Book Reviews

Spin labeling. The Next Millennium. Vol. 14. Biological Magnetic Resonance. By Lawrence J. Berliner (Ohio State University). Plenum Press: New York and London. 1998. xvii + 423 pp. $125.00. ISBN 0-306-45644-3.

This series, begun in 1972, provides a meeting place for those interested in applying magnetic resonance techniques to biological problems. The conceit of this volume is to show spin labeling techniques that are not yet mature but are promising—good wine to be drunk in forthcoming years.

The editor begins this volume with a brief historical perspective describing how McConnell, as a young physical chemist at Stanford, and his group synthesized the stable radicals invented by Rozantsev in the USSR and unavailable in the USA. Rozantsev had managed to trap an unpaired electron within an organic nitroxide that could remain stable for years. His chemistry remains a landmark. McConnell's group prepared maleimide derivatives of these nitroxides and used them to spin-label a variety of proteins. Analysis of the line shapes reported the molecular motion of these proteins, and the new method of spin labeling was born.

The application of lipid spin labels to membrane structure continues the most important application of the technique today. The first chapter, by Sankaram and Marsh, describes a new method for analysis of inhomogeneously broadened lines. Inhomogeniety can arises from the spatial distribution of lipid labels in lipid bilayers. If these bilayers are composed of lipids that segregate into domains with different connectivity, as given by percolation theory, these domains and their composition can be distinguished by this method. Disconnected domains in bilayers were earlier described using fluorescence (Thompson, T.E.; Sankaram, M.B.; Biltonen, R.L.; Marsh, D.; Vaz, W.L. *Mol. Membr. Biol.* **1995**, *12*, 157−62). Marsh, Páli, and Horváth provide elegant theoretical underpinnings for using saturation techniques, both continuous wave and saturation transfer, for measuring of rates of lipid exchange at lipid−protein interfaces. Additional applications included accessibility of spin-labeled lipids in bilayers to oxygen or water-soluble paramagnetic ions, rates of translational diffusion, and distance measurements between lipids and proteins. Smirnov, Belford, and Clarkson compare X-band (9.5 GHz) EPR with W-band (95 GHz) EPR of nitroxide spin-labeled lipids and proteins. High magnetic field EPR provides different information on motional anisotropy as shown in numerous examples but is limited experimentally by the difficulties of sample size (internal tube diameters of 0.15 mm) as well as spin exchange by dissolved oxygen. Solution of these difficulties using gas-permeable plastic capillaries, as described, permitted collecting spectra of even a few spin-labeled proteins in addition to lipids.

Khramtsov and Volodarsky describe the usefulness of imidazole nitroxides. This group discussed this class of nitroxides in 1978 in volume 2 of this series and now provides novel applications for them in the measurement of pH, thiols, and nitric oxide. The most important application is for pH measurement, especially for local concentrations and nontransparent solutions. Disulfide biradicals exhibit marked spectral changes when this disulfide is cleaved, enabling estimates of concentration of thiols as well as the kinetics. While NO is paramagnetic, is cannot be detected by ESR without trapping. Nitronyl nitroxides are used to follow kinetics and quantitate nitroxides in vivo. Makinen, Mustafi, and Kasa use electron nuclear double resonance (ENDOR) of spin labels to dissect molecular structures and conformations. The technique was applied to several enzyme intermediates and can be applied to many structure−function problems with proteins, but the conformation of a spin-labeled penicillin and the mechanism for hydrolysis were especially striking displays of the power of the method. Feix and Klug describe how spin labels can be specifically introduced after genetically engineering cysteine into critical locations in proteins. This method is based on the maleimide spin label introduced by McConnell (see above). So, in contrast to some of the other methods described in this volume, this is a mature method. Several nice examples in working out topology, demonstrating α-helix and β-pleated sheet within membrane proteins, are presented. These methods are or will become standard ones for those membrane proteins for which crystal structures are not available. Keyes and Bobst describe how a nucleotide can be spin labeled and then introduced into nucleic acids. The narrative takes the reader along the paths of possibilities answering questions as they occur to the reader, like a good whodunit. Applications include detecting local Z-structure, bending, and protein−nucleic acid interactions. Hemminga and van den Dries use the maleimide spin label with ST-ESR to characterize the viscoelastic properties of bread dough containing the protein, gluten, important in food science. This is a valiant attempt to understand the local environments present in a difficult, heterogeneous system—an example one hopes others will emulate with other, significant systems. Swartz and Halpern summarize the plethora of activity in using spin labels in vivo, estimating the amount of oxygen, pH, molecular motion, viscosity, polarity, temperature, and redox potential, as well as local perfusion, permeability, and distribution. This list is exhausting, and by the time these authors had referenced these activities with some completeness, they left the reader with only their brief comments. Without a good story or two, how is the reader encouraged to read deeper into the list? The last contribution is in the appendix by Marsh and Schorn, giving hyperfine splittings that will improve estimation of order parameters and be useful for simulations in intermediate motional regimes.

