Water in Organic Synthesis

Environmental concerns of the last few decades are driving the search for synthetic methods in more environmentally benign media. For obvious reasons, water would be considered the best solvent for organic synthesis if it actually dissolved organic compounds. The aim of *Water in Organic Synthesis*, edited by Shū Kobayashi, is to persuade organic chemists to forgo this "minor" limitation and consider water as a solvent of choice for organic reactions.

Right at the start, I wish to say that this is the most comprehensive book on the subject of organic synthesis in water or aqueous media. It consists of eight chapters, including two by the editor—"Introduction" and "Perspective"—that cover practically every aspect of organic chemistry in the aqueous phase. The introduction describes Lewis-acid-catalyzed reactions in water, while the second chapter, by Otto and Engberts, is devoted to the structure of water, its properties, and its interactions with organic compounds. This chapter is particularly useful for synthetic organic chemists, who are often not aware of the origin of water–solute interactions that can influence the kinetics and selectivity of organic transformations.

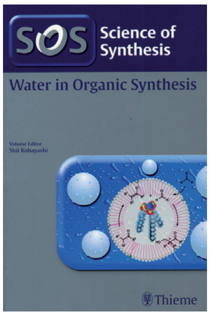
Each of the following chapters combines a number of reviews written by established experts, which deal with important classes of organic reactions taking place in water or in the presence of water. For example, Chapter 3 describes the reactive properties of C–C multiple bonds under such conditions, including oxidation, hydrogenation, hydroformylation, conjugate addition, cyclopropanation, and metathesis reactions. The topics are covered extensively, with much of the material conveniently presented as tables. Chapter 4 deals with the reactions of carbonyl and imino groups, with the focus on reduction, metal-catalyzed alkylation and arylation, aldol reactions, and Mannich reactions. Here again, extensive information on each of the topics is provided. Since many of the reactions that are described use very similar catalytic systems, a certain amount of duplication of the information is evident when one reads the book as a whole. This is to be expected, because each of the reviews deals with a specific functional group modification. Chapter 5 combines the reactions not covered in the preceding two chapters. Cycloaddition and pericyclic reactions co-exist in the same chapter with cross-coupling and Heck reactions, together with asymmetric α-functionalization of carbonyl compounds, free-radical transformations and polymerization, nucleophilic ring-opening of strained heterocycles, and oxidation reactions. Altogether, Chapters 3–5 cover most of those transformations commonly utilized in organic synthesis that can be performed in the aqueous phase.

Chapter 6 discusses special techniques with water. One such technique is organic synthesis under "on water" conditions, which involve heterogeneous mixtures of organic compounds with water. Chanda and Fokin describe many cases in which these conditions produce an increased reaction rate and/or an improvement in selectivity. Although there is still no clear understanding about the nature of these effects, the "on water" synthesis technique is very attractive from the practical point of view, and several representative procedures nicely illustrate this point. In the next review, Kruse and Dinjus describe chemistry performed in subcritical or supercritical water. I believe that many organic chemists will be intrigued to discover the wealth of synthetically useful transformations that can be performed at temperatures above 200 °C! The last review describes aqueous organic chemistry of β-cyclodextrin including many examples of practical synthetic transformations discussed in Chapters 3–5.

Using water instead of organic solvents in industrial applications, the topic of Chapter 7, is crucial to validating the claim of "green-ness" for water as a solvent. The detailed analysis by Wiebus, Schmid, and Cornils of the Ruhrchemie/Rhône-Poulenc propene hydroformylation to butanals provides impressive validation of this kind. Operating on a hundreds of thousands ton scale per year, this aqueous biphasic process is more efficient and selective (for the linear product) than the competing conventional processes, while only generating well under 100 g of waste per kg of the product. The second review in this chapter describes applications of aqueous organic synthesis in the pharmaceutical industry. Although scale-wise the benefits are not as spectacular as for hydroformylation, the review describes a great diversity of aqueous organic transformations that can be applied in the preparation of biologically active compounds on a kilogram scale.

