Achieving Faster GPC Separations using Novel High Pore Volume Columns and Conventional Instruments

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Introduction

GPC is an important technique for determining the molecular weight distribution of a polymer and for comparing batch-to-batch polymer quality. In common with other liquid chromatographers, GPC users are making more demands on the technique both in terms of speed of analysis and quality of results. These additional demands have to be balanced with the need to control costs, and the purchase of new specialized instrumentation to achieve performance gains may not be justified. The combined requirements for faster size-based separations and the use of conventional instrumentation could be achieved using novel GPC column technology.

Columns packed with particles that have a very high pore volume deliver significantly increased resolution compared to a conventional GPC/SEC column set. Run times can be decreased by employing shorter column lengths and higher linear velocities, without sacrificing separation quality. Using industry-standard, highly cross-linked polystyrene/divinylbenzene (PS/DVB) particles with a 3 µm diameter maintains compatibility with conventional GPC instruments.

We analyzed polymer samples on an Agilent 1260 Infinity GPC/SEC with an RI detector to compare a conventional column set with Agilent PL Rapide and ResiPore columns. The comparison demonstrates significant reductions in analysis time while maintaining acceptable results, without the need for specialized instrumentation.

Experimental

Samples

Three customer-supplied samples, believed to be Kratons - styrenic block copolymers consisting of polystyrene blocks and rubber blocks, with two peaks in each sample (copolymer and homopolymer or diblock and triblock copolymers) and expected molecular weight < 400,000 g/mol.

Conventional GPC Approach

The original customer method used six individual porosity PLgel 7.5 x 300 mm columns (10 µm 10^6, 2 x 5 µm 10^5, 5 µm 10^4, 5 µm 10^3, and 5 µm 500), with a run time of 70 min. In our conventional method we opted to use four columns, with porosity of 10^3 to 10^6 as the lower pore diameter column and the duplication of 10^5 columns does not contribute to the separation.

Conventional method conditions

Columns:	Agilent PLgel 10 µm 106 7.5 x 300 mm, PLgel 5 µm 10^5 7.5 x 300 mm, PLgel 5 µm 10^4 7.5 x 300 mm, PLgel 5 µm 10^3 7.5 x 300 mm
Standards:	Agilent EasiVial PS-H, (MW 162 to 6,000,000)
Mobile phase:	THF
Flow rate:	1.0 mL/min
Sample conc:	1.5 mg/mL
Injection vol:	100 µL
Column temp:	30 °C
System:	Agilent 1260 Infinity GPC/SEC system with RI detector and Agilent GPC/SEC software

Faster GPC Approach

The particles in Agilent PL Rapide columns have a very high pore volume to deliver significantly increased resolution compared to a conventional GPC/SEC column set. This allows run times to be decreased, with shorter column lengths and higher linear velocities, without sacrificing separation quality.

We used a three-column set of PL Rapide L columns to provide resolution over the expected sample molecular weight range (up to 400,000 g/mol), with a flow rate of 1.5 mL/min. Resolution was further improved by increasing column temperature to 50 °C, well within the maximum for PL Rapide columns (150 °C), and decreasing injection volume to 5 µL.

Faster GPC method conditions

Columns:	3 x Agilent PL Rapide L, 10 x 100 mm, 3 µm
Standards:	Agilent EasiVial PS-M (MW 162 to 400,000)
Mobile phase:	THF
Flow rate:	1.5 mL/min
Sample conc:	1.5 mg/mL
Injection vol:	5 µL
Column temp:	50 °C
System:	Agilent 1260 Infinity GPC/SEC system with RI detector and Agilent GPC/SEC software

Optimized Faster GPC Approach

Agilent PlusPore columns are also packed with particles that have a very high pore volume to provide significantly increased resolution compared to a conventional GPC/SEC column set. In addition, PlusPore columns are available in 4.6 mm id, which allow the use of lower flow rates and therefore less solvent. ResiPore columns were selected to provide resolution over the expected sample molecular weight range (up to 400,000 g/mol). The high efficiency, 3 µm particles used in ResiPore columns can be operated at higher linear velocities without sacrificing resolution, and so a two-column set was used with a flow rate of 0.6 mL/min to achieve resolution and keep run time to a minimum. The pressure generated was well within the ResiPore maximum limit of 180 bar.

