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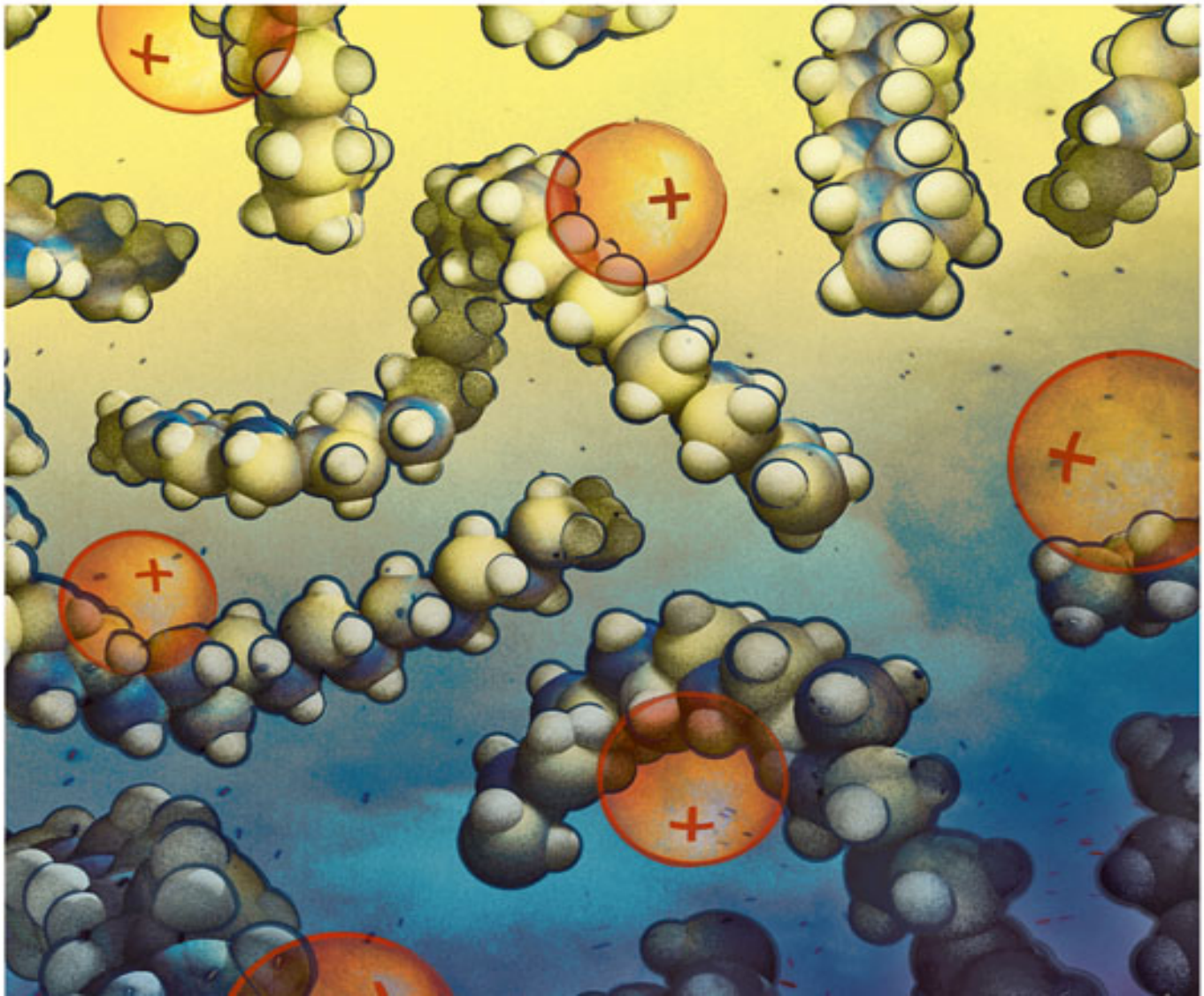
Mass Spectrometry in Polymer Chemistry



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Introduction

Christopher Barner-Kowollik, Jana Falkenhagen, Till Gruendling, and Steffen Weidner

