J. B. P. Soares, T. F. L. McKenna

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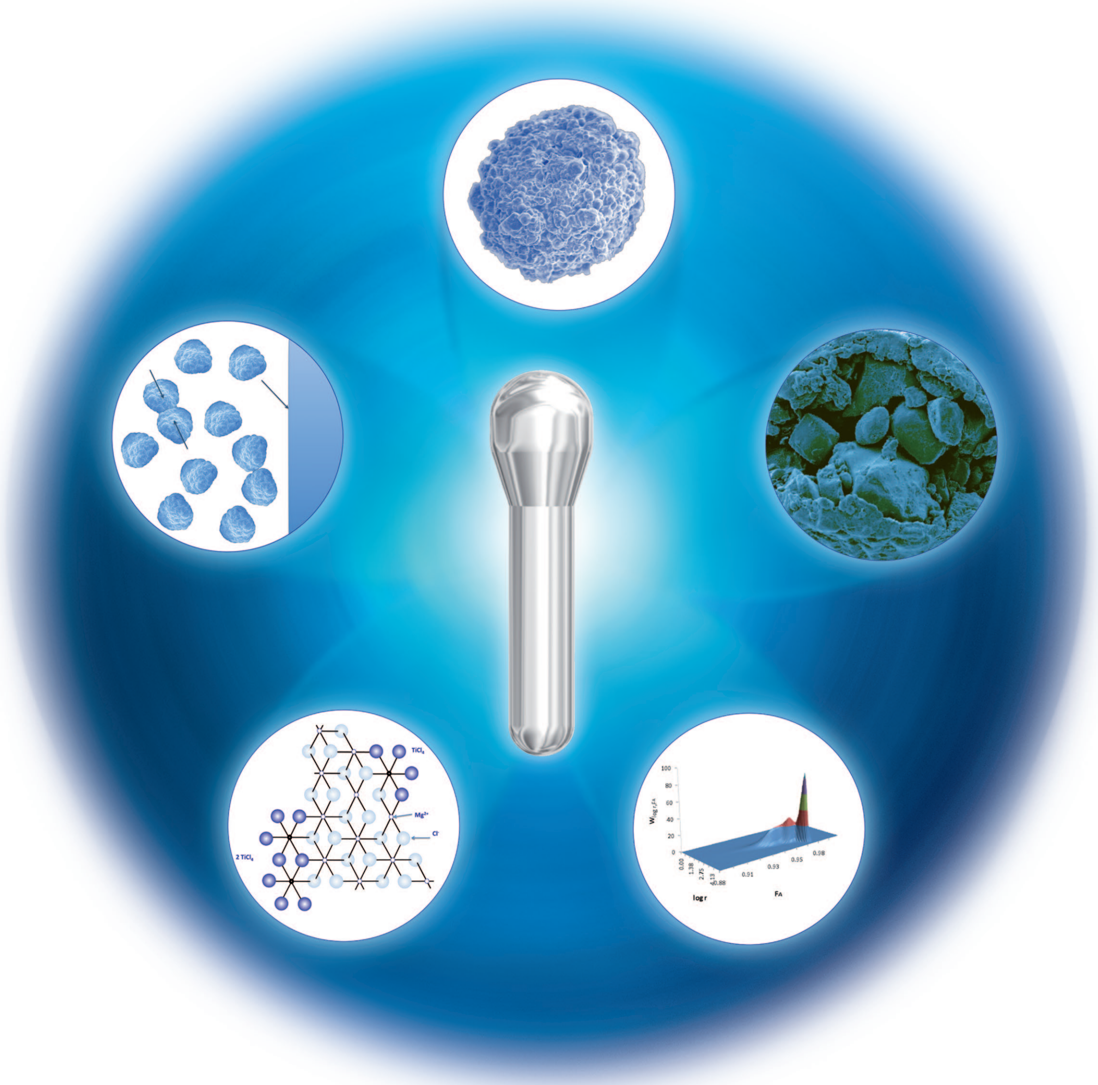
Polyolefin Reaction Engineering



