Comprehensive separation of a graft copolymer by GPC/SEC and Polymer-HPLC (LAC)

Application Note Chemical Manufacturing

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A peculiarity of copolymers is the simultaneous presence of a molar mass and a chemical composition distribution. Gradient polymer-HPLC in addition to multidetection GPC/SEC allows identification of all components in a graft copolymer.

Introduction

Graft copolymers are complex products as they exhibit a molar mass, a chemical composition and a structural type distribution simultaneously. During synthesis side reactions as the formation of homopolymers due to non-grafted species may occur.

GPC/SEC dual detection can be used to determine the concentration profiles of the comonomers as function of molecular size, if e.g. one of the comonomers contains chromophores.

Polymer-HPLC (Liquid Adsorption Chromatography, LAC) separates based on composition and therefore can differentiate between sample components which cannot be resolved by the size based separation in GPC/SEC due to co-elution.

This application compares the results of a poly(methyl methacrylate)-graft-poly(styrene) copolymer obtained with GOC/SEC dual detection and Polymer-HPLC.

System Requirements

	Conditions
Pump	PSS SECcurity GPC1260 quaternary pump • flow rate [mL/min]: 1.00 • mobile phase: GPC/SEC: THF LAC: $CHCl_3$/THF p.a. gradient
Injection system	PSS SECcurity GPC1260 Autosampler • variable injection volume GPC/SEC: 50 µL LAC: 10 µL
Columns	GPC/SEC: • PSS SDV linear XL 5 µm 8 x 300 mm LAC: • Macherey & Nagel Nucleosil 300Å 5µm, non-modified silica 4.6 x 250 mm

Detectors	GPC/SEC: • SECcurity 1260 UV/VIS at λ=254 nm • SECcurity 1260 RI LAC: • SECcurity ELS1260
Software	PSS WinGPC UniChrom with copolymer analysis module

Procedure, Results & Discussion

The sample, a poly(methyl methacrylate)-graft-poly(styrene), was synthesized by slowly adding poly(methyl methacrylate) (PMMA) with a broad molar mass distribution to a solution of living poly(styrene) (PS) having a narrow molar mass distribution and a M_w of approximately 5 000 Da.

GPC/SEC Results

First multidetection GPC/SEC was used to to analyze the product. As poly(styrene) (PS) can be detected at 254 nm a combination of an UV/VIS detector and an RI detector was applied.

The results of the GPC/SEC analysis are shown in Figure 1. It shows 3 separated peaks for both detectors. PS and PMMA homopolymers were used to determine the UV and RI detector response factors. These factors allow calculating the PS content for every fraction at each elution volume slice.

