
NOVEL APPLICATIONS OF SIZE EXCLUSION CHROMATOGRAPHY COUPLED TO ONLINE SOFT IONIZATION MASS SPECTROMETRY IN FREE RADICAL POLYMERIZATION

Till Gruendling (1,2), Thomas Junkers (1), Michael Guilhaus (2) and Christopher Barner-Kowollik (1)*

(1) Preparative Macromolecular Chemistry, Institut für Technische und Polymerchemie, Universität Karlsruhe (TH)/Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany, * christopher.barner-kowollik@polymer.uni-karlsruhe.de

(2) Bioanalytical Mass Spectrometry Facility, UNSW Analytical Centre, The University of New South Wales, Sydney, New South Wales 2052, Australia

A method is presented that allows determination of accurate and absolute molecular weight distributions (MWDs) as well as absolute concentrations of the individual macromolecular components in mixtures of polymers of the same monomer class yet differing in their endgroups. Data gained from size exclusion chromatography coupled online to refractive index (RI) detection and electrospray ionization mass spectrometry (ESI-MS) is processed by a sophisticated computer algorithm based on the maximum entropy (MaxEnt) principle. The procedure yields, for the first time, absolute molecular weight distributions of each component corrected for chromatographic band broadening. Molecular weights up to 10 kDa are accessible with a conventional quadrupole ion-trap mass analyzer.

Determination of accurate molecular weight distributions by quantitative SEC/ESI-MS finds a number of applications in the characterization of functional synthetic polymers, in the elucidation of reaction mechanisms and kinetics constants in free radical polymerization as well as in polymer endgroup degradation studies. Examples will be given from the past and ongoing work. The described method was recently applied to determine the progress of synthetic endgroup conversion of polymers synthesized by controlled radical polymerization. Further work focused on the transfer of the accurate calibration in size exclusion chromatography obtained from mass spectrometry to traditional single detection SEC-systems using the concept of Universal Calibration. Accurate determination of the kinetic rate constant of propagation in free radical polymerization, regardless of monomer identity is made possible using pulsed laser polymerization (PLP) with determination of the molecular weight distribution by quantitative SEC/ESI-MS.

References:

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2. Gruendling, T.; Guilhaus, M.; Barner-Kowollik, C. *Macromolecules*, revisions received.