HYPHENATED CHARACTERIZATION TECHNIQUES FOR POLYMERS: FROM LC/MALDI- AND UPLC/ESI-TOF-MS TO CID TANDEM MASS SPECTROMETRY

Jana Falkenhagen and Steffen Weidner

BAM, Federal Institute of Materials Research and Testing, Richard-Willstätter-Str. 11, 12489 Berlin, Germany, jana.falkenhagen@bam.de

The development of new polymer systems for specific applications is not conceivable without multidimensional high level characterization procedures. Depending on the aims, e.g. the determination of polymer heterogeneity regarding to molecular mass, functionality, topology or/and chemical composition of blends or copolymers, it is necessary to select the most useful chromatographic mode (Liquid Adsorption Chromatography; Size Exclusion Chromatography; Liquid Adsorption Chromatography at Critical Conditions, LACCC) resp. their two-dimensional combination. Recently, the Ultra High Pressure Liquid Chromatography (UPLC) was introduced. This method promises ultrafast separation with consistent resolution.

Matrix-assisted Laser Desorption / Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) is a very sensitive and fast analytical method for the identification of chromatographically separated fractions. In contrast to MALDI-TOF-MS without previous separation, the spraying or spotting techniques for LC/MS coupling offer a few important advantages, the most promising of them are higher reproducibility of spectra due to better homogeneity and, in particular, a higher sensitivity.

Furthermore the online coupling of UPLC with Electrospray-Ionization Time-of-Flight Mass Spectrometry (ESI-TOF-MS) was used. Both methods are complementary to each other regarding mass range or sample preparation. Aside from time saving in the chromatographic mode and excluding matrix effects, ESI-TOF-MS predominantly can be used for accurate mass determination, e.g. for differentiation of isobars and end groups and exact determination of copolymer composition.

Due to overlapping e.g. compositional and end group information the clear assignment of end groups and side products is very difficult. In those cases CID tandem mass spectrometry is applied. Fragmentation of suitable precursor ions resulted in typical fragment ion patterns. This technique enables a fast and unambiguous determination of end groups, composition (e.g. sequences), structural defects and topology of complex polymer mixtures. Examples will be demonstrated concerning copolyester and silsesquioxane mixtures.

References:

[1] J. Falkenhagen, H. Jancke, R.-P. Krüger, E. Rikowski, G. Schulz; Rapid Commun. in Mass Spectrom. 17, (2003), 285-290
[2] St. Weidner, J. Falkenhagen, R.-P Krüger, U. Just; Anal. Chem. 2007, 79, 4814-4819
[3] J. Falkenhagen, S. Weidner; Anal. Chem., 2009, 81 (1), pp 282–287
[4] S. Weidner, J. Falkenhagen, K. Knopp, A.Thünemann, Rapid Commun. Mass Spectrom. 2009, 23, 2768-2774