The first mass spectrometric experiment was arguably conducted by J. J. Thomson in the late 19th century, when he measured mass-to-charge ratios (m/z) in experiments that would eventually lead to the discovery of the electron [1]. By 1912, Thomson's investigations into the mass of charged atoms resulted in the publication of details of what could be called the first mass spectrometer [2, 3]. Interestingly, Thomson also employed one of the first man-made polymeric materials in his design of the parabola spectrograph: a material with trade name Ebonite or Vulcanite, a highly crosslinked natural rubber, which, although it was fairly brittle, provided an excellent electrical insulator and could easily be milled into shape. At the time, Thomson was most likely unaware of its chemical identity, as Staudinger's ground breaking macromolecular hypothesis was not to be established until a few years later [4]. By 1933 – the same year in which German chemist Otto Röhm patented and registered Plexiglas as a brand name – F. W. Aston had firmly established mass spectrometry as a field of analytical chemistry. Using the technique, he ascertained the isotopic abundances of essentially all of the chemical elements [5]. Thomson, Aston, and Staudinger were later to receive the Nobel Prize for their individual achievements.

Today, mass spectrometry provides the synthetic polymer chemist with one of the most powerful analytical tools to investigate the molecular structure of intact macromolecules. The development of technology that would be able to achieve this task was not realized until the late 1980s. Indeed, the mass analyzers themselves were not the key problem, as they were already fairly advanced at the time. An ionization technique that allowed the entire synthetic macromolecule to be transferred into the gas phase as ions without fragmentation could, however, only be realized in the late 1980s. The application of traditional MS ionization techniques requiring thermal evaporation of the sample to the large and entwined macromolecules was considered quite impossible, although notable attempts existed at employing the more traditional ionization techniques to polymeric material [6–8]. This perception had to undergo a drastic revision in 1988 and thereafter, the years in which electrospray ionization mass spectrometry (ESI) [9] and matrix assisted laser desorption and ionization (MALDI) [10, 11] were first reported of being capable to ionize proteins and synthetic polymers. Largely on the back of the work of four researchers, Karas [12–14], Hillenkamp [10, 12, 13], Tanaka [11], and Fenn [9, 15, 16], these new soft ionization mass spectrometry techniques commenced their success story initially in the field of biochemistry and later in synthetic polymer chemistry. Since the early 1990s, soft ionization mass spectrometry techniques have become an important part of polymer chemistry, ranging from unraveling polymerization mechanisms, assessing copolymer structures to studying the degradation of polymeric materials on a molecular level. However, a case can nevertheless be made that mass spectrometry is an underutilized tool in polymer chemistry compared to its high potential [17]. Such a

notion is underpinned by an analysis of the current literature: of the approximately 10 000 studies conducted upon – for example – polyacrylates (which are readily ionizable) from 2000 until 2010, NMR spectroscopy played a significant role in ~15% of these studies, whereas soft ionization mass spectrometry played a significant role in only about 3% of these studies. This is despite of the fact that soft ionization mass spectrometry technology has – due to its dominance as a highly applicable analytical tool in the biological sciences – become almost as readily available as NMR. To date, mass spectrometry remains the only technique with the power to isolate (provided the correct mass analyzer is employed) and image individual polymer chains on a routine basis.

Although there have been some notable books addressing the field of mass spectrometry applied to synthetic polymers [18–20], no publication especially dedicated to the needs of synthetic polymer chemists exists, which could aid in the selection of appropriate mass spectrometric tools. Specifically, most books on polymer mass spectrometry do not engage with the topics of living/controlled radical polymerization methods and their mechanistic underpinnings or the mass spectrometric investigation of polymerization processes in general. In addition, an up-date on the current situation of polymer mass spectrometry is required. With the present compilation, we wish to close this critical gap in the literature and provide a state-of-the-art overview on the applications of mass spectrometry in molecular polymer chemistry to the reader. In this edited publication, a series of leading researchers in the field will present their expert perspectives on several – in our view – important topics in contemporary mass spectrometry. It is thus no surprise that the large majorities of authors

contributing to the present book are chemists by training, as we have attempted to provide a book that addresses the analytical requirements posed in contemporary polymer chemistry.

