Waters™

Nota de aplicación

Using Advanced Polymer Chromatography with Quaternary Solvent Manager and Evaporative Light Scattering Detection for Gradient Polymer Elution Chromatography

Jennifer Gough, Will Martin, Neil J. Lander

Waters Corporation

Abstract

The APC with QSM is specifically designed for aggressive solvents used in the polymer industry. The Waters ACQUITY Advanced Polymer Chromatography (APC) System is designed to operate consistently using harsh solvents like THF, chloroform, and dimethyl sulfoxide. By adding the flexibility of a quaternary pump to the industry-accepted APC system, polymer analysis techniques are no longer limited to HPLC technology.

Benefits

- p-QSM with aggressive solvent compatibility right out of the box.
- Reverse-phase, normal-phase, and size-based separations provide flexible analysis.
- The low dispersion APC with p-QSM uses less solvent than HPLC or GPC, which makes it more sustainable
- High resolution with sub-3-µm BEH column technology

Introduction

The gradient polymer elution chromatography (GPEC) chromatogram in Figure 1 has a run time of 30 minutes using an Alliance HPLC (high-performance liquid chromatography) system. If this method is transferred to an UltraPerformance Liquid Chromatography (UPLC) system, the run time could be significantly shortened. However, most UPLC systems are not compatible with organic solvents, such as tetrahydrofuran (THF), and are not robust enough to constantly use 100% organic solvent.

The Waters ACQUITY Advanced Polymer Chromatography (APC) System is designed to operate consistently using harsh solvents like THF, chloroform, and dimethyl sulfoxide. Originally, the APC system was designed for gel permeation chromatography (GPC) using an isocratic pump. By adding the polymer quaternary solvent manager (p-QSM) for gradient elution and an evaporative light scattering detector (ELSD) to the APC system, GPEC can be accomplished in less than 10 minutes (Figure 1).

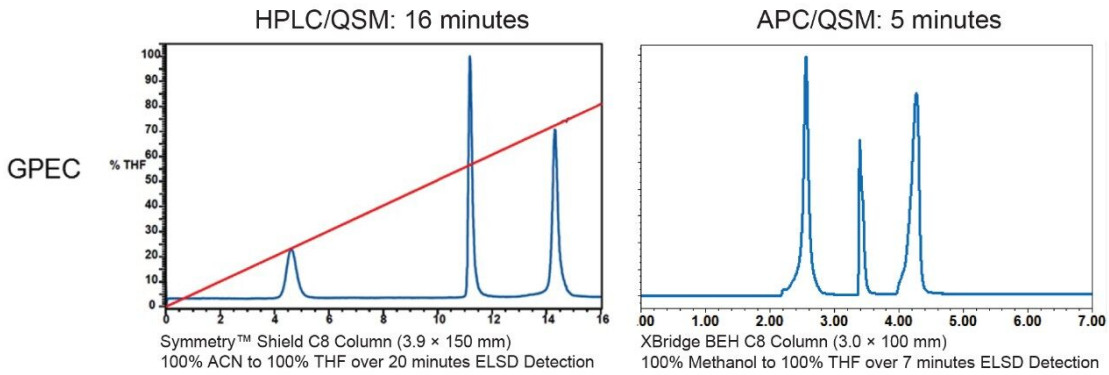

Figure 1. GPEC comparison of HPLC and UPLC analysis times.

Experimental

System:	APC with p-QSM
Column:	XBridge BEH C8, *XP*, 2.5 µm, 3.0 × 100 mm (p/n 186006047)
Mobile phase A/B:	Methanol
Mobile phase C/D:	Tetrahydrofuran
Flow rate:	0.7 mL/min
Column temp.:	40 °C
Injection volume:	1 µL
Sample concentration:	PMMA (1 mg/mL), PS (0.12 mg/mL), PBD (0.5 mg/mL)

Gradient:

