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Application Note

APC Analysis of Polyamides in HFIP as an Alternative to High Temperature GPC

Donald A. Trinite, Jennifer Gough

Waters Corporation

Abstract

This application note demonstrates the Waters ACQUITY Advanced Polymer Chromatography (APC)™ System for polyamide GPC analysis using HFIP as a more sustainable alternative when compared to traditional separation techniques.

Benefits

- Alternative analytical approach to high temperature Gel Permeation Chromatography (GPC) applications for polymers soluble in HFIP
- A 15-minute per sample analysis time compared to traditional GPC of 45-minute run time
- Lower hazardous waste and organic solvent consumption Polyamide GPC option
- APC Isocratic Solvent Manager (ISM) system with years of consistently successful use with HFIP

Introduction

Polyamides are an integral part of our daily lives, even if we do not readily see them performing their functions. Nylon 6,6 is a commodity polyamide named for its six-carbon monomer starting materials, adipic acid and hexamethyl diamine. Two examples of nylon products are car parts and electrical wiring, and these require heat and chemical resistance.[1] Due to the chemical resistance of polyamides, dissolving the polymer in an organic solvent for GPC analysis is challenging. Many manufacturers use high temperature GPC (>100 °C) to determine the molecular weight distribution of these nylon polymers, and the analysis often uses m-cresol or N-Methyl pyrrolidone as the mobile phase.[2,3]

An alternative GPC analysis of difficult to dissolve polyamide Nylon 6,6 is using hexafluoro isopropanol (HFIP) as a mobile phase. HFIP is a viscous solvent at room temperature: 1.65 cP at 20 °C. Compared to the viscosity of tetrahydrofuran, 0.48 cP at 25 °C, HFIP as a mobile phase requires consideration for LC system operating parameters with a 45-minute analysis time with liters of very expensive solvent and hazardous waste.[4–7]

HFIP as a mobile phase in a high-pressure system, such as an Advanced Polymer Chromatography (APC) System with a limit of 15,000 psi, adds new advantages to this routine analysis. This low dispersion system has a unique capability of being designed to maintain the high resolution of the Waters BEH small particle columns. One can imagine the challenges of putting a viscous mobile phase through a small particle column at high pressure and needing some extra consideration to overcome the physical limitations of HFIP. Many scientists find the UPLC advantages of efficient method development and faster analysis time as a strong motivator and have succeeded is using HFIP in their experiments with published results.[8]

Experimental

In this APC analysis, an HFIP mobile phase with salt additive is used to run a size-based separation of various polyamides, and the instrument parameters are listed in the LC Conditions table. Samples are dissolved in HFIP at 1 mg/mL overnight in scintillation vials and transferred to instrument vials.

LC Conditions

System:	ACQUITY Advanced Polymer Chromatography (APC) System with ISM

Pump:	Isocratic
Mobile phase:	Hexafluoro-2-propanol w/0.1 % sodium Trifluoroacetate (NaTFA)
Wash/purge:	Hexafluoro-2-propanol
Seal wash:	80/20 Water/Isopropanol
Seal wash rate:	2.00 min. intervals
Flow rate:	0.45 mL/min.
Run time:	15 min.
Sample temp:	20 °C
Syringe draw rate:	Automatic
Sample conc:	1 mg/mL
Injection vol:	20 µL
Column temp:	50 °C
Column set:	ACQUITY APC XT™: 900 Å, 450 Å (2.5 µm, 4.6 x 75mm), p/n: 186007253 200 Å (2.5 µm, 4.6 x 150mm), p/n: 186007005 125 Å (2.5 µm, 4.6 x 75mm), p/n: 186006998 45 Å (1.7 µm, 4.6 x 75mm), p/n: 186006993
Detector:	RI (50 °C)

Column Bank Assembly

Note the column bank selection of five columns. This is a creative solution to managing five columns in a space typically used for three 150 mm length columns. The column bank example shown in Figure 1 does not have a 150 mm 200 A column that covers a molecular weight range of 3K–70K Daltons. The column compartment has four eCord™ connections which enable traceability. The fifth column will not have a connection for the e-cord magnet, and therefore will not be captured in the Empower™ Software. This fifth column is helpful during screening for the molecular weight range of an unknown sample. Once the range is determined, the column bank can be optimized to four columns.

