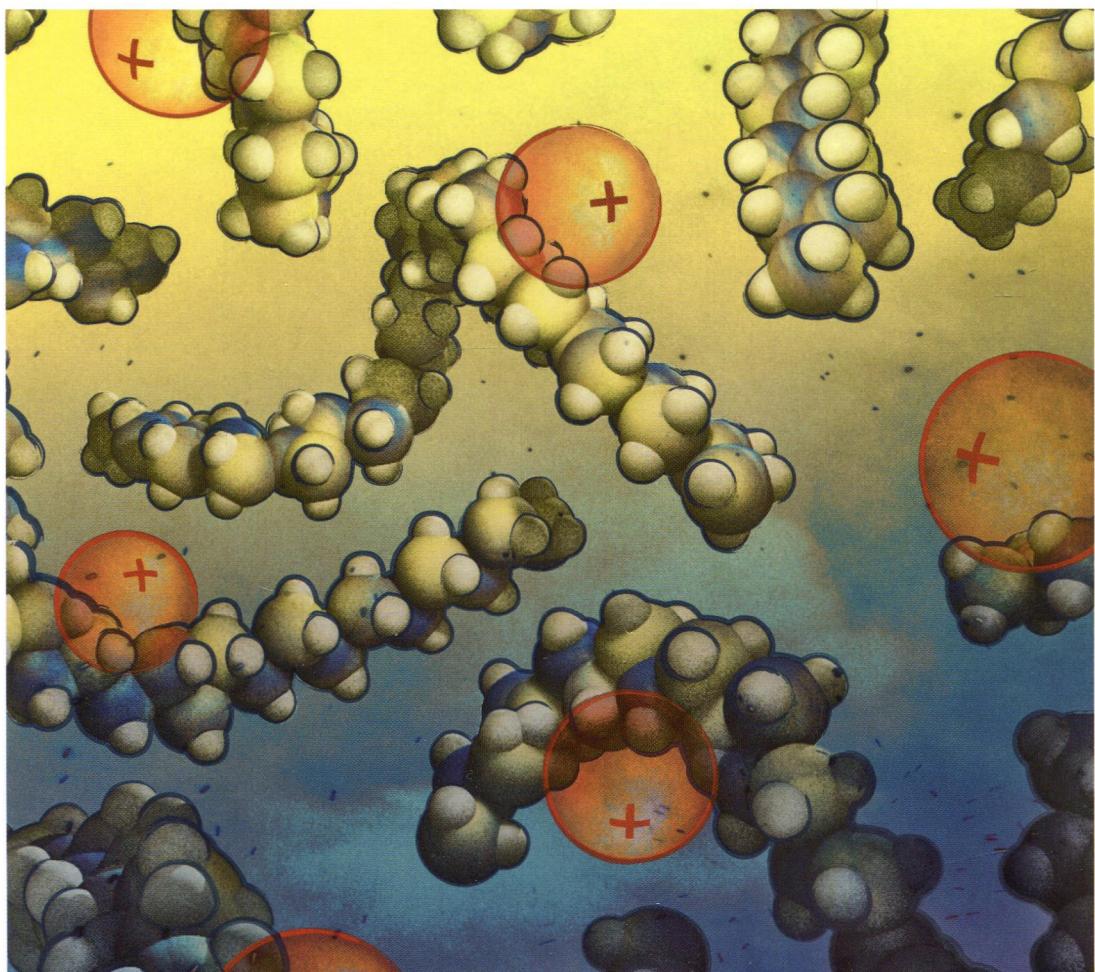


Edited by C. Barner-Kowollik,
T. Gründling, J. Falkenhagen, S. Weidner

WILEY-VCH

Mass Spectrometry in Polymer Chemistry



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

**Mass Spectrometry
in Polymer Chemistry**



WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Dr. C. Barner-Kowollik

Karlsruhe Institute of Technology (KIT)
Engesserstr. 18
76128 Karlsruhe
Germany

Dr. Till Gruendling

Karlsruhe Institute of Technology (KIT)
Engesserstr. 18
76128 Karlsruhe
Germany

Dr. Jana Falkenhagen

Federal Institute for
Mat. Research & Testing (BAM)
Richard-Wallst tter-Str. 11
12489 Berlin
Germany

Dr. Steffen Weidner

Federal Institute for
Mat. Research & Testing (BAM)
Richard-Wallst tter-Str. 11
12489 Berlin
Germany

Cover:

Wiley-VCH thanks Gene Hart-Smith for the permission to use the cover illustration.