Sr. No	Time	Flow (mL/min)	%A	%B	%C	%D	Curve
1	Initial	0.700	100.0	0.0	0.0	0.0	Initial
2	1.00	0.700	60.0	0.0	40.0	0.0	11
3	2.00	0.700	35.0	0.0	65.0	0.0	11
4	3.00	0.700	15.0	0.0	85.0	0.0	11
5	4.00	0.700	15.0	0.0	85.0	0.0	11
6	5.00	0.700	0.0	0.0	100.0	0.0	6
7	6.00	0.700	100.0	0.0	0.0	0.0	6
8	7.00	0.700	100.0	0.0	0.0	0.0	11

In order to precipitate a polymer onto the column, the polymer solubility in the gradient blend of solvents needs to be determined. The accepted method in literature is to titrate a known concentration of polymer solution (10^{-2} to 10^{-3} mg/mL) with a non-solvent (poor solvent). As the titration progresses, the polymer solution will appear cloudy as the polymer aggregates and precipitates: the polymer is repelled by the non-solvent and the polymer molecules are forced together in aggregation. The volume fraction of the non-solvent is calculated using Equation 1, where phi (F) equals the cloud point (CP) divided by 100, which equals the volume of the non-solvent (Vns) divided by the sum of polymer volume, good solvent volume, and non-solvent volume (Vp + Vs + Vns). This technique is called cloud-point determination.[4,5]

Eq 1. F = CP/100 = Vns / Vp + Vs + VNS

If the linear gradient cannot be optimized to achieve reproducible peak areas, a step gradient may be needed. The GPEC of three polymers, polystyrene (PS), polybutadiene (PBD), and polymethylmethacrylate (PMMA), are used for this experiment (Table 1). The linear gradient produces poor peak area reproducibility for PS and PMMA, and the PBD does not elute.

	1	2	3
Sample	Polybutadiene (PB)	Polystyrene (PS)	Polymethylmethacrylate (PMMA)
Molar mass (g/mol)	120,000	200,000	200,000
Chromatographic cloud points [MeOH (non-solvent)/THF]	30/70	46/54	65/35

Table 1. Polymers used in GPEC experiment.

Therefore, a step gradient method is used to control the amount of time the polymers spend in the insoluble regions of the gradient. A steep curve is used for the insoluble regions (11) of the gradient profile, while the soluble region is a less steep curve (6) as seen in the gradient table and resulting chromatography (Figure 2).

