Polymer Reaction Engineering

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Preface

Synthetic polymers are found in such a large variety of products that they have shaped modern life. The extraordinary versatility of the polymer materials in terms of properties is due to the variety and complexity of the polymer microstructure (chemical composition, chemical composition distribution, molecular weight distribution, polymer architecture, chain configuration and phase morphology).

Polymers are "product-by-process" whose microstructure, and hence their final properties, are mostly determined in the reactor. Therefore, the understanding of the processes occurring in the reactor is crucial to achieve an efficient, consistent, safe and environmentally-friendly production of polymer materials with improved performance.

This book provides the link between fundamentals of polymerization kinetics and the polymer microstructure achieved in the reactor. The aim is to instill a firm understanding of the effect of polymerization kinetics on both reactor performance and polymer quality, learning how to manipulate the process variables to achieve the process goals.

The vast majority of the polymers are produced using a few classes of polymerizations (coordination polymerization, free-radical polymerization and step-growth polymerization). The type of polymerization determines not only the kind of polymer obtained, but also the reactor configuration and the way in which the process is conducted. Therefore, the book is organized according to the type of polymerization.

The production of polyolefins by means of coordination polymerization, which is the highest tonnage polymerization process, is discussed first. The following chapters present the production of polymers by free-radical polymerization in homogeneous, heterogeneous and dispersed (suspension and emulsion) media. Afterwards, the reaction engineering of step-growth polymerization is discussed. The last chapter is devoted to the control of polymerization reactors.

Each chapter starts with a description of the main polymers produced by the particular method, the key microstructural features, the applications and the sought properties. Then the polymerization kinetics and its effect on the configuration of industrial reactors is discussed. Afterwards the mass and energy balances for the reactors are developed. The examples focus on the main polymers produced by the particular class of polymerization, but the general concepts, principles and methodology are emphasized.

The book is addressed to chemists and engineers taking their first steps in the industry, to those beginning an academic research project in the area, as well as to students of both advanced undergraduate and graduate courses in polymer reaction engineering. The book would help them to overcome the gap between a general understanding of

polymer chemistry or engineering and the specifics of working in this field. It is expected that the reader is familiar with the basic notions of polymers, chemical kinetics and mass and heat balances.

The book became a reality through the enthusiastic work of the chapter authors. I am indebted to each of them. I also would like to thank my wife Esmeralda and our daughter Leire for their support and the understanding shown during the preparation of this book.

Notation

a^*	interfacial area per unit volume of the reactor [$m^2\ m^{-3}$]
a_s	surface area of the polymer particles covered by 1 mol of surfactant under saturation [$m^2\ mol^{-1}$]
A_i	pre-exponential factor for rate coefficient of mechanism i [same units as rate coefficient]
A_p^*	surface area of the polymer particles [m^2]
A_w	total heat transfer area of the reactor [m^2]
Al	cocatalyst/activator
c	pseudo-first-order rate coefficient for termination (combination + disproportionation) in the polymer particles ($(k_{tc} + k_{td})/2N_A v_p$) [$s^{-1}$]
c_c	pseudo-first-order rate coefficient for termination by combination in the polymer particles ($k_{tc}/2N_A v_p$) [s^{-1}]
c_d	pseudo-first-order rate coefficient for termination by disproportionation in the polymer particles ($k_{td}/2N_A v_p$) [s^{-1}]
c_p	heat capacity [$kJ\ kg^{-1}\ K^{-1}$]
c_{pi}	heat capacity of compound i in the reactor [$kJ\ kg^{-1}\ K^{-1}$]
$c_{pi\text{in}}$	heat capacity of compound i in the feed [$kJ\ kg^{-1}\ K^{-1}$]
c_{pw}	heat capacity of the cooling fluid [$kJ\ kg^{-1}\ K^{-1}$]
C	catalyst
C^*	active center
C_d	deactivated active center
C_H^*	metal hydride active center
cmc	critical micelle concentration [$mol\ \ell^{-1}$]
CTA	chain transfer agent [mol]
C_{tr}^j	ratio of chain transfer rate (k_{tr}^j, j = mon, pol, sol, CTA, Al, H) to propagation rate coefficients
d_p	diameter of polymer particles [m]
d_{32}	Sauter mean diameter [m]
d_{50}	mean particle diameter [m]
D_a	dispersion coefficient [$m^2\ s^{-1}$]
DB	terminal double bonds [mol]
D_I	impeller diameter [dm]
D_{Mh}	diffusion coefficient of the monomer in phase h [$m^2\ s^{-1}$]

