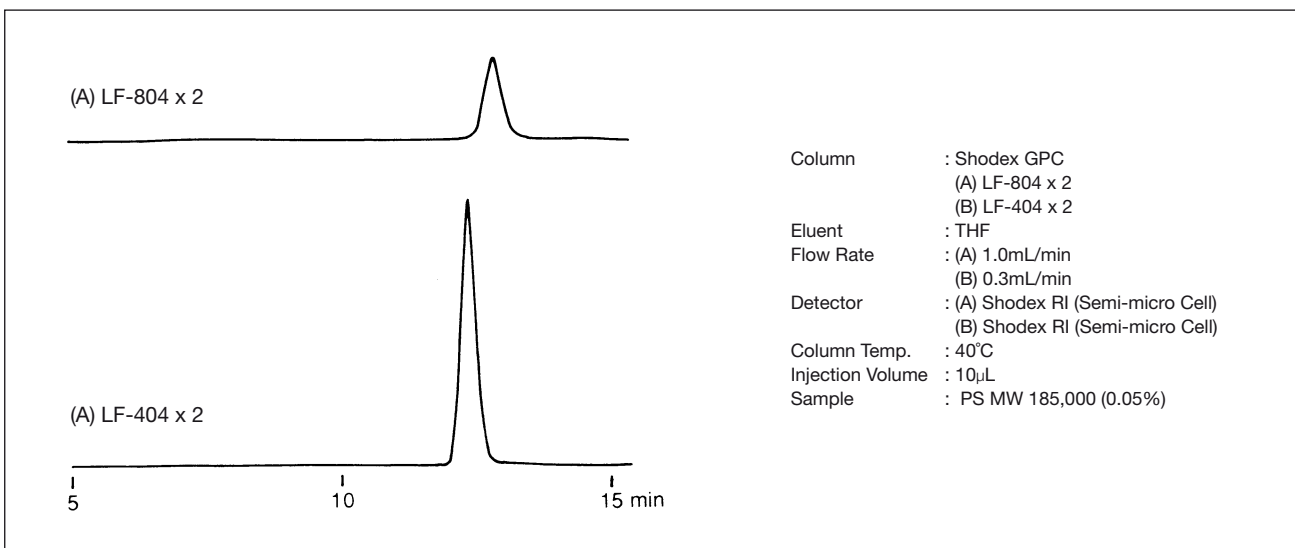


Figure 14. Comparison of Detection Sensitivity

(4) Offers an Equivalent Resolution to Conventional Columns with a Reduction of Solvent Consumption

LF-604 has an inside diameter of 6 mm and a length of 15 cm and is suitable for highspeed separation. LF-404 has an inside diameter of 4.6 mm and a length of 25 cm and is suitable for high-resolution separation. These two columns have nearly the same capacity, so that solvent consumption per run is nearly the same.

Figure 15 is a comparison of the separation performance of LF-404 (semi-micro analytical GPC) with LF-804 (general-purpose GPC). The resolution of LF-404 was comparable to that of LF-804, according to the results of a standard mixture of nine polystyrenes.

There is the additional advantage regarding reduction of solvent consumption. The solvent consumption of one analysis is reduced to one-fourth level with LF-404 (6.9 mL) compared to LF-804 (26 mL).

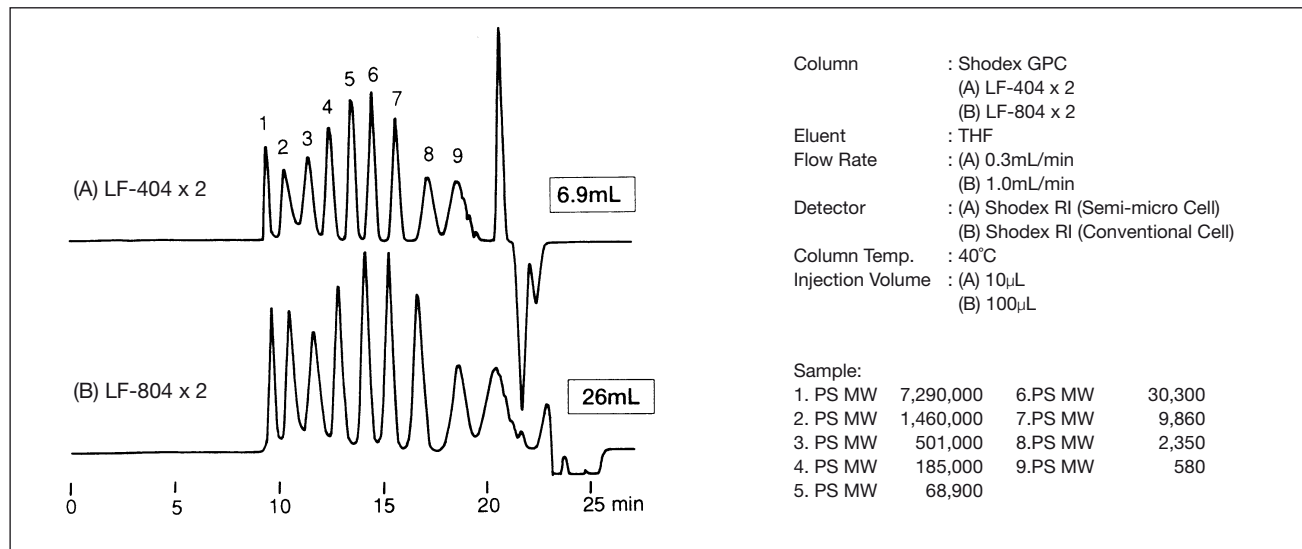


Figure 15. Comparison of the Separation Performance LF-404 vs LF-804

3.3. Highspeed Analysis

Figure 16 shows chromatograms obtained by analyzing the standard polystyrene mixture using one, two, and three units of LF-404.