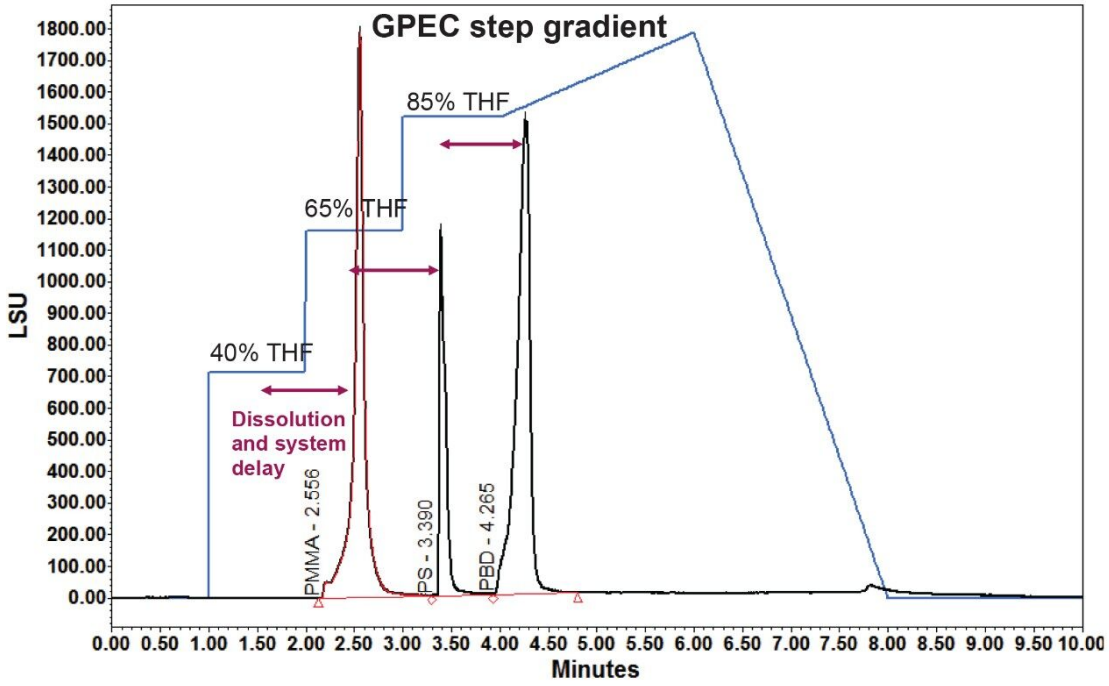

Figure 2. Empower overlay of the GPEC analysis of PMMA, PS, and PBD.

By using the Empower 3 CDS custom calculations and report features, there is no need to export data into a separate spreadsheet. The report in Figure 3 has the peak area ratios and the gradient ratios calculated within Empower. The complete GPEC project and detailed GPEC guide are available on the Waters website and in the Empower marketplace.

