

**Viscosimetry of Polymers and Polyelectrolytes.** By Werner-Michael Kulicke and Christian Clasen (Universität Hamburg). Springer-Verlag: Berlin, Heidelberg, New York. 2004. xviii + 120 pp. \$59.95. ISBN: 3-540-40760-X.

According to its preface, this short book (109 pages of text) was developed from material used in a “practical laboratory course in polymer analytics”. Perhaps for that reason, much of the presentation is somewhat superficial, without derivations one might normally expect to see and sometimes with a discussion that tends to obscure the relevant physical chemistry. The book is divided into eight chapters, accompanied by a list of symbols and abbreviations, 191 references, and a subject index (there is no author index). The English is generally readable, though the phrasing is often awkward, and there are lapses; e.g., “Nobel price lecture” and “bodily biopolymers” greet the reader in Chapter 1. Also in Chapter 1, and reappearing throughout the book, is a representation of the excluded volume effect in flexible chain polymers as being caused by a “solvating envelope around the polymer chain”, with accompanying cartoons of the effect. This is, at the very least, a naïve description that may seriously mislead the novice on the nature of the interaction potentials involved (one should realize that the chain is solvated at all conditions in solution). In this same chapter,  $\Theta$  conditions are said to apply when the dependence of the intrinsic viscosity  $[\eta]$  on molecular weight  $M$  gives a Mark–Houwink exponent  $a = \partial \ln [\eta] / \partial \ln M = 0.5$  and the second virial coefficient  $A_2$  vanishes. In fact, the correct criterion has  $A_2 = 0$ , and one often sees  $a \approx 0.5$  for low  $M$  flexible-chain polymers in solutions for which  $A_2 > 0$ , indicating “good solvent” conditions; for semiflexible chains,  $a$  may exceed 0.5 even though  $A_2 = 0$ .

Chapter 3 is a discussion of capillary and rotational viscometers (“viscosimeters” in the book’s notation), including schematic drawings, the relevant equations relating the observables to the viscosity, and comments on the advantages and drawbacks of many of the instruments. The discussion does not include the derivation of any of the expressions presented and often does not provide the reader with a citation to the literature for such. Although the notation used is close to standard in most cases, it is peculiar to see the term “Dynamic viscosity” applied to values of the viscosity of low molecular weight compounds; the authors mean to designate the (linear or Newtonian) shear viscosity by this term, perhaps thinking of the limiting value of the dynamic viscosity for zero frequency for fluids, although the frequency-dependent viscoelastic properties are not discussed in the book.

In Chapter 4, the authors discuss some of the usual methods to analyze data on the relative viscosity  $\eta_r$  as a function of concentration to determine  $[\eta]$  and the Huggins parameter  $k'$ , including the analysis of  $\eta_{sp}/c = (\eta_r - 1)/c$ ,  $\ln(\eta_r)/c$ , and  $\{2(\eta_{sp} - \ln \eta_r)\}^{1/2}/c$  as functions of  $c$ . Unfortunately, they do not clearly show how each of these relate to the usually valid expansions in Taylor series in  $c$ , such that each of these functions must extrapolate to the same intercept ( $[\eta]$ ) at zero  $c$ , with initial tangents that must provide the same value for  $k'$ , with the final

variant providing a good approximation to  $[\eta]$  for  $c$  greater than zero, provided  $k' \approx 1/3$ .

In the final chapters of the book, the authors provide a discussion of the dependence of  $[\eta]$  on  $M$  and the chain dimensions, including the well-known Flory–Fox expression with  $[\eta]M$  proportional to the cube of the root-mean-square radius of gyration, and the dependence of  $\eta_r$  on  $c$ ,  $M$ , and, for polyelectrolytes, the supporting electrolyte concentration; the latter includes the often observed strong increase of  $\eta_{sp}/c$  with decreasing  $c$  with low electrolyte concentration. Cartoons depicting a dilute solution as comprising well-separated coils are presented, when in fact, flexible chain polymers interpenetrate and interact at all concentrations; e.g., the effects monitored by  $A_2$ . The reader would be advised to supplement reading of these chapters with additional reading in the primary and review literature. Unfortunately, the references provided by the authors will be of limited use for this. For example, a full 80% of the citations predate 1990, and nearly 60% are to citations in 1980 or earlier.

