POLYMERIZATION PROCESS MODELING

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ADVANCES IN INTERFACIAL ENGINEERING SERIES

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Where microstructures dominate, the manufacturing process becomes the product. At the Center for Interfacial Engineering, a National Science Foundation Research Center, researchers are working together to develop the control over molecular behavior needed to manufacture reproducible and reliable interfacial products.

The books in this series represent an intellectual collaboration rooted in the disciplines of modern engineering, chemistry, and physics that incorporates the expertise of industrial managers as well as engineers and scientists. They are designed to make the most recent information available to the students and professionals in the field who will be responsible for future optimization of interfacial processing technologies.

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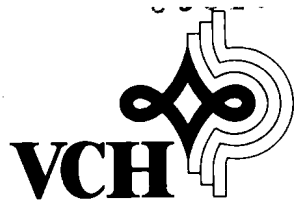

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PREFACE

Polymerization is one of the fundamental paths—along with self-assembly, association, crystallization, and other physical routes—to building microstructured organic materials. In contrast to the other processes, polymerization involves covalent bond formation, building up large molecules which, in turn, impart a range of unique and desirable properties to the polymeric materials thus made. In conjunction with self-assembly, crystallization, and other physical processes, polymerization can be used to lend permanence and mechanical robustness to engineered microstructures. We emphasize the term "microstructure" because this book is about how to model the chemical microstructure of macromolecules produced in polymerization reactors. The details of polymeric microstructure determine the properties of the product, often in multiphase systems—systems with interfaces. Specification of the desired characteristics of a polymeric material is a more complex endeavor than for any other kind of chemical product, because of the variety and complexity of microstructure.

Patricia Layman, writing in *Chemical and Engineering News* (October 31, 1994), reports on some industrial perspectives for the future on polymer manufacturing. Prominent on the list of new processes are approaches "to tailor a polyethylene molecule more accurately." The language itself reflects the significantly different kind of challenge that a polymerization engineer faces; no one talks about "tailoring" ethylene. Its polymer, however, can be tailored, and among the means to do such are new catalysts, new comonomers, and the modification of molecular weight distribution. Fundamentally, each of these new approaches requires the engineered adjustment of the polymeric microstructure—in this case, of molecular weight distribution or copolymer attributes—to obtain better performance in processing or end-use application. Tools of both the polymer scientist and the engineer can be used to these ends; new synthetic chemistry and new reactor configurations and control schemes each play a role. Ultimately, however, for the engineer to have any power to predict the effects that these innovations will have on the complex aspects of polymer product quality, the relationship between *formation* (which involves both chemistry and reactor environment) and *structure* must be understood.

This book lays out, in a comprehensible manner, the tools available to do this for a wide range of situations, emphasizing fundamental methods and approaches. This is not an advanced, state-of-the-art compendium or review book for the practicing polymerization engineer, though some in this situation might

well find the material useful. The aim, rather, is to educate and inform those who are either engineers entering the field (say as chemical or mechanical engineering students) or chemists, engaged in or collaborating on a polymerization reaction engineering project. We view this book as a bridge between the *chemistry of polymerization*, which focuses on mechanism and kinetics, and *reactor design* and *control*, where the predictive power of the engineer must be implemented. George Odian's *Principles of Polymerization* is an excellent source dedicated to polymerization kinetics and mechanism; *Control of Polymerization Reactors*, by Joe Schork et al., aims at the implementation phase of reactor design. This book, we feel, fills a need between these two. The motivation for analysis of the development of microstructure (particularly molecular weight distribution) is given in the first chapter. In subsequent chapters, we bring out the particular features of different categories of polymerizations which are industrially significant. We try to instill, in the text and in worked examples, an understanding of how the various tools of analysis work and when to employ them. More importantly, through the development and solution of models of polymerization processes, we try to bring out, in a way we have not seen brought together in a single volume, a firm understanding of how various types of polymerization work—that is, what they develop in the way of product distributions of molecular weight, composition, sequence, and so on. The book is reasonably self-standing in that not very much polymer science is assumed, though a basic polymer science course would be a very useful predecessor or prerequisite to a course derived from this book. On the other hand, it is expected that the reader is familiar with chemical kinetics and basic notions of mass and energy balances.