D_n dead polymer chains of length n [mol]
$D_{n,b}$ dead polymer chains of length n with b branching points [mol]
$D_n^{=}$ dead polymer chains of length n with terminal insaturation [mol]
$\overline{=}D_n$ dead polymer chain with an internal double bond [mol]
DP_n number-average degree of polymerization
DP_n^{inst} instantaneous number average degree of polymerization
DP_{nb} number-average degree of polymerization of branched polymers
DP_w weight-average degree of polymerization
D_R reactor diameter [m]
D_{wi} diffusion coefficient of water in phase i ($i = p$ (polymer); g (gas)) [$m^2 s^{-1}$]
E_i activation energy of the rate coefficient for mechanism i [kJ mol^{-1}]
$E(t)$ residence time distribution in the reactor
f initiator efficiency (Equation 3.1)
f_{av}^* average number of functional groups per monomer molecule (Equation 7.18)
f_i mol fraction of monomer i in monomer mixture
f_i^j fugacity of compound i in phase j
F_{iin} inlet molar flow rate of component i [mol s^{-1}]
F_{iout} outlet molar flow rate of component i [mol s^{-1}]
F_{pi} cumulative mol fraction of monomer i in the copolymer
F_{pi}^{inst} instantaneous mol fraction of monomer i in the copolymer chains being formed
h_p heat transfer coefficient at the polymer particle surface [kJ $m^{-2} s^{-1} K^{-1}$]
H total height of the reaction mixture [m]
i_{crit} critical length of the oligoradicals formed from desorbed radicals
$[i]_j$ concentration of species i in phase j [mol ℓ^{-1}]
I initiator [mol]
Inh inhibitor, poison
j_{crit} critical length of the oligoradicals formed from the initiator
k_a rate coefficient for radical entry into polymer particles [ℓ mol^{-1} s^{-1}]
k_{ac} rate coefficient for catalyst activation [s^{-1}]
k_{am} rate coefficient for radical entry into micelles [ℓ mol^{-1} s^{-1}]
k_{bb} rate coefficient for intramolecular H-abstraction (backbiting) [s^{-1}]
k_d rate coefficient for radical exit from the polymer particles [s^{-1}]
k_{dac} rate coefficient for catalyst deactivation [s^{-1}]
k_{dacI} rate coefficient for catalyst deactivation by impurity [ℓ mol^{-1} s^{-1}]
k_{dep} rate coefficient for depropagation [s^{-1}]
k_i rate coefficient for chain initiation [ℓ mol^{-1} s^{-1}]
k_I rate coefficient for thermal initiator decomposition [s^{-1}]
$\hat{k}_j$ pseudo-kinetic constant for mechanism j (Table 2.12)
k_L^a mass transfer coefficient [s^{-1}]
k_p rate coefficient for propagation and rate constant for forward polyamidation reactions [ℓ mol^{-1} s^{-1}]
$\overline{k}_p$ average propagation rate coefficient in copolymerization (Equation 3.44) [ℓ mol^{-1} s^{-1}]
k_{pij} rate coefficient for propagation of radicals with terminal unit i with monomer j [ℓ mol^{-1} s^{-1}]