The picture displayed here is an example of a four-column bank. To fit two 75 mm length columns in the space of the 900 Å column shown (150 mm length), the Pre-column filter will have to be removed, and the connectors are shaped for compacting into the column oven. Once the column bank is optimized to four columns, the pre-column filter can be re-installed.

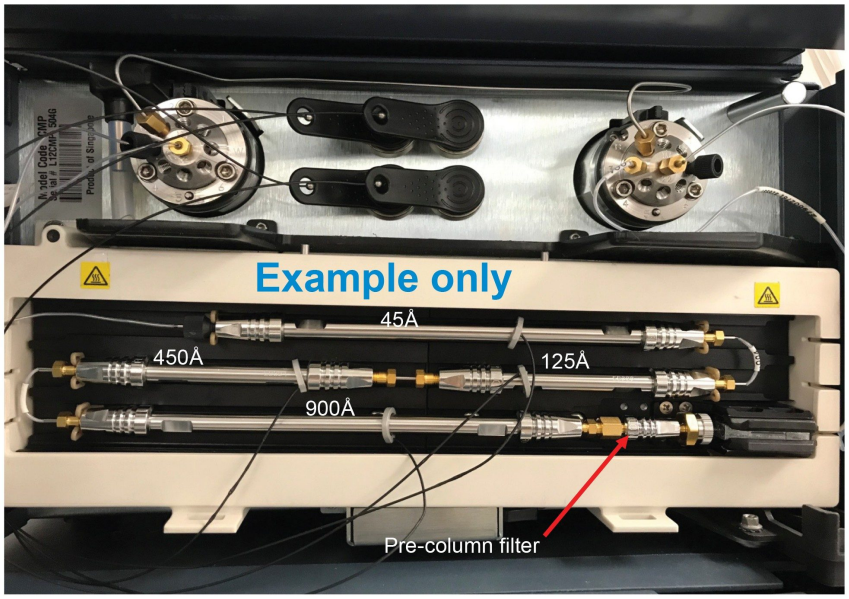


Figure 1. The example of a four-column configuration of ACQUITY APC XT Columns.

Data Management

Instrument control as well as data acquisition and processing were done by Empower 3 Chromatography Data System, FR5

Results and Discussion

Once the column bank and method are optimized to 15 minutes per injection, the polymethyl methacrylate (PMMA) calibration standards are run to establish a range of molecular weight range in Figure 2 and relative calibration curve (Figure 3).[9]