The general pattern of theory, experimental considerations, and interesting applications makes for a rich feast, nourishing for those biophysicists, chemists, biologists, and biochemists, both practitioners and students, looking for new applications of spin labeling techniques in the next millennium.

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Scanning Probe Microscopy of Polymers. Edited by Buddy Ratner and Vladimir V. Tsukruk. American Chemical Society: Washington, DC. 1998. 384 pages. $125.00. ISBN 0-8412-3562-7.

This book was compiled from a symposium on the scanning probe microscopy (SPM) of polymers, sponsored by the Division of Polymer Chemistry at the 1996 National ACS Meeting in Orlando, FL. According to the editors, the goal of the symposium was "to stimulate discussion of SPM applications among a wide range of polymer scientists". Judging by the broad participation in the program and in the proceedings volume, one would have to say that the organizers achieved their goal. Of the 65 papers presented, 21 were selected for the proceedings volume. As with all collections of this kind, the quality of the contributions is somewhat uneven; nevertheless, on the whole the book provides a solid and reasonably timely introduction to this rapidly growing field.

The book is divided into an introductory chapter and five technical sections. The first three of these sections deal broadly with polymer morphology and structure as applied to crystals/fibers, composites/biopolymers, and molecular films/interfaces. The final two sections cover the measurement of local surface properties (i.e., friction) and the development of novel imaging techniques, respectively.

The introductory chapter by Overney and Tsukruk is quite well done and is probably the most valuable article in the collection for workers in this field. After a brief overview of basic AFM principles and imaging modes, the authors give a detailed and well-organized review of polymer SPM. This chapter would be an excellent place for someone interested in entering this field to begin to learn the literature. There are over 200 primary literature citations, which are organized in tables according to keywords such as polymer type, surface morphology, mechanical properties, surface treatments, LB films, and biopolymers. Regarding the technical articles, the chapters by Güntherodt et al. on resolution limits in AFM and by Lieber et al. and Tsukruk et al. on chemical force microscopy are solid introductions to these two topics. The Güntherodt article, in particular, should be required reading for any prospective atomic force microscope user. Drawing on diverse results from the physics literature, the authors present a concise overview of the most important issues relating to the achievement of true atomic resolution in AFM, in terms the nonphysicist can understand. The Lieber article briefly introduces the technique of chemical force microscopy

with a discussion of that group's recent work on the use of chemically functionalized silicon nitride tips to study the frictional properties of chemically modified surfaces, while the Tsukruk article extends this work to the study of model organic surfaces (self-assembled monolayers).

Considering the cost of the book, it is worth commenting on the quality of the figures and the referencing. The good news is that, for the most part, the reproductions of the scanning probe images are of decent to high quality. Unfortunately, the same cannot be said about the quality of the line art (schemes, diagrams, and the like), which is often disappointing and certainly detracts from the overall quality of the volume. Finally, it is clear that the editors paid attention to keeping the references as up to date as possible. Most references are within 5 years of the symposium date, which is about as current as one can expect in a book such as this (citations up to early 1997 are included).

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Matrix-Isolation Techniques: A Practical Approach. The Practical Approach in Chemistry Series. By Ian R. Dunkin (University of Strathclyde). Oxford Press: New York. 1998. 242 pp. $105.00. ISBN 0-19-855863-5.

This book does a wonderful job of covering the practical aspects of matrix isolation and is a must for any matrix isolation research group or any researchers considering applying the technique to their chemical problem. For the beginner, it offers a step-by-step guide on how to set up the necessary equipment and carry out the experiments. For the expert, it is a handy compendium of practical tips and suggestions. The book is divided into six chapters, with the first four being a "how-to" and the last two covering typical matrix isolation experiments, with the only omission being the use of lasers for generating matrix species.

