アプリケーションノート

Solvent Flexibility for Size-Based Polymer Analysis Using the Advanced Polymer Chromatography (APC) System

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Abstract

Changing solvents in polymer analysis is a seldom performed practice due to current limitations of gel-based stationary phases. The ACQUITY APC System combined with ACQUITY APC Columns allows polymer scientists the versatility to rapidly analyze their polymers in the ideal solvent for their application without the cost of maintaining multiple columns sets.

Benefits

- Eliminates the need to dedicate and maintain multiple columns in different solvents.
- Fast re-equilibration of the APC System and columns for rapid solvent changeover.

Introduction

Gel-permeation chromatography (GPC) columns are commonly packed with gel-based stationary phases such as styrene-divinylbeneze or methacrylate polymers. These stationary phases require sufficient conditioning to allow the particles to swell to an appropriate size in the mobile phase solvent that is being used. To ensure proper performance of these columns, the particles are often packed in the mobile phase solvent (or solvent with similar properties) used in the application. Therefore, commercially-available columns of a particular pore size are frequently available for purchase in different solvents. This minimizes any loss of column performance due to changes in the particle properties, should a different mobile phase be used.

There are clear limitations to using gel-based packing materials in chromatographic analysis. Should a change in mobile phase solvent be required, polymer chemists must purchase a new column in the appropriate mobile phase or use an existing column, perform a lengthy equilibration and accept the potential for compromised column performance. In addition, gel-based stationary phases can suffer from mechanical instability at higher backpressures and must be used gently to ensure the particles do not collapse.

Waters Advanced Polymer Chromatography (APC) Columns for the analysis of polymers contain high-strength, sub-3µm hybrid silica particles which are resilient to solvent changes. Since there is little to no swelling of the particle in different solvents, column performance is maintained across the use of many common mobile phases. The versatility of APC Columns enables polymer scientists to analyze their samples in the most appropriate solvent for their application, while minimizing the number of columns in the lab. Using the low-dispersion ACQUITY APC System in combination with robust APC Columns, high backpressures can be accommodated, allowing the use of faster flow rates. This results not only in significant time-savings for polymer sample analysis, but also in considerable resource savings through faster overall system equilibration and by using the same bank of columns for multiple applications.

Experimental

ACQUITY APC System Conditions

Detection:	ACQUITY RI
RI flow cell:	35 °C
Mobile phase:	THF, Toluene, or DMF with 10mM LiCl
Flow rate:	1 mL/min
Columns:	ACQUITY APC XT 450 Å, 4.6 x 150 mm 2.5 µm (single)

	ACQUITY APC XT 450Å and 125Å, 4.6 x 150 mm 2.5 µm (in series)
Column temp.:	35 °C
Sample diluent:	THF, toluene, or DMF with 10 mM LiCl
Injection volume:	20 µL
Data management:	Empower 3 CDS

Sample preparation

Standards:	Waters Polystyrene ReadyCal Standards Kit (p/n WAT058931) at 1 mg/mL
Samples:	Polystyrene 180K narrow sample at 1 mg/mL in THF, poly(methyl methacrylate co ethyl acrylate in THF, poly(9,9 di-n-fluorenyl 2,7-diyl) in toluene, poly(bisphenol A co epichlorohydrin) in DMF with 10 mM LiCl

Results and Discussion

Traditional columns for polymer analysis commonly consist of polymeric stationary phases, such as polystyrene cross-linked with divinylbenzene. These require proper equilibration in the mobile phase to allow the particles to swell to their final size. As the particles swell, they are less stable and require gentle packing and running pressures to ensure long-term stability of the columns. Changing mobile phase solvents is generally discouraged, since the particles may swell differently in alternate solvents and alter the packing efficiency and long-term reproducibility of the columns. If a change in mobile phase solvent is required, a lengthy transfer and equilibration process is employed. The new solvent is typically run at very low flow rates, ramped up slowly to the operating flow rate, and flowed for an extended period of time to ensure thorough equilibration of the particles in the new mobile phase. Rather than perform this time-consuming procedure, new columns may be purchased and shipped in the mobile phase solvent of anticipated use. However, the necessity to purchase several columns, each in different solvents is cumbersome and expensive. Adding to the expense is the fact that columns are commonly connected in series for polymer analysis which means that multiple column sets in various solvents are needed for the analysis of polymers with different solvent requirements.

The use of hybrid silica particle columns in Advanced Polymer Chromatography (APC) allows chromatographers to select their ideal mobile phase for polymer analysis. Compared to polymeric stationary phases, hybrid silica particles are not prone to swelling and shrinking, allowing users to easily switch between different mobile phase solvents for reproducible results time after time. In addition, the use of high strength hybrid silica particles allows for high flow rates to be used, enabling chromatographers to take advantage of the faster runtimes, better peak shape, and resolution that the APC System offers.