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

  2012 Wiley-VCH Verlag & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photostriping, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Cover Design Formgeber, Eppelheim

Typesetting Thomson Digital, Noida, India

Printing and Binding Fabulous Printers Pte Ltd,
Singapore

Printed in Singapore

Printed on acid-free paper

Print ISBN: 978-3-527-32924-3

ePDF ISBN: 978-3-527-64184-0

eBook ISBN: 978-3-527-64182-6

ePub ISBN: 978-3-527-64183-3

Mobi ISBN: 978-3-527-64185-7

Contents

List of Contributors XIII

Introduction 1

Christopher Barner-Kowollik, Jana Falkenhagen,

Till Gruendling, and Steffen Weidner

References 4

1 Mass Analysis 5

Gene Hart-Smith and Stephen J. Blanksby

1.1 Introduction 5

1.2 Measures of Performance 5

1.2.1 Mass Resolving Power 6

1.2.2 Mass Accuracy 8

1.2.3 Mass Range 9

1.2.4 Linear Dynamic Range 9

1.2.5 Abundance Sensitivity 10

1.3 Instrumentation 12

1.3.1 Sector Mass Analyzers 12

1.3.2 Quadrupole Mass Filters 15

1.3.3 3D Ion Traps 17

1.3.4 Linear Ion Traps 19

1.3.5 Time-of-Flight Mass Analyzers 20

1.3.6 Fourier Transform Ion Cyclotron Resonance Mass Analyzers 22

1.3.7 Orbitraps 24

1.4 Instrumentation in Tandem and Multiple-Stage

Mass Spectrometry 25

1.5 Conclusions and Outlook 29

References 30

2 Ionization Techniques for Polymer Mass Spectrometry 33

Anthony P. Gies

2.1 Introduction 33

2.2 Small Molecule Ionization Era 34

| | | |
|----------|--|-----------|
| 2.2.1 | Electron Ionization (EI) | 34 |
| 2.2.2 | Chemical Ionization (CI) | 36 |
| 2.2.3 | Pyrolysis Mass Spectrometry (Py-MS) | 37 |
| 2.3 | Macromass Era of Ionization | 38 |
| 2.3.1 | Field Desorption (FD) and Field Ionization (FI) | 38 |
| 2.3.2 | Secondary Ion Mass Spectrometry (SIMS) | 40 |
| 2.3.3 | Fast Atom Bombardment (FAB) and Liquid Secondary Ion Mass Spectrometry (LSIMS) | 42 |
| 2.3.4 | Laser Desorption (LD) | 43 |
| 2.3.5 | Plasma Desorption (PD) | 44 |
| 2.3.6 | Other Ionization Methods | 45 |
| 2.4 | Modern Era of Ionization Techniques | 45 |
| 2.4.1 | Electrospray Ionization (ESI) | 46 |
| 2.4.2 | New Trends | 48 |
| 2.4.3 | Atmospheric Pressure Chemical Ionization (APCI) | 49 |
| 2.4.4 | New Trends | 49 |
| 2.4.5 | Matrix-Assisted Laser Desorption/Ionization (MALDI) | 49 |
| 2.4.6 | New Trends | 52 |
| 2.5 | Conclusions | 53 |
| | References | 53 |
| 3 | Tandem Mass Spectrometry Analysis of Polymer Structures and Architectures | <i>57</i> |
| | <i>Vincenzo Scionti and Chrys Wesdemiotis</i> | |
| 3.1 | Introduction | 57 |
| 3.2 | Activation Methods | 59 |
| 3.2.1 | Collisionally Activated Dissociation (CAD) | 59 |
| 3.2.2 | Surface-Induced Dissociation (SID) | 60 |
| 3.2.3 | Photodissociation Methods | 60 |
| 3.2.4 | Electron Capture Dissociation and Electron Transfer Dissociation (ECD/ETD) | 61 |
| 3.2.5 | Post-Source Decay (PSD) | 62 |
| 3.3 | Instrumentation | 62 |
| 3.3.1 | Quadrupole Ion Trap (QIT) Mass Spectrometers | 63 |
| 3.3.2 | Quadrupole/time-of-flight (Q/ToF) Mass Spectrometers | 69 |
| 3.3.3 | ToF/ToF Instruments | 72 |
| 3.4 | Structural Information from MS ² Studies | 75 |
| 3.4.1 | End-Group Analysis and Isomer/Isobar Differentiation | 75 |
| 3.4.2 | Polymer Architectures | 75 |
| 3.4.3 | Copolymer Sequences | 76 |
| 3.4.4 | Assessment of Intrinsic Stabilities and Binding Energies | 77 |
| 3.5 | Summary and Outlook | 78 |
| | References | 79 |