As is reviewed in the "Perspectives" chapter, there are many reactions for which the presence of water is essential. The book would gain further impact if this aspect was emphasized more strongly throughout the text, in addition to the potential environmental benefits.

The navigation through the numerous topics discussed in the book is easy, thanks to the extensive keyword and author indexes while the abundance of reaction procedures greatly helps to evaluate the reaction protocols without extensive searching of the original papers. In conclusion, *Water in Organic Synthesis* deserves to be in every well-maintained library. It will be very helpful for



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chemists who are interested in more environmentally benign organic processes, or who are searching for new opportunities in synthesis.

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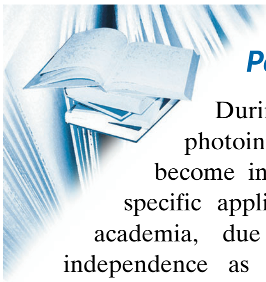
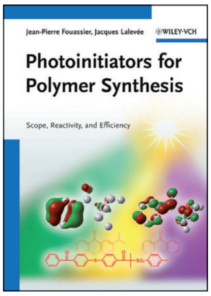


Photoinitiators for Polymer Synthesis



Photoinitiators for Polymer Synthesis
Scope, Reactivity, and Efficiency. By Jean-Pierre Fouassier and Jacques Lalavée. Wiley-VCH, Weinheim, 2012. 476 pp., hardcover, € 149.00.—ISBN 978-3527332106

During the last two decades, photoinitiation processes have become increasingly important for specific applications in industry and academia, due to their temperature independence as well as the associated temporal and spatial resolution opportunities. Most of these applications require a photoinitiator with properties that are suitable for the particular application. Thus, the main challenges are to synthesize new photoinitiator molecules and to characterize their decay mechanisms, decay rates, and cleavage products. A further important aspect is the need for analytical methods to determine the molecular structures of the final reaction products, which in most cases are polymers or radiation curing materials.

The book *Photoinitiators for Polymer Synthesis* describes the basic principles and applications of photopolymerization reactions in the areas of polymer science and materials science, and covers all currently available photoinitiating systems. The book provides a nearly complete overview of the photoinitiators and mechanisms involved. Furthermore, it discusses the latest developments in all fields of photoinitiator research.

The handbook is divided into four parts. Part I consists of seven chapters presenting the basic concepts of photopolymerization, such as light sources, experimental devices, applications, possible photopolymerization reactions, photosensitive systems, analytical techniques for elucidating the photochemical and chemical reactive behavior, and the efficiency of photopolymerization reactions (Chapters 1–7). All in all, Part I summarizes fundamental aspects for scientists working with photoinitiators.

The main part of the book is Part II, which consists of four chapters on free-radical photoinitiating systems. In Chapters 8 and 9, the most important one-component and two-component photoinitiation systems are highlighted. Part II also describes multicomponent photoinitiating systems (Chapter 10) as well as special photoinitiation systems (e.g., self-assembled photoinitiator monolayers, Chapter 11). Unfortunately, Part II does not contain much information about the mass-spectrometric post-mortem analysis of photolytically generated polymers to obtain qualitative data about initiation by individual radical fragments.

In Part III, all non-radical photoinitiating systems, including cationic photoinitiating systems (Chapter 12), anionic photoinitiators (Chapter 13), and photoacid and photobase generator systems (Chapters 14 and 15) are discussed.

Part IV provides a general discussion of the reactivity and efficiency of photoinitiating systems. Chapter 16 describes the influences of various experimental conditions on the performance of free-radical photoinitiators. The reactive properties and efficiency of free-radical photoinitiators in various reaction media are discussed in Chapter 17. Chapters 18 and 19 summarize the reactivity of free-radical photoinitiators towards oxygen, hydrogen donors, monomers, additives, and the oxidation process.

In summary, it can be stated that *Photoinitiators for Polymer Synthesis* is very well structured and is an important—albeit not fully complete—information resource for both experienced scientists and post-graduate students, and also, in part, for undergraduate students, who can use the book as a valuable resource to support their fundamental lectures in polymer chemistry.

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