k_{pLBC}	rate coefficient for macromonomer propagation [ℓ mol^{-1} s^{-1}]
k_p^{eff}	effective propagation rate coefficient (Equation 3.23) [ℓ mol^{-1} s^{-1}]
k_p^{pol}	rate coefficient for propagation of terminal double bonds [ℓ mol^{-1} s^{-1}]
k_r	rate coefficient for reverse hydrolysis reactions of amide links [ℓ mol^{-1} s^{-1}]
k_s	mass-transfer coefficient in the boundary layer surrounding the polymer particle [m s^{-1}]
k_t	rate coefficient for termination (combination + disproportionation) [ℓ mol^{-1} s^{-1}]
$\overline{k}_t$	average termination (combination + disproportionation) rate coefficient in copolymerization (Equation 3.48) [ℓ mol^{-1} s^{-1}]
k_{tc}	rate coefficient for termination by combination [ℓ mol^{-1} s^{-1}]
k_{td}	rate coefficient for termination by disproportionation [ℓ mol^{-1} s^{-1}]
k_{therm}	rate coefficient for monomer thermal initiation (ℓ^2 mol^{-2} s^{-1} for styrene, Equation 3.19)
k_{tr}^j	rate coefficient for chain transfer to species j (mon, pol, sol, CTA, Al, H) [ℓ mol^{-1} s^{-1}]
k_{tw}	rate coefficient for termination in the aqueous phase [ℓ mol^{-1} s^{-1}]
$k_{t\beta}$	rate coefficient for β-hydride elimination [s^{-1}]
$k(v, v')$	rate coefficient for coagulation of particles of volumes v and v' [ℓ part^{-1} s^{-1}]
K_a	apparent equilibrium constant in step-growth polymerization
K_{eq}	equilibrium constant [units depend on stoichiometry]
K_i^j	partition coefficient of monomer i between phase j and aqueous phase
K_D	lumped constant for catalyst deactivation (Equation 2.57) [s^{-1}]
K_{TR}	lumped constant for all transfer reactions (Equations 2.14 and 2.56) [s^{-1}]
LCB_{chain}	number of long chain branches per polymer chain
$\dot{m}_w$	mass flow rate of the cooling fluid [kg s^{-1}]
M	monomer [mol]
M_i	amount of monomer i in the reactor [mol]
M_{i0}	initial amount of monomer i in the reactor [mol]
$[M_i]_p$	concentration of monomer i in the polymer particles [mol ℓ^{-1}]
$[M_i]_w$	concentration of monomer i in the aqueous phase [mol ℓ^{-1}]
$\overline{M}_n$	number-average molecular weight [kg kmol^{-1}]
$\overline{M}_n^{inst}$	instantaneous number-average molecular weight [kg kmol^{-1}]
$\overline{M}_w$	weight-average molecular weight [kg kmol^{-1}]
$\overline{M}_w^{inst}$	instantaneous weight-average molecular weight [kg kmol^{-1}]
$\overline{n}$	average number of radicals per particle
n_m	surfactant aggregation number [molecules micelle^{-1}]
$n(v)$	number density distribution of particles with volume v [ℓ^{-1}]
$n_{in}(v)$	number density distribution of particles with volume v in the reactor feed [ℓ^{-1}]
N	impeller speed [s^{-1}]
N_A	Avogadro's number [mol^{-1}]
N_i	moles of compound i in the reactor [mol]
$N_i(n)$	fraction of all monomer i sequences in the copolymer that are n units long
N_m	number of micelles in the reactor

N_p	number of polymer particles in the reactor
$N_{p(n)}$	number of particles with n radicals in the reactor
p	conversion of the limiting functional group in step growth polymerization
P	impeller power consumption [kJ s^{-1}] and pressure in Equation 3.14 [Pa]
PDI	polydispersity index ($\overline{M}_w/\overline{M}_n$)
P_i	fraction of growing polymer chains with ultimate unit of type i in copolymerization
P_{ij}	probability that monomer i follows monomer j in the copolymer chain (Equation 3.36)
P_{1jcrit}	radicals of critical length formed from the initiator [mol] (Equation 6.18)
P_{Micrit}	radicals of critical length formed from desorbed radicals [mol] (Equation 6.18)
P_n^i	growing chains of length n terminated in monomer type i
P_n	growing polymer chains of length n [mol]
$P(n)$	probability that a molecule randomly picked from a reaction mixture is of length n
$P_{n,b}$	growing polymer chains of length n with b branch points [mol]
$P_{\overline{n}}X$	dormant species of length n
P_{tot}	total number of moles of radicals in the system [mol]
$[P_{tot}]_h$	concentration of radicals in phase h (p: polymer particles; w: aqueous phase) [mol ℓ^{-1}]
Q_{in}	volumetric inlet flow rate for continuous reactors [ℓ s^{-1}]
Q_{loss}	heat losses to the reactor surroundings [kJ s^{-1}]
Q_{out}	volumetric outlet flow rate for continuous reactors [ℓ s^{-1}]
Q_r	rate of heat generation by polymerization [kJ s^{-1}]
$Q_{removal}$	rate of heat removal [kJ s^{-1}]
$Q_{stirring}$	rate of heat production by stirring [kJ s^{-1}]
r	stoichiometric ratio of mutually reactive groups in step-growth polymerization ($A_0/B_0 \leq 1$)
r_i	reactivity ratio for monomer i (e.g., $r_1 = k_{p11}/k_{p12}$)
r_v	polymer particle volumetric growth rate [ℓ s^{-1}]
R	ideal gas constant [kJ mol^{-1} K^{-1}]
R_c	radius of the catalyst fragment
R_{init}	rate of initiation from initiator [mol ℓ^{-1} s^{-1}]
R_I	rate of initiator decomposition (mol ℓ^{-1} s^{-1})
R_{LCB}	rate of formation of long-chain branches [mol ℓ^{-1} s^{-1}]
R_{mic}	radius of microparticle [m]
R_{mac}	radius of polymer (macro) particle [m]
R_{nuc}	rate of particle nucleation [particles ℓ^{-1} s^{-1}]
R_p	polymerization rate [mol ℓ^{-1} s^{-1}]
R_p^{pol}	rate of propagation of terminal double bonds (Equation 3.30) [mol ℓ^{-1} s^{-1}]
R_{prop}	rate of propagation [mol ℓ^{-1} s^{-1}]
R_{term}	rate of termination [mol ℓ^{-1} s^{-1}]
R_{tr}	rate of chain transfer [mol ℓ^{-1} s^{-1}]
R_{ν_k}	rate of change of moment ν_k [ℓ mol^{-1} s^{-1}]
s_i	radical reactivity ratio (Equation 3.47)

