TSKgel® High Temperature GPC Column Durability

TSKgel
APPLICATION NOTE

Introduction

In gel permeation chromatography (GPC), just like all chromatography modes, the heart of the separation lies in the quality, applicability and selectivity, or resolution, of the column. The selectivity of a GPC column is based on the ability of the pores in the column packing material to differentiate between species of varying hydrodynamic volume. The pores of the packing material within a GPC column are sampled by the analytes as they travel through the column in a size dependent manner. Due to their size, the larger components of the analyte sample either a smaller number of pores or, within a given pore, a smaller pore volume than the smaller components of the analyte, thus the larger components elute from the column prior to the smaller components.

GPC is considered a low resolution technique and does not provide infinite resolution of species with different hydrodynamic volume. As a result of the low resolution of the separation technique, each slice eluting from the GPC column has some residual polydispersity. This residual polydispersity, combined with extra dead volume in detectors and instrument tubing, leads to the overestimation of sample polydispersity because the peak eluting from the GPC column is broadened and appears to cover a wide molar mass range.[1] The superficial broadening of the molar mass range due to the resolution of a GPC column has a direct impact on accuracy of the molar mass averages. The accuracy of the number and *z*-average molar masses, M_n and M_z respectively, can decreases by more than 10% as the resolution of a GPC column set decreases, while the accuracy of the weight-average molar mass, M_w, remains virtually unaffected by resolution.[1, 2]

The ability to obtain accurate molar mass averages for polymers by GPC, without superficially broadening the distribution, is essential as the molar mass averages and distributions affect the processing and end-use properties of materials. To obtain the best separation, thus most accurate molar mass averages possible, a GPC column must provide a linear calibration in the molar mass range of interest, narrow particle size distribution of the packing material, a large number of theoretical plates or high resolving power and durability.[2] Column manufactures, such as Tosoh, focus their innovations in GPC column technology on these characteristics as they directly affect column quality, applicability and selectivity, or resolution.

Column characteristics such as column durability become even more important in high temperature GPC analysis as these columns are not only exposed to harsh organic solvents but are also continuously exposed to extreme temperatures and repetitive temperature cycling. Here we have studied the durability and stability of Tosoh's new TSKgel high temperature GPC columns compared to other commercially available columns for polymer analysis at temperatures above 80 °C.

Experimental Conditions

Sample analysis was performed on a system consisting of an EcoSEC® High Temperature GPC System (HLC-8321 GPC/HT) equipped with RI detector. Separation of unfiltered 200 µL injections occurred over a column bank consisting of one 7.8 mm ID × 30 cm, 13 µm particle size TSKgel GMH$_{HR}$-H(S) HT column (exclusion limit 4 × 10^8 g/mol) (PN 18393) (Tosoh Bioscience LLC) or one 7.8 mm ID × 30 cm, 13 µm particle size, commercially available high temperature GPC column. The mobile phase and solvent were 1-chloronaphthalene (Fisher) at a flow rate of 1.0 mL/min. Detector, pump oven, and column oven were maintained at 220 °C. The polymer samples were dissolved in 1-chloronaphthalene at 250 °C for one hour using the Tosoh sample prep system (PN 23801). The final sample concentrations were approximately 2.0 g/L. Data was processed with the EcoSEC GPC Workstation software.

Temperature cycling was performed by flowing 1-chloronaphthalene through the EcoSEC High Temperature GPC System at a flow rate of 1.0 mL/min and slowly raising the column oven to 220 °C over nine hours. Samples were injected and molar mass averages were determined after the system reached equilibration at 220 °C. The EcoSEC High Temperature GPC System requires three hours to equilibrate. Temperature cycling times were extended beyond the equilibration time to test the column durability when exposed to extreme temperatures for a prolonged period. Following sample analysis 1-chloronaphthalene remained flowing through the EcoSEC High Temperature GPC System at a flow rate of 1.0 mL/min and the column oven temperature was slowly lowered from 220 °C to room temperature over nine hours. After the EcoSEC High Temperature GPC System was lowered to room temperature the flow was stopped. The entire temperature cycling process was performed multiple times to test column durability.

Molar mass averages were determined for each polymer sample using a calibration curve. A calibration curve for each column set was created for the RI detector at 220 °C using Tosoh polystyrene standards A-500, F-1, F-4, F-10, and F-40. Polystyrene standards were prepared for a final concentration of 10 g/L.