| | |
|----------|---|
| 4 | Matrix-Assisted Inlet Ionization and Solvent-Free Gas-Phase Separation Using Ion Mobility Spectrometry for Imaging and Electron Transfer Dissociation Mass Spectrometry of Polymers 85 <i>Christopher B. Lietz, Alicia L. Richards, Darrell D. Marshall, Yue Ren, and Sarah Trimpin</i> |
| 4.1 | Overview 85 |
| 4.2 | Introduction 87 |
| 4.3 | New Sample Introduction Technologies 92 |
| 4.3.1 | Laserspray Ionization – Ion Mobility Spectrometry-Mass Spectrometry 95 |
| 4.3.2 | Matrix Assisted Inlet Ionization (MAII) 99 |
| 4.3.3 | LSIV in Reflection Geometry at Intermediate Pressure (IP) 100 |
| 4.4 | Fragmentation by ETD and CID 102 |
| 4.5 | Surface Analyses by Imaging MS 103 |
| 4.5.1 | Ultraf Fast LSII-MS Imaging in Transmission Geometry (TG) 105 |
| 4.5.2 | LSIV-IMS-MS Imaging in Reflection Geometry (RG) 106 |
| 4.6 | Future Outlook 109 |
| | References 110 |
| 5 | Polymer MALDI Sample Preparation 119 <i>Scott D. Hanton and Kevin G. Owens</i> |
| 5.1 | Introduction 119 |
| 5.2 | Roles of the Matrix 120 |
| 5.2.1 | Intimate Contact 121 |
| 5.2.2 | Absorption of Laser Light 121 |
| 5.2.3 | Efficient Desorption 122 |
| 5.2.4 | Effective Ionization 123 |
| 5.3 | Choice of Matrix 125 |
| 5.4 | Choice of the Solvent 125 |
| 5.5 | Basic Solvent-Based Sample Preparation Recipe 127 |
| 5.6 | Deposition Methods 127 |
| 5.7 | Solvent-Free Sample Preparation 130 |
| 5.8 | The Vortex Method 132 |
| 5.9 | Matrix-to-Analyte Ratio 134 |
| 5.10 | Salt-to-Analyte Ratio 136 |
| 5.11 | Chromatography as Sample Preparation 138 |
| 5.12 | Problems in MALDI Sample Preparation 140 |
| 5.13 | Predicting MALDI Sample Preparation 142 |
| 5.14 | Conclusions 143 |
| | References 144 |
| 6 | Surface Analysis and Imaging Techniques 149 <i>Christine M. Mahoney and Steffen M. Weidner</i> |
| 6.1 | Imaging Mass Spectrometry 149 |
| 6.2 | Secondary Ion Mass Spectrometry 150 |