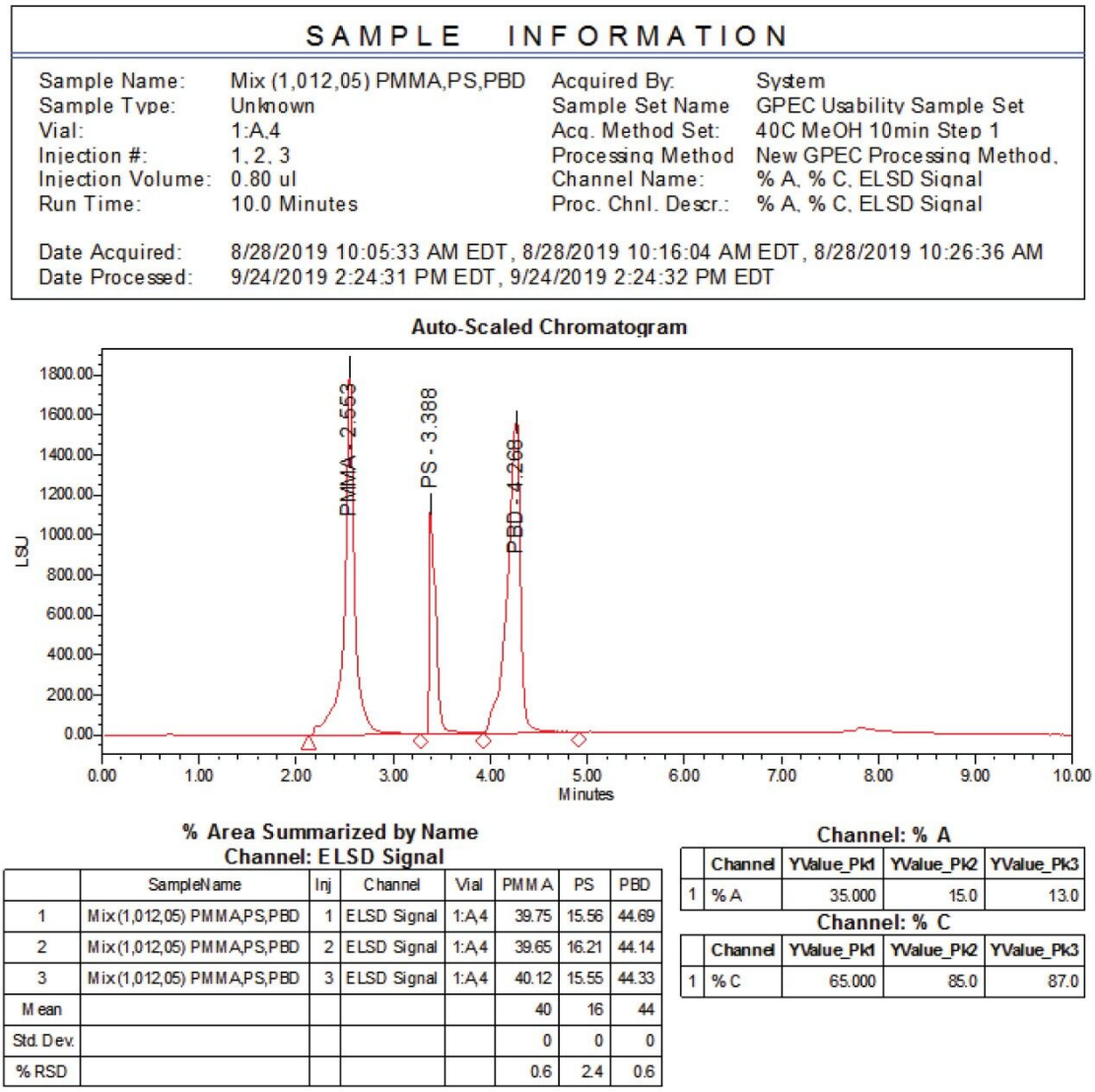

Figure 3. Empower report for the GPEC analysis of three separate injections with gradient custom calculation.

Results and Discussion

GPEC is not GPC. In the example chromatograms of Figure 4, three chemically different polymers co-elute using a GPC separation, because they have similar hydrodynamic volumes. If reversed-phase separation is used to separate these polymers, they would remain partially soluble throughout the separation and not baseline separate: partially overlapping. The GPEC method purposefully precipitates the polymers

temporarily onto the column or column frit until the gradient ratio of good solvent reaches the polymer's solubility point, releasing the polymer from the surface of the column. Instead of using the size-based separation of GPC, the polymers are separated by their chemical solubility using GPEC. GPEC is an LC application and is completely different from a GPC application.[1]

