# GOING INSIDE STRUCTURAL AND PHYSICOCHEMICAL PROPERTIES OF POLYMERS USING ION MOBILITY-MASS SPECTROMETRY

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Ion Mobility Spectrometry (IMS) is a gas phase technique which separates ions according to their charge, mass and shape. The shape descriptor is estimated through the Collision Cross-Section (CCS). The CCS of an ion can be approximated to the averaged two-dimensional projection of the three-dimensional structure (i.e. the shape) of the ion. Coupling tandem Mass Spectrometry to ion mobility (IM-MS) enables the mass-to-charge ($m/z$) ratio determination of the ions, leading to the identification of the polymer and their cation complex stoichiometries.

Studies on synthetic polymers have been undertaken for two decades[1–3], but the potential to build a general model in order to correlate their CCS trends as a function of the mass, has not yet been explored. A single Electrospray (ESI) MS experiment of polydisperse synthetic polymers leads to the observation of several charge states ($z$, i.e. number of cations complexing the polymer chains) spread over a wide mass range. The increasing $m/z$ ratios lead to large data sets for building CCS evolutions as a function of the degree of polymerization.

We used IM-MS and MS/MS ion activation techniques to analyze polymers whose monomers differ only by their side chains, such as methyl, ethyl, propyl,… All polymers bearing different side chains yielded distinct CCS trends, enabling their identification. As the chemical nature of the monomeric subunits is constant for given synthetic homopolymers, a growing polymer chain does not modify the essence of the intramolecular interactions. We developed a CCS trend fitting method allowing the extraction of the polymers' physicochemical properties. Indeed, the measured CCS values are correlated to the enthalpic, i.e. charge solvation and coordination, and entropic factors yielding the three-dimensional structures in the gas phase.

Finally, the applicability domain of IM-MS for polymer characterization is discussed, using examples of different isomeric polymer side chains, polymer architectures and using a case study of poly(acrylamide). The data interpretation issues encountered for poly(acrylamide) lead to general guidelines for confident IM-MS data interpretations.

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