S_T	total amount of surfactant in reactor [mol]
S_w	amount of surfactant in aqueous phase [mol]
t	polymerization time [s]
$\bar{t}$	mean residence time [s]
$t_{1/2}$	initiator half-life time [s]
T	reactor temperature [K]
T_e	temperature of the feed [K]
T_g	glass transition temperature [K]
T_{jin}	inlet temperature of the cooling fluid in the reactor jacket [K]
T_{jout}	outlet temperature of the cooling fluid in the reactor jacket [K]
T_m	melting temperature [K]
T_w	average temperature of the coolant [K]
u	velocity [$m\,s^{-1}$]
U	overall heat transfer coefficient [$kJ\,m^{-2}\,s^{-1}\,K^{-1}$]
U_j	free volume [ℓ]
v_p	volume of a monomer swollen polymer particle [ℓ]
V	reactor volume [ℓ]
V_d	volume of monomer droplets in the reactor [ℓ]
V_i	volume of monomer i in the reactor [ℓ]
Vis	viscosity dimensionless number
V_p	volume of monomer swollen polymer particles in the reactor [ℓ]
V_{pol}	volume of polymer in the reactor [ℓ]
V_w	volume of the aqueous phase in the reactor [ℓ]
V_{water}	volume of water in the reactor [ℓ]
W	condensation byproduct
W_i	mass of compound i [kg]
w_i	molecular weight of compound i ($i = m$ for the repeat unit in the polymer chain) [$kg\,mol^{-1}$]
$w(n)$	weight distribution of polymer chains of length n
We	Weber dimensionless number
x	conversion
$x(n)$	mol fraction of n-mers
X	mediating species in stable free-radical polymerization (Equation 3.75)
Z	polymer linkages in step growth polymers [mol]

Greek letters

α	parameter defined by Equation 2.119
α^*	branching coefficient (Equation 7.21)
α_c^*	critical value of the branching coefficient
α_{eff}	effective thermal diffusivity [$m^2\,s^{-1}$]
γ_i	activity coefficient for compound i
δ	fraction of termination events that occur by disproportionation (Equation 3.8)
$\delta(x)$	Kronecker delta function
δ_z	minimum length of the radicals generated from the initiator to enter into the polymer particles

ΔG_p	free energy of propagation [kJ mol^{-1}]
ΔH_p	enthalpy of propagation ($\Delta H_p \approx \Delta H_r$) [kJ mol^{-1}]
$(\Delta H_r)_i$	polymerization heat of monomer i under the reactor conditions [kJ mol^{-1}]
ΔS_p	entropy of propagation [kJ mol^{-1}]
ΔT_{ml}	logarithmic mean temperature difference [K]
ΔV_i	activation volume (Equation 3.14) [ℓ mol^{-1}]
ε	volume contraction factor
$\overline{\varepsilon}$	energy dissipation rate [kJ kg^{-1}s^{-1}]
ε_b	porosity of the bed of particles
ε_p	porosity of the polymer (macro) particle
ζ_k	kth moment for bulk (living + dead chains) polymer [mol]
η	viscosity [Pa s^{-1}]
$[\eta]$	intrinsic viscosity [ℓ mol^{-1}]
κ	parameter defined in Equation 2.110
λ	kinetic chain length
μ_k	kth moment of growing polymer chain distribution [mol]
ν_k	kth moment of dead polymer chain distribution [mol]
ρ	density [kg ℓ^{-1}]
σ	interfacial tension [N m^{-1}]
τ	ratio of all transfer reaction rates to propagation rate (Equation 2.84)
τ^*	ratio of all transfer reaction rates plus rate of LCB formation to rate of propagation
τ_s	tortuosity of polymer particle
φ	volume fraction of dispersed phase
ϕ_i^j	volume fraction of compound i in phase j
χ	Flory–Huggins interaction parameter

