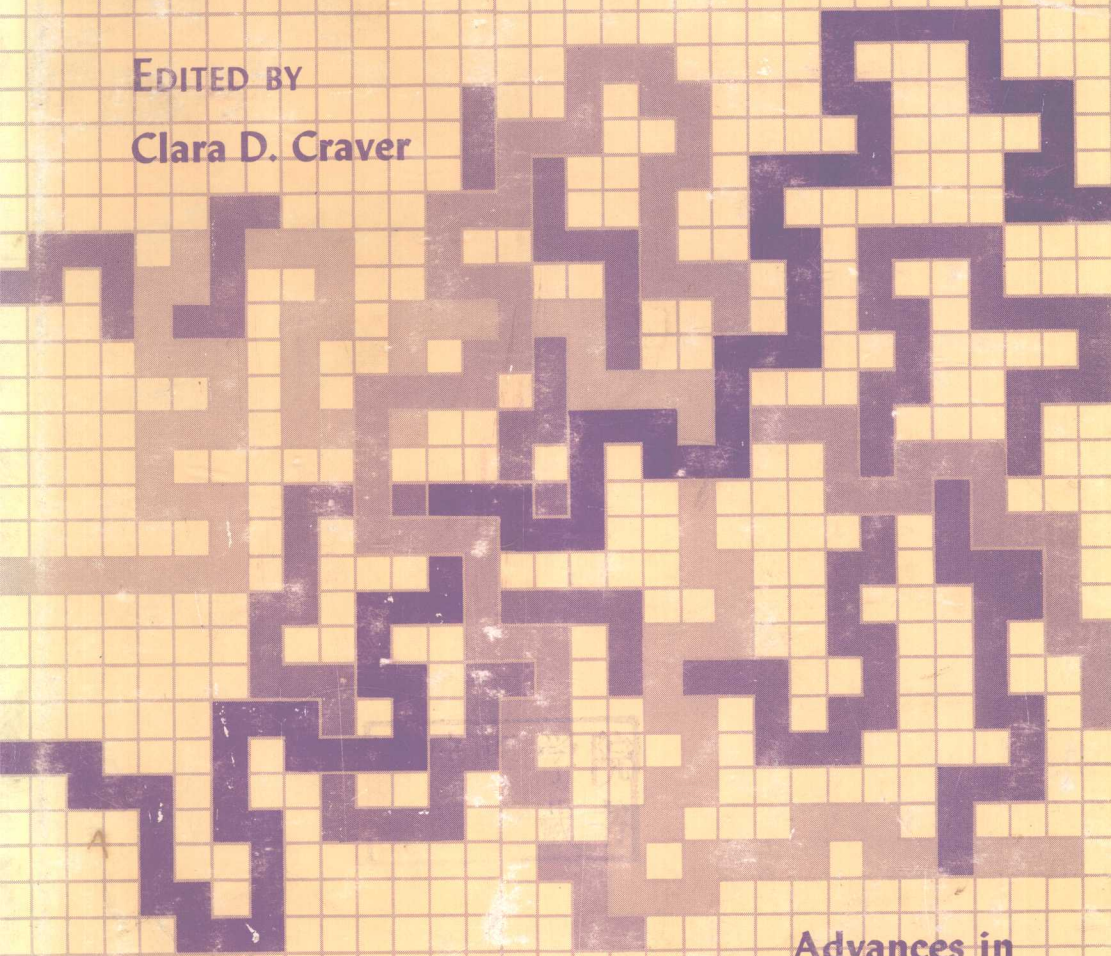
Polymer Characterization

Spectroscopic, Chromatographic, and Physical Instrumental Methods

EDITED BY
Clara D. Craver



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Polymer Characterization

Spectroscopic, Chromatographic, and Physical Instrumental Methods

Clara D. Craver, EDITOR
Chemir Laboratories

Based on a symposium sponsored
by the ACS Macromolecular Secretariat
at the 181st Meeting
of the American Chemical Society,
March 29–April 3, 1981,
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FOREWORD

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, their papers, distributed among several journals or not published at all. Papers are reviewed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Volumes in the ADVANCES IN CHEMISTRY SERIES maintain the integrity of the symposia on which they are based; however, verbatim reproductions of previously published papers are not accepted. Papers may include reports of research as well as reviews since symposia may embrace both types of presentation.