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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.
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> *Aristotle (384–322 BC)*
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> 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 We felt that this approach would lead to a long and tedious text that would become quickly outdated; several excellent reviews summarizing the most recent findings on polyolefin manufacturing and characterization are published regularly and are more adequate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	ethylaluminoxane
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	*n*-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
*t*BAO	*t*-butylaluminoxane
TCB	tricholorobenzene
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
$[\mathrm{AS}^*]$	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
$[\mathrm{C}_0]$	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)
$\overline{f_r}$	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
$\overline{F_\mathrm{A}}$	average comonomer molar fraction in the copolymer
$F_{\mathrm{B}r}$	molar fraction of comonomer B as a function of chain length
$F_\mathrm{M,in}$	molar flow rate of the monomer feed to the reactor
$F_\mathrm{M,out}$	molar flow rate of the monomer exiting the reactor
g	branching index, Eq. (2.18)
g'	viscosity branching index, Eq. (2.17)
ΔG	Gibbs free energy change

h	average convective heat transfer coefficient between the macroparticle and surroundings
ΔH	enthalpy change
ΔH_p	average enthalpy of polymerization
ΔH_r	enthalpy of reaction
ΔH_u	enthalpy of melting for a crystallizable repeating unit, Eq. (2.26)
ΔH_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 β-agostic interaction; thermal conductivity
k_fL	effective thermal diffusivity in the macroparticle
k_fp	thermal conductivity of the polymer layer around the catalyst fragment in the microparticle
k_iH	rate constant for initiation of metal hydride active sites
k_p	propagation rate constant
k_p'	apparent propagation rate constant, Eq. (5.115)
$\hat{k}_\mathrm{p}$	pseudo-propagation rate constant
$\tilde{k}_\mathrm{p}$	apparent propagation rate constant
$k_{\mathrm{p}i}$	propagation rate constant for monomer type i (Bernoullian model)
$k_{\mathrm{p}ij}$	propagation rate constant for chain terminated in monomer type i coordinating with monomer type j (terminal model)
$k_{\mathrm{p}ijk}$	propagation rate constant for chain terminated in monomer types i and j coordinating with monomer type k (penultimate model)
k_pm	propagation rate constant for meso insertion (propylene)
k_pr	propagation rate constant for racemic insertion (propylene)
k_r	reverse rate constant for reversible monomer coordination or β-agostic interaction
k_tAl	rate constant for transfer to cocatalyst
$k_{\mathrm{t}\beta}$	rate constant for β-hydride elimination
k_tH	rate constant for transfer to hydrogen
k_tM	rate constant for transfer to monomer
K	Mark–Houwink equation constant, Eq. (2.7)
K_a	initiation frequency, $k_\mathrm{a}[\mathrm{Al}]$
K_eq	equilibrium constant for dormant sites, Eq. (5.67)
$K_\mathrm{g-l}$, $K_\mathrm{g-l}^*$	gas–liquid partition coefficients, Eq. (5.113)

$K_{\mathrm{g-s}}$, $K^*_{\mathrm{g-s}}$, $K'_{\mathrm{g-s}}$	gas–solid partition coefficients, Eqs (5.111) and (5.114)
$K_{\mathrm{l-s}}$	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)
$K_{\mathrm{T}}^{\mathrm{H}}$	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
$\dot{m}_{\mathrm{vap}}$	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
$n_{\tilde{\mathrm{C}}_0}$, n_{C_0}	number of moles of catalyst
n_{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
$\mathrm{P}_r{}^i$	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
$\mathrm{P}^*{}_{r,i}$	living polymer chain of length r having i long-chain branches
$\tilde{\mathrm{P}}_1$	dormant site due to β-agostic interaction, Table 5.5
$\tilde{\mathrm{P}}_r$	dormant site for Ni-diimine catalysts, Table 5.8
P_{t}	termination probability
PDI	polydispersity index

$\overline{\mathrm{PDI}}$	polydispersity index for chains containing long-chain branches
$\mathrm{PDI}_{F_\mathrm{A}}$	polydispersity index as a function of copolymer composition
PDI_k	polydispersity index for chain with k long-chain branches, Eq. (6.106)
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
$\overline{r_\mathrm{n}}$	number average chain length for chains containing long-chain branches, Eq. (6.107)
$\tilde{r}_\mathrm{n}$	number average molecular weight that would result in the absence of long-chain branch formation reactions, see footnote 13 in Chapter 6
$r_{\mathrm{n}F_\mathrm{A}}$	number average chain length as a function of copolymer composition
$r_{\mathrm{n}k}$	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
$\overline{r_\mathrm{w}}$	weight average chain length for chains containing long-chain branches, Eq. (6.108)
$r_{\mathrm{w}F_\mathrm{A}}$	weight average chain length as a function of copolymer composition
$r_{\mathrm{w}k}$	weight average chain length for chains with k long-chain branches, Eq. (6.104)
r_{z_k}	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
$\left\langle R_\mathrm{g}^2 \right\rangle_\mathrm{b}$	squared radius of gyration of branched chains
$\left\langle R_\mathrm{g}^2 \right\rangle_\mathrm{l}$	squared radius of gyration of linear chains
R_L	macroparticle radius (multigrain model)
R_p	polymerization rate
$\overline{R_\mathrm{p}}$	average polymerization rate per unit volume of the reactor
$\overline{R_\mathrm{p}}'$	average polymerization rate per polymer particle
R_S	microparticle radius (multigrain model)
R_t	chain-transfer rate
Re	Reynolds number
ΔS	entropy change
Sc	Schmidt number
Sh	Sherwood number
t	time