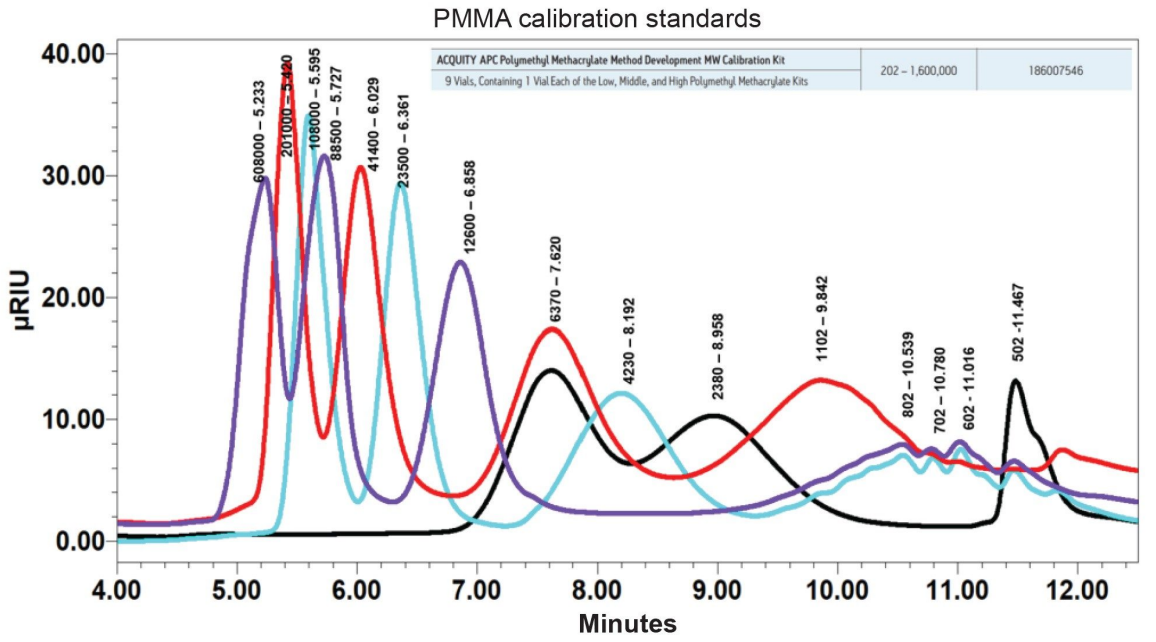
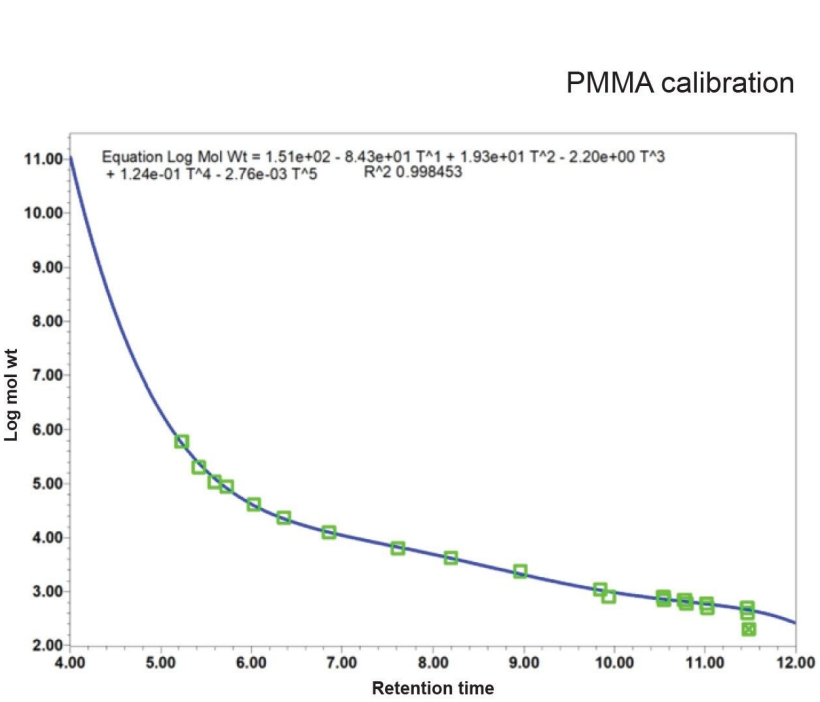


Figure 2. Chromatographic overlay of PMMA calibration standards.

The highest molecular weight points are on a bend in the calibration curve, and this is due to the lower resolution of a shorter separation path and shorter column, yet this does not affect the quality of the unknown polyamide sample analysis due to their eluting in the linear range of the curve. A 5th order curve was used to obtain the best R^2 value of 0.998453 (Figure 3).



