

Chromatographic Characterization of Polymers

Hyphenated and
Multidimensional Techniques



EDITED BY
Theodore Provder, Howard G. Barth,
and Marek W. Urban

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Chromatographic Characterization of Polymers

Hyphenated and Multidimensional Techniques

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FOREWORD

The ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented because their papers would be distributed among several journals or not published at all.

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ABOUT THE EDITORS



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He was chairman of the ACS Division of Polymeric Materials: Science and Engineering, Inc., and has served on the advisory board of the ACS Books Department and the editorial advisory board for ACS's *Industrial & Engineering Chemistry Product Research and Development* journal. He is a member of the editorial boards for the *Journal of Coatings Technology* and *Progress in Organic Coatings*. He is also the treasurer for the Joint Polymer Education Committee of the Divisions of Polymeric Materials: Science and Engineering, Inc. and Polymer Chemistry, Inc.

He is a recipient of an SCM Corporation Scientific and Technical Award in the area of computer modeling and two Glidden Awards for Technical Excellence for advanced latex particle size analysis methods and instrumentation development. In addition, he received the coatings industry's highest honor by being awarded the 1987 Joseph J. Mattiello Lecture at the annual meeting of the Federation of Societies for Coatings Technology. In 1989, he was awarded the ACS Division of Polymeric

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HOWARD G. BARTH is a senior research associate of the Corporate Center for Analytical Sciences at the DuPont Experimental Station in Wilmington, Delaware. Before joining the DuPont Company in 1988, he was a research scientist and group leader at Hercules Research Center. He received his B.A. in 1969 and his Ph.D. in 1973 in analytical chemistry from Northeastern University. His specialties include polymer characterization, size-exclusion chromaography, and high-performance liquid chromatography. He has published more than 70 papers in these and related

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MAREK W. URBAN received his M.S. degree in chemistry from Marquette University in 1979, followed by his Ph.D. from Michigan Technological University in 1984. Before joining North Dakota State University in 1986, he spent two years as a research associate in the Department of Macromolecular Science at Case Western Reserve University in Cleveland.

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Spectroscopy of Molecules and Macromolecules of Surfaces (Wiley-Interscience), and he edited two books in the Advances in Chemistry series and two books in the ACS Symposium Series. He is also the editor of the ACS book series "Polymer Surfaces and Interfaces", which is part of the Professional Reference Books. His research interests range from characterization of polymer networks and surfaces using FTIR spectroscopy to structure-property relationships at surfaces and interfaces, and from spectroscopic measurement of diffusion in polymer networks to nonequilibrium thermodynamics. His academic research group is involved in the studies of polymer surfaces and interfaces using vibrational spectroscopic methods. For his pioneering work on rheophotoacoustic spectroscopy, he was awarded the 1990 Megger's Award presented for the most outstanding paper published in the *Applied Spectroscopy Journal*. The award is given by the Federation for Analytical Chemistry and Spectroscopy Societies. He also is credited with two patents in this area. For five consecutive years, from 1986 to 1991, he was honored by the 3M Company with the Young Faculty Award. From 1987 to 1988, he served as chair for the Society for Applied Spectroscopy, Minnesota Chapter. He is an invited speaker at many international conferences, Gordon Research conferences, and industrial laboratories. He serves as a consultant to several chemical companies.

His involvement in ACS symposia began in 1991, when he co-chaired the International Symposium on Spectroscopy of Polymers in Atlanta, Georgia, from which *Structure-Property Relations in Polymers* (Advances in Chemistry Number 236) was derived. He co-chaired the 1993 Symposium on Hyphenated Techniques in Polymer Characterization, which was held in Chicago, Illinois, during the ACS National Meeting, and served as chair of the International Symposium on Polymer Spectroscopy, which was held in Washington, D.C., in 1994. He is also a lecturer

in spectroscopy workshops offered by ACS. At North Dakota State University, he is chair of the Polymers and Coatings Department, director of the summer coatings science short courses, and director of the National Science Foundation's Industry–University Coatings Research Center at North Dakota State University.

PREFACE

THE GLOBAL, OPERATIVE BUSINESS AND SOCIETAL DRIVING FORCES of the mid-1990s are causing polymer-related industries to focus strongly on their core businesses and technological competencies. This focusing has produced a more directed approach to product development and a significant change in corporate R&D culture. The product development process is no longer a sequential process from R&D to product introduction into the marketplace. Instead, the process is highly nonlinear, nonsequential, and iterative in order to speed up product innovation, product development, and market introduction. Improving the effectiveness of the R&D process must be done in conjunction with strong regard for safety, health, and environmental values; waste reduction; energy conservation; product quality; improved product-process-customer economics; the need to satisfy and delight the customer; and the need to improve shareholder value.

The polymer science and technology required to meet product and market needs in the context of improving the effectiveness of the R&D process are generating highly complex polymeric systems that may be blends or composites of a variety of materials. As a result, measurement of average properties is no longer adequate to characterize and elucidate the nature of such complex polymeric materials. A combination of polymer analytical and characterization techniques or multidimensional analytical approaches is required to provide a synergism of analytical and characterization information to establish structure, property, and morphology processing relationships that can form a knowledge bridge between polymerization mechanisms and end-use performance. Advances in instrumentation technology and the need for analytical and characterization information synergism have led to an increase in the development of hyphenated characterization techniques and their application to polymeric materials characterization.

This book covers some of the significant advances in hyphenated chromatographic separation methods for polymer characterization. Chromatographic separation techniques in this volume include size-exclusion chromatography, liquid chromatography, and field flow fractionation methods that are used in conjunction with information-rich detectors such as molecular size-sensitive or compositional-sensitive detectors or coupled in cross-fractionation modes.