| | | |
|----------|---|------------|
| 6.2.1 | Static SIMS of Polymers | 150 |
| 6.2.1.1 | The Fingerprint Region | 151 |
| 6.2.1.2 | High-Mass Region | 162 |
| 6.2.2 | Imaging in Polymer Blends and Multicomponent Systems | 168 |
| 6.2.3 | Data Analysis Methods | 171 |
| 6.2.4 | Polymer Depth Profiling with Cluster Ion Beams | 174 |
| 6.2.4.1 | A Brief Discussion on the Physics and Chemistry of Sputtering and its Role in Optimized Beam Conditions | 180 |
| 6.2.5 | 3-D Analysis in Polymer Systems | 182 |
| 6.3 | Matrix-Assisted Laser Desorption Ionization (MALDI) | 184 |
| 6.3.1 | History of MALDI Imaging Mass Spectrometry | 184 |
| 6.3.2 | Sample Preparation in MALDI Imaging | 185 |
| 6.3.3 | MALDI Imaging of Polymers | 188 |
| 6.3.4 | Outlook | 192 |
| 6.4 | Other Surface Mass Spectrometry Methods | 192 |
| 6.4.1 | Desorption Electrospray Ionization | 192 |
| 6.4.2 | Plasma Desorption Ionization Methods | 194 |
| 6.4.3 | Electrospray Droplet Impact for SIMS | 194 |
| 6.5 | Outlook | 196 |
| | References | 196 |
| 7 | Hyphenated Techniques | 209 |
| | <i>Jana Falkenhagen and Steffen Weidner</i> | |
| 7.1 | Introduction | 209 |
| 7.2 | Polymer Separation Techniques | 210 |
| 7.3 | Principles of Coupling: Transfer Devices | 214 |
| 7.3.1 | Online Coupling Devices | 214 |
| 7.3.2 | Off-Line Coupling Devices | 218 |
| 7.4 | Examples | 220 |
| 7.4.1 | Coupling of SEC with MALDI-/ESI-MS | 220 |
| 7.4.2 | Coupling of LAC/LC-CC with MALDI-/ESI-MS | 224 |
| 7.5 | Conclusions | 228 |
| | References | 228 |
| 8 | Automated Data Processing and Quantification in Polymer Mass Spectrometry | 237 |
| | <i>Till Gruendling, William E. Wallace, Christopher Barner-Kowollik, Charles M. Guttman, and Anthony J. Kearsly</i> | |
| 8.1 | Introduction | 237 |
| 8.2 | File and Data Formats | 237 |
| 8.3 | Optimization of Ionization Conditions | 239 |
| 8.4 | Automated Spectral Analysis and Data Reduction in MS | 241 |
| 8.4.1 | Long-Standing Approaches | 242 |
| 8.4.2 | Some New Concepts | 243 |
| 8.4.3 | Mass Autocorrelation | 243 |

| | | |
|-----------|--|------------|
| 8.4.4 | Time-Series Segmentation | 245 |
| 8.5 | Copolymer Analysis | 248 |
| 8.6 | Data Interpretation in MS/MS | 251 |
| 8.7 | Quantitative MS and the Determination of MMDs by MS | 252 |
| 8.7.1 | Quantitative MMD Measurement by MALDI-MS | 253 |
| 8.7.1.1 | Example for Mixtures of Monodisperse Components | 256 |
| 8.7.1.2 | Example for Mixtures of Polydisperse Components | 257 |
| 8.7.1.3 | Calculating the Correction Factor for Each Oligomer | 260 |
| 8.7.1.4 | Step by Step Procedure for Quantitation | 261 |
| 8.7.1.5 | Determination of the Absolute MMD | 262 |
| 8.7.2 | Quantitative MMD Measurement by SEC/ESI-MS | 266 |
| 8.7.2.1 | Exact Measurement of the MMD of Homopolymers | 266 |
| 8.7.2.2 | MMD of the Individual Components in Mixtures of Functional Homopolymers | 270 |
| 8.7.3 | Comparison of the Two Methods for MMD Calculation | 273 |
| 8.7.4 | Simple Methods for the Determination of the Molar Abundance of Functional Polymers in Mixtures | 274 |
| 8.8 | Conclusions and Outlook | 276 |
| | References | 276 |
| 9 | Comprehensive Copolymer Characterization | 281 |
| | <i>Anna C. Crecelius and Ulrich S. Schubert</i> | |
| 9.1 | Introduction | 281 |
| 9.2 | Scope | 282 |
| 9.3 | Reviews | 282 |
| 9.4 | Soft Ionization Techniques | 283 |
| 9.4.1 | MALDI | 283 |
| 9.4.2 | ESI | 292 |
| 9.4.3 | APCI | 294 |
| 9.5 | Separation Prior MS | 297 |
| 9.5.1 | LC-MS | 297 |
| 9.5.2 | Ion Mobility Spectrometry-Mass Spectrometry (IMS-MS) | 299 |
| 9.6 | Tandem MS (MS/MS) | 301 |
| 9.7 | Quantitative MS | 303 |
| 9.8 | Copolymers for Biological or (Bio)medical Application | 304 |
| 9.9 | Software Development | 307 |
| 9.10 | Summary and Outlook | 309 |
| | References | 309 |
| 10 | Elucidation of Reaction Mechanisms: Conventional Radical Polymerization | 319 |
| | <i>Michael Buback, Gregory T. Russell, and Philipp Vana</i> | |
| 10.1 | Introduction | 319 |
| 10.2 | Basic Principles and General Considerations | 320 |
| 10.3 | Initiation | 321 |