The material contained in this volume has been used as the basis for courses in polymerization modeling at the University of Massachusetts and the University of Minnesota (and elsewhere) numerous times over the last decade or more. The material can be covered in a ten-week, quarter-length course directed at engineering seniors and graduate students. Matt Tirrell, Rafael Galván, and Neil Dotson have each instructed such a course at Minnesota. A fuller development of this material can be accomplished in a fifteen-week, semester-length course, as has been done by Bob Laurence at Massachusetts. The text contains tried and true problems for homework or for the self-teacher.

Assistance from the Center for Interfacial Engineering at the University of Minnesota was essential in bringing this book to its final form; Hertha Schulze, Mark Swanson, and Susan Mehle were of particular help. Before the final stages, though, we received generous financial contributions from E. I. duPont de Nemours Co., Inc., EXXON Corporation, and S. C. Johnson and Sons, all of which were vital in keeping the work on this book moving. Colleagues from these companies and others also provided useful feedback on the contents of this book, as did those who peer-reviewed the book.

Matt Tirrell was the beneficiary of the Shell Oil Company Distinguished Chair in Chemical Engineering at Minnesota and the Olaf A. Hougen Visiting Professorship in Chemical Engineering at the University of Wisconsin, which provided both

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NOMENCLATURE

The tables that follow list nomenclature for variables and acronyms sufficiently common to be present in the text without local definition (i.e., definition within the section or subsection in which an item appears). The text contains more variables and acronyms than are listed here, but all others are defined locally or used only locally (e.g., in the analysis of a particular problem).

Variable	*Chapters*	*Meaning*
A	2, 5	concentration of A-type functional groups
A_p	7	total surface area of polymer particles
a_s	7	specific surface area of surfactant
A_0	2, 5	initial concentration of A-type functional groups
$(A_2)_0$	2	initial concentration of A_2 monomers
B	2	concentration of B-type functional groups
B_0	2	initial concentration of B-type functional groups
$(B_2)_0$	2	initial concentration of B_2 monomers
C_m	5, 7	transfer to monomer constant, $k_{tr,m}/k_p$
C_p	5	transfer to polymer constant, $k_{tr,p}/k_p$
C_s	5, 6	transfer to agent constant, $k_{tr,s}/k_p$
d	3, 6	parameter in free-radical polymerization, defined in Chapter 3
Da	6	Damköhler number of the first kind, being the ratio of rate of reaction to rate of exit from reactor
DP_n	1–7	number-average degree of polymerization, μ_1/μ_0
DP_w	1–6	weight-average degree of polymerization, μ_2/μ_1
DP_n^{inst}	3	instantaneous number-average degree of polymerization of dead chains
DP_w^{cumu}	3, 5	cumulative weight-average degree of polymerization of dead chains
DP_w^{inst}	3, 5	instantaneous weight-average degree of polymerization of dead chains
DP_z	1, 6	z-average degree of polymerization, μ_3/μ_2
DP_{z+1}	1, 6	(z + 1)-average degree of polymerization, μ_4/μ_3
$E(N_A^{in})$	2, 5	expected number of monomers looking into an A group
$E(N_A^{out})$	2, 5	expected number of monomers looking out of an A group
$E(W_A^{out})$	2, 5	expected weight looking out of an A group
$E(W_B^{out})$	2, 5	expected weight looking out of a B group
f	3–6	initiator efficiency factor
	5, 6	functionality of multifunctional monomer
f_i	4, 6	mole fraction of monomer i in the comonomer mixture
$f_{i,0}$	4	initial mole fraction of monomer i in the comonomer mixture
$f(\theta')d\theta'$	6	residence time distribution
F_i	4, 6	instantaneous mole fraction of monomer i incorporated into copolymer

