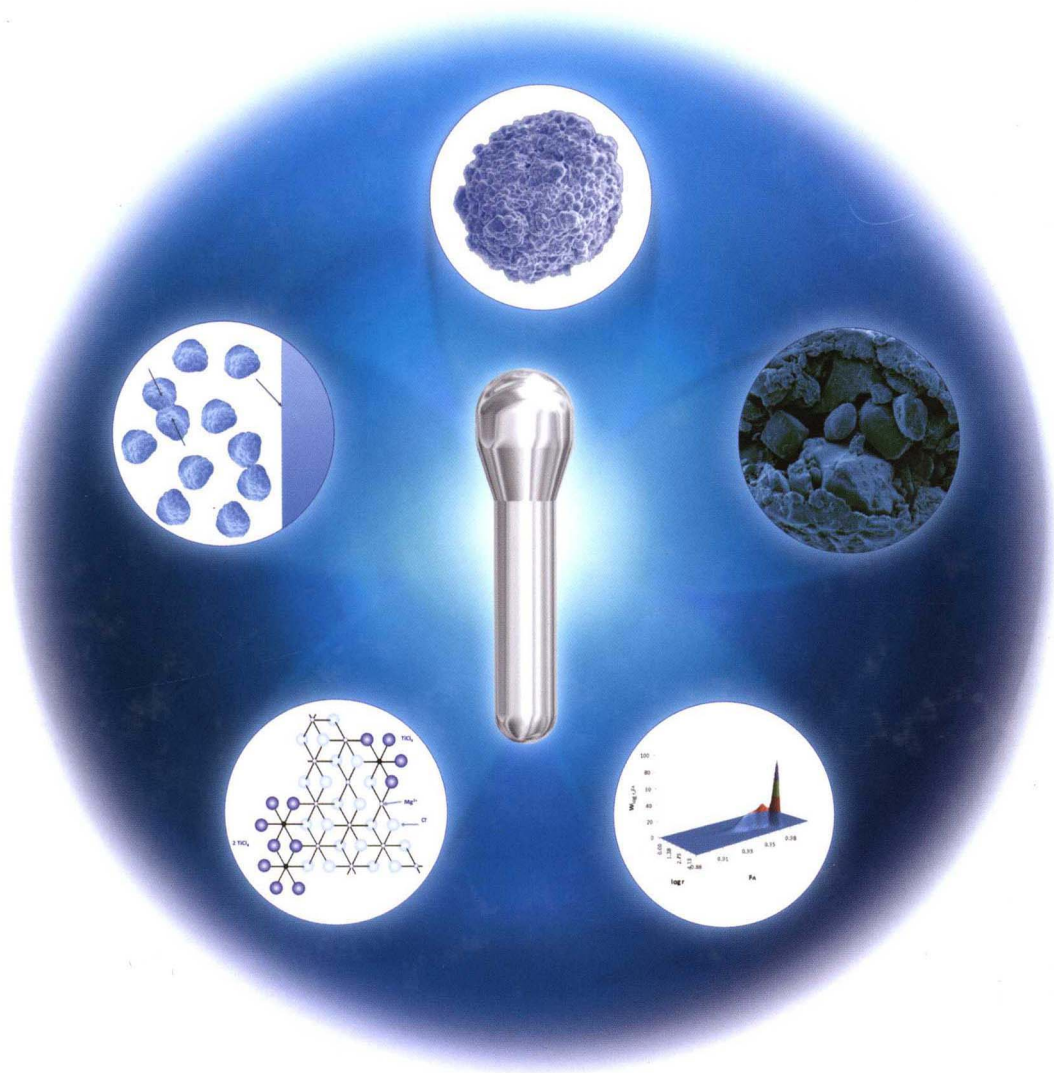


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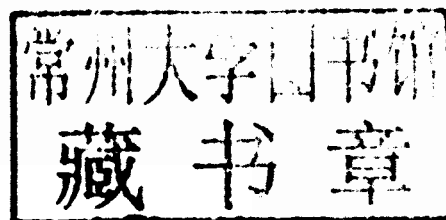
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# Polyolefin Reaction Engineering



*João B. P. Soares and Timothy F. L. McKenna*

## **Polyolefin Reaction Engineering**



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## The Authors

### **Prof. Dr. João B. P. Soares**

University of Waterloo  
Department of Chemical Engineering  
University Avenue West 200  
Waterloo, ON N2L 3G1  
Canada

### **Prof. Dr. Timothy F. L. McKenna**

C2P2 UMR 5265  
ESCPE Lyon, Bat 308F  
43 Blvd du 11 Novembre 1918  
69616 Villeurbanne Cedex  
France

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*To our wives, Maria Soares and Salima Boutti-McKenna, for their love, dedication, and patience while we wrote this book, not to mention the interminably long hours we spent discussing polyolefins in their presence. This book belongs to both of you, but you don't need to read it – you have heard all about it already.*

*João Soares and Timothy McKenna*

## Acknowledgments

*Personally I'm always ready to learn, although I do not always like being taught.*

Sir Winston Churchill (1874–1965)

Several of the concepts covered in this book arose from our daily interactions with students and colleagues in academia and industry. They are too many to be named individually here, but we would like to express our sincere gratitude to their outstanding contributions that are summarized in this work. We did like being thought by all of you.