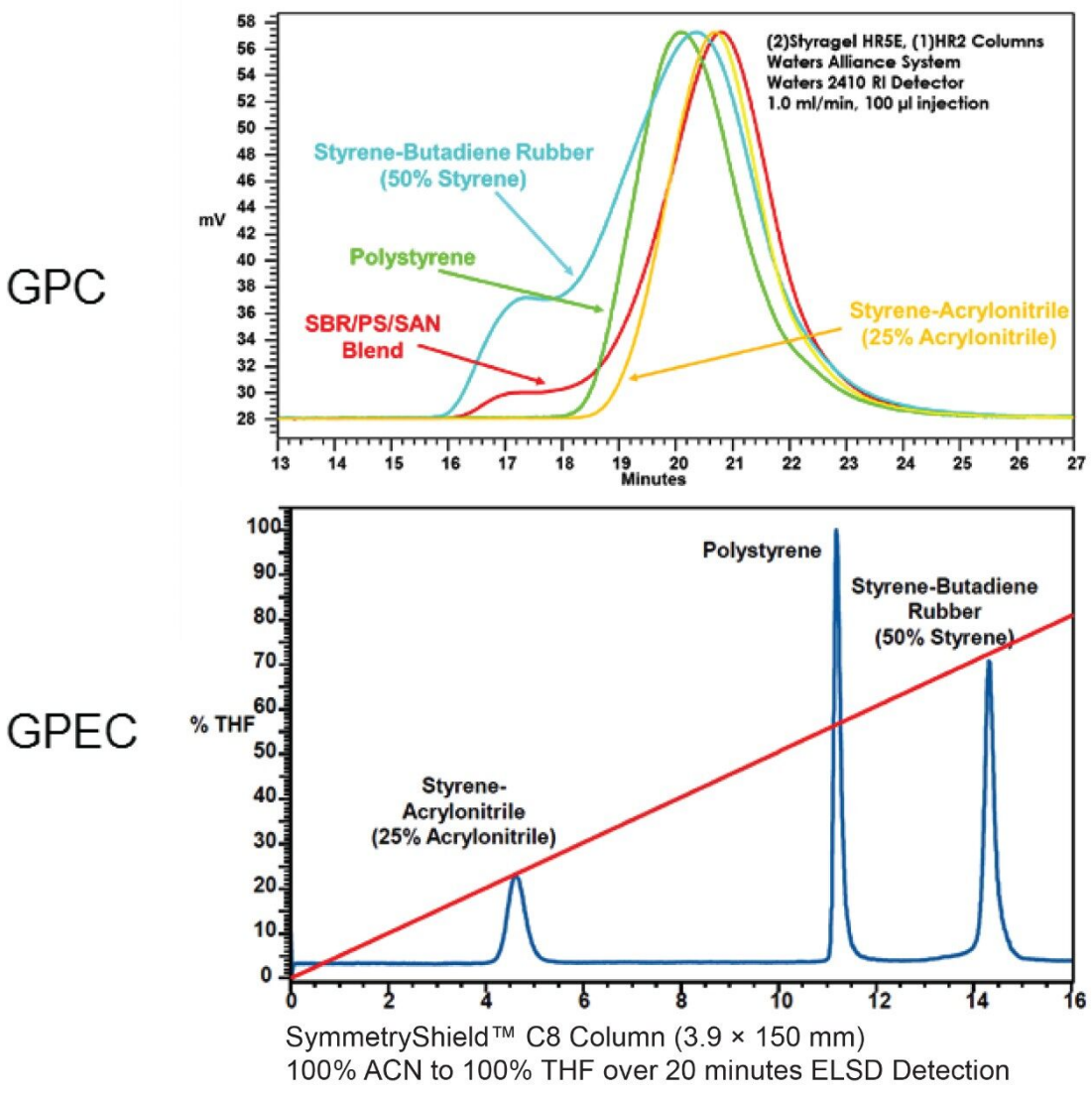

Figure 4. GPC and GPEC of three polymers using an Alliance System.

The APC system designed for GPEC has a new configuration (Figure 5). The polymer isocratic solvent manager (p-ISM) has been replaced with a polymer quaternary solvent manager (p-QSM) to accommodate gradient elution with 100% organic solvent. The refractive index (RI) detector has been replaced with an evaporative light scattering detector (ELSD), because RI is not compatible with gradient elution. A

photodiode array (PDA) is not used for this application example, because not all polymers are UV active.[2,3]

Figure 5. APC System with p-QSM and ELSD.

Conclusion

GPEC is a complementary analysis to GPC, when co-eluting peaks interfere with determining polymer ratios in a mixture. This uncommon analysis technique has been used for decades but has been limited to traditional HPLC instruments. UPLC instruments have solvent compatibility limitations that can limit analysis options like GPEC. The APC with QSM is specifically designed for aggressive solvents used in the polymer industry. By adding the flexibility of a quaternary pump to the industry-accepted APC system, polymer

analysis techniques are no longer limited to HPLC technology.

References

1. Uliyanchenko, E.; van der Walac, S.; Schoenmakers, P.J., Challenges in Polymer Analysis by Liquid Chromatography. *Polym. Chem*. 2012, 3, 2313–2335. https://pubs.rsc.org/en/content/articlelanding/2012/py/c2py20274c#!divAbstrac.
2. Waters ACQUITY UPLC ELS Detector, https://www.waters.com/waters/nav.htm?cid=514219.
3. ACQUITY UPLC Evaporative Light Scattering Detector Getting Started Guide, https://www.waters.com/webassets/cms/support/docs/71500109303rd.pdf.
4. Klumperman, B.; Cools, P.; Philipsen, H.; Staal, W. (1996), A Qualitative Study to the Influence of Molar Mass on Retention in Gradient Polymer Elution Chromatography (GPEC). Macromol. Symp., 110: 1–13. doi:10.1002/masy.19961100102, https://onlinelibrary.wiley.com/doi/abs/10.1002/masy.19961100102.
5. Klenin, V. J.; Shmakov, S.L. Features of Phase Separation in Polymeric Systems: Cloud-Point Curves (discussion). *Universal Journal of Materials Science* 2013, 1 (2), 39–45. https://pdfs.semanticscholar.org/44cf/8e3fc4396d2d8bc6bc55 b5be0b2648e70619.pdf.

Featured Products

ACQUITY Advanced Polymer Chromatography System <https://www.waters.com/134724426>

Empower 3 Chromatography Data Software <https://www.waters.com/513188>

720006705 November 2019