

Preface

The application of nature's toolset is a fast-growing area in several industries, such as food, fine chemicals and polymers. Specifically in vitro enzymatic catalysis has seen a steady increase in (industrial) applications where enzyme catalysis has established itself as an indispensable tool in the synthesis of small molecules. Examples can be found in the production of pharmaceutical intermediates, where biotechnology generates significant turnover and reduces the environmental impact. In recent years, enzyme catalysis was also successfully applied in polymer synthesis. The motivation for using enzymes in polymer synthesis was initially mainly scientific curiosity, but as this technology started to produce results comparable to conventional polymerizations, the potential was recognized. The possibility of making polymers that are not available from conventional methods and their natural character make enzymes a particularly promising catalytic system. The goal of this book is to provide an overview of enzyme catalysis in polymer synthesis structured according to the different enzyme classes used in these reactions. Notably, three of the six enzyme groups have been reported in enzymatic polymerization in vitro, i.e. oxidoreductases, transferases and hydrolases.

Chapter 1 reviews recent advances in the field of biocatalytic synthesis of water-soluble conducting polymers using oxidoreductases. This class of enzymes catalyses the reduction or oxidation of functional groups. Horseradish peroxidase (HRP), obtained from natural and renewable sources, efficiently catalyzes the oxidative polymerization of aniline and phenol-based monomers under benign conditions. In addition, the technologically relevant conjugated polymer poly-3,4-ethylenedioxythiophene (PEDOT) can be accessed using HRP catalysis. This biocatalytic method results in PEDOT materials that show a high electrical conductivity and possess excellent film formation, making it a valuable tool in the preparation of functional polymers.

Chapter 2 summarizes the application of transferases in polymer chemistry. Transferases are enzymes transferring a group from one compound (donor) to another compound (acceptor). Of the three classes of enzymes used in polymer science, transferases are the least frequently applied, which is due to their sensitivity. Nonetheless, several transferases such as phosphorylases and synthases have been

found to be effective for catalyzing the *in vitro* synthesis of polysaccharides and polyesters and well-defined polymers with a variety of architectures have become available.

Enzymes that belong to the class of hydrolases are by far the most frequently-applied enzymes in polymer chemistry and are discussed in Chaps. 3–6. Although hydrolases typically catalyse hydrolysis reactions, in synthetic conditions they have also been used as catalysts for the reverse reaction, i.e. the bond-forming reaction. In particular, lipases emerged as stable and versatile catalysts in water-poor media and have been applied to prepare polyesters, polyamides and polycarbonates, all polymers with great potential in a variety of biomedical applications.

Chapter 3 focuses on the increased understanding in enzymatic strategies for the production of well-defined polymers. A wide variety of (co)polymers has been synthesised and explored in a variety of applications using lipase catalysts. On the other hand, detailed studies also revealed the limitations of the use of lipases: as a result of the monomer-activation mechanism, polymers of low polydispersity and quantitative degree of end-group functionality are difficult to attain.

Chapter 4 shows that the range of polymeric structures from enzymatic polymerization can be further increased by combination with chemical methods. The developments in chemoenzymatic strategies towards polymeric materials in the synthesis of polymer architectures such as block and graft copolymers and polymer networks are highlighted. Moreover, the combination of chemical and enzymatic catalysis for the synthesis of unique chiral polymers is discussed.

Chapter 5 shows that the application of hydrolytic enzymes is a powerful yet mild strategy to directly improve polymer surface properties (i.e. hydrophilicity) or activate materials for further processing. The surface hydrolysis of polyamides (PA), polyethyleneterephthalates (PET) and polyacrylonitriles (PAN) is discussed, as well as the mechanistic details on the enzymatic surface hydrolysis. The mechanistic data, combined with advances in structural and molecular biology, help to explain different activities of closely related enzymes on polymer surfaces.

Finally, Chap. 6 deals with the exploitation of biocatalysis in generating supramolecular polymers, a class of polymers where the monomers are connected via non-covalent bonds. This approach provides highly dynamic and reversible supramolecular structures, inspired by biological polymeric systems found in the intra- and extracellular space. A number of potential applications of enzymatic supramolecular polymerizations are discussed in the context of biomedicine and nanotechnology.

From the present book and the work of numerous researchers in the field, it becomes clear that enzymatic polymerization presents a serious alternative to chemical synthesis. Significant progress has been achieved in recent years in this relatively young polymerization technique. As with all polymerization techniques, enzymatic polymerizations have their advantages and disadvantages. It is clear that many challenges still have to be overcome, even for polymer systems in which the enzymatic processes have significantly advanced, as is the case for polyester synthesis. Nevertheless, enzymes hold significant promises with respect to green polymer chemistry and as an additional tool for the synthesis of functional polymers. However, the

advantages of enzymes are not directly transferable from small molecule synthesis to polymers. While much fundamental research has been done in the past and will be needed in the future on this topic, we are approaching a transition towards the development of integrated green processes in polymer science, and enzymatic polymerization is one element of this transition.

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