

Preface

Due to the possibility that petroleum supplies will be exhausted in the next decades to come, more and more attention has been paid to the production of bacterial plastics including polyhydroxyalkanoates (PHA), polylactic acid (PLA), poly(butylene succinate) (PBS), biopolyethylene (PE), poly(trimethylene terephthalate) (PTT), and poly(p-phenylene) (PPP). These are well-studied polymers containing at least one monomer synthesized via bacterial transformation.

Among them, PHA, PLA and PBS are well known for their biodegradability, whereas PE, PTT and PPP are probably less biodegradable or are less studied in terms of their biodegradability. Over the past years, their properties and applications have been studied in detail and products have been developed. Physical and chemical modifications to reduce their cost or to improve their properties have been conducted.

PHA is the only biopolyester family completely synthesized by biological means. They have been investigated by microbiologists, molecular biologists, biochemists, chemical engineers, chemists, polymer experts, and medical researchers for many years. PHA applications as bioplastics, fine chemicals, implant biomaterials, medicines, and biofuels have been developed. Companies have been established for or involved in PHA related R&D as well as large scale production. It has become clear that PHA and its related technologies form an industrial value chain in fermentation, materials, feeds, and energy to medical fields.

In this monograph, *Dr. Yaacov Okon* and his lab focus their attention on PHA as energy and intracellular carbon storage compounds that can be mobilized and used when carbon is a limiting resource. They describe the phenomena of intracellular accumulation of PHA, which enhances the survival of several bacterial species under environmental stress conditions imposed in water and soil, such as UV-irradiation, salinity, thermal and oxidative stress, desiccation, and osmotic shock. The ability to endure these stresses is linked to a cascade of events concomitant with PHA degradation and the expression of the genes involved in protection against damaging agents.

Dr. Sang Yup Lee reviews the strategies for the metabolic engineering of PHA producers, genomic and proteomic studies performed to understand the PHA biosynthesis in the context of whole cell metabolism and to develop further engineered strains. Finally, he suggests strategies for systems metabolic engineering of PHA

producers, which will make it possible to produce PHA with higher efficiencies and to develop tailor-made PHAs by systems-level optimization of metabolic network and establishment of novel pathways.

Drs. Martin Koller and Gerhart Braunegg suggest that facilities for the production of biopolymers, biofuels and biochemicals should be integrated into existing production lines, where the feedstock directly accrue as waste streams, to save costs on transportation. They point out that the utilization of waste streams for production of value-added products not only enhances the economics of such products, but also provides the industry with a strategy to overcome disposal problems.

Dr. José M. Luengo found that unusual polyhydroxyalkanoates (UnPHAs) constitute a particular group of polyoxo(thio)esters belonging to the PHA family, which contain uncommon monomers. He classifies the UnPHAs into four classes and discusses some of their characteristics and biotechnological applications.

Despite some successes in PHA production by plants, *Drs. Yves Poirier and Stevens Brumbley* believe production of PHA in crops and plants remains a challenging project. The challenges for the future are to succeed in the synthesis of PHA co-polymer with a narrow range of monomer composition, at levels that do not compromise plant productivity, and to find methods for efficient and economical extraction of polymers from plants. These goals will undoubtedly require a deeper understanding of plant biochemical pathways and advances in biorefinery.

Dr. Manfred Zinn focuses on the production of medium-chain-length poly[(R)-3-hydroxyalkanoates] (mcl-PHAs) in pseudomonads. He reviews the biosynthesis of mcl-PHA in high cell density cultures that is economically very important.

Dr. Isao Noda has been working on the family of PHA called Nodax™ that consists of (R)-3-hydroxyalkanoate comonomer units with medium size chain side groups and (R)-3-hydroxybutyrate. Because of the unique design of their molecular structure, the Nodax™ class PHA copolymers have a set of useful attributes, including polyolefin-like thermo-mechanical properties, polyester-like physico-chemical properties, and interesting biological properties. Therefore, a broad range of industrial and consumer product applications are anticipated.

Drs Tadahisa Iwata and Toshihisa Tanaka succeeded in obtaining strong fibers, using two new ways of drawing techniques, from microbial PHA polyesters produced by both wild-type and recombinant bacteria. The improvement in the mechanical properties of the fibers is due not only to the orientation of molecular chains but also to the generation of a planar zigzag conformation. They present the processing, mechanical properties, molecular and highly-ordered structure, enzymatic degradation, and bioabsorption of strong fibers and nanofibers produced from microbial polyesters.

Drs. Philippe Guérin, Estelle Renard and Valérie Langlois found that all polyesters are susceptible to degradation by simple hydrolysis to some extent. The degradation rate is highly dependent on the chemical structure and material crystallinity. One way to obtain more hydrophilic PHA is to introduce specific functions in the macromolecular side chains. The combination of bioconversion and organic chemistry allows modulating the physical properties of these bacterial polyesters as solubility,

hydrophilic/hydrophobic balance, and water stability in the perspective of biomedical applications.

Drs. K. Jim Jem, Johan F. van der Pol and Sicco de Vos calculated lactic acid derivatives back to the equivalent amount of original lactic acid, and they concluded that the total global market volume in 2008 is estimated at around 260,000 metric tons of lactic acid (calculated at 100% concentration) for traditional applications (excluding PLA). They claim that today more than 95% of lactic acid produced is derived from biological sources (e.g. sucrose or glucose from starch) by microbial fermentation, which typically produces the L(+) form of lactic acid.

Besides lactic acid, *Dr Jun Xu* opines that increasing demand on biodegradable poly(butylene succinate) (PBS) will open a new market for succinic acid produced via microbial fermentation. He reviews the synthesis of succinic acid, PBS polymerization, crystalline structure, thermal and mechanical properties, and biodegradability.

Polyethylene is an important engineering material. It has been traditionally produced through the ethylene polymerization process. Ethylene can be produced through steam cracking of ethane, steam cracking of naphtha or heavy oils, or ethanol dehydration. With the increase in oil prices, bio-ethylene, produced through ethanol dehydration, is a more important production route for ethylene. Based on the ethanol dehydration chemistry principle, *Dr. He Huang* describes the research and development progress on catalysts and the process of ethanol dehydration to form ethylene.

Poly(trimethylene terephthalate) (PTT) fiber, as a new type of polyester, has been characterized by much better resilience and stress/recovery properties than poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). *Dr Dehua Liu* proved that PTT is highly suitable for uses in fiber, carpet, textile, film, and engineering thermoplastic applications. With this in mind, his lab has developed highly efficient fermentation technology based on glycerol for 1,3-propanediol (PDO) which is a monomer of PTT.

Benzene *cis*-diols, namely, *cis*-3,5-cyclohexadien-1,2-diols abbreviated as DHCD, can be used for synthesis of poly(*para*-phenylene) (PPP), which is a material with high thermal stability and electricity conducting ability when doped. Several types of bacterial dioxygenases, that can catalyze the conversion of aromatic compounds to their corresponding *cis*-diols, which can be polymerized to form PPP, are discussed.

With the support of the above experts, we are able to offer the readers up-to-date information on the bacterial plastics. We are grateful to the authors who have contributed these excellent chapters. Our thanks also go to Springer for publishing this monograph, especially to Jutta Lindenborn for all his/her effort in helping us.

Finally, I (George Guo-Qiang Chen) would also like to thank my wife Sherry Xuanming Xu and daughter Jenny Jiani Chen for supporting my effort to bring out this monograph.

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