

## Mass spectrometry methods for the characterization of new synthetic polymers and self-assembling supramolecules

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Matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) have enabled mass spectrometry (MS) analyses for a wide variety of synthetic polymers. MS experiments provide the mass-to-charge ratios ( $m/z$ ) of the constituent  $n$ -mers of a polymeric analyte, from which compositional heterogeneity, molecular weight, and functionality distributions can be deduced. Considerable challenges still exist, however. Polymerizations may create complex mixtures, which are difficult or impossible to characterize by single-stage MS because of discrimination effects in the ionization and detection steps and/or because the polymer may contain isobaric components or a mixture of isomeric architectures that cannot be identified by  $m/z$  measurement alone. These problems can be partly overcome by combining MS with fragmentation and a second stage of mass analysis, i.e. by tandem mass spectrometry (MS<sup>2</sup>) [1]. Depending on the functional groups present in the backbone and end groups, and the nature of the ionic site, a polymer cation or anion subjected to MS<sup>2</sup> via collision-activated dissociation (CAD) decomposes by charge-site reactions, homolytic cleavages, or charge-remote rearrangements. Either type of dissociation yields useful structural insight, as will be demonstrated for several new or uniquely functionalized polymers and copolymers. For example, the charge-catalyzed fragmentations ensuing from linear polyphosphazene anions enable definitive identification of the respective chain end groups and point to a tadpole structure. Similarly, the fragments arising from charge-remote hydrogen rearrangements in metalated aliphatic polyesters allow one to distinguish linear from branched architectures and to determine likely branching points [2]. Meanwhile, the homolytic cleavages taking place in silverated or lithiated polystyrenes [1,3,4] lead to unique fragmentation patterns that reveal unequivocally the corresponding architecture (linear vs. cyclic), functionality location (at the chain end vs. in-chain) and comonomer sequence (for styrenic copolymers). Polymer ions can alternatively be induced to fragment by electron-transfer dissociation (ETD), which promotes degradation by electron exchange. ETD of synthetic polymers most commonly involves reduction of a multiply charged precursor cation by a reagent anion. ETD of polyester

homo- and copolymers results in bond scissions which are not observed in CAD, thereby producing complementary structure and sequence information. For the characterization of more complex polymer systems, MS and MS<sup>2</sup> must be interfaced with separation methods, such as liquid chromatography (LC) or ion mobility (IM) spectrometry. Interactive LC (i.e. adsorption-mode LC) is found ideally suitable for the separation of oligomer mixtures with constituents of different polarities. This capability will be demonstrated with poly(ethylene oxide) / poly(propylene oxide) copolymers as well as sorbitan-based surfactant blends. In LC-MS, separation takes place before ionization. IM-MS may be viewed as a chromatographic method that disperses post-ionization according to mass, charge, and shape. Since it does not involve interactions with a solid or liquid stationary phase, it is particularly useful for labile and weakly bonded species which may decompose or react if sent through an LC-column. Our group has used IM-MS to characterize supramolecular polymers, self-assembled from designed building blocks via coordinative (i.e. metal-ligand) or  $\pi$ - $\pi$  interactions [5-7]. Self assembly generally creates many different isomers and conformers (architectures); these have identical  $m/z$  ratios but distinct shapes and, thus, can be separated and identified by IM-MS, as will be shown for metallomacrocycles and  $\pi$ - $\pi$  bonded nanoparticles. Further insight about the binding interactions in these materials is gained from their dissociation energetics, assessed through three-dimensional IM-MS<sup>2</sup> experiments.

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