GPC/SEC Analysis of Nylon Using Agilent PLgel Columns with HFIP and m-Cresol Solvents

Application Note

Materials Testing & Research

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Introduction

Analysis of a polymer by the LC technique of GPC/SEC reveals information that influences many of the key physical parameters of such material, including strength, brittleness, melt flow, and how easily the material is processed. As such, GPC/SEC is a very important technique for those synthesizing polymers of all kinds. However, for many polymer systems, the choice of solvent for the analysis is complex. Many polymers are soluble in only a small number of solvents, and the choice of solvent dictates the running conditions of the analysis. Many of the solvents required are exotic by HPLC standards and often are relatively unpleasant to handle and use from a health and safety perspective.

An example of such an analysis is that of nylon, a common polyamide that has a range of uses, most commonly in clothing. Despite the ubiquitous nature of nylon, the polyamide is only soluble in a few solvents that are suitable for use in GPC/SEC molecular weight distribution determinations. Two such solvents are 1,1,1,3,3,3-hexafluoro-2-isopropanol (HFIP) and meta-cresol. Both can be used to solubilize polyamides and have advantages and drawbacks when used as solvents in GPC/SEC.

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HFIP

HFIP is a viscous, colorless liquid with a pungent odor. It is an excellent solvent for polyamides and esters and can be used to analyze nylon. Typically, a small amount of sodium trifluoroacetate is added to the eluent to reduce sample aggregation. HFIP is viscous but has a low boiling point and so the analysis is often performed at 40 °C to reduce the back pressure in the column. HFIP is also highly polar and can cause calibrations to become non-linear for MIXED-bed columns. Therefore, Agilent produced a special PL HFIPgel column for use in this solvent, with a multipore structure that is unaffected by the solvent. This work shows the analysis of 2 samples of nylon in HFIP.

Materials and methods

The system was calibrated using polymethylmethacrylate standards and, therefore, all molecular weight values quoted are relative to these standards (Figure 1). Both samples were prepared as 0.1% w/v solutions and found to be fully soluble in the eluent, HFIP + 0.02 M NaTFAc.

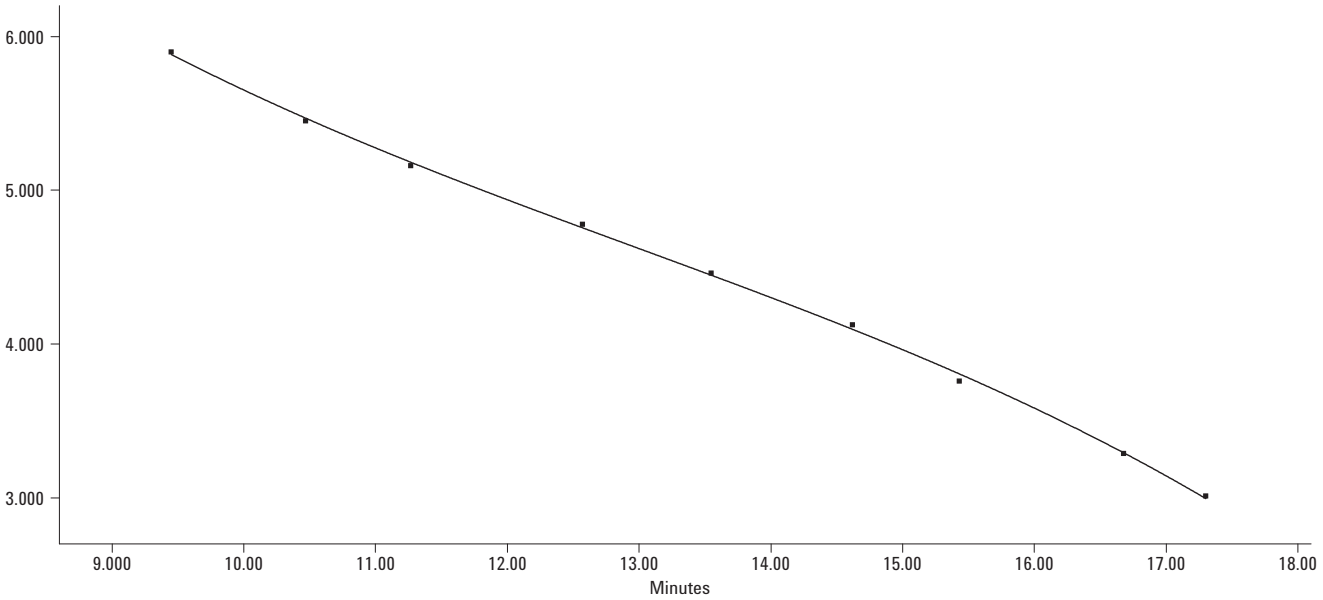

Figure 1. Calibrating an Agilent PL HFPgel column using polymethylmethacrylate narrow standards.