Results and Discussion

Column durability in high temperature GPC polymer analysis is essential as these columns are continuously exposed to harsh organic solvents, extremely elevated temperatures and temperature cycling as GPC systems are turned on and off. The durability of a high temperature GPC column directly influences the quality, applicability and selectivity, or resolution, of the GPC column, thus the accuracy of the molar mass averages obtained. A durability and stability study of Tosoh's new TSKgel high temperature GPC columns was performed and the results compared to another commercially available column for polymer analysis at 220 °C.

The weight-, number-, and *z*-average molar mass values, M_n, M_w, and M_z respectively, obtained for a polymer sample on both a TSKgel GMHHR-H(S) HT column and a commercially available high temperature GPC column initially and after multiple temperature cycles are given in *Table 1*. Little to no variation of the molar mass averages, especially the number- and *z*-average molar mass values, is seen with the TSKgel GMHHR-H(S) HT column, while significant fluctuations on the other commercially available high temperature GPG column are evident. The repeatability (column accuracy) of the molar mass averages obtained on the TSKgel GMHHR-H(S) HT column after temperature fluctuations is an indication that when the TSKgel GMHHR-H(S) HT column is exposed to extreme temperatures and temperature cycling, column resolution is not compromised. If the resolution of the TSKgel GMHHR-H(S) HT column was compromised due to high temperature GPC experimental parameters, as in the other commercially available high temperature GPC column, fluctuations in molar mass averages would be observed between those obtained before and after temperature cycling.

Table 1. Molar mass averages and polydispersity for a polymer before and after temperature cycling obtained using a TSKgel GMHHR-H(S) HT column and a commercially available high temperature GPC column.

Column	M_n (g/mol)	M_w (g/mol)	M_z (g/mol)	PDI[a]
TSKgel GMHHR-H(S) HT				
Before	3.9×10^3	1.8×10^4	3.6×10^4	4.6
After	3.6×10^3	1.7×10^4	3.5×10^4	4.7
Commercial column				
Before	6.7×10^3	1.9×10^4	4.4×10^4	2.9
After	4.1×10^3	2.4×10^4	9.3×10^4	5.8

[a] $PDI = M_w/M_n$

The deterioration of the other commercially available high temperature GPC column is also observed in the GPC elution profiles, *Figure 1*, as the resolution between the sample and solvent peaks decreases after the column is exposed to temperature cycling. The GPC elution profiles obtained before and after temperature cycling are slightly shifted for the other commercially available high temperature GPC columns while the GPC elution profile for the TSKgel GMHHR-H(S) HT column remain superimposable, *Figure 2*. As a high temperature GPC column begins to fail or lose resolution due to the extreme experimental conditions required for high temperature GPC polymer analysis, the number- and *z*-average molar mass values obtained become inflated and the GPC elution profile begins to shift due to a decrease in multiple factors that affect the ability of the columns to separate species varying in hydrodynamic volume.

Figure 1. GPC elution profile for a polymer before and after temperature cycling obtained using a commercially available high temperature GPC column

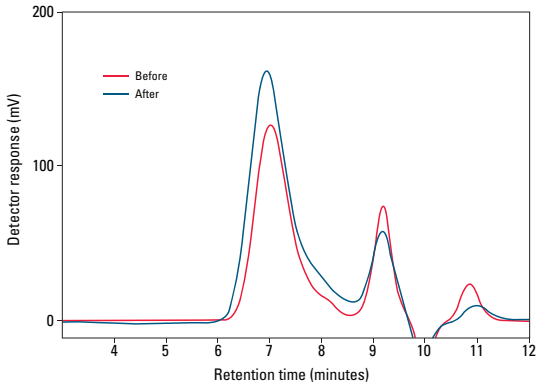
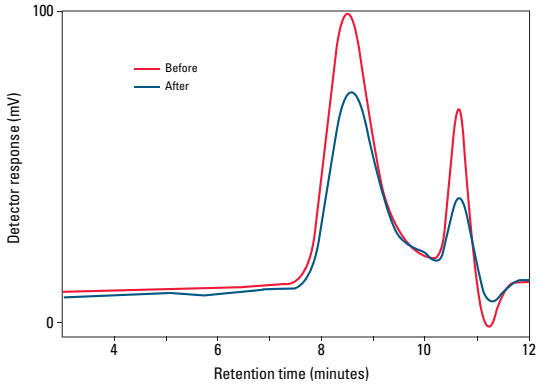


Figure 2. GPC elution profile for a polymer before and after temperature cycling obtained using a TSKgel GMHHR-H(S) HT column



