

Review of Conjugated Polymer Synthesis: Methods and Reactions

Conjugated Polymer Synthesis: Methods and Reactions. Edited by Yoshiaki Chujo. (Kyoto University, Japan). WILEY-VCH Verlag & Co. KGaA: Weinheim. 2010. xvi + 314 pp. \$215. ISBN 978-3-527-32267-1.

The design, synthesis, and application of conjugated polymer systems, sometimes referred to as conducting polymers, have long been of high interest to synthetic chemists, electrochemists, physicists, and materials engineers. The control of electro-optical functionality has always been the main objective, which involves increasing π -conjugation leading to better control of electron delocalization or generation charge carriers. An electrochemist, physicist, or physical chemist will tend to focus on the electrochemical—doping and dedoping—and physicochemical phenomena of a new material. An engineer, on the other hand, will focus on the processing and fabrication of such materials for specific applications. However, an innovative and skilled organic or organometallic synthetic chemist will see that the design of a new macromolecule is but an application of a well-honed synthetic methodology or a chance to stretch the limit of macromolecular design. This book enables the synthetic polymer chemist to appreciate the vast array of methodologies available for the design and synthesis of conjugated polymer systems, which includes linear systems, macrocycles, as well as hyperbranched and liquid crystalline ordered systems. The editor has done a good job in assembling a group of authors to sample the field while focusing also on their expertise. Although this book is not claimed to be a comprehensive treatise on the various methods and architectures available, it represents some of the major classes and subclasses of these materials.

Yamamoto's opening chapter of the book is a review of polycondensation or coupling methods to form conjugated polymers based on organometallic C–C chemistry, which results in the formation of aryl, ethynyl, and ethylene, as well as coupling and cross-coupling products. The vast majority of conjugated polymers with well-defined architectures have primarily benefitted from such exact C–C bond-coupling methods. The relevance of this as a starting point is important, given that the Nobel Prize winners in Chemistry for 2010, Heck, Negishi, and Suzuki, have contributed much to the field of metal-mediated cross-coupling reactions in organic chemistry. This chapter is followed by one by Yokozawa on catalyst-transfer condensation polymerizations and further defines the utility of C–C coupling to form “blocks” that can be utilized and transformed as macroinitiators for further addition polymerization. The types of aromatic and heteroaromatic monomers presented are varied and described specifically in the succeeding chapters. Polythiophenes, perhaps one of the most well-studied conjugated polymers to date, have been synthesized to form regioregular and regiosymmetric architectures as highlighted by the McCullough group in Chapter 3. The various methods utilizing the GRIM and Rieke methods have enabled the formation of highly crystalline materials with functional end groups amenable to block-copolymer formation. Their electro-optical

properties have been found to be superior to those of the nonregioregular derivatives.

Acetylene polymerization, an important type of addition polymerization, is described in Chapter 4 by Tang and coauthors and can serve as a building block for various hyperbranched and network structures. The use of group 5 and 6 metal and organometallic catalysts for producing polyacetylenes is well-known and analogous to their application in polyolefin coordination chemistry. However, the ability to obtain hyperbranched and cyclization chemistry with acetylenes is unique.

An interesting class of through-space conjugated polymers is reviewed by Morisaki and Chujo, who discuss work coming from various scaffold and ring precursor systems. The importance of this topic is that it enabled the through-space phenomena of the π -electron cloud and the charge-carrier mechanism to be truly represented as part of the field of conjugated polymers. The chapter on macrocycles by Takase and Iyoda highlights the possibility of creating nano-objects out of macrocyclic derivatives based on controlled ring-formation chemistry. Other specific chapters that are of relevance include ones on organoboron-containing conjugated polymers (Nagai and Chujo), phosphorus-containing π -conjugated polymers (Siu and Gates), organo-arsenic and antimony conjugated polymers (Naka and Chujo), and other hetero and heteroaromatic structures that contain a contribution of the inorganic component via donor–acceptor systems.

The chapter on synthetic strategies for conjugated main-chain metallopolymers is authored by Schubert and co-workers. It is a summary of the ability to utilize multidentate systems and metals to form macromolecular architectures. Lastly, the chapter by Akagi on helical polyacetylenes prepared in liquid crystal fields is of high interest for the formation of beautiful and dimensional hierarchical structures.

The book is quite readable. A knowledgeable synthetic chemist can appreciate the detail and the examples that have been highlighted to emphasize the importance of each methodology. On the other hand, the book is not for the physicist or physical chemist (except for adventurous ones) who will tend to focus on the electro-optical properties or try to understand the structure–property relationships, especially with the newly reported or less studied conjugated polymer systems. The book does not cater to that.

Topics that should have been included in the book include dendrimeric systems, supramolecular assemblies, or even a chapter on polyradicals. Although the editor has priorities and specific topics on which to focus, inclusion of these chapters would have made the book a bit more comprehensive. Overall, however, the book is very good and a worthwhile addition to the libraries of those who appreciate synthetic chemistry in conjugated polymers.

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