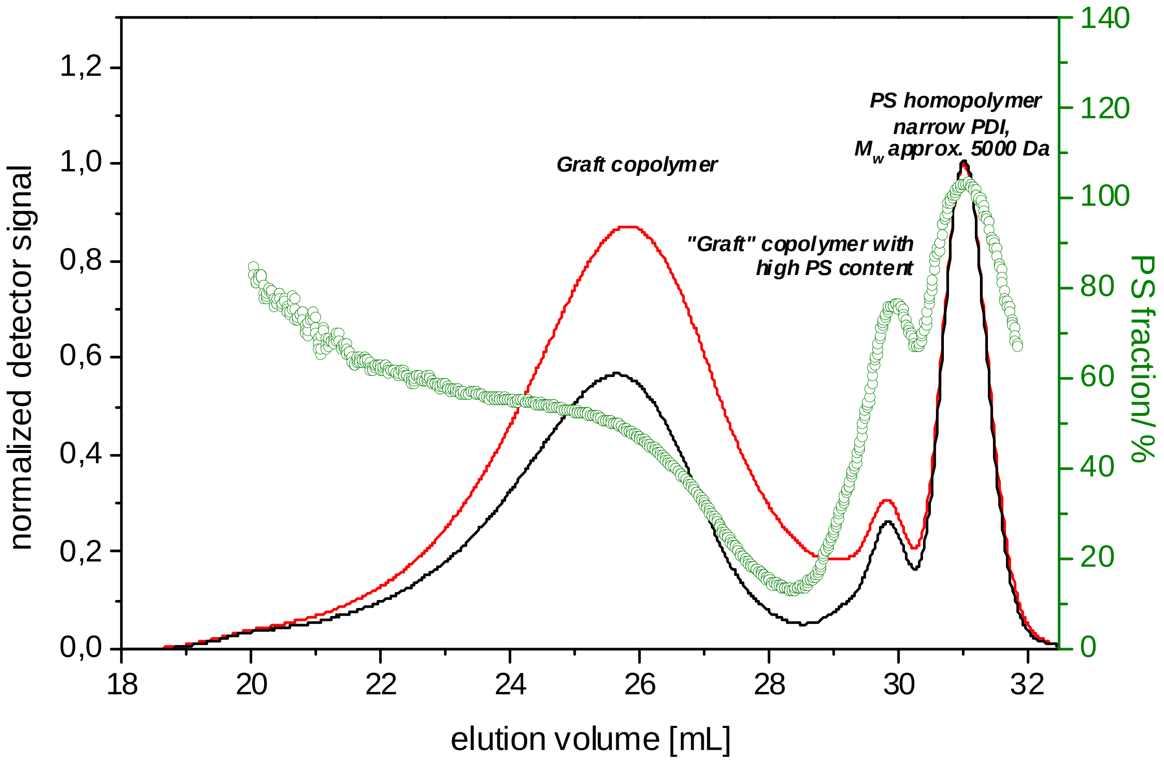

Fig. 1:
UV254 nm and RI traces for the final product. The PS content was calculated based on both detectors signals using the four response factors (UV(PS), RI(PS), UV(PMMA), RI(PMMA)).

Figure 2 shows the normalized RI signal (red) and the normalized concentration profiles for PS (green) and PMMA (blue) as a function of GPC/SEC elution volume.

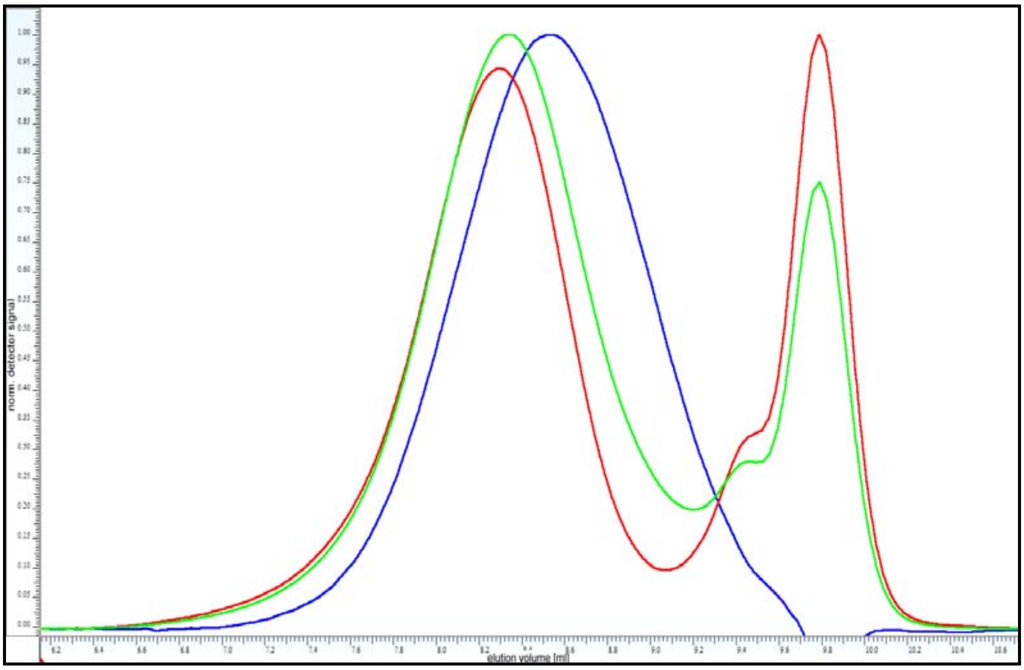

Fig. 2:
Normalized RI detector signal (red) overlaid with the PS (green) and PMMA (blue) concentration curves for the graft copolymer obtained with GPC/SEC dual detection UV/RI.