Optimized method conditions

Columns:	2 x Agilent ResiPore, 4.6 x 250 mm, 3 µm
Standards:	Agilent EasiVial PS-M (MW 162 to 400,000)
Mobile phase:	THF
Flow rate:	0.6 mL/min
Sample conc:	1.5 mg/mL
Injection vol:	2 µL
Column temp:	50 °C
System:	Agilent 1260 Infinity GPC/SEC system with RI detector and Agilent GPC/SEC software

Results

Table 1. Separation and % comparison, all samples

Columns	Tr (Peak 2)	Rs	N/m (Peak 2)	α	Area (%)	Height (%)
Sample A						
4 x PLgel	27.04	2.23	10612	1.10	10	12
3 x PL Rapide L	7.04	1.88	20277	1.12	10	13
2 x ResiPore	6.34	1.90	13764	1.11	11	13
Sample B						
4 x PLgel	28.46	1.22	5653	1.05	8	7
3 x PL Rapide L	7.41	1.13	23727	1.06	7	7
2 x ResiPore	6.66	1.10	14510	1.05	8	8
Sample C						
4 x PLgel	27.85	2.87	10292	1.17	11	16
3 x PL Rapide L	7.24	2.15	19130	1.19	12	18
2 x ResiPore	6.52	2.10	11370	1.17	16	21

Table 2. MW results comparison, all samples

	Mp	Mn	Mw	PD	Mp	Mn	Mw	PD
Sample A								
	Peak 1				**Peak 2**			
Mean	398198	373794	404895	1.08	106700	100498	103831	1.03
% RSD	11	7	7	1	3	1	1	1
Sample B								
	Peak 1				**Peak 2**			
Mean	110262	107964	111181	1.03	56041	51015	53208	1.05
% RSD	3	1	1	0	5	8	5	4
Sample C								
	Peak 1				**Peak 2**			
Mean	576906	472410	562185	1.19	74817	57671	66091	1.15
% RSD	4	5	3	4	4	5	2	6

Table 3. Methods - cost comparison

Columns	Run Time (min)	Saving (% Run time)	Flow Rate (mL/min)	Solvent (mL)	Saving (% Solvent)
4 x PLgel	50	0	1.0	50	0
3 x PL Rapide L	15	70	1.5	22.5	55
2 x ResiPore	15	70	0.6	9	82