To illustrate the solvent flexibility of the ACQUITY APC Columns, a comparison of the elution profiles for a narrow dispersity polystyrene sample across three mobile phases (THF, toluene and DMF) is shown in Figure 1.

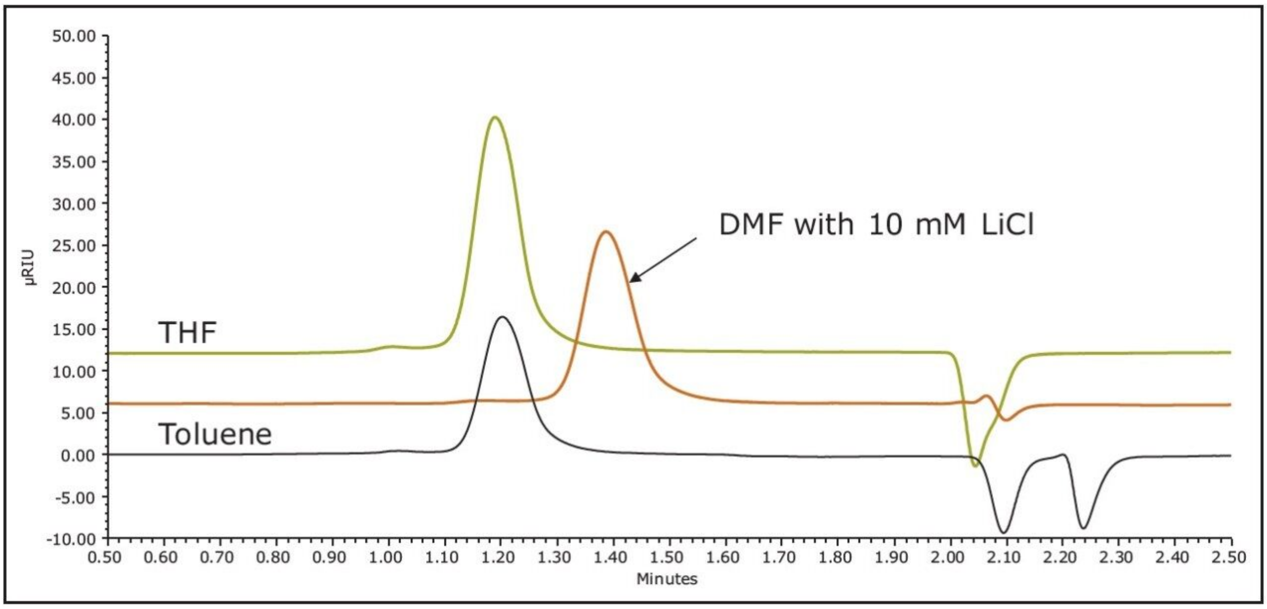


Figure 1. Comparison of elution of a polystyrene narrow sample using three different solvents (THF, toluene, and DMF) on an ACQUITY APC XT 450 Å 2.5 µm, 4.6 x 150 mm Column. Differences in elution times result from varying analyte characteristics in the different solvents.

For each solvent system, a calibration curve was generated using Waters ReadyCal Standards that were prepared in the respective solvents, shown in Figure 2.

