

2010

Book Review: Controlled and Living Polymerizations: From Mechanisms to Applications

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Book Review: Controlled and Living Polymerizations: From Mechanisms to Applications

Abstract

Controlled/living polymerization makes it possible to synthesize polymers of low polydispersity with a predefined molecular weight and specified chain architecture. Such polymers are desirable for a broad range of applications, including coatings, adhesives, and lubricants. Although living polymerization was first discovered in anionic polymerizations in 1956, several decades passed prior to the development of living polymerization techniques for carbocationic polymerization (1984) and ring-opening metathesis polymerization (1986). During the 1990s, several techniques were developed for controlled/living free radical polymerizations. The development of these techniques led to a dramatic increase in the number of research publications dedicated to improving the understanding of controlled/living polymerization mechanisms, the synthesis and characterization of novel polymer architectures, and the applications of these polymers. In fact, a search on the Web of Science shows that in the past 20 years the number of references to living or controlled polymerization in the literature has increased from 48 to 1594. Therefore, the publication of this book, which reviews the various living/controlled polymerization techniques developed to date and the synthesis of a wide range of polymer architectures, is certainly timely and provides a much-needed resource for chemical professionals working with polymers.

Disciplines

Chemical Engineering | Polymer Science

Comments

This is a book review from *Journal of the American Chemical Society* 132 (2010): 10206, doi: [10.1021/ja105230x](https://doi.org/10.1021/ja105230x). Posted with permission.

Chiral Ferrocenes in Asymmetric Catalysis: Synthesis and Applications. Edited by Li-Xin Dai and Xue-Long Hou (both at Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, People's Republic of China). WILEY-VCH GmbH & Co. KGaA: Weinheim. 2010. xviii + 414 pp. \$215.00. ISBN 978-3-527-32280-0.

This book is a compilation of 12 chapters from different authors, including many leaders in this field. Predictably, it opens with a chapter from the editors summarizing some fundamental chemistry of the ferrocene scaffold, including stability, chirality, and derivatization.

Snieckus and co-workers provide the second chapter on stereoselective syntheses of planar chiral ferrocene derivatives. As you might expect, the emphasis here is on directed asymmetric metalation, but the authors did not neglect other methods, e.g., enzyme-mediated resolutions, that are outside their immediate field of interest. This chapter, and most of the others in the book, ends with about four experimental procedures, presumably chosen by the authors because they are of special importance and representative of the different methods that may be used.

Functionalization of the ferrocene core to create ligands can be achieved in a limited number of ways, and this makes it easy to classify the products. Thus, Chapters 3–9 deal with ligands that are monodentate chiral; 1,2-*P,P*-bidentate; 1,2-*P,N*-bidentate; *O,N*-bidentate; symmetrical 1,1'-bidentate; unsymmetrical 1,1'-bidentate; and S-, Se-, and biferrocene-containing. This way of "carving up" the literature does not eliminate duplication or make it completely unambiguous about where to look in the book, but it is good enough. Each of these chapters focuses on the particular applications of these different types of ligands in catalysis. Marion and Fu in Chapter 11 cover different reactions of ferrocene derivatives with N- or P-atoms substituting for CH in a cyclopentadiene ring, and Chapter 12 deals with complexes involving metalation of the Cp-units.

Two types of researchers will be attracted to this book: those looking to apply ferrocene-based ligands in reactions they are working on, and those who specialize in making these types of ligands. The latter group is going to want to have a copy because the slant of the text is ideal for them. A good index is important for the former type of reader. Unfortunately his book's index reads as if it were professionally done by someone who understands more about indexing than about chemistry or reading chemistry books. For instance, under "hydrogenation, -asymmetric" we are directed to "see asymmetric hydrogenation", but under "hydrogenation, -enantioselective" we are given the page numbers directly, which seems a little odd. In general, the advantage of sending readers to "see this and that" rather than write the page numbers in two places is something I have never understood. Nevertheless, readers interested in a particular type of catalysis will be able to find it from the index, and even better, if they are only interested in using a particular metal, they will be able to find it too.