Molar masses can be obtained for the PS homopolymer using a PS calibration with PSS Polystyrene ReadyCal Standards. In case of a linear block copolymer the copolymer module would also allow to determine the copolymer molar mass by using a copolymer calibration curve derived from the corresponding PS and PMMA calibration curves and the weight fraction of the comonomers at each elution volume slice. However since the final product is a branched copolymer these molar masses would still be apparent molar masses due to the different hydrodynamic volumes of linear and branched structures. The application of a molar mass sensitive detector, e.g. a viscometer, could overcome this problem.

LAC Results

Although clear differences in chemical composition can be identified by dual detection, it is unclear whether all PMMA chains are grafted.

A solution to overcome this is separating by chemical composition. Therefore gradient chromatography was applied.

Figure 3 shows the results for the gradient run with evaporative light scattering detection. Only here the PMMA homopolymer can be identified. This component is co-eluting with the actual graft copolymer in GPC/SEC and was therefore not recognized when using a size based separation.

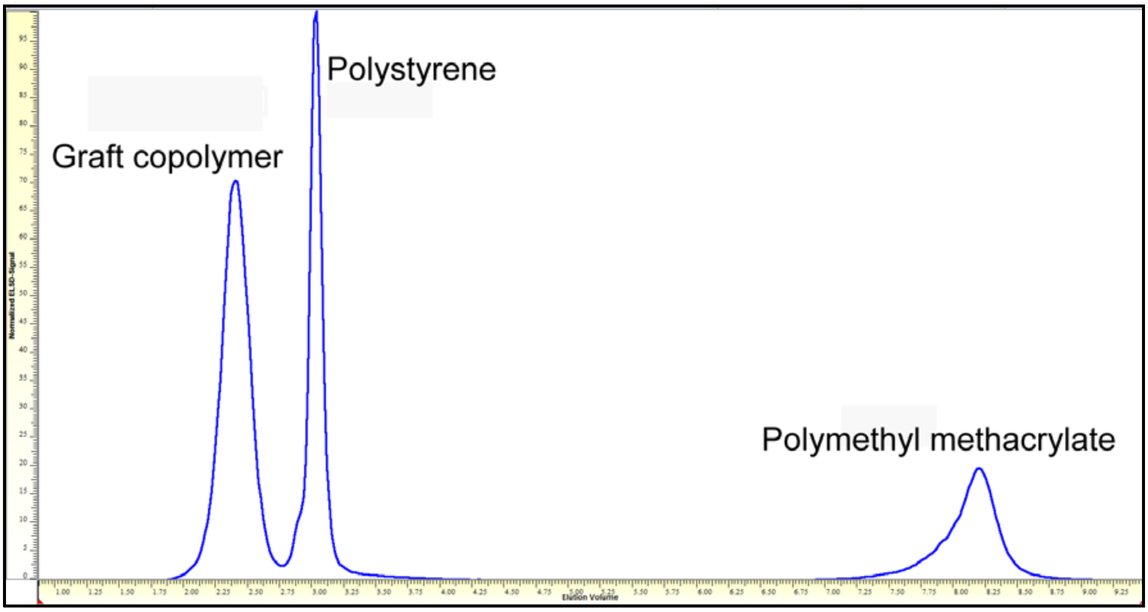

Fig 3:
Polymer-HPLC chromatogram showing the 3 species present in the graft copolymer

A comprehensive characterization, including molar mass determination and composition determination, is possible by 2-dimensional chromatography. The results for these separations, as well as the branching analysis using GPC/SEC-viscometry, will be published in separate application notes.