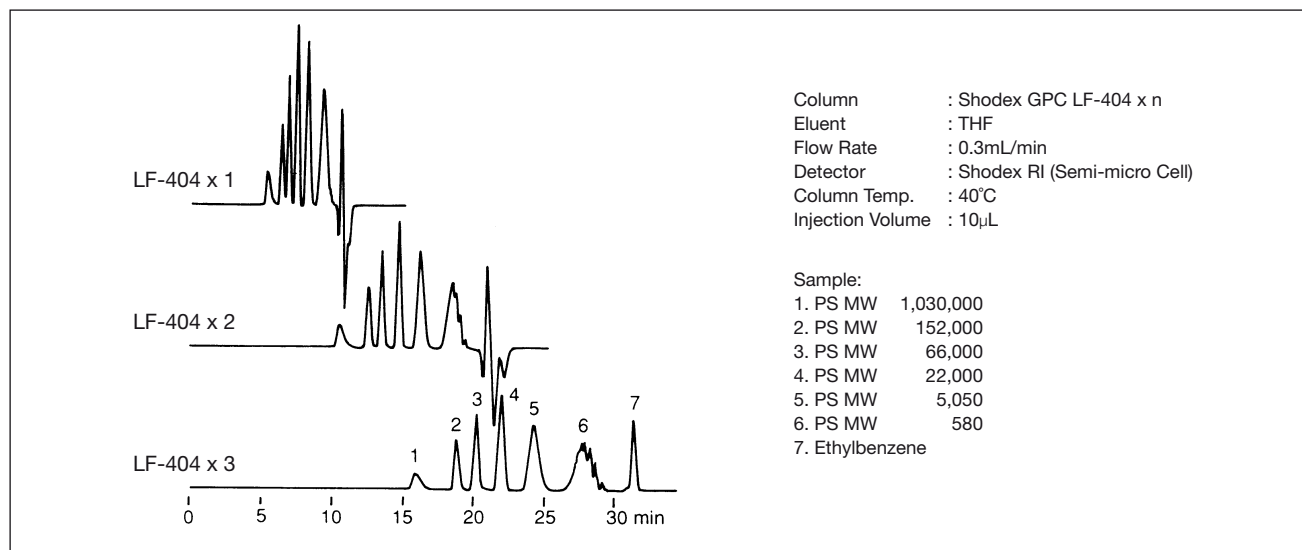


Figure 16. Chromatogram of Standard Polystyrene Mixture with LF-404

Figure 17 compares chromatograms obtained by analyzing the standard polystyrene mixture using one, two, and three units of LF-604. Even when a single unit of the column was used, seven peaks were separated within 7 minutes on the LF-604 column as compared to the same seven peaks separating in 12 minutes on the LF-404. Therefore, the LF-604 is particularly well suited to high-throughput GPC to quickly determine rough molecular weight distributions.

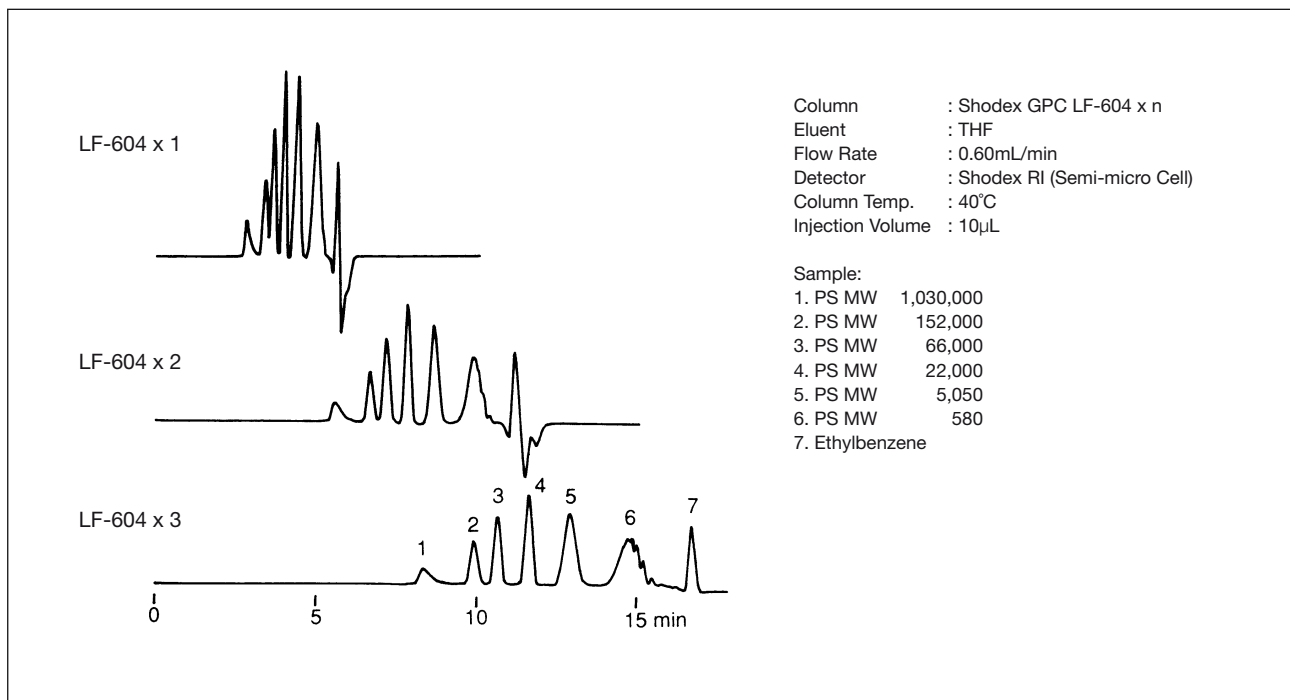


Figure 17. Chromatogram of Standard Polystyrene Mixture with LF-604

Figures 18 to 21 compare chromatograms obtained by analyzing EPON1009 and polycarbonate using one, two, and three units of each of LF-404 and LF-604.