Electronic searching is so easy these days that to realize their full potential, compilations like this need to have critical

overviews of where the field has been and where it is going. Some of the chapters mentioned above have sections dedicated to perspectives and conclusions, but not all. Chapter 12 is followed by another chapter, cryptically marked "A", which is a graphical summary of the most effective ligands and complexes in various catalytic reactions. This is useful because it ignores relatively inaccessible and/or ineffective ligands that have more historical than chemical value. Nevertheless, it might have been useful if a dominant figure in the area had given a "bigger picture opinion" in the book and addressed some questions that are sometimes painful to face. Here are a few that I can imagine. Are ferrocene-based ligands superior to other types and why? My answer is "sometimes"; when they are, it is for reasons that are too varied to go into here, but it might have been useful to read about them. Is development of chiral ferrocene ligands a mature area or are there new topics to be mined within this field? In my opinion, there probably is nothing to be discovered in the design of ferrocenyl ligands that will significantly change the field, and most of the new work is likely to be incremental improvements. If that is true, this book might stand out as a landmark summary that marks the sunset of an intense area of research.

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JA105679W

10.1021/ja105679w

Controlled and Living Polymerizations: From Mechanisms to Applications. Edited by Axel H. E. Müller (Universität Bayreuth, Germany) and Krzysztof Matyjaszewski (Carnegie Mellon University, Pittsburgh, USA). WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim. 2009. xxii + 612 pp. \$195. ISBN 978-3-527-32492-7.

Controlled/living polymerization makes it possible to synthesize polymers of low polydispersity with a predefined molecular weight and specified chain architecture. Such polymers are desirable for a broad range of applications, including coatings, adhesives, and lubricants. Although living polymerization was first discovered in anionic polymerizations in 1956, several decades passed prior to the development of living polymerization techniques for carbocationic polymerization (1984) and ring-opening metathesis polymerization (1986). During the 1990s, several techniques were developed for controlled/living free radical polymerizations. The development of these techniques led to a dramatic increase in the number of research publications dedicated to improving the understanding of controlled/living polymerization mechanisms, the synthesis and characterization of novel polymer architectures, and the applications of these polymers. In fact, a search on the Web of Science shows that in the past 20 years the number of references to living or controlled polymerization in the literature has increased from 48 to 1594. Therefore, the publication of this book, which reviews the various living/controlled polymerization techniques developed to date and the synthesis of a wide range

of polymer architectures, is certainly timely and provides a much-needed resource for chemical professionals working with polymers.

The term “living polymerization” was first defined in 1956 by Michael Szwarc as a chain polymerization from which chain transfer and chain termination are absent. Thus, living polymerizations typically lead to very narrow molecular weight distributions and allow for the synthesis of block copolymers by sequential addition of monomers. However, a living polymerization does not necessarily allow for controlling the molecular weight or chain architectures of polymers. In 1987, the term “controlled polymerization” was introduced by Müller and Matyjaszewski to describe synthetic methods to prepare polymers with well-defined topology (e.g., linear, star-shaped, comb-shaped, dendritic, and cyclic), terminal functionality, composition, and comonomer arrangement (e.g., statistical, gradient, block, and graft). The first four chapters of this book are descriptions of the controlled/living polymerization of vinyl monomers. All of these chapters are thoroughly referenced and include the most current information available at the time of publication. Chapters 1, 3, and 4 provide clear fundamental descriptions of controlled/living anionic, free-radical, and coordination polymerizations, respectively, as well as the pertinent results of the cited literature. In addition, Chapter 3 is a helpful summary of the advantages and disadvantages of several controlled/living free radical polymerization techniques, including stable free-radical polymerization, atom-transfer radical polymerization, and reversible addition–fragmentation chain-transfer polymerization. However, Chapter 2 is somewhat lacking in the discussion of the cited literature regarding controlled/living carbocationic polymerization and reads primarily as a list of references.

Chapters 5 and 6 cover anionic and cationic ring-opening polymerization and ring-opening metathesis polymerization, respectively. Both are well-referenced and include discussions of the most current literature. Chapter 6, which is written as a self-described “user’s manual”, is particularly useful for chemical professionals who are new to the area of controlled/living polymerization.

Chapters 7 and 8 provide a comprehensive review of the synthesis of polymers with precisely defined macromolecular architectures—such as block copolymers, graft copolymers, star polymers, and dendrimers—by the techniques described in the first six chapters. The advantages and disadvantages of these techniques for such syntheses are also discussed. The schematics in these chapters are particularly helpful. Chapter 9 deviates from the synthetic focus of the book with a complementary review of the self-assembly of segmented copolymers into nanostructured morphologies in bulk, thin films, and solution. The final chapter includes numerous examples of industrial applications that require polymers with the precisely defined macromolecular architectures that can only be synthesized by controlled living polymerization.