The first chapter gives the background for the matrix isolation technique and what one might hope to accomplish using the technique. The second chapter gives the nuts and bolts of how to actually put a cold cell together from scratch. The chapter covers all of the important points regarding closed-cycle and open-cycle refrigerators, temperature measurement and control, vacuum systems, and sample holders as well as the care and maintenance required for a matrix isolation system. The third chapter covers coupling the cold cell with various spectroscopic techniques as well as sample preparation and the generation of reactive species. The fourth chapter discusses how to prepare matrixes and gives a variety of useful protocols, as well as discussing the various issues involved when manipulating gases and volatile materials in vacuum lines.

The final two chapters present a variety of actual matrix experiments. The fifth chapter discusses photochemistry in matrices and spectroscopy using plane-polarized light, which seems to be the author's area of interest. The final chapter gives a compendium of "Classic Matrix Experiments" which is very useful. This chapter explains, in detail, how to perform a variety of matrix experiments. The species presented in these experiments cover a wide variety of experiments where matrix isolation is a useful tool for determining what is occurring on a molecular level. The author begins with stable molecules, moves on to forming molecular complexes in matrices, and concludes with forming reactive species for study in matrices. The last chapter is a wonderful guide for anyone who is just beginning in matrix isolation. One can easily find an experiment to use as a check for determining if ones matrix setup is working properly or to show that a new student has the technique down. This book is absolutely essential for anyone who is interested in learning the various intricacies of the matrix isolation technique.

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Expanded, Contracted & Isomeric Porphyrins. By Jonathan L. Sessler and Steven J. Weghorn (University of Texas at Austin). Pergamon Press: New York. 1997. 503 pp. $48.50. ISBN 0-08-042093-1.

This monograph is a comprehensive overview of organic synthesis devoted to expanded, contracted, and isomeric porphyrins. Considering the extent of worldwide research on "the pigment of life", it is amazing that the structural modification of the chromophoric macrocycle itself is just beginning to attract the attention of the broader scientific community. This book contains all that is needed to secure more well-deserved recognition for this field. Comprehensive and very well written, it is rewarding for both specialists and readers from allied fields with little expertise. It consists of 10 chapters with 856 references to early as well as current literature, and a subject index. Numerous illustrations present the structures of the final conjugated macrocycles and their cation complexes, frequently supported by X-ray data, and succinct synthetic schemes.

The introduction chapter is followed by a review of synthesis and metalation chemistry of contracted porphyrins. A puzzling ring contraction of isomeric porphyrins, indicative of the serendipity and pioneering spirit often encountered in this book, and the elegant ring expansion of subphthalocyanines, pointing toward supra- and macromolecular perspectives of this field, may be particularly impressive. In addition, chapter 2 includes questions on aromaticity related to the macrocyclic analogy of benzene and its "contracted" cyclopentadiene anion, or to nitrogen-, oxygen-, and sulfur-bridged [18]annulenes. After a concise summary of the probably least explored isomeric porphyrins in chapter 3, the major topic of the book, expanded porphyrins, follows. Chapter 4 emphasizes many elaborate ways to insert oligoene, oligoyne, cumulene, and arene units into the original porphyrin framework to give beautifully circular torands, dibenzofuran cavitands, and so on. Somewhat surprisingly, the organic dye with the highest molar extinction known today (1.6 millions (!) for the sharp Soret band of a vinylogous tetraoxaporphyrin) appears in this chapter as well. Many of the structural motifs introduced here are revisited in the subsequent chapters on larger rings. It is satisfying to note that the complete coverage of pentapyrrolic systems includes some oligomers and conjugates that serve as effective reminders of the applicability of "advanced" porphyrin chemistry to expanded, isomeric, and contracted systems (chapters 5 and 6). Further ring expansion leads to the expected bathochromic shifts and multiple cation-binding domains (chapter 7). However, beginning with octapyrrolic systems, a remarkable structural change occurs: the few higher oligomers prepared so far have a marvelously twisted "figure-eight" conformation instead of the familiar planes (chapter 8). The book concludes with an excursion on the Schiff base chemistry in expanded nitrogen-bridged macrocycles (chapter 9) and an introduction to applications that emphasizes contrast agents, photosensitizers, catalysts for oligonucleotide cleavage, and mediators of anion transport (chapter 10).

Readers of this monograph will experience the fresh flavor of a juvenile field throughout a very readable and well-referenced text. Naturally, most attention is given to a contemporary account of synthetic feasibility. Readers other than synthetic chemists who miss a similar treatment of their particular interests could (and maybe should?) be enticed to make the field ready for equally stimulating monographs on physical, spectroscopic, catalytic, supramolecular, and biological aspects of these sophisticated macrocycles.

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