| | | |
|-----------|---|------------|
| 10.3.1 | Radical Generation | 321 |
| 10.3.1.1 | Thermally Induced Initiator Decomposition | 321 |
| 10.3.1.2 | Photoinduced Initiator Decomposition | 331 |
| 10.3.1.3 | Other Means | 334 |
| 10.3.2 | Initiator Efficiency | 335 |
| 10.4 | Propagation | 335 |
| 10.4.1 | Propagation Rate Coefficients | 336 |
| 10.4.2 | Chain-Length Dependence of Propagation | 340 |
| 10.4.3 | Copolymerization | 342 |
| 10.5 | Termination | 347 |
| 10.6 | Chain Transfer | 351 |
| 10.6.1 | Transfer to Small Molecules | 351 |
| 10.6.2 | Acrylate Systems | 356 |
| 10.7 | Emulsion Polymerization | 364 |
| 10.8 | Conclusion | 365 |
| | References | 365 |
| 11 | Elucidation of Reaction Mechanisms and Polymer Structure: Living/Controlled Radical Polymerization | 373 |
| | <i>Christopher Barner-Kowollik, Guillaume Delaittre, Till Gruendling, and Thomas Paulöhrl</i> | |
| 11.1 | Protocols Based on a Persistent Radical Effect (NMP, ATRP, and Related) | 374 |
| 11.2 | Protocols Based on Degenerative Chain Transfer (RAFT, MADIX) | 386 |
| 11.3 | Protocols based on CCT | 393 |
| 11.4 | Novel Protocols and Minor Protocols | 397 |
| 11.5 | Conclusions | 398 |
| | References | 399 |
| 12 | Elucidation of Reaction Mechanisms: Other Polymerization Mechanisms | 405 |
| | <i>Grażyna Adamus and Marek Kowalcuk</i> | |
| 12.1 | Introduction | 405 |
| 12.2 | Ring-Opening Polymerization Mechanisms of Cyclic Ethers | 406 |
| 12.3 | Ring-Opening Polymerization Mechanisms of Cyclic Esters and Carbonates | 408 |
| 12.4 | Ring-Opening Metathesis Polymerization | 423 |
| 12.5 | Mechanisms of Step-Growth Polymerization | 425 |
| 12.6 | Concluding Remarks | 430 |
| | References | 431 |
| 13 | Polymer Degradation | 437 |
| | <i>Paola Rizzarelli, Sabrina Carroccio, and Concetto Puglisi</i> | |
| 13.1 | Introduction | 437 |
| 13.2 | Thermal and Thermo-Oxidative Degradation | 438 |

| | | |
|------|--|-----|
| 13.3 | Photolysis and Photooxidation | 449 |
| 13.4 | Biodegradation | 454 |
| 13.5 | Other Degradation Processes | 455 |
| 13.6 | Conclusions | 457 |
| | References | 461 |
| 14 | Outlook | 467 |
| | <i>Christopher Barner-Kowollik, Jana Falkenhagen, Till Gruendling, and Steffen Weidner</i> | |
| | Index | 469 |