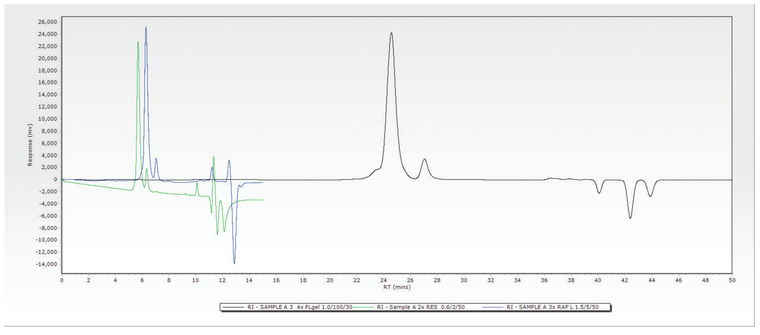

Figure 1. Sample A overlays - normalized response

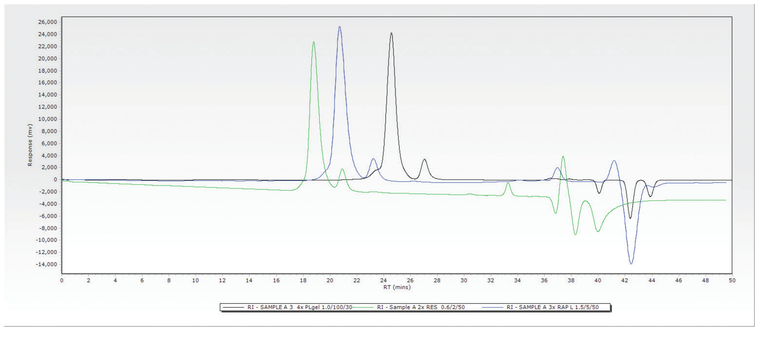

Figure 2. Sample A overlays - normalized response and retention

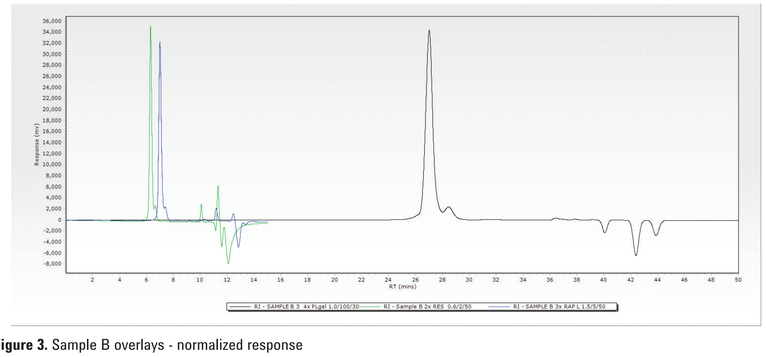

Figure 3. Sample B overlays - normalized response

Results

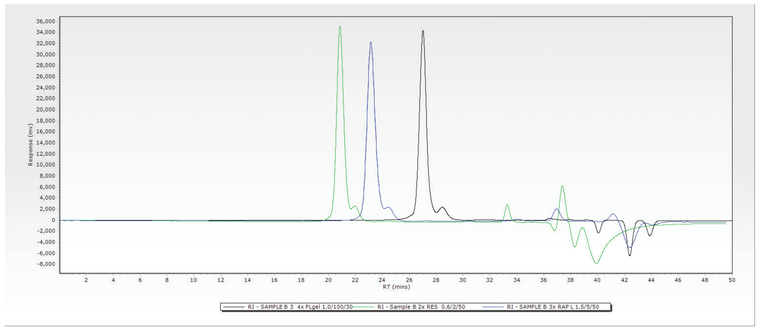

Figure 4. Sample B overlays - normalized response and retention

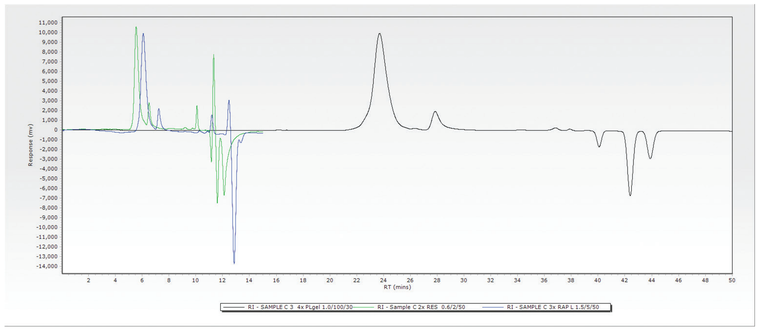

Figure 5. Sample C overlays - normalized response

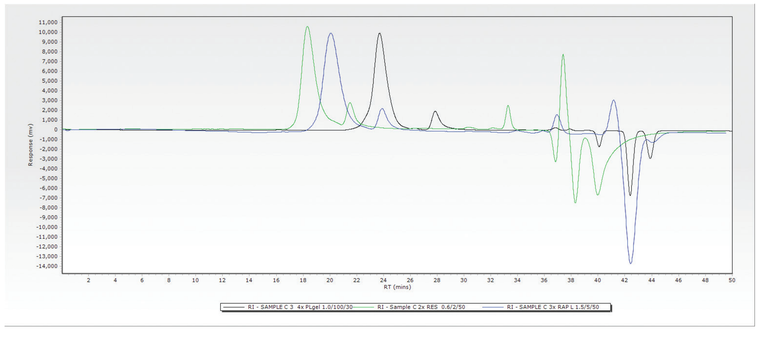

Figure 6. Sample C overlays - normalized response and retention

Conclusions

Faster GPC

Agilent PL Rapide L columns **reduced analysis time by 70%**, with a **55% saving in solvent costs**. The quality of results was maintained with the response ratio between resolved peaks and average molecular weight results consistent between conventional and fast GPC (within expected errors). This increase in productivity and reduction in costs was achieved using a conventional GPC system.

Optimized Faster GPC

Agilent ResiPore columns **reduced analysis time by 70%**, with an **82% saving in solvent costs**. Again, the quality of results was maintained with the response ratio between resolved peaks and average molecular weight results consistent between conventional and fast GPC (within expected errors). This further reduction in costs was also achieved using a conventional GPC system.

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