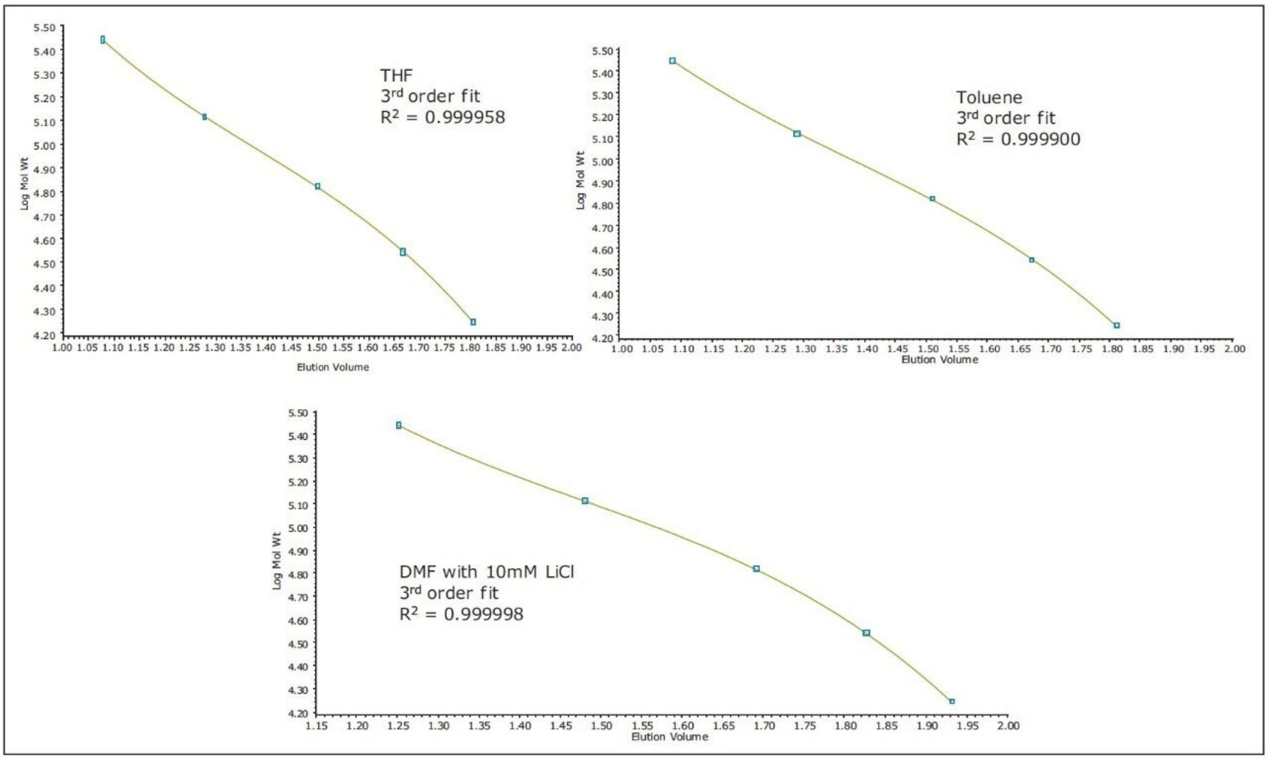


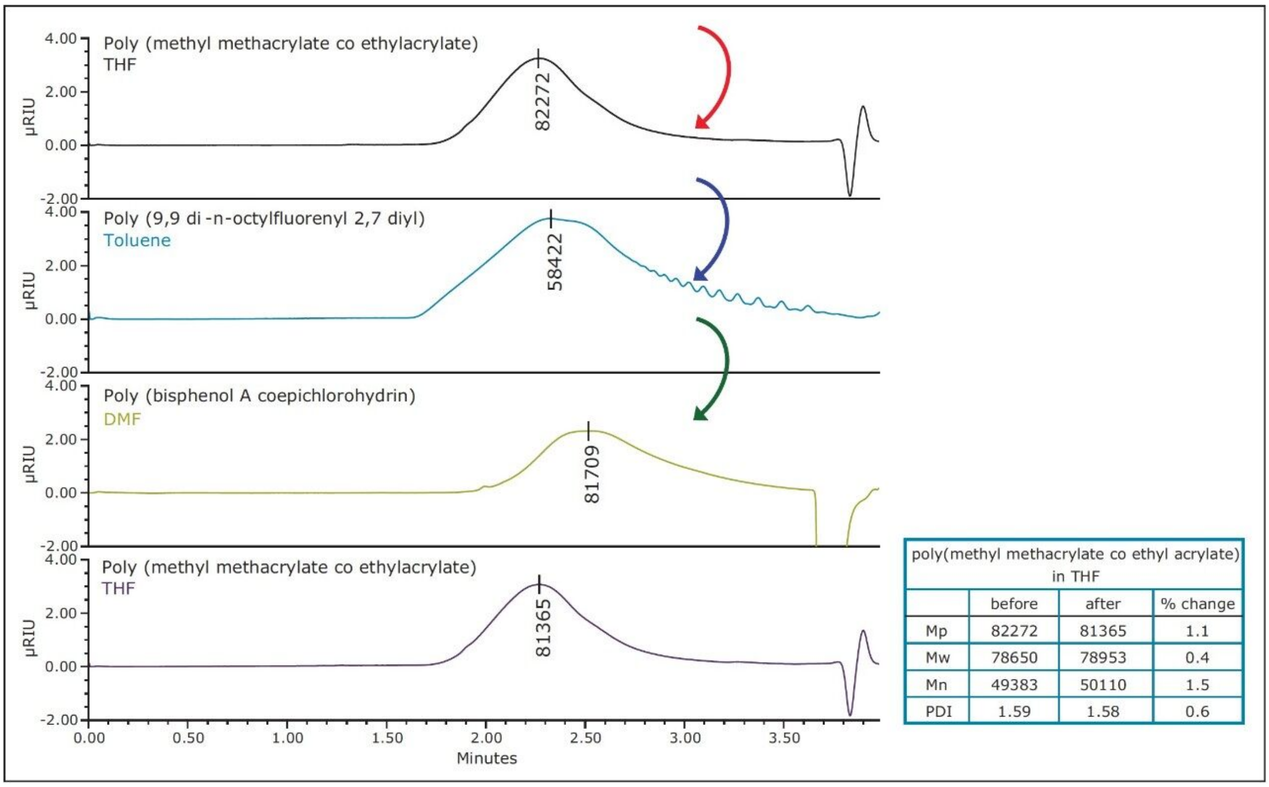
Figure 2. Comparison of polystyrene calibration curves (MW range: 17.6 K to 277 K) on the same ACQUITY APC XT 450Å 4.6 x 150 mm Column across different solvents (THF, toluene, and DMF) showing excellent fit in different solvents.