The first section of this book focuses on general considerations con-

cerning hyphenated polymer chromatographic separation methods. The second section focuses on the use of light scattering and viscometry molecular size sensitive detectors, the issue of multidetection calibration, and some unique applications of these detectors. The third section focuses on the analysis and elucidation of compositional heterogeneity in copolymers and blends by using cross-fractionation approaches with compositional and molecular size sensitive detectors.

We hope this book will encourage and catalyze additional activity and method development in hyphenated chromatographic separation methods for polymer characterization.

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CONTENTS

Preface	xiii
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GENERAL CONSIDERATIONS

1. Hyphenated Polymer Separation Techniques: Present and Future Role	3
Howard G. Barth	
2. Limiting Conditions in the Liquid Chromatography of Polymers ...	13
David J. Hunkeler, Miroslav Janco, Valeria V. Guryanova, and Dusan Berek	
3. Isoperichoric Focusing Field-Flow Fractionation Based on Coupling of Primary and Secondary Field Action	21
Josef Janča	
4. Size-Exclusion Chromatography with Electrospray Mass Spectrometric Detection	41
William J. Simonsick, Jr. and Laszlo Prokai	

LIGHT SCATTERING AND VISCOMETRY: MULTIDETECTION CALIBRATION AND APPLICATION

5. Concerns Regarding the Practice of Multiple Detector Size-Exclusion Chromatography	59
Christian Jackson and Howard G. Barth	
6. Computer Simulation Study of Multidetector Size-Exclusion Chromatography: Flory-Schulz Molecular Weight Distribution ...	69
Christian Jackson and Wallace W. Yau	
7. Eliminating Lag Time Estimation in Multidetector Size-Exclusion Chromatography: Calibrating Each Detector Independently	79
Kevin G. Suddaby, Ramin A. Sanayei, Kenneth F. O'Driscoll, and Alfred Rudin	
8. Determination of Molecular Weight and Size of Ultrahigh Molecular Weight Polymers Using Thermal Field-Flow Fractionation and Light Scattering	93
Seungho Lee and Oh-Seung Kwon	
9. Molecular Characterization Using a Unified Refractive Index-Light-Scattering Intensity Detector	109
Robyn Frank, Lothar Frank, and Norman C. Ford	
10. Size-Exclusion Chromatography with Light-Scattering Detection at Two Angles: Polystyrene in Tetrahydrofuran	123
Thomas H. Mourey and Hans Coll	

11. Characterization by Size-Exclusion Chromatography with Refractive Index and Viscometry: Cellulose, Starch, and Plant Cell Wall Polymers	141
Judy D. Timpa	
12. Size-Exclusion Chromatography of Dextrans and Pullulans with Light-Scattering, Viscosity, and Refractive Index Detection . . .	151
William S. Bahary, Michael P. Hogan, Mahmood Jilani, and Michael P. Aronson	
13. Star-Branched Polymers in Multidetector Gel Permeation Chromatography	167
James Lescq, Michèle Millequant, Maryse Patin, and Philippe Teyssie	
ANALYSIS OF COMPOSITIONAL HETEROGENEITY IN COPOLYMERS AND BLENDS	
14. Determination of Molecular Weight and Composition in Copolymers Using Thermal Field-Flow Fractionation Combined with Viscometry	183
Martin E. Schimpf	
15. Compositional Heterogeneity of Copolymers by Coupled Techniques with Chromatographic Columns and Multidetectors . . .	197
John V. Dawkins	
16. Size-Exclusion Chromatography and Nonexclusion Liquid Chromatography for Characterization of Styrene Copolymers	211
Sadao Mori	
17. Two-Dimensional Chromatography for the Deformulation of Complex Copolymers	223
P. Kilz, R.-P. Krüger, H. Much, and G. Schulz	
18. Characterization of Block Copolymers Using Size-Exclusion Chromatography with Multiple Detectors	243
Elizabeth Meehan and Stephen O'Donohue	
19. Use of a Gel Permeation Chromatography-Fourier Transform Infrared Spectrometry Interface for Polymer Analysis	253
James N. Willis and L. Wheeler	
20. Size-Exclusion Chromatography-Fourier Transform IR Spectrometry Using a Solvent-Evaporative Interface	265
P. C. Cheung, S. T. Balke, and T. C. Schunk	
Author Index	283
Affiliation Index	283
Subject Index	284

GENERAL CONSIDERATIONS

Hyphenated Polymer Separation Techniques

Present and Future Role

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An overview is presented on recent developments in the use of hyphenated multidimensional separation and detection techniques for the characterization of polymeric materials. Emphasis has been placed on the use of on-line molecular-weight-sensitive detectors for size-exclusion chromatography (SEC). These detection systems are based on measuring Rayleigh light-scattering or intrinsic viscosity of the eluting polymer. With these types of detectors, one can determine absolute molecular weights as well as branching, molecular size, and polymer conformation as a function of molecular weight, without the use of column calibration. The determination of compositional heterogeneity using SEC with on-line selective detectors, such as UV, Fourier transform infrared, mass spectrometry, NMR, and even Raman spectrometry, is now being investigated. Multidimensional hyphenated techniques, such as orthogonal chromatography, temperature-rising elution fractionation-SEC, and SEC-high-performance liquid chromatography, are briefly discussed.

POLYMERS ARE TYPICALLY COMPLEX MIXTURES in which the composition depends on polymerization kinetics and mechanism and process conditions. As we enter the twenty-first century, polymeric materials are becoming even more complex, consisting of polymer blends, composites, and branched and grafted structures of unusual architecture. To obtain polymeric materials of desired characteristics, polymer processing must be carefully controlled and monitored. Furthermore, we need to understand the influence of molecular parameters on polymer properties and end-use performance. As a result, we are faced with unprecedented

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