

Preface

It is the mark of an instructed mind to rest satisfied with the degree of precision which the nature of the subject permits and not to seek exactness where only an approximation of the truth is possible.

Aristotle (384-322 BC)

The art of being wise is the art of knowing what to overlook.

William James (1842 – 1910)

The manufacture of polyolefins with coordination catalysts has been a leading force in the synthetic plastic industry since the early sixties. Due to constant developments in catalysis, polymerization processes, and polyolefin characterization instruments, it continues to be a vibrant area of research and development today.

We have been working in this area for over fifteen years, always feeling that there was a need for a book that summarized the most important aspects of polyolefin reaction engineering. This book reflects our views on this important industry. It grew out of interactions with the polyolefin industry through consulting activities and short courses, where we first detected a clear need to summarize, in one single source, the most generally accepted theories in olefin polymerization kinetics, catalysis, particle growth, and polyolefin characterization.

As quoted from Aristotle above, we will *rest satisfied with the degree of precision which the nature of the subject permits* and hope that our readers agree with us that this is indeed *the mark of an instructed mind*. It was not our intention to perform an extensive scholarly review of the literature for each of the topics covered in this book. We felt that this approach would lead to a long and tedious text that would become quickly outdated; several excellent reviews summarizing the most recent findings on polyolefin manufacturing and characterization are published regularly, and are more adequate for this purpose. Instead, we present our very personal interpretation of the field of polyolefin reaction engineering. Since any selection process is always subjective, we may have left out some approaches considered to be relevant by others, but we tried to be as encompassing as possible considering the limitations of a book of this type. We have also made sparse use of references in the main body of the chapters, but added reference sections at their end where we discussed some alternative theories, presented exceptions to the general approach followed in the chapters, and suggested additional readings. The reference sections are not meant to be exhaustive compilations of the literature, but sources of supplemental readings and a door to the vast literature in the area. We hope this approach will make this book a pleasant reading and also provide the reader with additional sources of reference.

Chapter 1 introduces the field of polyolefins, with an overview on polyolefin types, catalyst systems, and reactor configurations. We also introduce our general philosophy of using mathematical models to link polymerization kinetics, mass and heat transfer processes at several length scales, and polymer microstructure characterization for a complete understanding of olefin polymerization processes.

We discuss polyolefin microstructure, as defined by their distributions of molecular weight, chemical composition, stereo- and regioregularity, and long chain branching in Chapter 2. It is not an overstatement to say that, among all synthetic polymers, polyolefins are the ones where microstructure control is the most important concern. Polyolefin microstructure is a constant theme in all chapters in this book, and our best guide to understanding catalysis, kinetics, mass and heat transfer resistances, and reactor behavior.

Chapter 3 is dedicated to polymerization catalysis and mechanisms. The field of coordination catalysis is huge and, undoubtedly, the main driving force behind innovation in the polyolefin manufacturing industry; to give it a complete treatment, a separate book would be necessary. Rather, we decided to focus on the most salient aspects of the several classes of olefin catalysts, their general behavior patterns and mechanisms, and how they can be related to polymerization kinetics and polyolefin microstructural properties.

The subject of Chapter 4, polymerization reactors, is particularly dear to us, polymer reactor engineers. In fact, polyolefin manufacturing is a “dream come true” for polymer reactor engineers, because practically all possible configurations of chemical reactors can be encountered. A great deal of creativity went into reactor design, heat removal strategies, series and parallel reactor arrangements, and cost reduction schemes of polyolefin reactors. We start the chapter by discussing reactor configurations used in olefin polymerization and then follow with a description of the leading processes for polyethylene and polypropylene production.

Chapter 5 is the first chapter dedicated to the mathematical modeling of olefin polymerization. We will start our derivations with the standard model for olefin polymerization kinetics and develop, from basic principles, its most general expressions for the rates of catalyst activation, polymerization and catalyst deactivation. The standard model, albeit widely used, does not account for several phenomena encountered in olefin polymerization; therefore, some alternative polymerization kinetic schemes are discussed at the end of this chapter.

In Chapter 6 we develop mathematical models to describe the microstructure of polyolefins. This is one of the core chapters of the book, and helps connect polymerization kinetics, catalysis, and mass and heat transfer resistances to final polymer performance. We opted to keep the mathematical treatment as simple as possible, without compromising the most relevant aspects of this important subject.

Particle fragmentation and growth are covered in Chapter 7. These models are collectively called single particle models, and can be subdivided into polymer growth models and morphology development models. The two most well-established particle growth models are the polymeric flow model and the multigrain model. These models are used to describe heat and mass transfer in the polymeric particle after fragmentation takes

place. The fragmentation of the catalyst particles themselves (described with morphology development models) is much harder to model and there is still no well accepted quantitative model to tackle this important subject. We will review the main modeling alternatives in this field. Finally, particle-to-particle and particle-to-wall interactions, equally important and hard subjects, will also be covered in Chapter 7.

Finally, Chapter 8 is dedicated to macroscopic reactor modeling. This chapter is, in a way, the most conventional chapter from a chemical engineering point of view, since it involves well-known concepts of reactor residence time distribution, micromixing and macromixing, and reactor heat removal issues. The combination of macroscopic reactor models, single-particle models, detailed polymerization kinetics and polymer microstructural distributions, however, is very challenging and represents the ultimate goal of polyolefin reactor engineers.