Molar Mass and Chemical Composition 2D Analysis for Thermoplastic Elastomers

Application Note Chemical Manufacturing

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Gradient HPLC can be hyphenated with GPC/SEC in a fully automated setup to measure molar mass and chemical composition distribution of copolymers simultaneously with highest peak capacity.

Introduction
Thermoplastic elastomers (TPEs) are copolymers or blends consisting of materials with thermoplastic and elastomeric properties. There are several classes of TPEs. Block copolymers with thermoplastic poly(styrene) blocks are one of them.

Block copolymers are a typical example for complex polymers as they exhibit polydispersity in chemical composition and molar mass, which cause co-elution in LC.

While GPC/SEC is the established method for the determination of molar mass averages and distribution, gradient HPLC can be applied to separate based on chemical composition. 2D chromatography allows to measure unbiased multiple distribution simultaneously. The most suitable 2D combination for block copolymers is the use of gradient Polymer HPLC for the first dimension and GPC/SEC for the second dimension.[1]

For this work poly(styrene) block copolymers with different macroscopic properties but comparable GPC/SEC traces were investigated to answer the question why they behave so differently in the application tests.

System Requirements

	Conditions 1st dimension	***Conditions 2nd dimension***
Pump	PSS SECcurity GPC1260 quaternary gradient pump • flow rate [mL/min]: 0.1 • mobile phase: n-Hexane/THF p.a. gradient	PSS SECcurity GPC1260 isocratic pump • flow rate [mL/min]: 6.25 • mobile phase: THFp.a.
Injection system	PSS SECcurity GPC1260 Autosampler • injection volume variable	• PSS 2D tandem transfer valve with two 100 µL loops
Columns	• PSS Si-60 5 µm	• PSS HighSpeed SDV 5µ 10 000 Å (20*50 mm)
Loading	• 2 mg/mL, 20 µL injection volume	
Detectors		• PSS SECcurity UV detector @ 254 nm
Software	• PSS WinGPC UniChrom with ChromPilot control, 2D, Copolymer and Chemical Heterogeneity modules	

Figure 1 shows a schematic 2D setup. The 2D tandem switching valve is fully controlled by WinGPC Software and collects a new fraction while the previous one is injected and analyzed.
To speed up the 2nd dimension special GPC/SEC HighSpeed columns with large inner diameter are used.[2] These columns can be operated at higher flow-rates. A single GPC/SEC analysis needs then 2 minutes to be completed. The amount of solvent per analysis is the same as when standard analytical GPC/SEC columns are used (approx. 12.5 mL). The advantage of the HighSpeed columns is that they decrease the analysis time significantly (by a factor of 6.25) and therefore allow on-line hyphenation and many fractions to be analyzed in short time.[3, 4]

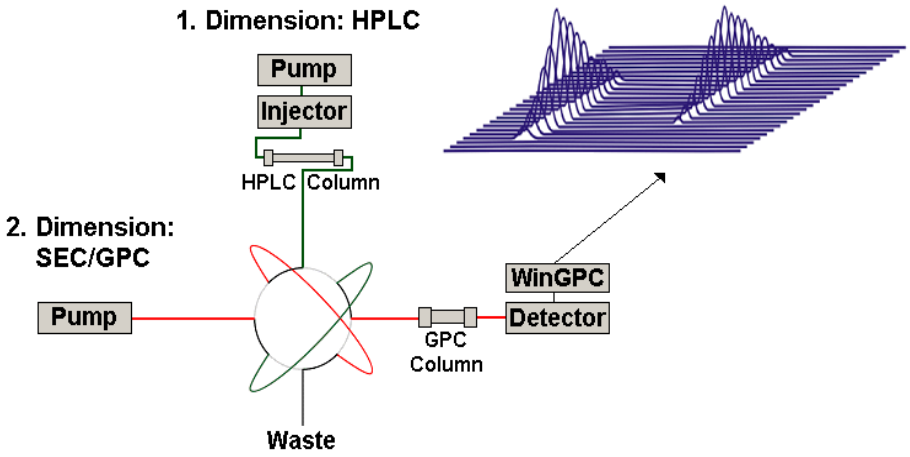

Fig. 1: Scheme for an online 2D (HPLC -GPC/SEC) setup. One loop of the switching valve is filled by the first dimension while the second loop is injected onto the GPC/SEC HighSpeed column

Results & Discussion

Three different samples have been investigated. First the single methods, GPC/SEC and Polymer HPLC, have been tested. They showed the following results:

Table1: Observations for the single experiments

sample	GPC/SEC results	HPLC results
A	only one peak detected	broad multi modal distribution with many shoulders
B	only one peak detected, compared to A: slight shift to lower molar mass	broad multi modal distribution with many shoulders
C	one peak with a small shoulder detected, approx. same molar mass as B	one peak with a small shoulder detected

Since these results did not allow a precise data analysis and interpretation, HPLC and GPC/SEC separation were hyphenated online. The results are shown in figures 2 to 4 as

contour plot. The contour plots show clearly resolved peaks and allow a much better understanding of the differences.