GPC calibration table

	Retention Time (min)	Mol Wt (Daltons)	Log Mol Wt	Calculated Weight (Daltons)	% Residual
1	5.227	608000	5.7839	578385	5.120
2	5.729	88500	4.9469	82183	7.686
3	6.858	12600	4.1004	12630	-0.236
4	10.537	802	2.9042	728	10.190
5	10.766	702	2.8463	659	6.542
6	11.014	602	2.7796	592	1.634
7	11.463	502	2.7007	463	8.434
8	5.233	608000	5.7839	559948	8.581
9	5.727	88500	4.9469	82738	6.964
10	6.858	12600	4.1004	12629	-0.231
11	10.539	802	2.9042	727	10.317
12	10.780	702	2.8463	655	7.148
13	11.016	602	2.7796	592	1.749
14	11.467	502	2.7007	462	8.688
15	5.420	201000	5.3032	239185	-15.965
16	6.029	41400	4.6170	39575	4.611
17	7.620	6370	3.8041	6689	-4.773
18	9.842	1102	3.0422	1063	3.703
19	5.595	108000	5.0334	125110	-13.676
20	6.361	23500	4.3711	22380	5.002
21	8.192	4230	3.6263	4165	1.552
22	9.935	802	2.9042	1001	-19.871
23	10.543	702	2.8463	726	-3.249
24	10.793	602	2.7796	652	-7.614
25	11.024	502	2.7007	590	-14.868
26	11.466	402	2.6042	462	-12.985
27	7.617	6370	3.8041	6705	-4.993
28	8.958	2380	3.3766	2122	12.171
29	11.481	202	2.3054		

Figure 3. Empower calculated PMMA calibration curve.

The unknown polyamide samples were integrated and calculated using the relative calibration PMMA standard curve (Figure 4).

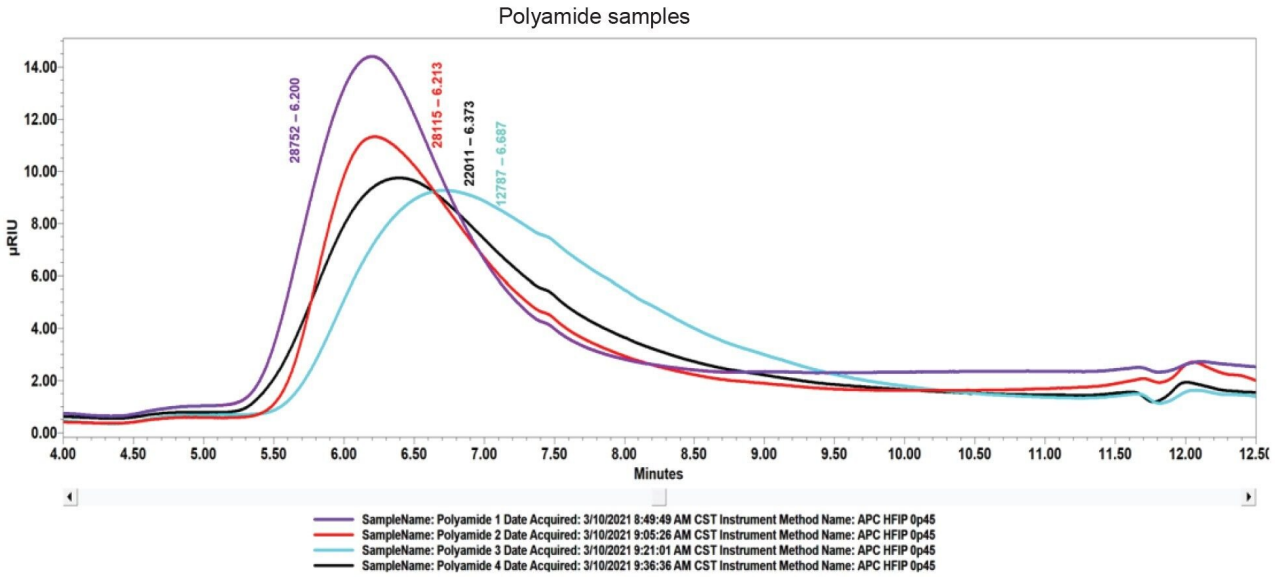


Figure 4. Empower 3 chromatographic overlay of four unknown polymer samples ranging from peak molecular weight of 128K to 288K.

Conclusion

The results from the experiments described demonstrate that the APC has the capability to analyze polyamides dissolved in HFIP with a calibration curve having and R^2 value of 0.9985.

This analytical method delivers the results three times faster than traditional GPC with a 15-minute analysis per injection. The shorter run time uses less than 7 mL of HFIP solvent per injection, as compared to traditional GPC using greater than 22 mL per injection.[10]

Taken together, this method described here has the potential to increase laboratories sample throughput offering a more sustainable, cost-effective separation option and a viable alternative to high temperature GPC.

References

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