First, we would like to thank our former mentors, who trusted and guided us when we were starting our careers, and kept encouraging us throughout these years. Their mentoring, support, and friendship are greatly appreciated.

This book could not have been written without the dedication of our graduate students, post-doctoral fellows, and research assistants, who toiled day after day in our laboratories to propose and test hypotheses, challenge us with unexpected new results, and in the process advance our understanding of polyolefin reaction engineering. Several of their results are interspersed throughout this book and constitute main contributions to the field of olefin polymerization science and engineering. We are very thankful to their hard work, perseverance, and confidence in us as their supervisors.

We would also like to thank our academic and industrial collaborators who over the years helped us better understand olefin polymerization and polyolefin characterization, often kindly allowing us to use their laboratory facilities (for free!) to complement the work done in our institutions. We are indeed indebted to these extraordinary colleagues and look forward to continue working with them in the future.

Finally, we would like to thank the polyolefin companies all over the world that have hired us as consultants and instructors of our industrial short course on *Polyolefin Reaction Engineering*. This book is a result, in large part, from the stimulating discussions we had with the scientists and engineers who took these courses. If it is true, as said by Scott Adams, the creator of the comic strip *Dilbert*, that “Give a man a fish, and you’ll feed him for a day. Teach a man to fish, and he’ll buy a funny hat. Talk to a hungry man about fish, and you’re a

*consultant*”, then we hope that talking to the course participants over these years has at least stimulated them to look deeper into the vast sea of polyolefin reaction engineering.



## 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 1960s. Owing to the 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 15 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 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 sparsely used 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 of this book and is 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 proper 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 continue 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 start our derivations with what we like to call the fundamental 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 fundamental 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 review the main modeling alternatives in this field.

Finally, Chapter 8 is dedicated to macroscopic reactor modeling. This chapter is, in a way, the most conventional chapter from the 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.

## Nomenclature

What's in a name? William Shakespeare (1564–1616)

### Acronyms

CCD	chemical composition distribution
CEF	crystallization elution fractionation
CFC	cross-fractionation
CGC	constrained geometry catalyst
CLD	chain length distribution
CRYSTAF	crystallization analysis fractionation
CSLD	comonomer sequence length distribution
CSTR	continuous stirred tank reactor
CXRT	computed X-ray tomography
DEAC	diethyl aluminum chloride
DIBP	di-iso-butylphthalate
DSC	differential scanning calorimetry
EAO	ethylaluminumoxane
EB	ethyl benzoate
EDX	energy dispersive X-ray spectroscopy
EGMBE	ethylene glycol monobutylether
ELSD	evaporative light scattering detector
EPDM	ethylene-propylene-diene monomer rubber
EPR	ethylene-propylene rubber
FBR	fluidized bed reactor
FFF	field flow fractionation
FTIR	Fourier-transform infrared
GPC	gel permeation chromatography
HDPE	high-density polyethylene
HMDS	hexamethyldisilazine
HPLC	high-performance liquid chromatography
HSBR	horizontal stirred bed reactor

IR	infrared
LALLS	low-angle laser light scattering
LCB	long-chain branch
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LS	light scattering
MALLS	multiangle laser light scattering
MAO	methylaluminoxane
MDPE	medium-density polyethylene
MFI	melt flow index
MFR	melt flow rate
MGM	multigrain model
MI	melt index
MWD	molecular weight distribution
MZCR	multizone circulating reactor
NMR	nuclear magnetic resonance
NPTMS	<i>n</i> -propyltrimethoxysilane
ODCB	orthodichlorobenzene
PDI	polydispersity index
PFM	polymer flow model
PFR	plug flow reactor
PP	polypropylene
PSD	particle size distribution
RND	random number generated in the interval [0,1]
RTD	residence time distribution
SCB	short-chain branch
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SLD	sequence length distribution
SPM	single particle model
<i>t</i> BAO	<i>t</i> -butylaluminoxane
TCB	trichlorobenzene
TEA	triethyl aluminum
TEM	transmission electron microscopy
TGIC	temperature gradient interaction chromatography
TMA	trimethyl aluminum
TOF	turnover frequency
TREF	temperature rising elution fractionation
UHMWPE	ultrahigh-molecular weight polyethylene
ULDPE	ultralow-density polyethylene
VLDPE	very low-density polyethylene
VISC	viscometer
VSBR	vertical stirred bed reactor

