

INVESTIGATION OF POLYMER REACTIONS BY GPC/SEC WITH MASS SPECTROMETRY

Peter Kilz^{1,*} Christopher Barner-Kowollik,² Till Gründling³

¹PSS Polymer Standards Service, POB 3368, 55023 Mainz Germany, info@polymer.de

²KIT, Macromolecular Chemistry, Karlsruhe, Germany

³BASF SE, Ludwigshafen, Germany

ABSTRACT

GPC/SEC is the most versatile and widely used technique in macromolecular characterization. However, it suffers from limited selectivity which can be a major limitation in the analysis of complex macromolecules like copolymers, functionalized polymers and also in the determination of by-products which widely occur in any polymerization reaction and limit the efficiency of polymerisation processes. Moreover, GPC/SEC is a separation technique which cannot identify species even if they are well separated.

It has been shown that the combination of spectroscopic detection (e.g. FTIR) and size-separation can be efficiently used to elucidate polymerization pathways and identify multiple species simultaneously. Mass spectrometry is one of the most powerful spectrometric methods but has been difficult to interface with GPC/SEC systems (MALDI) or has been limited to the very low molar mass range (ESI).

The recent improvement in mass spectrometer design with efficient and gentle ionization and improved data analysis methods allows to apply these techniques to characterize complex macromolecules both from academia and industrial products alike by a hyphenation of GPC/SEC with MS devices. Research groups such as Karlsruhe Institut of Technology (KIT), National Institute of Standards and Technology (NIST), German Federal Institute for Materials Research and Testing (BAM), etc., have developed powerful analytical methods to successfully investigate polymers with mass spectrometry. The availability of GPC-MS software solutions designed for non-MS experts will enable each lab to take advantage of the new capabilities and obtain comprehensive information about new and complex macromolecules.

This presentation will present the latest findings and developments in overcoming the limitations of mass spectrometry with regard to synthetic polymers.

The high performance of modern MS instruments in combination with modern GPC-MS software empowers basically every lab to investigate not only the absolute molar mass, but also to disclose other properties, like:

- species with different end groups and cycles
- homopolymer contamination in copolymers
- functionalization efficiency and endgroup identity
- branch points in star and comb polymers
- analysis of chain termination in polymer synthesis
- information on chain degradation during aging/stress
- comprehensive out-of-spec tests

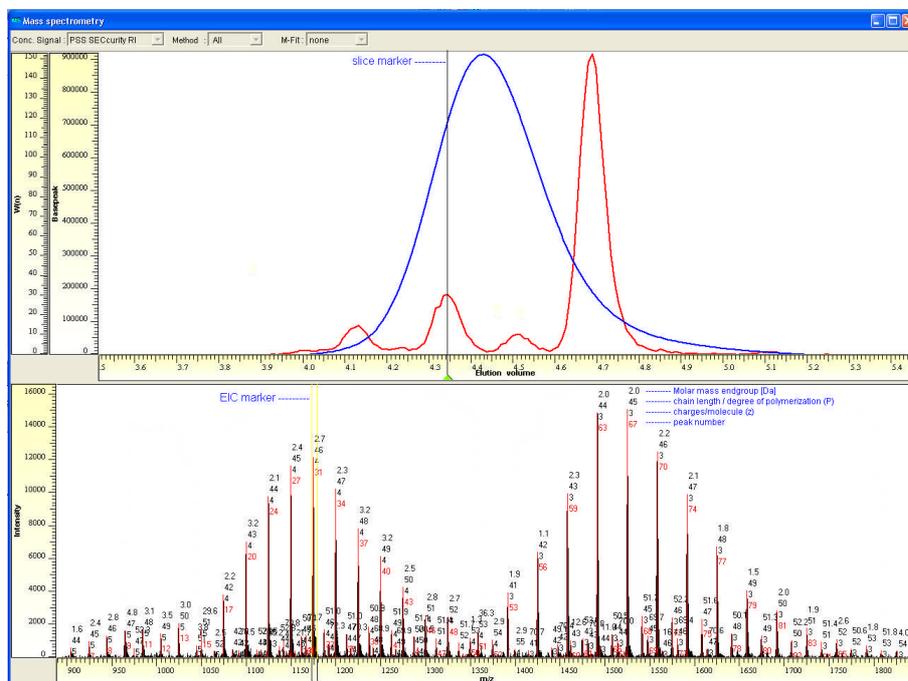


Fig. 1: WinGPC MS window: detector signals (top): RI (blue), MS TIC (red); bottom: mass spectrum at the elution volume of the green fraction marker with automatic assignment of charge-state, degree of polymerization and molar mass of end group

References:

1. W.J. Simonsick et al., *Rapid Comm. Mass Spec*, **1993**, 7, 853
2. C. Barner-Kowollik et al., *Macromolecules*, **2009**, 42, 6366