In summary, this book is an excellent resource for chemical professionals interested in controlled/living polymerization, and the clear, concise presentation of the mechanisms for such polymerizations accompanied by the comprehensive

literature references renders this book useful to both novices and experts.

Jennifer O’Donnell, Iowa State University

JA105230X

10.1021/ja105230x

Molecular Nano Dynamics, Volume 1: Spectroscopy Methods and Nanostructures, and Volume 2: Active Surfaces, Single Crystals and Single Biocells. Edited by Hiroshi Fukumura (Tohoku University, Japan), Masahiro Irie (Rikkyo University, Japan), Yasuhiro Iwasawa (University of Electro-Communications and University of Tokyo, Japan), Hiroshi Masuhara (Nara Institute of Science and Technology, Japan and National Chiao Tung University, Taiwan), and Kohei Uosaki (Hokkaido University, Japan). WILEY-VCH Verlag GmbH & Co. KGaA: Weinheim. 2009. xxii + 722 pp. \$460. ISBN 978-3-527-32017-2.

Recently, the study of chemical reaction dynamics in nano-systems has begun to draw significant attention as a result of great contemporary interest in nanoscience and nanotechnology. This book contains a systematic investigation of molecular nanosystems conducted under the KAKENHI (The Grant-in-Aid for Scientific Research) project on “molecular nano dynamics” from April 2004 to March 2007. This impressive two-volume set brings together more than 80 authors and includes thousands of published papers and presentations. It is broad in scope, providing numerous systems for the reader to explore and expand their knowledge using the supplied references, each of which is sufficient for a thorough introduction to the topic.

Volume 1 opens with an introduction to various new developments in spectroscopic methods for approaching the nano interfaces (Part 1, Chapters 1–9), including methods for simultaneous direct dynamic measurements in both time and real space domains. Good examples are provided of combining scanning probe microscopy with traditional spectroscopy, such as STM-Raman spectroscopy, tip-enhanced near-field nano-Raman microscopy, and near-field two-photon excitation. This part also places specific emphasis on nonlinear laser spectroscopic methods, including sum-frequency-generation spectroscopy, single particle spectroscopy, hyper-Raman spectroscopy, and multiphoton fluorescence. These new spectroscopic methods with novel space resolution, ultrafast time domain, and high sensitivity allow for an analysis of dynamics and mechanisms in terms of space and time in the nanosystems. Part 2 of Volume 1 covers the characteristics and dynamics of multiple nanostructures, including polymer thin films, self-assembled organic thin films, self-spreading lipid bilayer, and quantum dots. Although Parts 3 and 4 in Volume 2 are not primarily focused on nanosystems, they provide descriptions of fundamental approaches to the chemical reactions and dynamic mechanisms on large-scale surfaces and crystals, which offer an excellent understanding of the systems in the nano scale. Part 5 is a very thorough biological investigation of dynamics studies at the level of the single cell.

In summary, this two-volume set provides readers with a concise introduction to a broad and diverse research area. The discussions and references in this set will stimulate further advancements in the studies of chemical reaction

dynamics in nanosystems of supramolecules, colloids, and ultrasmall materials.

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JA1048175

10.1021/ja1048175

Practical Methods for Biocatalysis and Biotransformations. Edited by John Whittall (University of Manchester, U.K.) and Peter Sutton (GlaxoSmithKline R&D Ltd., U.K.). John Wiley & Sons, Ltd.: Chichester. 2010. xxx + 402 pp. \$170. ISBN 978-0-470-51927-1.

This book was written “to provide the readership with enough information to understand when a biocatalytic or biotransformation method would be a suitable practical method to carry out their synthetic transformation”, to quote from the Preface. The first two chapters offer, respectively, a review of biotransformation from an industrial pharmaceutical perspective and an introduction to molecular biology for nonexperts in this area. The remaining chapters cover key biotransformations from the literature, detailing the procedures used, the sources of the starting materials and reagents, references, and tips and advice, where appropriate. A brief subject index completes the book.

JA105554C

10.1021/ja105554c