## Symbols

$a$	Mark–Houwink equation constant, Eq. (2.7)
$a_s$	specific surface area of the support
$A$	monomer type A
$A$	total reactor heat transfer area
$A_i$	Arrhenius law preexponential factor for reaction of type $i$
$A_s$	support specific surface area
$Al$	cocatalysts
$[AS^*]$	concentration of active sites per unit surface area in the microparticle
$B$	monomer type B
$B_n$	average number of long-chain branches per polymer chain
$C$	catalyst precursor or active site
$C^*$	active site
$[C_0]$	initial concentration of active sites
$C_d$	deactivated catalytic site
$C_p$	heat capacity
$D_b$	bulk diffusivity
$D_{eff}$	effective diffusivity in the macroparticle
$d_p$	polymer (or catalyst) particle diameter
$D_p$	diffusivity in the primary particle
$D_r$	dead polymer chain
$D_{r,i}$	dead polymer chain of length $r$ having $i$ long-chain branches
$D_{r,i}^-$	dead polymer chain of length $r$ having $i$ long-chain branches and a terminal unsaturation (macromonomer)
$E(t)$	reactor residence time distribution
$E_i$	Arrhenius law activation energy for reaction of type $i$
$f^-$	molar fraction of macromonomers in the reactor
$f_i$	molar fraction of monomer type $i$ in the polymerization medium
$f_r$	frequency Flory chain length distribution, Eq. (6.13)
$\bar{f}_r$	overall frequency chain length distribution for chain having long-chain branches, Eq. (6.101)
$f_{rk}$	frequency chain length distribution for chains with $k$ long-chain branches per chain, Eq. (6.86)
$f_{\log r k}$	frequency chain length distribution for chains with $k$ long-chain branches per chain, log scale, Eq. (6.88)
$F$	monomer molar flow rate to the reactor
$F_A$	comonomer molar fraction in the copolymer
$\bar{F}_A$	average comonomer molar fraction in the copolymer
$F_{Br}$	molar fraction of comonomer B as a function of chain length
$F_{M,in}$	molar flow rate of the monomer feed to the reactor
$F_{M,out}$	molar flow rate of the monomer exiting the reactor
$g$	branching index, Eq. (2.18)
$g'$	viscosity branching index, Eq. (2.17)
$\Delta G$	Gibbs free energy change

$h$	average convective heat transfer coefficient between the macroparticle and surroundings
$\Delta H$	enthalpy change
$\Delta H_p$	average enthalpy of polymerization
$\Delta H_r$	enthalpy of reaction
$\Delta H_u$	enthalpy of melting for a crystallizable repeating unit, Eq. (2.26)
$\Delta H_{\text{vap}}$	enthalpy of vaporization
$I_1$	Bessel function of the first kind and order 1
$k_a$	site activation rate constant
$k_c, k_c^-$	forward and reverse rate constants, respectively, for the formation of dormant site with Ni-diimine catalysts, Table 5.8
$k_d$	first-order deactivation rate constant
$k_d^*$	second-order deactivation rate constant
$k_f$	forward rate constant for reversible monomer coordination or $\beta$ -agostic interaction; thermal conductivity
$k_{\text{fl}}$	effective thermal diffusivity in the macroparticle
$k_{\text{fp}}$	thermal conductivity of the polymer layer around the catalyst fragment in the microparticle
$k_{\text{iH}}$	rate constant for initiation of metal hydride active sites
$k_p$	propagation rate constant
$k'_p$	apparent propagation rate constant, Eq. (5.115)
$\hat{k}_p$	pseudo-propagation rate constant
$\tilde{k}_p$	apparent propagation rate constant
$k_{\text{pi}}$	propagation rate constant for monomer type $i$ (Bernoullian model)
$k_{\text{pij}}$	propagation rate constant for chain terminated in monomer type $i$ coordinating with monomer type $j$ (terminal model)
$k_{\text{pijk}}$	propagation rate constant for chain terminated in monomer types $i$ and $j$ coordinating with monomer type $k$ (penultimate model)
$k_{\text{pm}}$	propagation rate constant for meso insertion (propylene)
$k_{\text{pr}}$	propagation rate constant for racemic insertion (propylene)
$k_r$	reverse rate constant for reversible monomer coordination or $\beta$ -agostic interaction
$k_{\text{tAl}}$	rate constant for transfer to cocatalyst
$k_{\text{t}\beta}$	rate constant for $\beta$ -hydride elimination
$k_{\text{tH}}$	rate constant for transfer to hydrogen
$k_{\text{tM}}$	rate constant for transfer to monomer
$K$	Mark–Houwink equation constant, Eq. (2.7)
$K_a$	initiation frequency, $k_a[\text{Al}]$
$K_{\text{eq}}$	equilibrium constant for dormant sites, Eq. (5.67)
$K_{\text{g-l}}, K_{\text{g-l}}^*$	gas–liquid partition coefficients, Eq. (5.113)

