Introduction

Living systems are capable of the synthesis of a wide range of different polyesters. Most of them are synthesized by plants as structural components of the cuticle covering the aerial parts of plants, such as cutin and suberin, or by prokaryotic microorganisms as intracellular storage compounds. These PHAs are water-insoluble. Furthermore, water-soluble polyesters are synthesized by a few eukaryotic organisms. In addition, polymers of, e.g., 3-hydroxybutyrate exhibiting a rather low degree of polymerization were detected, which are complexed with other biopolymers such as calcium polyphosphate or proteins. The latter were found in almost any living system investigated. However, the physiological function(s) were not revealed yet.

The chemical composition of insoluble cytoplasmic inclusions in the Gram-positive bacterium *Bacillus megaterium* was identified by Lemoigne in 1926 as poly(3-hydroxybutyric acid). By the end of the 1950s, sufficient evidence was accumulated from physiological studies to suggest that this biopolymer functions as an intracellular reservoir of carbon and energy. Meanwhile, it is known that this or structurally related (see below) storage polyesters are synthesized by members of almost any phylogenetic taxon of prokaryotes. In 1974, the identification of 3-hydroxyalkanoates other than 3-hydroxybutyrate, such as 3-hydroxyvalerate and 3-hydroxyhexanoate, was reported in chloroform extracts of activated sludge. Since the 1980s, many bacteria were demonstrated to synthesize various types of polyesters containing 3-, 4-, and 5-hydroxyalkanoate units. To date, approximately 150 different hydroxyalkanoates are known as constituents of these polyesters which are, therefore, generally referred to as polyhydroxyalkanoates (PHA).

The onset of the molecular biology revolution during the late 1970s provided new tools for biological research, which were successfully used to decipher genetic information and to better understand the principles behind PHA biosynthesis at the molecular level. By the end of the 1980s, the genes coding for enzymes involved in PHA biosynthesis were cloned from *Ralstonia eutropha* (formerly known as *Alcaligenes eutrophus*), and the genes were also shown to be functionally active in *Escherichia coli*. So far, about 60 PHA synthase structural genes have been cloned from different bacteria. In addition, many genes encoding enzymes and proteins relating to PHA biosynthesis were cloned and characterized at the molecular level. This strongly stimulated research and provided new perspectives for biotechnological production of PHAs. This knowledge has been utilized to establish PHA biosynthesis in many prokaryotic organisms and plants. The methodology of metabolic engineering was successfully applied for effective production of various PHAs by fermentation biotechnology
or agriculture in economically feasible processes. In particular transgenic plants expressing
PHA biosynthesis pathways may provide potential producers of PHAs in the future. One
important aspect is the large-scale biotechnological production of PHAs by fermentative
processes and by agriculture from renewable carbon sources and CO₂, respectively.

The PHA family of polyesters is thermoplastic with biodegradable and biocompatible
properties. Many of these water-insoluble polyesters can be thermoformed to various types of
products such as bottles, films and fibers like established petrochemical-based thermo-
plastics by using conventional extrusion and molding equipment. Some PHAs have become
commercially attractive for applications in various areas. Applications are also known for the
water-soluble polyester poly(malic acid). This explains the interest of industry in PHAs and
other polyesters as large-scale biotechnological products. The physical and mechanical
properties can be regulated by varying the composition of the polyesters. As a result, PHA can
be made in a wide variety of polymeric materials, from hard crystalline plastics to very elastic
rubber. Besides thermoplasticity, one of the most important characteristics of PHA products
is their biodegradability. PHA products such as films and fibers are degraded in soil, sludge
and seawater. Under optimum conditions the degradation rate is extremely fast. Many
prokaryotic and eukaryotic microorganisms excrete extracellular PHA depolymerases to
hydrolyze PHA products, and they utilize the decomposed compounds as nutrients. These
genes have also been cloned and characterized at a molecular level. Today, interdisciplinary
research and development of biological polyesters are rapidly expanding in both the
biological and polymer sciences. Concerted multidisciplinary scientific approaches have
been directed to elucidate various new aspects of PHA. One important impact of studying
and introducing natural polyesters was that efforts to establish new synthetic biodegradable
materials were strongly stimulated. As a consequence, many new biodegradable packaging
materials were developed by the chemical industry, and production processes for existing
synthetic polyesters were highly optimized. For example, polylactides, which were formerly
only affordable for medical applications, will now become also available for bulk applications.

This second volume on polyesters will focus on the biodegradability and further properties
of PHAs and other, synthetic polyesters and on the various methods for chemical synthesis of
polyesters. This volume starts with a description of the current and most effective methods to
reveal and determine the chemical composition of PHAs (Chapter 1). The intracellular
degradation of storage PHAs is described (Chapter 2) as well as our current knowledge on
extracellular PHA depolymerases (Chapter 3) and on extracellular degradation of these
polymers (Chapter 4). This part of the volume is completed by the description of the
influence of the structure and chemical composition of PHAs on their biodegradability
(Chapter 5). The following three chapters focus on various physical and other properties
such as solubility, crystallization and chemical stability of polyesters (Chapters 6-8). Next, the
technical processing and various applications of polyesters are presented (Chapter 9).
Processes for the biotechnological production of organic acids and other metabolites that can
be used for chemical synthesis of polyesters are described (Chapter 10). In the last part of this
volume (Chapters 11-13) methods of chemical synthesis of polyesters are described in detail.

These topics reflect the recent progress on polyester research, and we hope that these three
volumes will provide useful new information and knowledge for scientists of many
disciplines and to engineers from industry and for all others who want to gain deeper
knowledge on the biology of naturally occurring and synthetic polyesters and their
properties. Another aim of this book is to support ongoing interdisciplinary efforts to stimulate and improve the commercial production of polyesters and to broaden the uses and applications of these polymers.

We are very grateful to the many authors and experts in this field who contributed these excellent chapters to the three volumes on polyesters. The expertise, enthusiasm and the costly time, which they devoted to their chapters, is highly appreciated. We are well aware that all of them have many other obligations and duties. Without such committed individuals and scientists such a book could never have been prepared.

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