194
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Enzyme-Catalyzed Synthesis of Polymers

Volume Editors:
Shiro Kobayashi · Helmut Ritter · David Kaplan

With contributions by
D. L. Kaplan · S. Kobayashi · S. Matsumura · M. Ohmae
M. Reihmann · H. Ritter · A. Singh · H. Uyama · P. Xu

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Preface

This special volume on the enzyme-catalyzed synthesis of polymers focuses on various methods of polymer synthesis using enzymes as catalysts. There are three cases for such synthetic processes: (1) In living cells (in vivo) enzymes catalyze the synthesis of all biopolymers besides other biological substances via biosynthetic (metabolic) pathways. In test tubes (in vitro) enzymatic catalysis is achieved for the synthesis of polymers via (2) biosynthetic pathways or (3) non-biosynthetic pathways. The present volume is concerned with case (3). Therefore, studies such as the synthesis of polyesters via fermentation using micro-organisms and synthesis of proteins using *E. coli* are not included.

All enzymes are categorized into six groups: (1) oxidoreductases, (2) transferases, (3) hydrolases, (4) lyases, (5) isomerases, and (6) ligases. They show respective catalytic functions specific to the substrate group in vivo. In this volume, however, each chapter is organized on the basis not of the enzyme category but on the class of polymers synthesized. Enzymatic synthesis of polymers (often referred to as enzymatic polymerization) is operated by in vitro enzymatic catalysis, which is close to or very similar to in vivo enzymatic catalysis depending on the reaction.

In vivo enzymatic catalysis has advantageous characteristics: high catalytic activity (high turnover), reactions under mild conditions with respect to temperature, pressure, solvent, neutral pH, etc., and excellent reaction control of stereo-, regio-, chemo-, enantio- and choro-selectivities. These characteristics can also be realized in vitro depending upon the catalyst. Therefore, the reactions contribute to the alleviation of environmental problems due to their low loading processes (energy saving), clean processes (without forming by-products), and the biodegradable nature of product polymers in many cases. These are often difficult to realize by conventional methods.

The first chapter by Reihmann and Ritter reviews the recent developments of peroxidase-catalyzed oxidative polymerization of phenol and derivatives with a phenolic OH group. The importance of enzymatic polymerization in general is emphasized. Properties of product polyphenols, characteristics of the enzyme catalysis, and significance of the process and the product are discussed. The second chapter by Uyama and Kobayashi is concerned with the oxidative polymerization of polyphenols, which are compounds containing more than two phenolic OH groups. These compounds include catechols and flavonoids

such as urushiol and catechin. The anti-oxidant properties of flavonoids were greatly enhanced by the polymerization. In the next chapter, Xu, Singh and Kaplan described the synthesis of polyaniline and their derivatives by using oxidoreductase enzymes and biomimetic catalysts. In the presence of templates, the polymer structure was controlled to produce processable materials, which can be used for electrical contact applications, such as synthetic–biological interfaces. The dip-pen nanolithography technique was used for the processing.

The fourth chapter by Matsumura overviews the lipase-catalyzed polyester synthesis via ring-opening polymerization of lactones. A hydrolysis enzyme of lipase, catalyzing the hydrolysis of esters to break the ester-bond in vivo, catalyzed the ester-bond formation to produce polyesters. In comparison with conventional methods, characteristics of the ring-opening polymerizability by lipase catalysis was pointed out, and the reaction mechanism was extensively discussed. A chemical recycling process using a polymer-oligomer equilibrium is proposed. The following chapter by Uyama and Kobayashi describes various polycondensations for the polyester synthesis catalyzed by lipase. Divinyl esters were found to be very effective monomers for the reactions. Dehydration was accomplished in water with lipase catalyst.

In the sixth chapter, Kobayashi and Ohmae reviewed polysaccharide synthesis by hydrolase-catalyzed polymerizations. The general characteristics of enzymatic polymerization and the importance of a new concept for monomer design called transition-state analogue substrates are mentioned. New enzyme-recognizable substrates were designed as two families, sugar fluoride monomers and sugar oxazoline monomers. The polycondensation of the former and the ring-opening polyaddition of the latter enabled the first successful chemical synthesis of natural polysaccharides like cellulose, xylan, chitin, hyaluronan, chondroitin and their derivatives as well as unnatural polysaccharides. Reaction mechanisms and high-order molecular structure formation from the product polymers are also discussed.

In the last chapter by Singh and Kaplan, vinyl polymerizations induced by oxidoreductase enzymes are described, where a mediator is normally used. The reaction is of radical-type to form a C – C bond main chain. Vitamin C-functionalized vinyl monomers and others were polymerized. Such in vitro reactions are unique because nature does not utilize the vinyl-type C – C bond formation reaction except for natural rubber synthesis via polycondensation.

The interdisciplinary topics presented are expected to bridge the fields of materials science (including polymer science) and life science.

Kyoto, Düsseldorf, Medford *Shiro Kobayashi, Helmut Ritter, David Kaplan*
October 2005

Contents