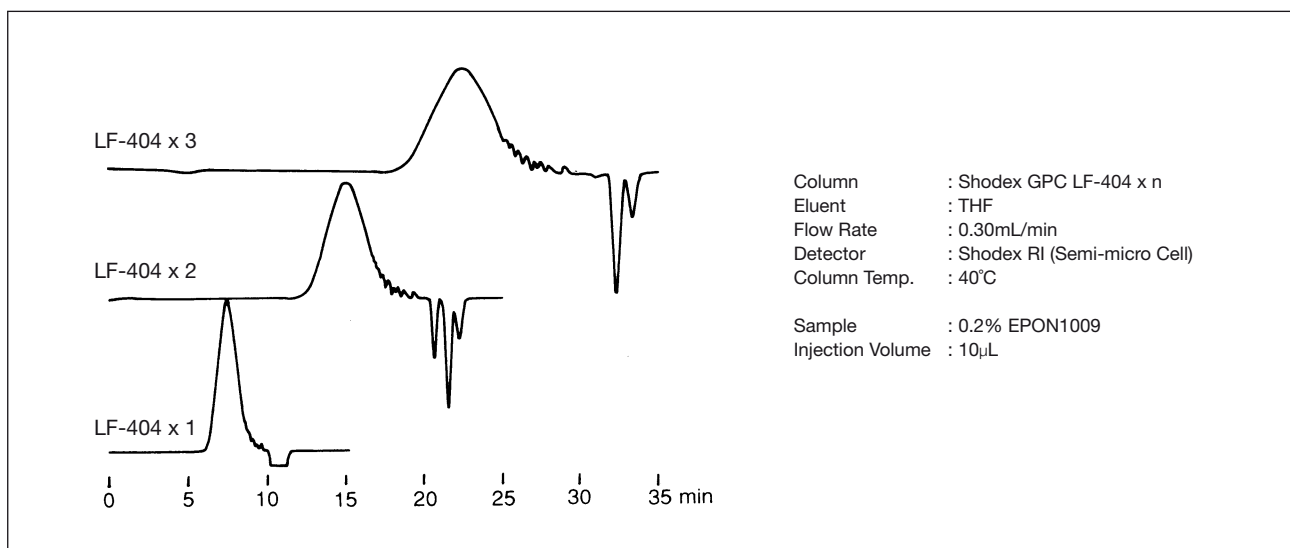


Figure 18. Chromatogram of EPON1009 with LF-404

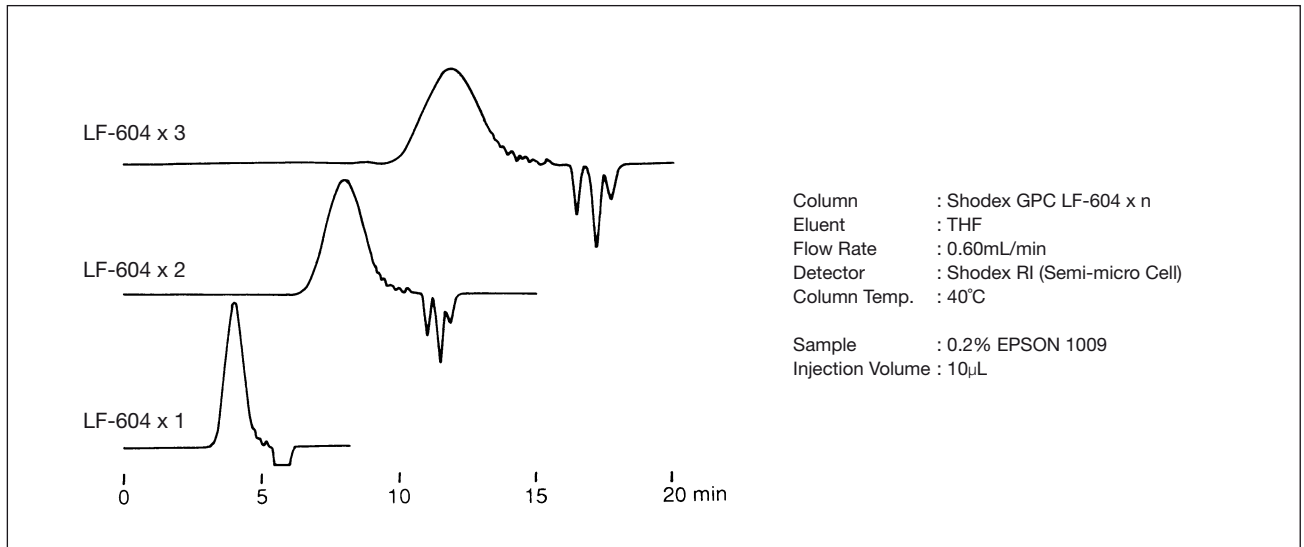


Figure 19. Chromatogram of EPON1009 with LF-604

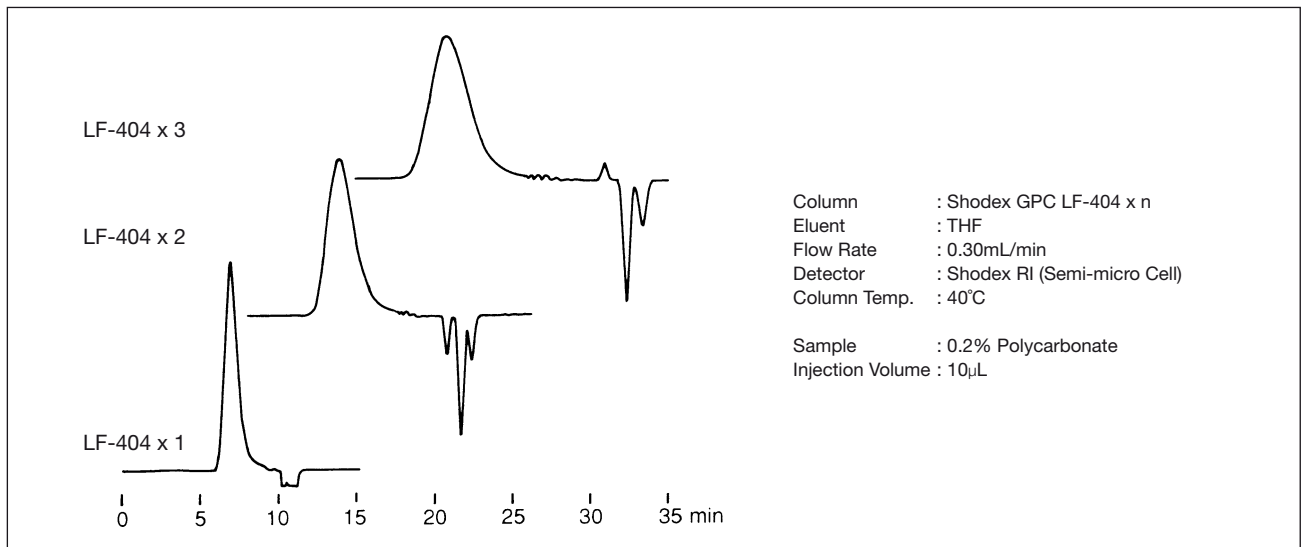


Figure 20. Chromatogram of Polycarbonate with LF-404

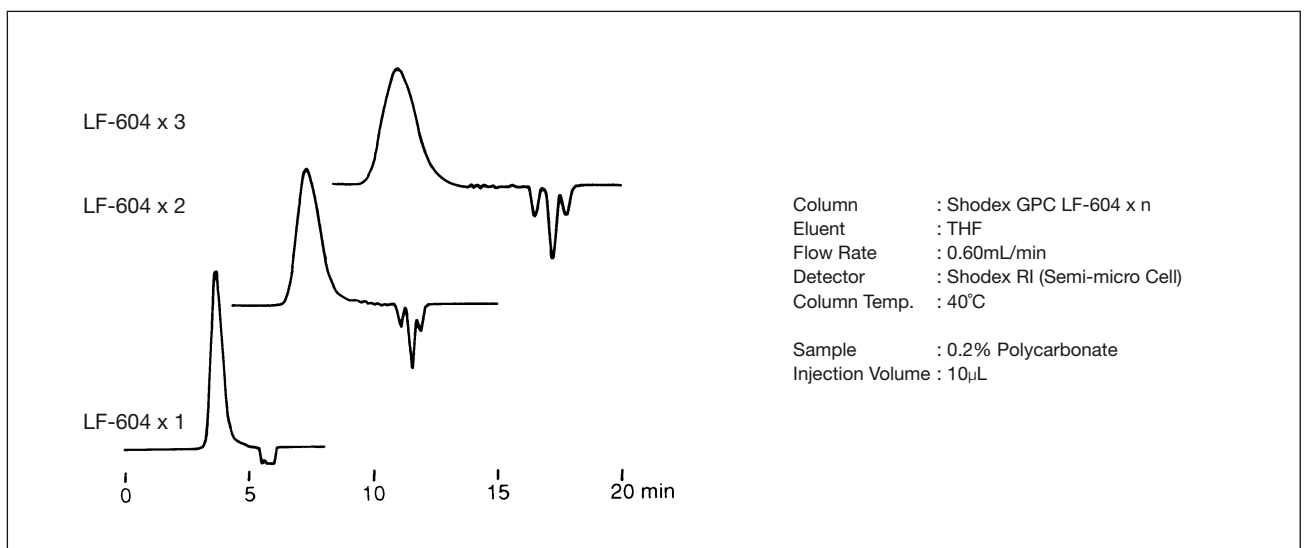


Figure 21. Chromatogram of Polycarbonate with LF-604

Table 3 shows the results of molecular weights and Mw/Mn ratios of a polystyrene standard having narrow molecular weight distribution, using different numbers of units of LF-404 and LF-604. (1 to 3 units). The weight-average of the sample's molecular weight was 185,000 and the Mw/Mn ratio was 1.03.

