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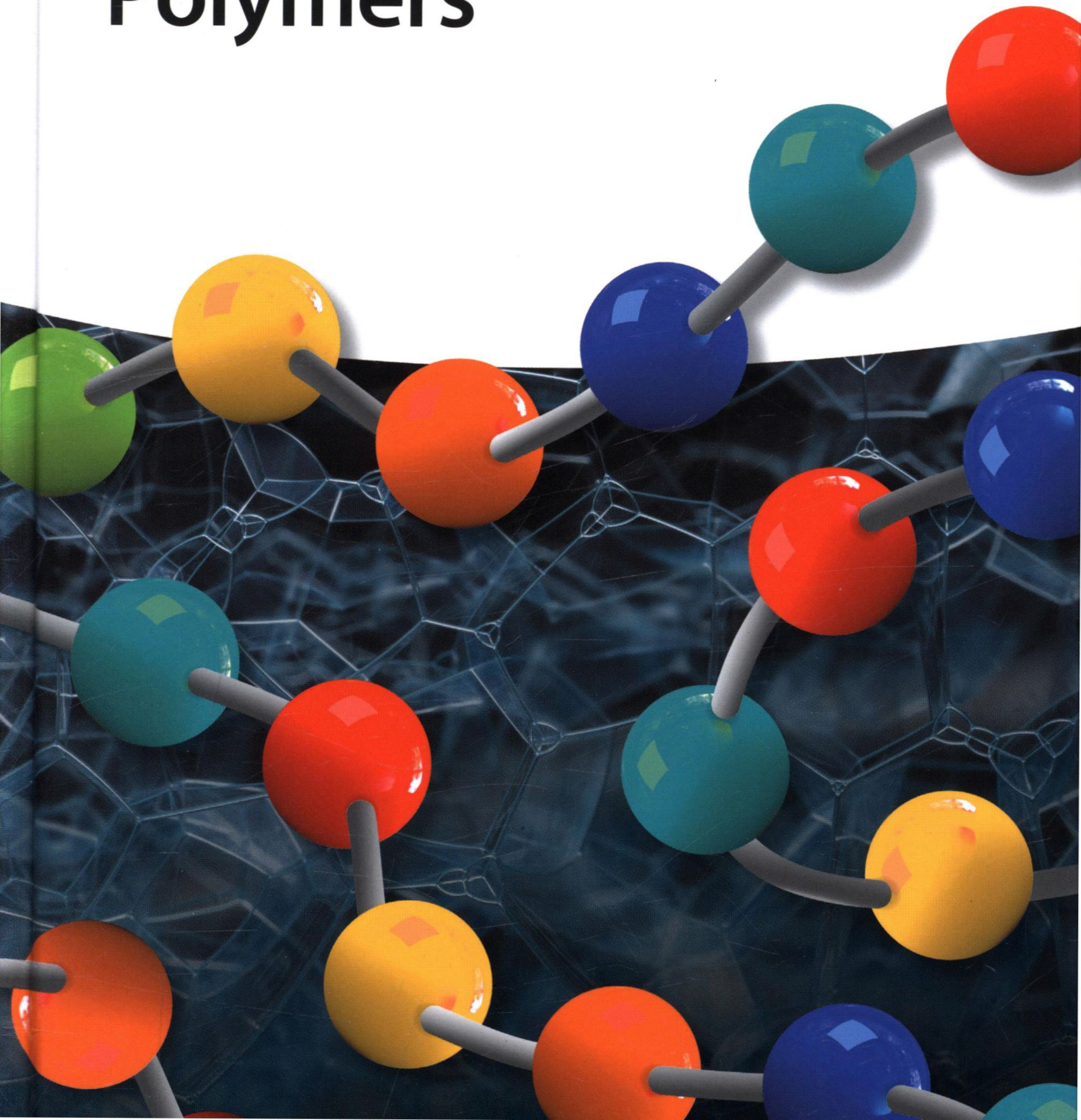
Jean-François Lutz

Sequence-Controlled Polymers



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Edited by a leading authority in the field, the first book on this important and emerging topic provides an overview of the latest trends in sequence-controlled polymers.

Following a brief introduction, the book goes on to discuss various synthetic approaches to sequence-controlled polymers, including template polymerization, genetic engineering and solid-phase chemistry. Moreover, monomer sequence regulation in classical polymerization techniques such as step-growth polymerization, living ionic polymerizations and controlled radical polymerizations are explained, before concluding with a look at the future for sequence-controlled polymers.

With its unique coverage of this interdisciplinary field, the text will prove invaluable to polymer and environmental chemists, as well as biochemists and bioengineers.

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He received in 2008 the prize of the polymer division of the French Chemical Society and he is listed since 2015 as an ISI Highly-Cited Researcher in Chemistry. He is also a European Research Council (ERC) laureate since 2010 through successive starting (StG 2010) and proofs of concept (PoC 2015) grants. His current research interests include the synthesis of sequence-controlled polymers, single-chain technologies and the preparation of information-containing macromolecules. He is the author of more than 200 publications.

