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BOOK REVIEWS

MALDI Mass Spectrometry for Synthetic Polymer Analysis. Edited by Liang Li (University of Alberta, Edmonton, Canada). From the series Chemical Analysis, Volume 175. Edited by J. D. Winefordner. John Wiley & Sons, Inc.: Hoboken, NJ. 2010. x + 300 pp. $89.95. ISBN 978-0-471-77579-9.

This book is an impressive compilation in 12 chapters of state-of-the-art developments in the field of MALDI-MS of synthetic polymers written by 16 experts in the field. It is well edited, and related subjects in different chapters are thoroughly cross-referenced. The authors do an excellent job presenting the latest capabilities of MALDI-MS for the analysis of synthetic polymers, which they illustrate with many examples. More importantly, the authors also stress the limitations of MALDI-MS for such analyses, and in doing so, they present a realistic and frank assessment of the capabilities of this technology.

A broad number of topics are included, ranging from the fundamentals of the MALDI process for synthetic polymers to a description of the LC-MALDI interface and applications of MALDI-MS to industrial polymers. Each chapter includes an extensive compilation of references related to the topic.

Chapter 1 is an overview by the editor of the role of MS in polymer analysis as well as other analytical techniques. He also presents a historical overview of the analysis of synthetic polymers with MS and underscores the complementary nature of both MALDI and ESI and the attributes of ESI in the analysis of water-soluble polymers, despite the formation of multiply charged ions during this process. Finally, he also sets a pragmatic tone about the capabilities of MALDI MS for the analysis of synthetic polymers, especially for samples with broad polydispersities, while emphasizing the importance of sample preparation for successful MALDI.

Readers probing the "whys" and "hows" of MALDI of synthetic polymers will find Chapter 2 by Zenobi a highly informative account of the ionization of polymers with detailed mechanisms and explanations of primary and secondary ionization events as well as a review of the use and proper selection of cationization agents. Detailed descriptions of sources that cause mass discrimination effects in the MALDI process and in MS detector systems are presented as the main limiting factors in obtaining accurate molecular mass distributions for polymers, particularly those with broad polydispersity. Discussion of the need for sample fractionation to achieve accurate characterization and presentation of an overview of the current gaps in the knowledge and challenges ahead for quantitative MALDI MS of synthetic polymers complete the chapter.

Li and Whittal provide a detailed introduction to the most common mass analyzer, the time-of-flight (TOF) instrument, coupled with MALDI. They focus on the earlier perceived poor resolution of TOF when coupled to MALDI, as it is the latter that introduces uncertainties in the time and energies of ion formation that affect the resolution achieved. The authors outline instrumental strategies, in both the ion source and mass analyzer, to compensate for this uncertainty and increase resolution. For those readers interested in the underlying equations for ion motion in TOF, there is plenty in this chapter. I found Section 3.5 particularly useful, where specific examples of the effect of instrumental settings on the quality of polymer mass spectra are presented.

Equally valuable is Chapter 4, in which Borgmann and Wilkins describe the use of Fourier Transform Mass Spectrometry (FTMS) for analyzing polymers. Here the authors discuss its virtues of high mass-resolving power, mass accuracy, and MS^n. A tutorial is provided on FTMS and the ionization processes used with this instrument, as is a table in which the advantages and disadvantages of different ICR cells for FTMS instruments are outlined.

Chapters 5 and 10 deal with tandem MS (MS/MS) of polymers. Chapter 5 by Polce and Wesdemiotis is a primer for Chapter 10 for those unfamiliar with the notation for and mechanisms of polymer fragmentation. The basic principles of MS/MS of polymers, the instrumentation for MS/MS, and the activation of precursor ions and the energies involved are reviewed in the first section, which could easily form part of a graduate level course in MS. The following section is a description of the mechanisms of polymer fragmentation that includes charge-induced fragmentations, charge-remote rearrangements, and charge-remote fragmentation via radical intermediates. The authors conclude by pointing out ETD and ECD as new ways to fragment synthetic polymers that deserve attention from the polymer scientist in the near future. The chapter includes over 200 references, making it a useful resource.