Even when a single unit of LF-604 was used, the weight-average molecular weight was determined to be 180,000, showing a fair agreement with the actual value; however, the Mw/Mn ratio was slightly higher at 1.06. This means that only one unit of column can determine a weight-average molecular weight or molecular weight distribution of a sample roughly and rapidly. For obtaining an accurate molecular weight distribution of a sample having narrow molecular weight distribution, it is better to use three units or more of columns.

Table 3. Results of Molecular Weights and Mw/Mn Ratios of Polystyrene Standard (MW 185,000)

Column (pcs)	Mw	Mn	Mw/Mn
LF-404 X 2	186,200	181,500	1,026
LF-404 X 3	182,600	178,800	1.021
LF-604 X 1	180,000	169,700	1.060
LF-604 X 2	181,500	175,100	1.037
LF-604 X 3	188,000	183,700	1.024

Table 4 shows the results of molecular weights and Mw/Mn ratios of a polystyrene standard having broad molecular weight distribution using different numbers of units of LF-404 and LF-604. (1 to 3 units).

In the case of a sample having broad molecular weight, the value obtained with one unit of LF-604 was nearly the same as the value obtained with three units.

This data was obtained using a general-purpose LC system, therefore a higher reproducibility is expected using a dedicated GPC system for both narrow MW and broad MW situations.

Table 4. Results of Molecular Weights and Mw/Mn Ratios of Polystyrene Standard

Column (pcs)	Mw	Mn	Mw/Mn
LF-404 X 2	274,100	121,200	2.262
LF-404 X 3	287,400	121,100	2.372
LF-604 X 1	278,000	124,600	2.232
LF-604 X 2	283,600	126,900	2.236
LF-604 X 3	271,900	122,000	2.228

Figures 22 to 26 show chromatograms obtained by analyzing several kinds of synthetic polymer using two units of LF-404.

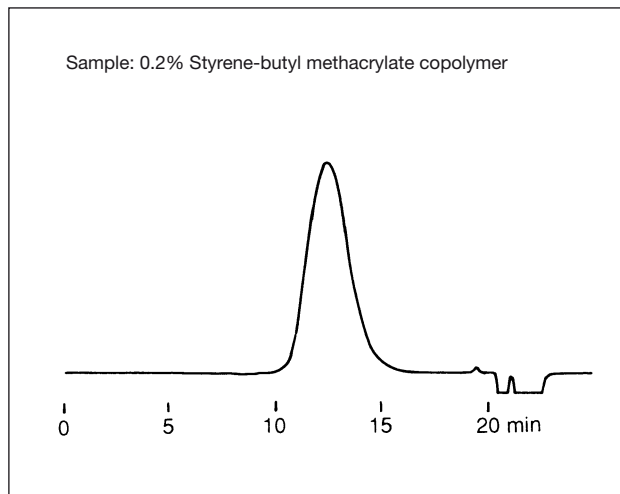


Figure 22. Styrene-butyl Methacrylate Copolymer

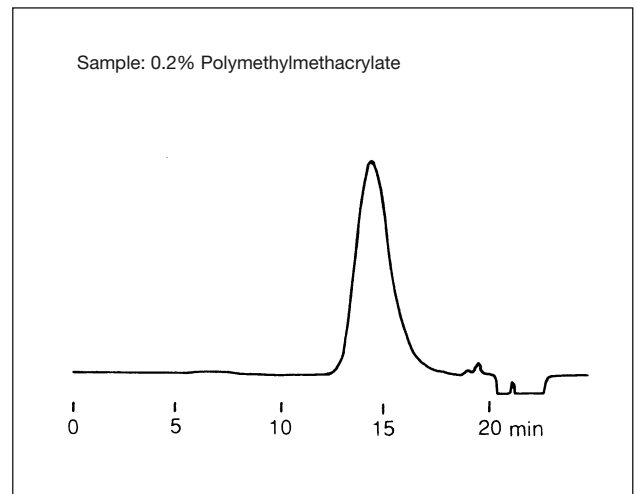


Figure 23. Polymethylmethacrylate

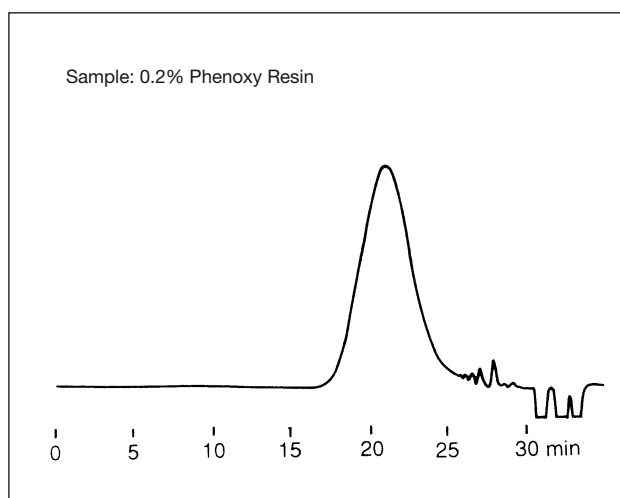


Figure 24. Phenoxy Resin

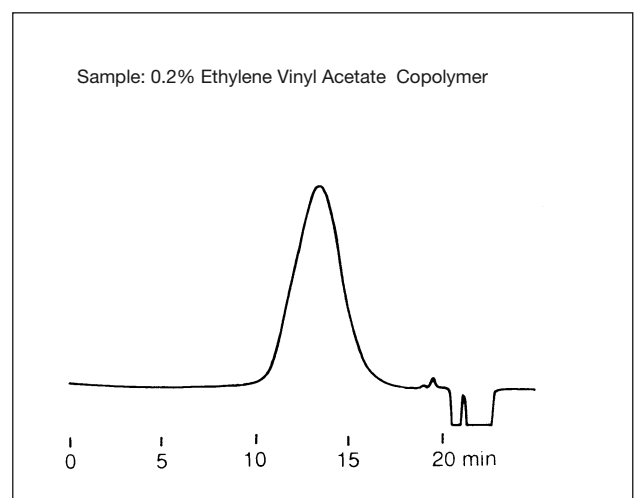


Figure 25. Ethylene Vinyl Acetate Copolymer

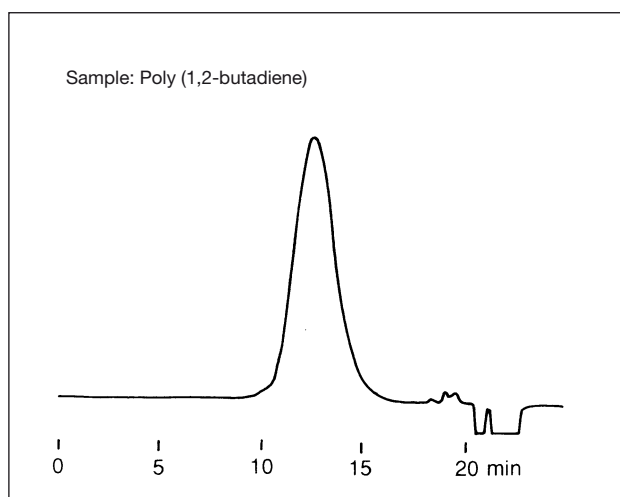


Figure 26. Poly (1,2-butadiene)