The narrow polystyrene sample was tested against the calibration curves and molecular weights (Mp, Mw, Mn) and polydispersity (PD) were calculated and compared for each solvent system, described in Table 1. All of the measurements showed good precision and accuracy on the ACQUITY APC System using the APC Column. For each molecular weight measurement, %RSD was <1 for triplicate injections and % change in molecular weight measurements of <3% were observed across the three different solvents systems used.

Solvent	Injection	Mw	Mn	PD
THF	1	170093	162305	1.05
THF	2	169765	162011	1.05
THF	3	170014	161989	1.05
	Average	**169957**	**162102**	**1.05**
	%RSD	**0.1**	**0.1**	**0.1**
Toluene	1	171228	167118	1.02
Toluene	2	170293	165109	1.03
Toluene	3	170771	166117	1.03
	Average	**170764**	**166115**	**1.03**
	%RSD	**0.3**	**0.6**	**0.3**
% Change compared to THF		**0.5**	**2.5**	**-1.9**
DMF	1	167856	163697	1.03
DMF	2	166593	161292	1.03
DMF	3	167501	163111	1.03
	Average	**167317**	**162700**	**1.03**
	%RSD	**0.4**	**0.8**	**0.4**
% Change compared to THF		**-1.6**	**0.4**	**-1.9**

Table 1. Comparison of Mw, Mn, and polydiversity (PD) measurements for a narrow dispersity polystyrene sample across three different solvents (THF, toluene, and DMF) on a single ACQUITY APC XT 450 Å 2.5 µm, 4.6 x 150 mm Column.

A separate example of the reproducibility of molecular weight results obtained for a polymer sample, after changing mobile phase solvents on the same bank of columns is shown in Figure 3. In this case, a two-column bank of 450 Å and 125 Å ACQUITY APC XT Columns in series was used. The columns were first equilibrated in THF and a sample of poly(methyl methacrylate co ethylacrylate) was tested to obtain molecular weight information including Mp, Mw, Mn, and polydispersity (PD), relative to a polystyrene calibration performed in THF. Next, using the same bank of columns on the ACQUITY APC System, the solvent was changed to toluene, primed, and equilibrated. A new polystyrene calibration was performed in toluene and a sample of poly (9,9 di-n-octylfluorenyl 2,7-diyl) was tested. The ACQUITY APC System and same column set were then changed to N,N-dimethylformamide (DMF) containing 10 mM LiCl for the analysis of poly(bisphenol-A co epichlorohydrin). Finally, the system was returned back to THF, a new polystyrene calibration was performed and poly(methylmethacrylate co ethylacrylate) was re-analyzed. Molecular weight results were compared before and after the solvent changeover. An overall difference of <2% was seen when comparing the results of poly(methylmethacrylate co ethylacrylate) in THF before and after the solvent changeover, demonstrating the high robustness of the particles after exposure to various solvent environments. Traditionally, this application may have taken days to complete, using multiple solvent-dedicated column sets. With the APC System, solvent changes can be performed in a matter of hours using the same set of APC Columns.



poly(methyl methacrylate co ethyl acrylate) in THF

	before	after	% change
Mp	82272	81365	1.1
Mw	78650	78953	0.4
Mn	49383	50110	1.5
PDI	1.59	1.58	0.6

Figure 3. Repeatable analysis of poly (methyl methacrylate co ethylacrylate) on the APC system, using the same two APC 4.6 x 150 mm columns (450 Å and 125 Å) in series after switching solvents from THF to toluene to DMF and back to THF.

Conclusion

Changing solvents in polymer analysis is a seldom performed practice due to current limitations of gel-based stationary phases. However, the hybrid silica particles packed in APC Columns allow the use of different mobile phase solvents without concern of swelling and shrinking of particles. This results in a repeatable, robust analysis of polymers on the same columns, even after exposure to different solvent environments. Further, the low dispersion, high backpressure capability of the APC System ensures fast equilibration of the column and system in the appropriate solvent. The ACQUITY APC System combined with ACQUITY APC Columns allows polymer scientists the versatility to rapidly analyze their polymers in the ideal solvent for their application without the cost of maintaining multiple columns sets.

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720004628, March 2013