The book opens with an overview of the available mass analyzers. Special consideration is given by the authors Steven Blanksby and Gene Hart-Smith to their uses in polymer chemistry. Various ionization techniques applicable in polymer mass spectrometry are then explored in-depth by Anthony Gies. Chrys Wesdemiotis subsequently takes a close look at tandem mass spectrometry, a highly important tool for the elucidation of polymer structure and one of the major contemporary fields of development in the mass spectrometry sector. Sarah Trimpin and colleagues follow with their contribution, describing gas-phase ion-separation procedures as applied to synthetic polymers. The ionization process of polymers via the MALDI approach requires a careful design of the sample preparation procedures. Scott Hanton and Kevin Owens therefore provide a close look at how polymer samples are best prepared. Synthetic polymers are not only important materials in their own right, but are also frequently employed to (covalently) modify variable surfaces. Surface analysis is notoriously challenging and a range of techniques have to be employed to map the chemical characteristics of surface-bound macromolecules. Christine Mahoney and Steffen Weidner provide a detailed description of the part which surface-sensitive mass spectrometric techniques play in elucidating a polymer surface's structure.

Soft ionization mass spectrometry techniques can be especially powerful when combined with chromatographic techniques such as size exclusion chromatography (SEC), liquid adsorption chromatography

at critical conditions (LACCCs) or both. Jana Falkenhagen and Steffen Weidner explore the wide variety of so-called hyphenated techniques and impressively demonstrate the information depth that can be attained by employing such technologies. While arguably the majority of molecular weight determination is carried out via SEC often equipped with refractive index as well as light scattering detectors, Till Gruendling, William Wallace, and colleagues demonstrate how MALDI-MS as well as SEC coupled to ESI-MS can be employed to deduce absolute molecular weight distributions. The chapter also provides an overview of contemporary automated data processing techniques for mass spectrometric data. Most polymers generated are arguably copolymers and it thus is mandatory to dedicate an entire chapter to the analysis of copolymers via mass spectrometry – Ulrich Schubert and Anna Crecelius provide an in-depth analysis. The field of living/controlled radical polymerization provides fascinating high precision avenues for the construction of complex macromolecular architectures and enables the generation of polymers with a high degree of end-group fidelity, which are often employed in cross-discipline applications (e.g., in biosynthetic conjugates). Soft ionization mass spectrometry plays an integral part in unraveling the mechanism of living/controlled radical polymerization processes as well as in the characterization of macromolecular building blocks: Christopher Barner-Kowollik and colleagues take a close look at the current state-of-the-art. Similarly, polymers generated via conventional radical polymerization can be readily investigated via mass spectrometry. Here, especially the investigation of the initiation process and of the generated end-group type is of high importance – Michael Buback, Greg Russell, and colleagues report. Finally, Grazyna Adamus and Marek Kowalczuk survey the field of mass spectrometry applied to polymers prepared

via nonradical methods such as coordination polymerization, polycondensation, and polyaddition. The question of polymer stability and a detailed understanding of polymer degradation processes on a molecular level are of paramount importance for an evaluation of the performance of a polymer in chemical applications or as a material. Sabrina Carroccio and colleagues survey the field of soft ionization mass spectrometry applied to the molecular study of degradation processes at the book's conclusion.

With the above spectrum, we hope to have covered most of what constitutes modern mass spectrometry applied to questions of organic polymer chemistry. The final chapter provides an outlook and evaluation – from our perspective – of what the important advances in mass spectrometry technology related to polymer chemistry could be and which important chemical questions are yet to be addressed by soft ionization techniques.

Karlsruhe and Berlin, February 2011
Christopher Barner-Kowollik
Jana Falkenhagen
Till Gruendling
Steffen Weidner

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Chapter 1

Mass Analysis

Gene Hart-Smith and Stephen J. Blanksby

1.1 Introduction

Modern day mass analyzer technologies have, together with soft ionization techniques, opened powerful new avenues by which insights can be gained into polymer systems using mass spectrometry (MS). Recent years have seen important advances in mass analyzer design, and a suite of effective mass analysis options are currently available to the polymer chemist. In assessing the suitability of different mass analyzers toward the examination of a given polymer sample, a range of factors, ultimately driven by the scientific questions being pursued, must be taken into account. It is the aim of the current chapter to provide a reference point for making such assessments.

The chapter will open with a summary of the measures of mass analyzer performance most pertinent to polymer chemists (Section 1.2). How these measures of performance are defined and how they commonly relate to the outcomes of polymer analyses will be presented. Following this, the various mass analyzer technologies of most relevance to contemporary MS will be discussed (Section 1.3); basic operating principles will be introduced, and the measures of performance described in Section 1.2 will be summarized for each of these technologies. Finally, an instrument's tandem and