Condition of Fig 22 to 26

Column : Shodex GPC LF-404 x 2
 Eluent : THF
 Flow Rate : 0.30mL/min
 Detector : Shodex RI (Semi-micro Cell)
 Column Temp. : 40°C

3.4. Applications with DMF Eluent

Figure 27 shows a calibration curve for polyethylene oxide analyzed using LF-604 with DMF as the eluent. The calibration curve was highly linear even when using DMF as the eluent.

Figures 28 to 32 show chromatograms obtained by analyzing phenoxy resin, polyvinylbutyral, polyvinyl pyrrolidone, N-vinylpyrrolidone-vinyl acetate copolymer, and vinylidene chloride-acrylonitrile copolymer, respectively, using two units of LF-604.

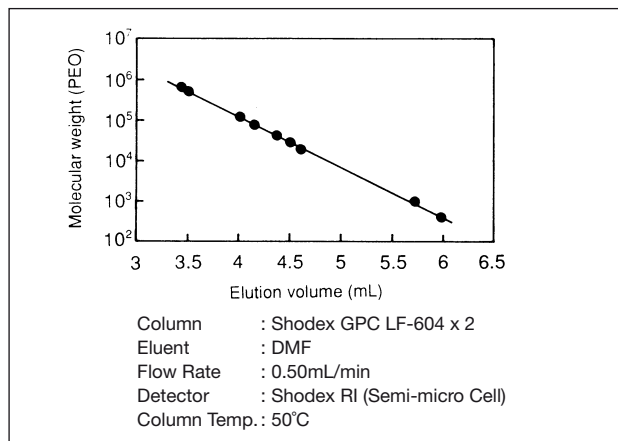


Figure 27. Calibration Curve of PEO with DMF

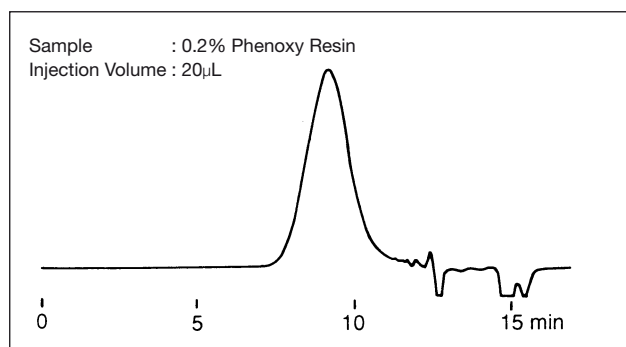


Figure 28. Phenoxy Resin

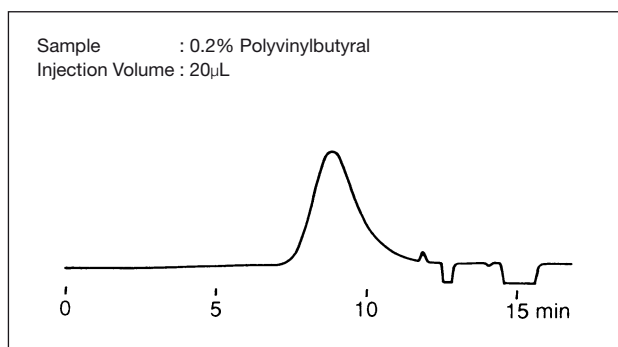


Figure 29. Polyvinylbutyral

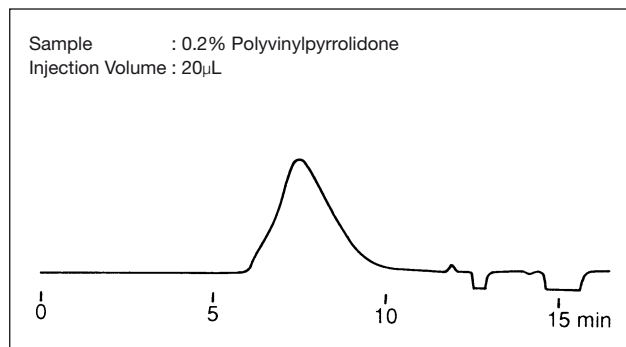


Figure 30. Polyvinylpyrrolidone

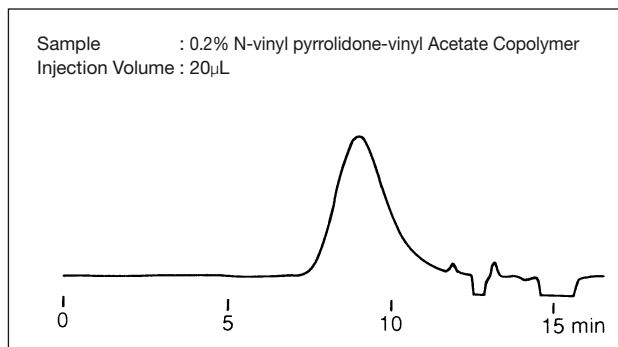


Figure 31. N-vinylpyrrolidone-vinyl Acetate Copolymer

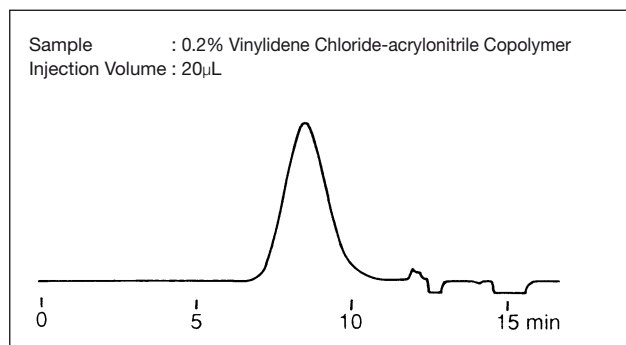


Figure 32. Vinylidene Chloride-acrylonitrile Copolymer

Conditions for Fig 28 to 32

Column : Shodex GPC LF-604 x 2
 Eluent : DMF
 Flow rate : 0.50mL/min
 Detector : Shodex RI (Semi-micro Cell)
 Column Temp. : 50°C

3.5. Applications with NMP Solvent

Figures 33 and 34 show calibration curves for polyethylene oxide and polystyrene obtained using LF-604 with N-methylpyrrolidone (NMP) as the eluent. The calibration curves were highly linear even when using NMP as the eluent. LF-604 is suited for applications with a highly viscous eluent like this.

