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

Theodore Provder, EDITOR
The Glidden Company
(Member of ICI Paints)

Howard G. Barth, EDITOR
DuPont

Marek W. Urban, EDITOR
North Dakota State University

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FOREWORD

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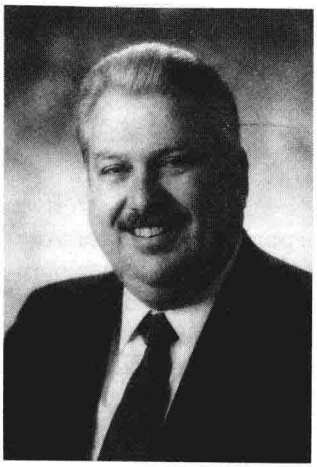

THEODORE PROVDER is principal scientist at the Glidden Company's Research Center and is responsible for the research activities of the Materials Science and Analytical Services Department. He received a B.S. degree in chemistry from the University of Miami in 1961 and a Ph.D. inphysical chemistry from the University of Wisconsin in 1965.

After receiving his doctorate, he joined the Monsanto Company in St. Louis as a senior research chemist and carried out research on the characterization and material properties of exploratory polymers and composites. While he was at Monsanto, his research interests focused on molecular weight characterization, particularly by size-exclusion chromatography. Recently, his research has focused on size-exclusion chromatography, particle size distribution analysis, cure chemistry and physics, and the application of computers in the polymer laboratory. He is the author of more than 100 publications, is credited with three patents, and has edited or co-edited 10 volumes in the ACS Symposium Series and co-edited two volumes in the Advances in Chemistry series.

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

Materials: Science and Engineering, Inc., Roy W. Tess Award in Coatings. In 1993, Provder received the University of Missouri—Rolla Coatings Institute Distinguished Scientist Award in recognition of distinguished work in the field of coatings and polymer science.

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 areas. Barth also edited the book *Modern Methods of Particle Size Analysis* (Wiley, 1984) and co-edited *Modern Methods of Polymer Characterization* (Wiley, 1991). He has edited five volumes on polymer characterization published in the *Journal of Applied Polymer Science* and co-edited two volumes in the ACS Symposium Series. Barth was on the instrumentation advisory panel of *Analytical Chemistry* and was associate editor of the *Journal of Applied Polymer Science.* He is cofounder and chairman of the International Symposium on Polymer Analysis and Characterization. He was recently appointed editor-in-chief of the *International Journal of Polymer Analysis and Characterization* (Gordon and Breach). Barth is past chairman of the Delaware Section of the American Chemical Society, and he presently serves as councillor. Barth is a member of the ACS Divisions of Analytical Chemistry, Polymer Chemistry, Inc., and Polymeric Materials: Science and Engineering, Inc.; the Society of Plastics Engineers; and the Delaware Valley Chromatography Forum. He is also a fellow of the American Institute of Chemists and a member of Sigma Xi.

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.

He is the author of more than 180 research papers, numerous review articles, and several book chapters and books, mostly published in the ACS Advances in Chemistry series. He is the author of *Vibrational 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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THEODORE PROVDER
The Glidden Company
ICI Paints in North America
16651 Sprague Road
Strongsville, OH 44136

HOWARD G. BARTH
DuPont
Central Research and Development
Corporate Center for Analytical Sciences
Experimental Station
P.O. Box 80228
Wilmington, DE 19880–0228

MAREK W. URBAN
Department of Polymers and Coatings
North Dakota State University
Fargo, ND 58105

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Hyphenated Polymer Separation Techniques

Present and Future Role

Howard G. Barth

DuPont, Experimental Station, Wilmington, DE 19880–0228

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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