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Mass Spectrometry of Synthetic Polymers: Backbone vs. End Group Reactivity Effects

Matrix-assisted laser desorption ionization (MALDI) and electrospray ionization (ESI) have become the most widely used ionization methods in mass spectrometry (MS) analyses of synthetic polymers. Both methods bring the polymer in intimate contact with solvents, cationizing salts, and/or matrices, with which acid/base or redox reactions may take place. Such reactions are partly desired to add a charge to the macromolecule and, thus, make it analyzable by MS methods. But this chemistry can also alter the composition or structure of a polymer, leading to misleading results, as will be demonstrated for polystyrene (PS) prepolymers functionalized with silane and thiol groups.

Polymers that lack basic or acidic substituents or polymers that are too large to be dissolved and ionized directly by desorption or spray techniques pose different analytical challenges. In these cases, chemical modification prior to MS analysis is required. We have found mild pyrolysis to be a simple and generally applicable functionalization / degradation process. It introduces ionizable end groups and/or reduces the molecular size via cleavages at predictable positions, creating mixtures (“polymer digests”) that can now be subjected to MALDI or ESI studies. This approach is illustrated with the characterization of polypropylenes and amphiphilic membranes, both of which cannot be analyzed by MS in their native states.

The intrinsic chemical properties of a macromolecule also affect the unimolecular chemistry occurring in tandem mass spectrometry (MS/MS) experiments. Depending on the functional groups present in the backbone and end groups, and the cationizing agent used, a macromolecular ion may preferentially depolymerize to small fragment ions, yield high-mass fragments through specific fragmentations at the end groups, or produce a series of abundant backbone ions; these fragmentation characteristics are observed for silverated polystyrenes, lithiated polydimethylsiloxanes, and lithiated polyethers, respectively. In certain cases, homolytically formed fragments are held together in ion-molecule complexes, in which inter-fragment reactions can take place.