Figures 35 to 39 show chromatograms obtained by analyzing phenoxy resin, N-vinylpyrrolidone-vinyl acetate copolymer, polyvinylbutyral, and vinylidene chloride-acrylonitrile copolymer, respectively. Low sensitivity experienced in the chromatogram of polyvinyl butyral is due to the small difference in the refractive index between the sample and the NMP eluent.

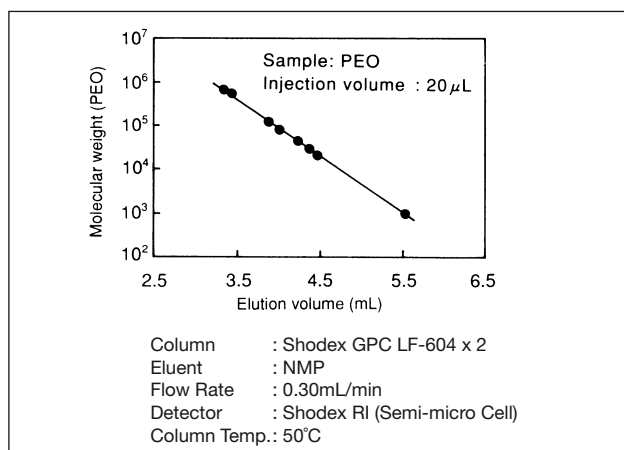


Figure 33. Calibration Curve of PEO with NMP

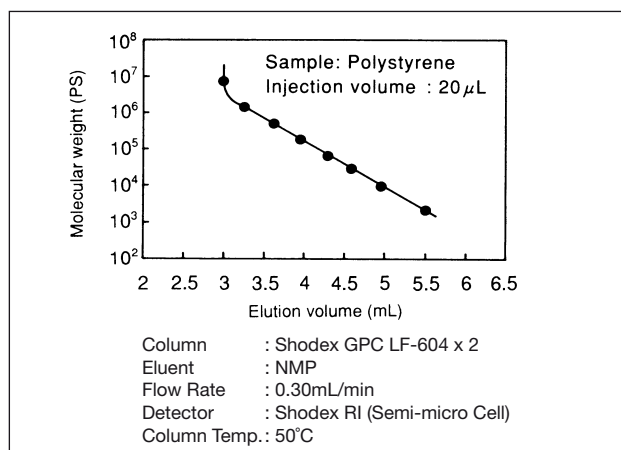


Figure 34. Calibration Curve of PS with NMP

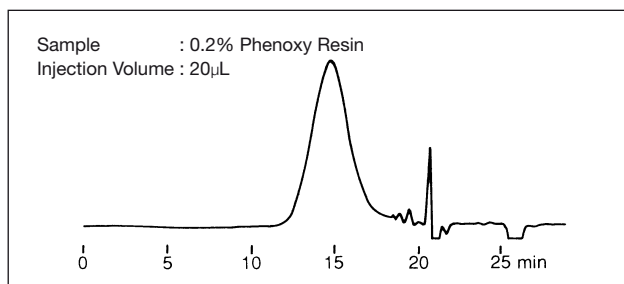


Figure 35. Phenoxy Resin

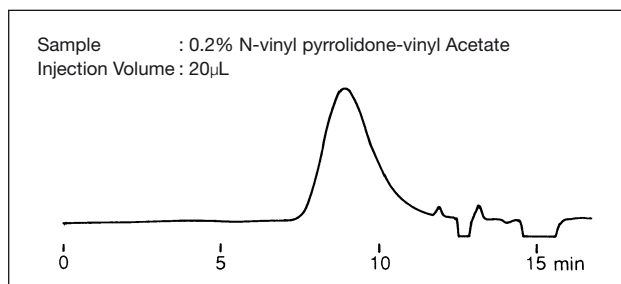


Figure 36. N-vinylpyrrolidone-vinyl Acetate Copolymer

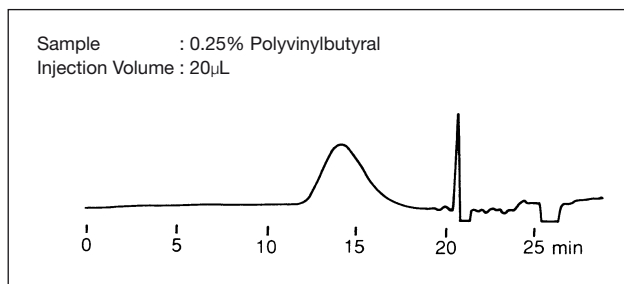


Figure 37. Polyvinylbutyral

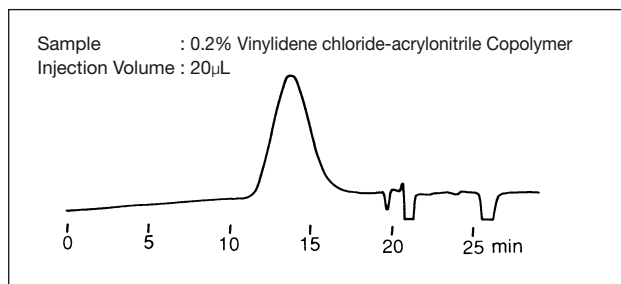


Figure 38. Vinylidene chloride-acrylonitrile Copolymer

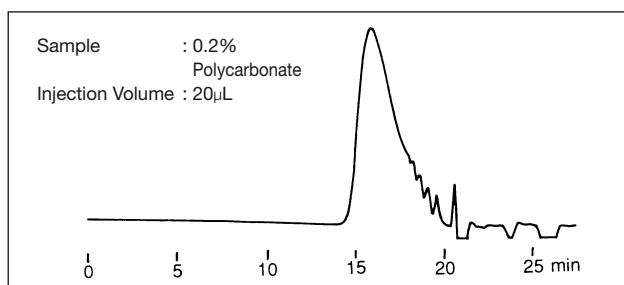


Figure 39. Polycarbonate

Condition of Fig 35 to 39

Column : Shodex GPC LF-604 x 2
 Eluent : NMP
 Flow rate : 0.30mL/min
 Detector : Shodex RI (Semi-micro Cell)
 Column Temp.: 50°C

3.6. Applications with HFIP Solvent

Figure 40 shows calibration curves for polymethyl methacrylate (PMMA) obtained using LF-404 and LF-604 with Hexafluoroisopropanol (HFIP) as the eluent. The calibration curve remained linear even when using the HFIP eluent.

Figure 41 compares chromatograms obtained by analyzing PMMA with different flow rates.

Figure 42 and 45 show the results of nylon 6/6 and polyethylene terephthalate, poly (trimethyl hexamethylene terephthalamide) and polyacetal.