Samples A and B, that show one narrow main peak in GPC/SEC, reveal in the 2D separation several peaks, that co-elute in GPC/SEC. For sample A four peaks are present, while Sample B shows only three peaks.
The HPLC separation shows that these species differ in composition and their poly(styrene) content.

Additional information is available from the color code. It indicates the concentration of each species and ranges from red (high concentration) to green/blue (low concentration/not present).

Quantification with simultaneous molar mass averages and composition results for each species can be determined after calibrating the GPC/SEC and HPLC axis.

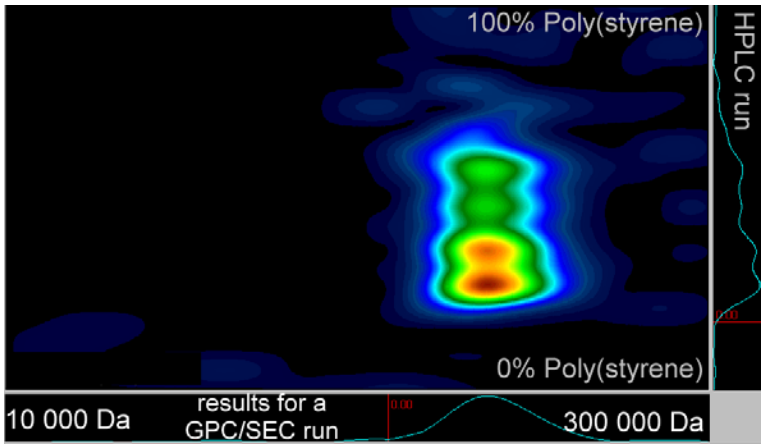

Fig. 2: Contour Plot for Sample A reveals 4 peaks, that co-elute in GPC/SEC (ordinate: composition, abscissa: molar mass)

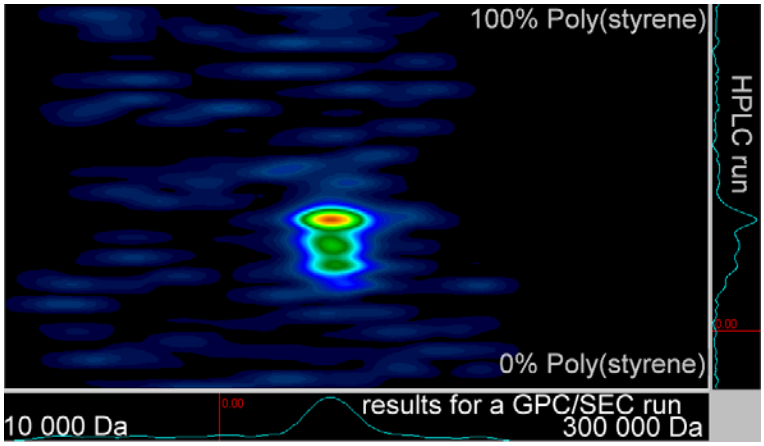

Fig. 3: Contour Plot for Sample B reveals 3 peaks, that co-elute in GPC/SEC (ordinate: composition, abscissa: molar mass)

The contour plot for sample C shows that this product is much more uniform in chemical composition. The enhanced peak capacity allows here to investigate the side peak with the low concentration.

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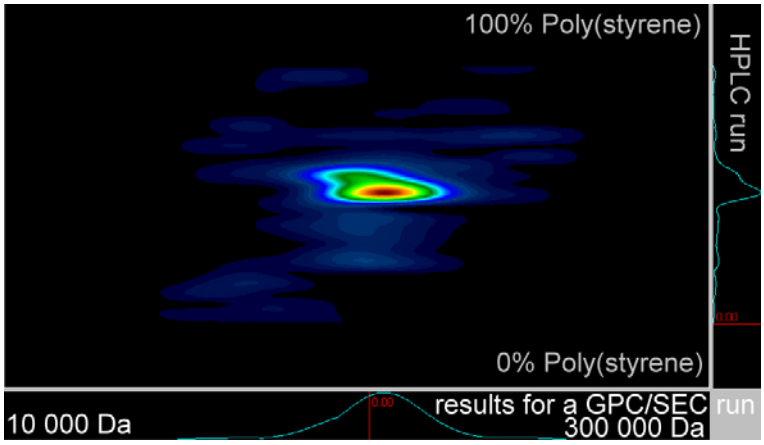

Fig. 4: Contour Plot for Sample C (ordinate: composition, abscissa: molar mass)

Summary

The online combination of gradient HPLC and GPC/SEC increases peak capacity of the separations and allows to evaluate peaks which cannot be separated by either method alone. The 2D approach is the only way to determine two property distributions independently and unambiguously.

A better understanding of the polymerization process and of structure - property relationships can be obtained that might help to tune products for specific applications.

Literature

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[4] M. Adler, P. Kilz , 2D polymer LC as a high-speed, high-throughout application, LC/GC Europe 19, 10, page 552, (2006)

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