In addition to molar mass averages, the polydispersity index, *PDI*, can also be compared when looking at column performance and durability. In GPC analysis it is often difficult to compare GPC elution profiles and molar mass averages obtained for a given polymer under different experimental conditions, *i.e.* different GPC columns, as GPC columns tend to vary ever so slightly from manufacturer to manufacturer. The molar mass distributions and the *PDI* values for a given polymer analyzed on a given column set should not change, unless the quality, applicability and selectivity, or resolution, of the column has been compromised. As seen in *Table 1* and *Figures 3 and 4*, the molar mass distribution and *PDI* values obtained for the polymer samples using the TSKgel GMHHR-H(S) HT column remain constant while those obtained using the other commercially available high temperature GPC column change after the columns are exposed to temperature cycling. In general, GPC columns have an expected lifetime that varies depending on analyte and experimental conditions but for high temperature GPC analysis the TSKgel GMHHR-H(S) HT column is shown to be more durable than other commercially available high temperature GPC columns.

Figure 3. Overlay of the differential molar mass distribution of a polymer before and after temperature cycling obtained using a commercially available high temperature GPC column

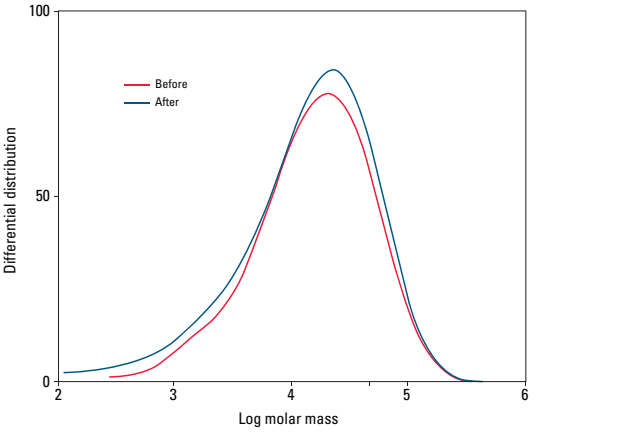
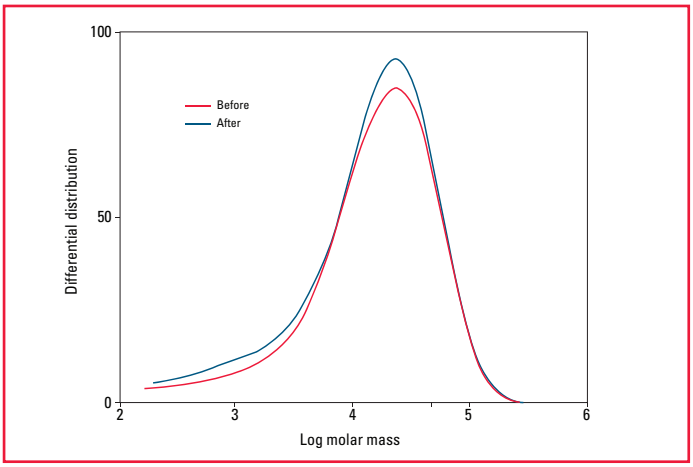


Figure 4. Overlay of the differential molar mass distribution of a polymer before and after temperature cycling obtained using a TSKgel GMH$_{HR}$-H(S) HT column



Conclusions

Column characteristics such as column durability become even more important in high temperature GPC analysis as these columns are not only exposed to harsh organic solvents but are also continuously exposed to extreme temperatures and repetitive temperature cycling. A decrease in column durability over time will result in superficial broadening of the molar mass range as a result of a decrease in the resolution of a GPC column thus directly impacting the accuracy of the molar mass averages. A durability and stability study of Tosoh's new TSKgel high temperature GPC columns was done and compared to another commercially available column for polymer analysis at 220 °C. The TSKgel GMH$_{HR}$-H(S) HT column was shown to be more durable than the other commercially available high temperature GPC column when exposed to temperature cycling as the molar mass averages and molar mass distribution obtained before and after temperature cycling showed less variation for the TSKgel GMH$_{HR}$-H(S) HT column compared to the other commercially available high temperature GPC column.

References

[1] Jackson, C.; Barth, H.G. Molecular weight-sensitive detectors for size exclusion chromatography. In: Wu C-S (ed) Handbook of size exclusion chromatography, Mercel Dekker, New York, 1995.

[2] deGroot, A.W. Quality control of columns for high-temperature gel-permeation chromatography. In: Wu C-S (ed) Column handbook of size exclusion chromatography, Academic Press: Sand Diego, 1999.

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