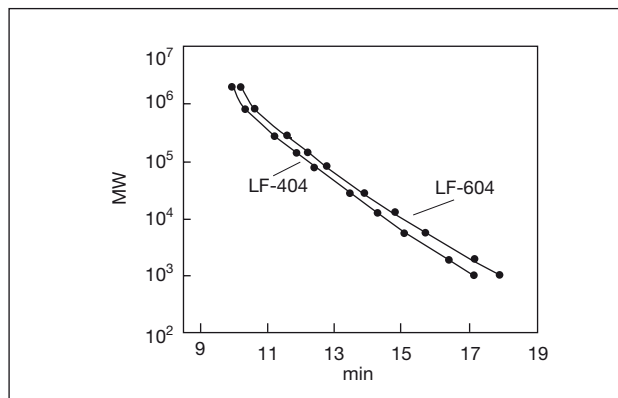


Figure 40. Calibration Curves of Standard PMMA using LF-404 and LF-604 with HFIP Solvent

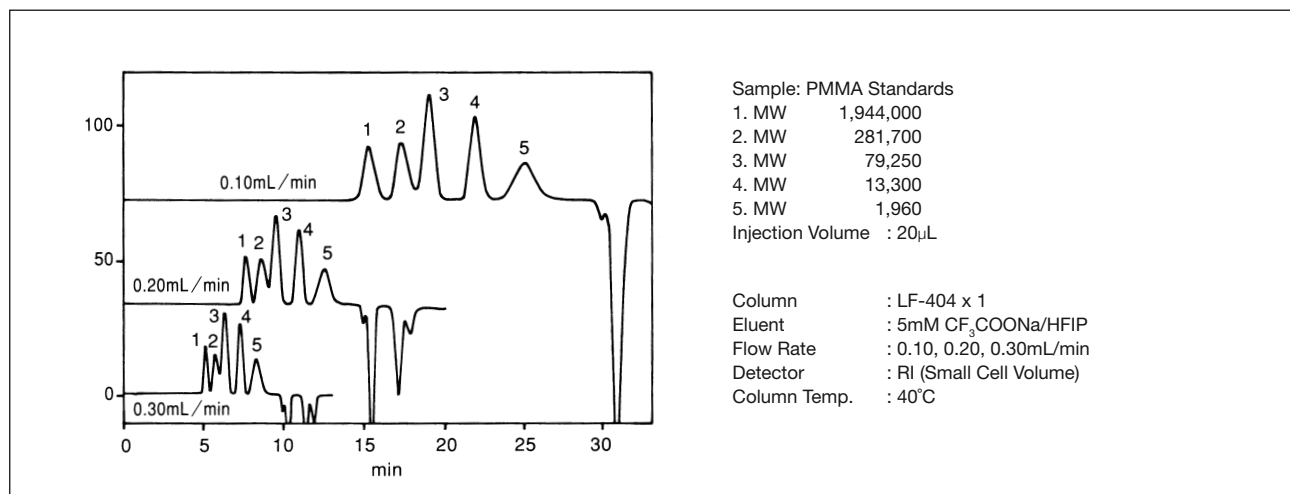


Figure 41. Effect of Flow Rate for Separation of PMMA

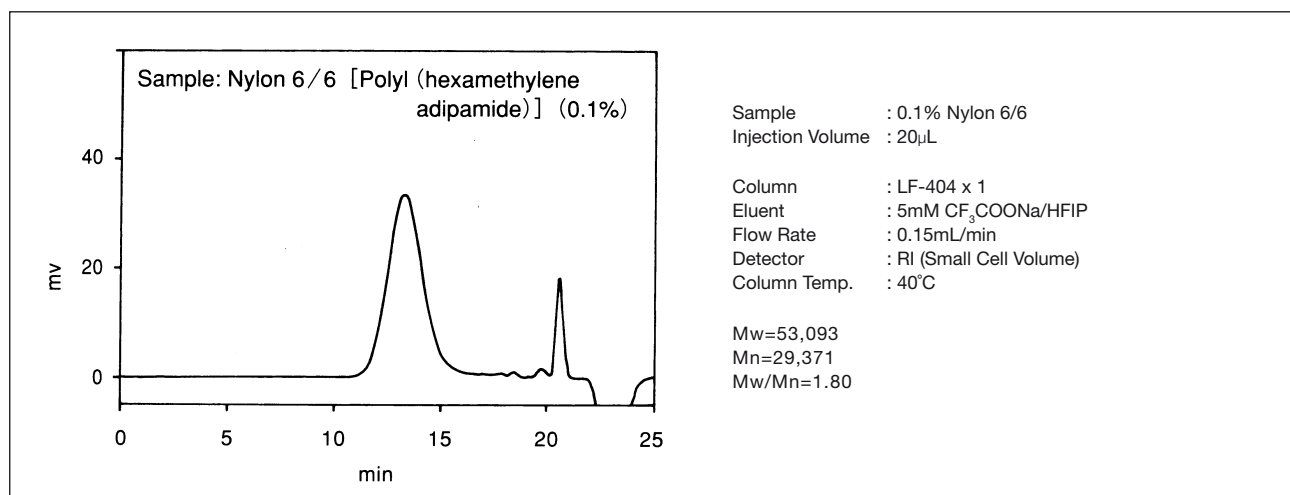


Figure 42. Nylon 6/6

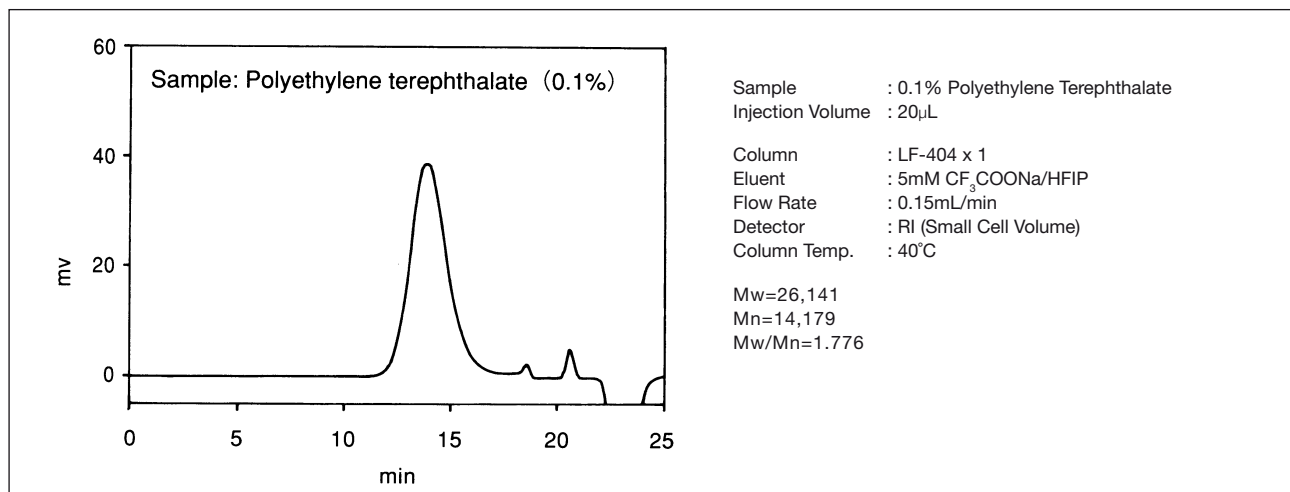


Figure 43. Polyethylene Terephthalate

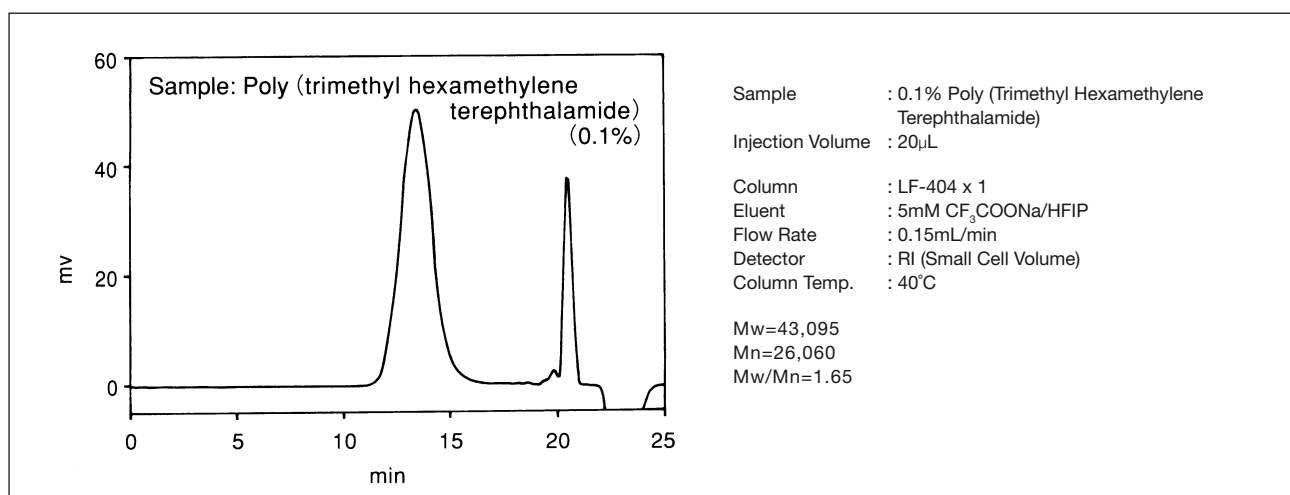


Figure 44. Poly (Trimethyl Hexamethylene Terephthalamide)

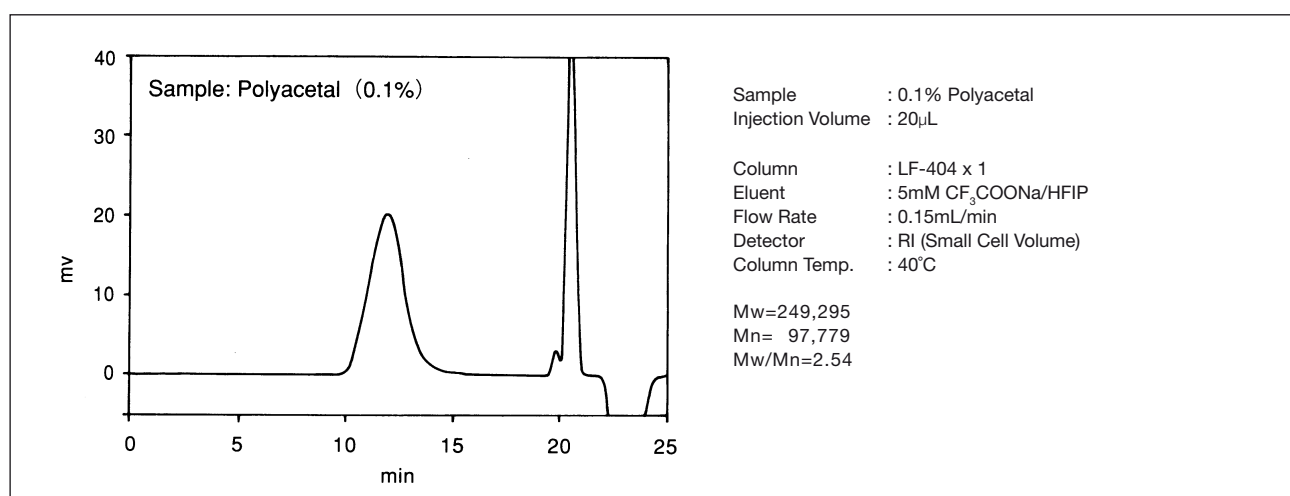


Figure 45. Polyacetal

4. Replacement of In-column Solvent of LF Series

Table 5 lists compatible solvents and maximum pressure for the LF series. Flow rate must be controlled to keep the back pressure lower than the maximum listed for each column. For high viscosity solvents, such as dimethylformamide (DMF), dimethylacetamide (DMAc), hexafluoroisopropanol (HFIP), n-methylpyrrolidone (NMP) and dimethylsulfoxide (DMSO), the column temperature must be set above 40 °C.

Table.5 Solvent Compatibility of LF Series

Column	LF-804	LF-604	LF-404
Maximum Pressure (< MPa)	3.5	2.0	3.5
THF	Y	Y	Y
Chloroform	Y	Y	Y
Carbon Tetrachloride	Y	Y	Y
Toluene	Y	Y	Y
Dimethylformamide (DMF)	H	H	H
Dimethylacetamide (DMAc)	H	H	H
Hexafluoroisopropanol (HFIP)	H	H	H
N-Methylpyrrolidone (NMP)	H	H	H
Dimethylsulfoxide (DMSO)	H	H	H
30%-m-Cresol/Chloroform	Y	Y	Y
30%-m-Chlorophenol/Chloroform	Y	Y	Y
Methyl Ethyl Ketone	Y	Y	Y