$K_{g-s}, K_{g-s}^*, K_{g-s}'$	gas–solid partition coefficients, Eqs (5.111) and (5.114)
$K_{l-s}$	liquid–solid partition coefficient, Eq. (5.112)
$K_H$	Henry law constant
$K_T$	lumped chain-transfer constant, Eq. (5.74)
$K_T^1$	lumped chain-transfer constant, Eq. (5.70)
$K_T^H$	lumped chain-transfer constant, Eq. (5.71)
$m_i$	mass fraction of polymer made on site type $i$
$m_k$	mass fraction of chains with $k$ long-chain branches
$m_p$	mass of polymer, polymer yield
$\dot{m}_{\text{vap}}$	vaporization rate
mw	molecular weight of repeating unit; in the case of copolymers, the average molecular weight of the repeating units
$M$	molecular weight
$M$	monomer
$M_C$	molar mass of catalyst
$M_n$	number average molecular weight
$M_v$	viscosity average molecular weight
$M_w$	weight average molecular weight
MW	polymer molecular weight
$n$	number of long-chain branches per chain; number of active site types
$n_c(v)$	polymer particle size distribution
$n_{C_0}, n_{C_0}$	number of moles of catalyst
$n_{\text{LCB}}$	average number of long-chain branches in a polymer sample
$n_M$	number of moles of monomer
$n_w$	weight average number of long-chain branches per chain
$N_A$	Avogadro number
$N_i$	flux of species $i$
$N_s$	number of macroparticles per unit volume of the reactor
Nu	Nusselt number
$P_A, P_B$	probability of propagation of monomers A and B, respectively
$P_H^*$	metal hydride active site
$P_M$	partial pressure of monomer
$P_p$	propagation probability
$P_r$	living chain with length $r$
$P_r^i$	living polymer chain with length $r$ terminated in monomer type $i$ (A or B for binary copolymers) or 1-2 or 2-1 insertions for polypropylene
$P_{r,i}^*$	living polymer chain of length $r$ having $i$ long-chain branches
$\tilde{P}_1$	dormant site due to $\beta$ -agostic interaction, Table 5.5
$\tilde{P}_r$	dormant site for Ni-diimine catalysts, Table 5.8
$P_t$	termination probability
PDI	polydispersity index



$\overline{\text{PDI}}$	polydispersity index for chains containing long-chain branches
$\text{PDI}_{F_A}$	polydispersity index as a function of copolymer composition
$\text{PDI}_k$	polydispersity index for chain with $k$ long-chain branches, Eq. (6.106)
$\text{Pr}$	Prandtl number
$\dot{Q}$	heat generation rate
$r$	polymer chain length
$r_i$	comonomer reactivity ratio
$r_L$	radial position in macroparticle (multigrain model)
$r_n$	number average chain length
$\bar{r}_n$	number average chain length for chains containing long-chain branches, Eq. (6.107)
$\tilde{r}_n$	number average molecular weight that would result in the absence of long-chain branch formation reactions, see footnote 13 in Chapter 6
$r_{nF_A}$	number average chain length as a function of copolymer composition
$r_{nk}$	number average chain length for chains with $k$ long-chain branches, Eq. (6.103)
$r_s$	radial position in the microparticle (multigrain model)
$r_w$	weight average chain length
$\bar{r}_w$	weight average chain length for chains containing long-chain branches, Eq. (6.108)
$r_{wF_A}$	weight average chain length as a function of copolymer composition
$r_{wk}$	weight average chain length for chains with $k$ long-chain branches, Eq. (6.104)
$r_{zk}$	z-average chain length for chains with $k$ long-chain branches, Eq. (6.105)
$\overline{r_0^2}$	root-mean-square end-to-end distance of a polymer chain
$R$	gas constant
$R_c$	catalyst fragment radius (multigrain model)
$R_i$	reaction rate of species $i$
$\langle R_g^2 \rangle_b$	squared radius of gyration of branched chains
$\langle R_g^2 \rangle_l$	squared radius of gyration of linear chains
$R_L$	macroparticle radius (multigrain model)
$R_p$	polymerization rate
$\overline{R_p}$	average polymerization rate per unit volume of the reactor
$\overline{R_p'}$	average polymerization rate per polymer particle
$R_S$	microparticle radius (multigrain model)
$R_t$	chain-transfer rate
$\text{Re}$	Reynolds number
$\Delta S$	entropy change
$\text{Sc}$	Schmidt number
$\text{Sh}$	Sherwood number
$t$	time