$\bar{t}$	average reactor residence time
t_R	reactor residence time
$t_{\frac{1}{2}}$	catalyst half-time
T	temperature
T_c	crystallization temperature
T_i0	reactor inlet temperature
T_m	melting temperature
T_m^0	melting temperature of an infinitely long polyethylene chain
T_S	temperature in the microparticle
T_w	reactor coolant temperature
U	global heat-transfer coefficient
V	Monte Carlo control volume; reactor volume
V_e	elution volume
V_i	interstitial volume
V_p	pore volume
V_R	reactor volume
$w_{\log \mathrm{r}}$	weight Flory chain length distribution, log scale, Eq. (6.24)
w_r	weight Flory chain length distribution, Eq. (6.17)
$\overline{w_r}$	cumulative weight Flory chain length distribution
$\overline{w_r}$	overall weight chain length distribution for chain having long-chain branches, Eq. (6.102)
w_{r,F_A}	Stockmayer bivariate distribution, Eq. (6.60)
w_{rk}	weight chain length distribution for chains with k long-chain branches per chain, Eq. (6.87)
$w_{\log rk}$	weight chain length distribution for chains with k long-chain branches per chain, log scale, Eq. (6.89)
$w_{\log \mathrm{MW},F_\mathrm{A}}$	Stockmayer bivariate distribution, log scale, Eq. (6.61)
$w_{r,F_\mathrm{A}k}$	trivatiate distribution of chain length, chemical composition, and long-chain branching, Eq. (6.117)
$w_{r\gamma}$	Stockmayer bivariate distribution, Eq. (6.56)
$w_{\log \mathrm{MW}}$	weight Flory molecular weight distribution, log scale, Eq. (6.32)
w_MW	weight Flory molecular weight distribution, Eq. (6.30)
W_C	mass of catalyst
x_c	mass fraction of catalyst in a supported catalyst
x_i	molar fraction of comonomer i in the copolymer
γ	deviation from average comonomer molar fraction in the copolymer, Eq. (6.57)
γ_k	molar fraction of chains with k long-chain branches
Y_i	ith moment of living polymer
$[\mathrm{Y}_0]$	total concentration of active sites or living polymer chains
Z	compressibility factor

Greek Letters

α	polymer chain hydrodynamic volume constant, Eq. (2.4); long-chain branching parameter, Eq. (6.93)
β, $\hat{\beta}$	Stockmayer bivariate distribution parameters, Eqs. (6.58) and (6.62), respectively
ε	exponent relating g' to g, Eq. (2.19); macroparticle void fraction
η	catalyst site efficiency, Eq. (5.45)
$[\eta]$	intrinsic viscosity
ϕ	fraction of actives sites with growing polymer chains, Eq. (5.55)
ϕ_i	fraction of living chains terminated in monomer type i
ϕ_k	Catalan numbers, Eq. (6.95)
Φ	polymer chain hydrodynamic volume constant defined in Eq. (2.4)
κ	size exclusion partition coefficient
λ, λ_n	number of long-chain branches per 1000 C atoms
μ	long-chain branching parameter, Eq. (6.94); viscosity
ρ_C	support (catalyst) density
$\overline{\rho C_p}$	average value of the heat capacity per unit volume of the macroparticle
τ	Flory most probable chain length distribution parameter; ratio of all chain-transfer rates to the propagation rate, Eq. (6.29); $\mathfrak{g}$ macroparticle tortuosity
$\hat{\tau}$	Flory most probable molecular weight distribution parameter, Eq. (6.31)
τ_B	chain length distribution parameter for polymers containing long-chain branches, Eq. (6.90)
τ_d	characteristic diffusion time in the macroparticle

Superscripts and Subscripts

ˆ	pseudokinetic constant
–	average
12, 21	1-2 or 2-1 propylene insertions
A, B	monomer types
bulk	bulk conditions
C	catalyst, monomer type C in the case of terpolymerization
l	liquid phase
M	monomer
MC	Monte Carlo simulation rates and constants
P	polymer
s	solid polymer phase