n-Hexane	N	N	N
Methanol	N	N	N

Y: Compatible; H: Compatible using more than 40 °C; N: Not Compatible

Procedure for Change-over of In-column Solvent

1. Change only between miscible solvents.
2. Use a reduced flow rate (0.3mL/min for LF-804, 0.2mL/min for LF-604 and 0.1mL/min for LF-404).
3. Flow three times of column volumes of a 1:1 mixture of current solvent and new solvent.
4. Flow three times of column volumes of the new solvent.
5. Set the flow rate to suitable level for the analysis

5. Conclusion

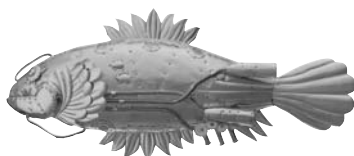
The Shodex GPC LF series offers easy-to-use columns for the analysis of molecular weight distribution. These columns can be used for the analysis of polymers having a wide range of molecular weight. Importantly, these columns provide linear calibration curves over a wide range of molecular weight. The unique 'multi-pore' property of a single gel containing a wide pore distribution creates the advantage of a broad linear calibration range. Now the LF series columns provide smooth chromatograms of molecular distribution without the inflection problems observed with mixed type linear columns.

Three types of columns are now available: LF-804 (8.0mmID x 300mm) for general purpose, LF-604 (6.0mmID x 150mm) for high speed analysis, and LF-404 (4.0mmID x 250mm) for high resolution analysis.

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