In the reviewer’s view, the book would be of limited value to a serious student of the subject, and some of the physics presented in the book could mislead the novice.

Guy C. Berry, *Carnegie Mellon University*

JA040940+

10.1021/ja040940+

**Handbook of Metalloproteins, Volume 3.** Edited by Albrecht Messerschmidt (Max-Planck-Institute for Biochemistry, Martinsried and University of Konstanz), Wolfram Bode (Max-Planck-Institute for Biochemistry, Martinsried), and Mirek Cygler (McGill University). John Wiley and Sons, Inc.: Hoboken, NJ. 2004. 768 pp. \$545.00. ISBN 0-470-84984-3.

This volume of *Handbook of Metalloproteins* focuses on metalloproteins containing calcium and zinc and provides information about their chemical, biological, physical, and medical properties. Color graphical representations of the three-dimensional structures of the metalloproteins are provided, and functional class, occurrence, and spectroscopic data are given as well. Calcium ions as secondary messengers in controlling biological processes is included among the topics. An index concludes the book.

JA040949B

10.1021/ja040949b

**Advanced Free Radical Reactions for Organic Synthesis.** By Hideo Togo (Chiba University). Elsevier: Amsterdam. 2004. xii + 258 pp. \$178.00. ISBN 0-08-044374-5.

This book provides a grab bag of organic radical reactions with a focus on synthetic applications. Its strengths lie in its many examples of addition, cyclization, hydrogen atom abstraction, and cascade reactions of radicals (Chapters 3–6). Chapters

7 and 8 on the Barton–McCombie reaction and the Barton decarboxylation reaction are especially well done. Many chapters contain an assortment of short experimental procedures that will appeal to those considering the various reactions. References span the 1980s and 1990s and move into 2000 and beyond. One cannot help but be impressed by the scope and diversity of radical chemistry after reading this book.

While the many reactions and conditions will appeal to synthetic chemists, the book is not very pedagogical; the emphasis is squarely on what has been done as opposed to why it works. Organization is not always clear, and certain topics appear in many places. This is because the author freely mixes methods to conduct radical reactions (tin hydride, for example) with the reactions themselves. The spartan index is a help for finding reactions, but does not list many reagents. Basic principles are provided at a low level, and the result is at times beneficial (simplified) and at times not (oversimplified or omitted). The rates of radical additions, for example, are presented only in the context of frontier molecular orbital theory and without discussion of steric or enthalpic effects. Ratios of products of competing bimolecular reactions are presented without reagent concentrations.

Beyond oversimplification, there are some questionable statements; benzene, for example, is said in several places to

be a good solvent because it stabilizes radicals by a weak orbital interaction, but there is no citation to support the statement. Likewise, despite many useful references to preparative work, key information such as rate constants is often presented without a citation. The book is also not critical, and problems range from small (incorrect steps in reactions) to large (I recommend that readers disregard the slim Chapter 9 on “Radical Reactions of Metal Hydrides” entirely).

Where does the book fit in? Given the lack of pedagogy and brief treatment of basic principles, it is not a good starting point for students. At the other end, my first stop for information on modern aspects of synthetic radical reactions is almost always Renaud and Sibi’s two-volume treatise on “Radical Reactions in Organic Synthesis”. Togo’s book falls between these two ends of the information spectrum. Readers can get a concentrated dose of synthetic radical chemistry in the core Chapters 2–8. From there, the next stop is back to basics to learn more about principles or on to Renaud and Sibi’s book, reviews, or the primary literature.

**Dennis P. Curran**, *University of Pittsburgh*

JA0409255

10.1021/ja0409255