Acronyms

AA	acrylic acid
ABS	acrylonitrile-butadiene-styrene copolymer
AIBN	2,2′-azobisisobutyronitrile
ATR-FTIR	attenuated total reflection infrared
ATRP	atom transfer radical polymerization
BA	butyl acrylate
BB	dichlorobutyl branch
BHET	bishydroxyethyl terephthalate
BMA	butyl methacrylate
BPO	benzoyl peroxide
CCD	chemical composition distribution
CFD	computational fluid dynamics
CHDF	capillary hydrodynamic fractionation chromatography
CGC	constrained geometry catalyst
CLD	chain length distribution
CRP	controlled radical polymerization
Crystaf	crystallization analysis fractionation
CSTR	continuous stirred-tank reactor
CTA	chain-transfer agent
CTD	crystallization temperature distribution
DA	dodecyl acrylate
DEB	diethyl branch
DMT	dimethyl terephthalate
DSC	differential scanning calorimetry
DSD	droplet size distribution
EAO	ethylaluminoxane
EG	ethylene glycol
EGDMA	ethylene glycol dimethacrylate
EKF	extended Kalman filter
EPDM	ethylene-propylene-diene monomer
EPS	expandable polystyrene
EVA	ethylene-vinyl acetate copolymer
FFF	field-flow fractionation

FODLS	fiber-optic dynamic light scattering
FRP	free-radical polymerization
FTIR	Fourier-transform infrared spectroscopy
GC	gas chromatography
GPC	gel permeation chromatography
HCPP	high-crystallinity polypropylene
HCSTR	homogeneous continuous stirred-tank reactor
HDPE	high density polyethylene
HIPP	high impact polypropylene
HIPS	high impact polystyrene
HLB	hydrophilic–lipophilic balance
HMD	hexamethylene diamine
HPMC	hydroxypropyl methylcellulose
IDP	iterative dynamic programming
KPS	potassium persulfate
LCB	long-chain branch
LCH	long-chain hypothesis
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
LS	light scattering
MA	methyl acrylate
MAO	methylaluminoxane
MFFT	minimum film forming temperature [K]
MFI	melt flow index
MGM	multigrain model
MIR	mid-range infrared
MMA	methyl methacrylate
MPD	most probable distribution
MSD	monomer sequence distribution
MW	molecular weight
MWD	molecular weight distribution
NBR	acrylonitrile-butadiene rubber
NIR	near infrared
NMP	nitroxide mediated polymerization
NMR	nuclear magnetic resonance
ODCB	orthodichlorobenzene
PAN	polyacrylonitrile
PBD	polybutadiene
PBE	population balance equation
PBT	polybutylene terephthalate
PET	polyethylene terephthalate
PFM	polymer flow model
PFR	plug flow reactor
PLP	pulsed-laser-induced polymerization
PMMA	poly(methyl methacrylate)
PS	polystyrene

PSD	particle size distribution
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
PVC	poly(vinyl chloride)
QSSA	quasi-steady-state assumption
RAFT	reversible addition-fragmentation chain transfer
RI	refractive index detector
RIM	reaction injection molding
RSA	random search algorithm
RSSA	reactor steady-state approximation
RSSH	reactor steady-state hypothesis
RTD	residence time distribution
S	styrene
SAN	styrene-acrylonitrile copolymer
SBR	styrene-butadiene rubber
SCB	short-chain branch
SCSTR	Segregated continuous stirred tank reactors
SEC	size exclusion chromatography
SFRP	stable free-radical polymerization
SPP	solid-phase polymerization
SQP	sequential quadratic procedures
SSP	solid-state polymerization
TCB	trichlorobenzene
TEA	triethyl aluminium
TEMPO	2,2,6,6-tetramethylpiperidinyloxy
TMA	trimethyl aluminium
TPA	terephthalic acid
TPFB	tris(pentafluorophenyl) borane
TREF	temperature rising elution fractionation
UHMWPE	ultra-high molecular weight polyethylene
ULDPE	ultra low-density polyethylene
VAc	vinyl acetate
VCM	vinyl chloride monomer
VISC	viscometer
VLDPE	very low-density polyethylene
VOC	volatile organic compound
WCLD	weight chain-length distribution

Contents