ABOUT THE EDITOR

CLARA D. CRAVER, president and founder (1958) of Chemir Laboratories, received her B.S. degree in chemistry from Ohio State University in 1945 and was awarded the honorary degree of Doctor of Science by Fisk University in 1974. Her work at Esso Research Laboratories, 1945–1949, resulted in patents on characterization of complex hydrocarbon mixtures. She established an infrared laboratory at Battelle Memorial Institute in 1949, and, acting as group leader until 1958, conducted spectroscopic work for Battelle's research projects as well as original research work that resulted in scientific publications in the areas of drying oils, asphalts, paper, and resins. Her work in organic coatings won her the 1955 Carbide and Carbon Award of the Division of Organic Coatings and Plastics Chemistry of the ACS. In 1975 she became chairman of that Division. She initiated the Coblentz Society's spectral publication program and is editor of five books of Special Collections of IR Spectra. She served as consultant to ASTM for the Evaluated IR Spectral Publication Program supported by the National Bureau of Standards, and is chairman of the Joint Committee on Atomic and Molecular Physical Data. She is past-chairman of the ASTM Committee on Molecular Spectroscopy, and was named a Fellow of ASTM in 1982 when she received that organization's highest honor, the Award of Merit. She is a Fellow of the American Institute of Chemists and a Certified Professional Chemist.

PREFACE

TODAY'S POLYMER SCIENTIST makes use of a large array of characterization methods to develop data relating the performance of polymeric materials to chemical and physical structure. Polymer applications demand conflicting performance characteristics: strong adhesion with easy peel, hardness with resiliency, flexibility with dimensional stability, inertness with miscibility, smoothness with paintability, rigidity with lack of brittleness, and crack resistance. The desired properties are obtained by the selection of chemical composition, including residual or grafted functional groups. Control of properties can be exercised by alternating structures, by alternating clumps of functional groups or by synthesizing interpenetrating polymer networks. Some properties are controlled by molecular dimensions: linear, branched, cross-linked. Others are controlled by molecular size, by curing conditions and cross-linking agents, by blending and by additives including plasticizers, antioxidants, surfactants, stabilizers, and fillers.

The characterization and resultant understanding of polymeric systems require input from many fields: chromatography, spectroscopy, rheology, surface chemistry, electron microscopy, thermal analysis, and physical testing. Other highly specialized techniques involve light scattering, neutron scattering, excimer fluorescence, photoacoustic spectroscopy, and pyrolytic degradation, with exact identification of small molecular subunits by chromatography combined with IR and mass spectrometry.

In drawing upon so many diverse and specialized fields, polymer characterization has profited by the cross-fertilization of ideas that occur when specialists meet and communicate with one another. Serving this purpose, the American Chemical Society Divisions of Organic Coatings and Plastics Chemistry, Polymer Chemistry, Rubber Chemistry, Colloid Chemistry, and Cellulose and Paper Chemicals hold cosponsored symposia at the National ACS meetings. The Macromolecular Secretariat, a programming group composed of all five divisions, designated Polymer Characterization as its topic for 1981, and with the participation of the Division of Analytical Chemistry, programmed a full week's symposium organized and chaired by the editor. This book, covering significant advances in polymer characterization, is based on that symposium. It is

organized around seven major methods with single chapters on a few new or highly specialized techniques.

Comprehensive coverage of dynamic mechanical methods is provided in nine chapters by experts selected by the 1978 Borden Award winner, John K. Gillham, of Princeton University. The latest developments in automation of equipment for dynamic mechanical spectroscopy, torsion pendulum and torsional braid analyses, and shear in polymer melts are reported. Applications include impregnated cloth analysis, mechanical analysis of organic coatings, and strength and viscoelastic characterization of polymeric solids.

The thermal characteristics of polymers bear important relationships to their performance. Thermal gravimetric analysis (TGA) may be used for identification or determination of purity of polymers. TGA can measure solvent retention and provide activation energies and heats of reactions. Bernhard Wunderlich, of Rensselaer Polytechnic Institute, describes sources of experimental errors in differential scanning calorimetry (DSC) and summarizes the state of the art in instrumentation. The treatment of kinetic data and kinetic modeling, including applications to polymer degradation, is reported by J. Flynn and B. Dickens of the National Bureau of Standards. Application to coatings is reported by investigators from Glidden Coatings and Resins Division of SCM Corporation.

Chromatographic methods of polymer fractionation and the resultant correlation of chromatograms with polymer composition and performance are among the most widely used methods of characterization. However, the data must be interpreted cautiously because many variables affect polymer distribution as reflected by chromatograms. Among these are nonuniformity of chemical composition of the various particle size ranges which in turn affect solubilities and detector response. The coverage of this subject as arranged by Theodore Provder, of SCM Corporation, includes the theory and understanding of calibration problems of polymer chromatography and techniques for minimizing them. Novel partition methods such as foam fractionation are also presented.

Studies of polymer surfaces by scanning electron microscopy alone and in combination with x-ray analysis and micro-Raman techniques is especially useful in organic coatings analysis and research. Results reported here include investigation of mildew attack on paint surfaces and corrosion of metal substrates in microscopic-sized blisters at the coating–metal interface. Raman microprobe, MOLE, permits chemical analysis of microareas. An example of its usefulness is the identification of "fisheyes" in a copolymer sheet as being homopolymer impurities. The capability of correlating metal analysis from x-ray maps of surfaces with organic analysis by Raman microprobe makes these combined

techniques a powerful research tool. L. H. Princen, USDA, organized an application-oriented report on these significant instrumental advances.