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Defining the Field of Sequence-Controlled Polymers

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1.1 Introduction

This book is fully devoted to an exploding area in fundamental and applied polymer science, namely the synthesis, characterization, and utilization of sequence-controlled polymers (SCPs) [1]. This topic is at the same time very old and very new: old because monomer sequence regulation is a central concept in biology and has therefore been thoroughly studied in biochemistry and biophysics for several decades. Thus, efficient methods are available for the synthesis and characterization of sequence-defined biopolymers such as deoxyribonucleic acid (DNA), ribonucleic acid (RNA), and proteins [2]. In comparison, however, the development of man-made polymers with controlled monomer sequences is a much more recent area of research. As pointed out in early essays and reviews [3–5], very little research efforts have been devoted to that topic until about 10 years ago. However, the subject has recently gained significant academic attention, in particular during the last 5 years. This recent emerging trend is actually what is described in the present book, and all the authors of the following chapters have been actively participating in the development of that new discipline. Yet, it should be clearly stated that the field of SCPs was not started 5 years ago. Studies on monomer sequences began with the development of the first synthetic copolymers and can therefore be tracked back to the early days of polymer science [6, 7]. However, as described in a recent historical summary [8], the subject has been stuck for more than 50 years and was mostly limited to the synthesis of classical copolymers such as statistical, alternating, periodic, and block copolymers. More complex degrees of sequence regulation were regarded by the polymer science community as difficult to achieve or as the preserve of biochemists. This state of mind is exactly what has changed during the last few years, which have witnessed the emergence of a large number of original ideas and concepts for making SCPs [1]. As a consequence, the description of monomer sequences in man-made polymers has started to get outdated in classical textbooks. In particular, many copolymers that have been reported in recent years are difficult to describe using current polymer nomenclature and

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terminology [9]. In this context, the objective of the present volume is to define, rationalize, and categorize that burgeoning new field of research.

As a key to decode the present volume, the reader should always keep in mind that the field of SCPs is actually a hybrid discipline located at the interface between biology and polymer science, as depicted in Figure 1.1. Biological polymers, such as nucleic acids and proteins, are indeed archetypal examples of macromolecules with perfectly controlled monomer sequences. Thus, one important trend in the field consists in using biological principles to synthesize SCPs. Protein engineering [10] and DNA-templated polymerizations [11] are good examples of strategies following this school of thought (see Chapters 3 and 4 of this volume for details). However, a second important trend in the field of SCPs aims to synthesize non-natural macromolecules that are as structurally defined as biopolymers [4]. In such approaches, man-made chemistry concepts are used to synthesize the polymers. These tools can be classical polymerization approaches such as chain-growth and step-growth polymerizations but also tools that are imported from other areas of chemistry such a solid-phase synthesis and molecular machines [12, 13]. Solid-phase iterative chemistry was first introduced for the chemical synthesis of biopolymers such as proteins [14, 15] and nucleic acids [16, 17]. However, it was later demonstrated that such approaches can also be used for preparing a wide variety of synthetic sequence-defined polymers (see Chapters 5–7 for details), which includes peptide–polymer bio-hybrid structures [18], peptidomimetics such as peptoids [19], as well as fully unnatural macromolecules such as information-containing polymers [20, 21]. Yet, such multistep growth approaches remain overall experimentally demanding as well as time consuming, and consequently more straightforward sequence-controlled polymerization strategies have been also investigated in the past years. For instance, living or pseudo-living chain-growth polymerizations such as carbanionic polymerization, cationic polymerization, and controlled radical polymerization have been extensively studied for monomer sequence regulation (see Chapters 8–11 for details). Original step-growth polymerization concepts have also been recently examined for the preparation of periodic SCPs (see Chapter 12 for details). Furthermore, efficient chemical transformations known as "click" reactions, which have become quite popular in synthetic polymer chemistry during the last decade [22, 23], have also been shown to be useful tools for the preparation and modification of sequence-controlled macromolecules (see Chapter 13).

This recent progress in the synthesis of SCPs has also raised a large number of new questions and challenges in the broad field of polymer science. Indeed, the emerging domain of SCPs is not restricted to polymer synthesis but also opens up new directions in polymer physics, analytical chemistry, engineering, materials science, and nanotechnology. For instance, the characterization of SCPs requires the development of new analytical approaches [24]. Besides standard polymer analytics such a nuclear magnetic resonance spectroscopy and size-exclusion chromatography, SCPs call for more specific sequencing methods that permit the full characterization of monomer sequences (see Chapter 16). As highlighted in Figure 1.1, engineering aspects will also probably play an increasing role in the field of SCPs in the near future. Indeed, although SCPs are