The reader already familiar with MALDI-MS knows the importance of sample preparation for successful analyte desorption/ionization in MALDI and that no amount of tuning or adjusting of instrumental parameters can improve the quality of the signal obtained from a poorly prepared sample. Appropriately, two chapters address sample preparation of synthetic polymers for MALDI analysis. Chapter 6 by Owens and Hanton is not a list of recipes for conventional preparation of samples, but rather it focuses on the fundamental and often complex interplay of the many variables involved: nature of the matrix, solvent(s), cationization agent, matrix/polymer ratio, use of additives, concentration of the analyte, order of mixing, MALDI plate surface, and the manner the sample is deposited onto the MALDI plate. For example, the authors provide insightful knowledge on the match of solubility parameters between the matrix and polymer to form a true solid solution. Each section addressing a sample preparation variable is illustrated with an example from the literature or from their own work, making this chapter easy to follow and highly informative to MALDI users. The chapter concludes with a detailed example, using the principles previously described, of a successful MALDI-MS analysis of a novel synthetic polymer.

The next chapter, by Trimpin, is devoted to solvent-free sample preparation for MALDI-MS analysis. She outlines the concept of preparing the polymer/matrix/salt solid solution without predissolving each component in "compatible" solvents, a process that can be difficult. The author describes the virtues of not having solvent in the recipe, thereby considerably simplifying the process because there is one less variable to optimize in a long list of permutations to test. Finally, a series of examples involving the analysis of insoluble polymers,

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systems with matrix/polymer segregation problems, and mixtures suffering from suppression is presented. Overall, I believe many investigators will find this chapter very useful in their research.

Extracting quantitative information about synthetic polymers from MALDI-MS data is of paramount importance and often the end goal of the polymer chemist when using this technique. Accuracy in determining values for the number-average relative molecular mass and the mass-average relative molecular mass is crucial in determining the polydispersity (PD) of a synthetic polymer, and considerable effort has been devoted to determining these values by MALDI-MS. Accordingly, Chapters 8 and 9 address these topics. Chapter 8 by Guttman and Wallace presents a detailed description of the uncertainties affecting the accuracy of the signal axis, which ultimately influence the accuracy of the estimated PD. Sources of variability include sample preparation; the laser desorption/ionization process, e.g., laser intensity; detector saturation; and detector mass-dependence of the ion-to-electron process. This is a must-read chapter for those wanting to extract useful quantitative information from MALDI-MS measurements. Chapter 9 on the other hand is geared for those investigators more interested in applying or developing novel chemometric approaches to extract useful and unbiased information from the data set. The authors, Wallace, Kearsley, and Guttman, dig into the nontrivialities in answering simple questions like "Where does the peak begin and end?" when analyzing a MALDI-mass spectrum of a synthetic polymer. Two approaches are presented that are operator independent in order to avoid bias: (1) autocorrelation to identify periodic signals within the noise and (2) time-series segmentation.

In Chapter 10, Jackson presents several examples of tandem mass spectra of synthetic polymers, each accompanied with detailed explanations of signal assignment and ion fragmentation. After introducing MS/MS, he presents several examples of tandem mass spectra for acrylic polymers, poly(styrene), polyethers, polyesters, and polyesteramides. In addition, a detailed description is given of end-group structure analysis by the use of equations that take into consideration the mass of the cations, fragment ions, and precursor ions to infer the mass of the end group.

To mitigate the problems usually associated with the MALDI-MS of polymer blends and polymers of high PD, liquid chromatography (LC) is commonly performed prior to MS analysis. This approach is described in Chapter 11 by Weidner and Falkenhagen. They outline online and offline coupling methods and then focus on several examples of offline LC-MALDI MS coupling: (1) Chemical composition distribution, e.g., determination of the degree of epoxidation of polybutadiene 5000; (2) topology type distribution, e.g., cyclic versus star configurations; and (3) functional type distribution, e.g., operation of SEC at near critical mode to differentiate end group functionality.

The final chapter, by Hanton and Owens, provides examples of the analysis of several industrial polymers with MALDI-MS, and as a result, this chapter also serves as an epilogue for the book. Because it is cross-referenced with almost all the other chapters in the book, it also serves as an excellent starting point, along with Chapter 1. Starting with a primer on MALDI and sample preparation, the authors then discuss a series of illustrative examples of MALDI MS analyses of polymers of increasing complexity, i.e., from simple homopolymers to the challenging analysis of polymer blends.

Overall, I highly recommend this book for any polymer scientist with access to MALDI-MS as it will aid in the better planning of experiments and interpretation of the results. This is definitely a book for beginning graduate students in the field and for MS facility managers who are constantly exposed to a wide variety of samples, with synthetic polymers being among them.

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