Conditions

Column(s):	2 × Agilent PL HFIPgel, 4.6 × 250 mm, 9 µm (p/n PL1514-5900HFIP)
Calibrants:	Agilent polymethylmethacrylate narrow standards
Eluent:	HFIP + 0.02 M NaTFAc
Sample concentration:	0.1% w/v
Injection volume:	100 µL
Flow rate:	0.3 mL/min
Temperature:	40 °C
Pressure:	30 bar
Detector:	DRI

Results and discussion

Figure 2 shows both samples eluting within the operating range of the PL HFIPgel column packing (2,000,000 to 500). Sample 2 displays the highest molecular weight.

An example of the molecular weight averages that can be calculated for one of the samples is shown in Table 1.

Table 1. Molecular weight characteristics of nylon with HFIP as solvent.

Mz+1	106,545
Mz	71,804
Mw	44,081
Mp	37,402
Mn	19,962
Mv	40,638
Polydispersity	2.208
Peak area	317,647

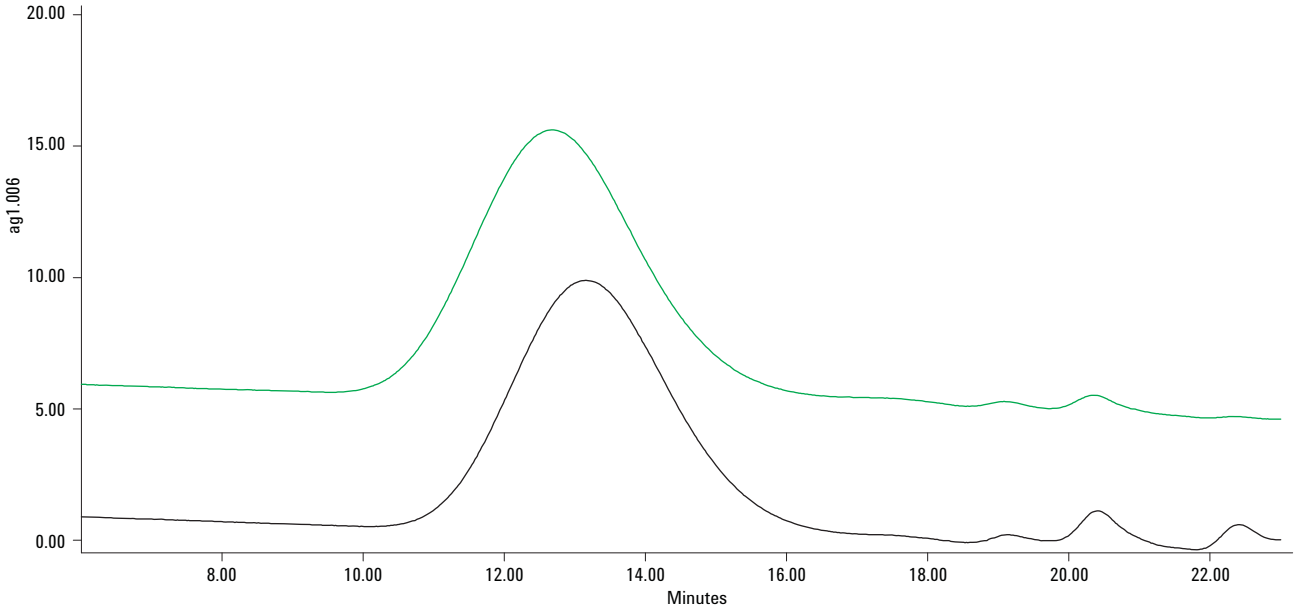

Figure 2. Raw data chromatogram of 2 nylon samples on a 2-column set of Agilent PL HFIPgel 9 µm columns with HFIP solvent.

Any differences or similarities that exist between samples are further highlighted in the combined molecular weight distribution plots in Figure 3.

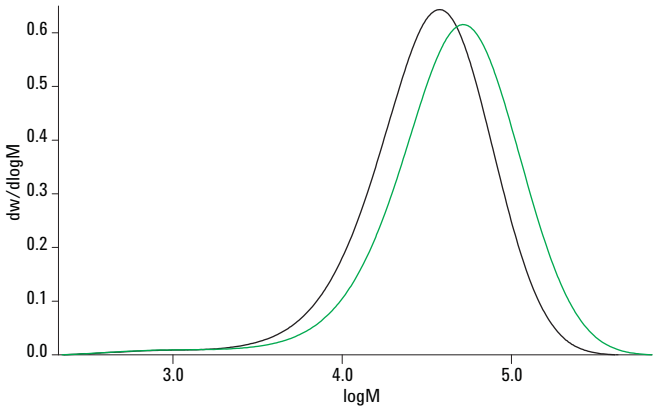

Figure 3. Overlaid molecular weight distributions of 2 nylon samples on 2 Agilent PL HFIPgel 9 µm columns.

Meta-cresol

Meta-cresol is a methyl phenol compound that is excellent at solubilizing many polymers, including polyamides such as nylon. It has a pungent 'moth-ball' aroma but is relatively safe to handle compared to HFIP. However, it is extremely viscous and requires running at an elevated temperature to reduce the backpressure in the columns.