Nearly half of the chapters in this book report on advances in the use of spectroscopy for polymer characterization. These tools are often combined, not only with each other, but with thermal and mechanical techniques to relate molecular structure to polymer performance and stability.

E. Brame, du Pont, has provided an overview of NMR applications. Advances in ^{13}C NMR, made possible by the increased sensitivity of pulsed Fourier transform instruments, provide improved determination of tacticity, comonomer sequence and branching of synthetic polymers. There are five full chapters reporting on advances in polymer structure determination by NMR including ^{1}H, ^{13}C, and ^{19}F. The chapter authored by Frank Bovey, of Bell Laboratories, is rich in interpretation of the significance of NMR data as applied to polymer synthesis, stability, and morphology. Practical use of sophisticated structural analysis arises from such findings as the detection of tertiary chloride atoms in poly(vinyl chlorine) which may contribute to its thermal instability.

NMR is usually carried out on polymers in solution or in the molten state. Only low resolution or broadline NMR has been attainable on solids. Recent advances in magic-angle spinning and dipolar decoupling along with multipulse NMR have made it possible to resolve individual resonances of solid state samples. Research directed toward describing the segmental motions in amorphous and semicrystalline polymers and understanding secondary transitions makes use of these NMR techniques applied to samples at varying temperatures.

IR spectroscopy has long been a valuable tool for chemical characterization of polymers and for following the chemical changes in curing or degradation reactions. The increased sensitivity now obtainable from computer averaging of data and the increased speed of determining a spectrum made possible by Fourier transform are expanding the applications of IR to minor composition differences and to conformation at surfaces and in bulk samples under stress. J. Koenig, Case Western Reserve University, arranged the coverage of this subject and included advances in the theory of IR intensities and developments in photoacoustic spectroscopy.

Advances in the techniques for observing microstructural changes by IR data simultaneously with stress–strain data are described by S. L. Hsu and D. J. Burchell, University of Massachusetts. Degradation studies of poly(ethylene terephthalate) and polyacrylonitrile polymers are reported by B. Bulkin, E. Pearce, and C. Chen, of the Polytechnic Institute of New York, and M. Coleman and G. Sivy of Pennsylvania State University, respectively. James Boerio, University of Cincinnati, describes

reflection/absorption spectra showing polymer orientation at interfaces of ultrathin coatings on polished metal surfaces. Advances in the application of photoacoustic Fourier transform IR to polymer analysis is discussed by Warren Vidrine of Nicolet Instruments.

Major advances have been made in the last few years in the theory of IR and Raman intensities. A wealth of molecular structure information is available from absolute band intensities, but spectroscopists have lacked the theoretical tools to interpret the significance of these intensities. The manuscript contributed by Giuseppe Zerbi, of Istituto Chimica, Milan, Italy, describes advances in this field. This contribution provides examples that demonstrate the significance of the breakthrough in theory to the understanding of molecular structure of polymers. Other new areas reported by Dr. Zerbi deal with the calculation of vibrational frequencies of very large molecules with no symmetry and the determination of chain lengths from the Longitudinal Acoustic Mode (LAM).

Improvements in techniques for pyrolytic degradation of polymers into reproducible fragments that can be analyzed by gas chromatography and mass spectrometry permit atom-by-atom molecular arrangements to be identified. The coverage of analytical pyrolysis was organized by Shirley Liebman, of Chemical Data Systems, Inc. S. Tsuge, of Nagoya University, Japan, discusses the fundamental conditions for obtaining characteristic and reproducible high-resolution pyrograms and the application to sequence distribution investigation in copolymers. The specificity of laser sources and the usefulness of being able to vary power densities is demonstrated in the report by David Hercules et al., University of Pittsburgh, on laser microprobe mass analysis (LAMMA). These techniques are applicable to diverse macromolecules. Coal characterization is reported by K. Voorhees and coworkers, Colorado School of Mines. Forrest Bayer provides an overview of the specificity and sensitivity of these techniques to a wide range of biopolymers. E. Reiner and F. Moran, of Georgia Institute of Technology, characterize details of pathogenic microorganisms and mammalian cells including ones reflecting genetic defects which may produce disease such as cystic fibrosis.

Larry Brydia, of Union Carbide, represented the Analytical Division and served as chairman for specialized techniques. Two subjects from that symposium that are covered in single chapters are advances in scattering techniques by R. S. Stein, University of Massachusetts, and the use of excimer fluorescence as a probe of polymer structure by C. W. Frank of Stanford University.

I am indebted to the subject chairmen and the authors for providing well-balanced coverage in each field. They have included advances in theory along with experimental details essential for obtaining good data. The practical value of the results from these major methods of chemical

and physical characterization of polymers has been interpreted in terms of stability and performance of the many polymers which were investigated. I am especially grateful to all of them for their cooperation and patience which made this book possible.

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PHYSICAL PROPERTIES