Materials and methods

The system was calibrated using polystyrene standards and, therefore, all molecular weight values quoted are relative to these standards. Agilent EasiCal calibrants were used to obtain a 10 point calibration from only 2 injections (Figure 4). The sample was prepared as a 0.2% w/v solution and found to be fully soluble in the chosen eluent, m-cresol. Overnight sample preparation was used as part of the dissolution process, with gentle warming of the sample solution prior to injection to ensure full solubility.

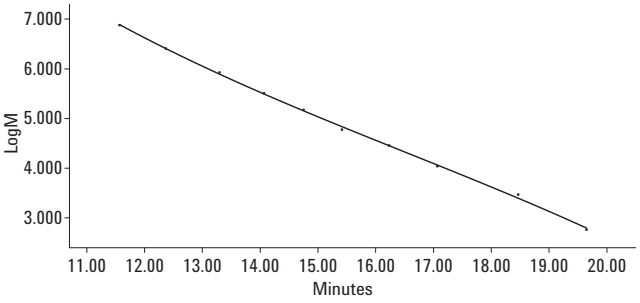

Figure 4. Calibrating the Agilent PLgel 10 µm MIXED-B column using Agilent EasiCal PS-1 standards.

Conditions

Column(s):	2 × Agilent PLgel 10 µm MIXED-B, 7.5 × 300 mm (p/n PL1110-6100)
Calibrants:	Agilent EasiCal PS-1 (polystyrene) (p/n PL2010-0501)
Eluent:	m-Cresol
Injection volume:	200 µL
Flow rate:	1.0 mL/min
Temperature:	100 °C
Pressure:	55 bar
Detector:	DRI

Results and discussion

Figure 5 shows repeat injections for a sample of nylon. A shoulder of high molecular weight material is clearly evident in the leading portion of the distribution.

Table 2 and Figure 6 show the calculated molecular weight averages for each injection, and Figure 6 demonstrates the good repeatability by comparison of the overlaid molecular weight distribution plots.

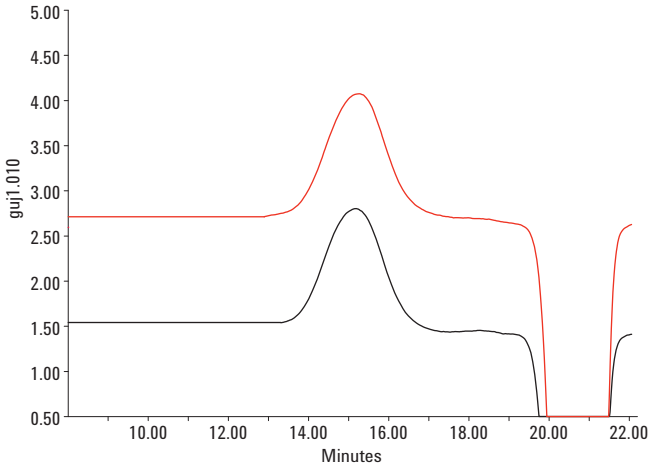

Figure 5. Raw data chromatogram of a sample of nylon on a 2-column set of Agilent PLgel 10 µm MIXED-B columns with m-cresol.

Table 2. Molecular weight characteristics of an injection of nylon with m-cresol as solvent.

Mz+1	1,509,517
Mz	506,837
Mw	151,806
Mp	91,715
Mn	75,874
Mv	131,838
Polydispersity	2.001
Peak area	28,822

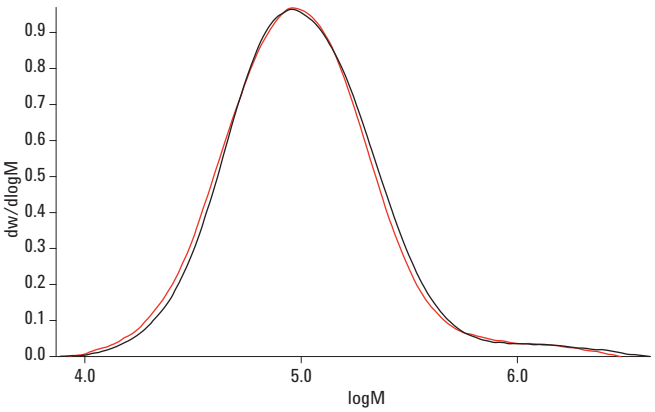

Figure 6. Overlaid molecular weight distributions of nylon samples on 2 Agilent PLgel 10 µm MIXED-B columns with m-cresol as solvent.

Conclusions

Nylon is a common material, but analysis by GPC/SEC requires the use of exotic solvents, such as HFIP and m-cresol, both of which place particular requirements on the experiment. This application illustrates the difficulty of performing GPC/SEC experiments on even the most common polymer types due to the limited solvent range available. However, with the range of columns, standards, and instruments available for GPC/SEC from Agilent Technologies, both versions of this difficult application can be performed routinely.

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