Variable	*Chapters*	*Meaning*
$G(s)$	2–7	moment generating function; $G(1)$ equals μ_0
$G_A(s)$	2	in $A_2 + B_2$ polymerization, the moment generating function of chains with A_2 groups on both ends; $G_A(1)$ equals the concentration of such chains
$G_B(s)$	2	in $A_2 + B_2$ polymerization, the moment generating function of chains with B_2 groups on both ends; $G_B(1)$ equals the concentration of such chains
$G_M(s)$	2	in $A_2 + B_2$ polymerization, the moment generating function of chains with an A_2 group on one end and a B_2 group on the other; $G_M(1)$ equals the concentration of such chains
$H(s)$	2–6	moment generating function of intermediate chains or polymeric by-product (cyclic species); $H(1) = \lambda_0$ (or R)
I	3–7	initiator concentration
I_0	3, 4, 6	initial initiator concentration
k	2, 5, 6	polycondensation rate constant
	3, 6	propagation rate constant for ionic polymerization
k_d	3–6	initiator decomposition rate constant
k_{ij}	4, 6	the rate constant for propagation of a radical of type i with a monomer of type j (terminal model)
k_p	3, 5–7	propagation rate constant
k_t	3, 6, 7	overall termination rate constant
k_{tc}	3, 5	rate constant for termination by combination
k_{td}	3, 5	rate constant for termination by disproportionation
k_{tij}	4, 6	termination rate constant between i- and j-type radicals (similarly defined for k_{tc} and k_{td})
$k_{tr,x}$	3, 5	rate constant for transfer to agent X
M	3–6	monomer concentration
M_{Af}	2, 5	mass of monomer A_f ($f = 2$ in Chapter 2)
M_{Bg}	2, 5	mass of monomer B_g ($g = 2$ in Chapter 2)
M_i	4	concentration of monomer i
$(M_i)_0$	4	initial concentration of monomer i
M_n	1, 2, 4, 5	number-average molecular weight
M_w	1, 2, 4, 5	weight-average molecular weight
M_z	1	z-average molecular weight
M_0	3, 5, 6	initial monomer concentration
$\overline{n}$	7	average number of radicals per particle
N	7	number of polymer particles
$(N_i)_n$	4	number-average sequence length for monomer i
$(N_i)_n^{cumu}$	4	cumulative number-average sequence length for monomer i
$(N_i)_n^{inst}$	4	instantaneous number-average sequence length for monomer i
$(N_i)_w$	4	weight-average sequence length for monomer i
p	2, 5, 6	conversion of (limiting) functional groups in stepwise polymerization
	3–6	conversion of monomers in chainwise (co)polymerization
P	2	molar concentration of polymer
p_c	5	critical conversion for gelation
$P(F_i^{out})$	5	probability of a finite structure looking out of monomer i
p_i	4	conversion of monomer i in free-radical copolymerization

Variable	*Chapters*	*Meaning*
P_i	1–6	molar concentration of chains of length i
$P_{i,j}$	2, 4	molar concentration of chains comprising i A_2 units and j B_2 units (for $A_2 + B_2$ step polymerization), or dead chains comprising i M_1 units and j M_2 units (for chain copolymerization)
$P(X_{i,f})$	5	probability of an f-functional crosslinker having i arms to the network
P_0	2, 6	initial molar concentration of polymer
$P_{1,0}$	5	initial molar concentration of A_f monomers
	6	concentration of monomer in stream 0
q	3, 5–7	probability of propagation
Q	1–3, 5–7	polydispersity, DP_w/DP_n (generally)
	6	volumetric flow rate for continuous reactors
r	2, 4, 5	stoichiometric ratio of mutually reactive groups, $A_0/B_0 \leq 1$ generally; $r = A_0/(B_0 + C_0) \leq 1$ for $A_2 + B_2 + C_2$ polymerization
R	3, 6	molar concentration of intermediate (active) chains (e.g., radicals)
	1, 5, 7	ideal gas law constant
r_i	4	the ratio of homo- to cross-propagation rate constants (k_{ii}/k_{ij}) for binary copolymerization (terminal model)
R_i	3, 5	molar concentration of intermediate (e.g., active) chains of length i
R_p	3, 6, 7	rate of chainwise polymerization, or equivalently of monomer consumption (generally free radical)
s	2, 3, 5–7	dummy variable for the generating function $G(s)$, defined within the unit circle on the complex plane
S	3, 5	concentration of transfer agent
	7	surfactant concentration
$S_{i,k}$	4	sequence length distribution; number or concentration of sequences of length k of monomer type i
$S_{i,k}^{cumu}$	4	cumulative sequence length distribution; number of sequences of length k of monomer type i in accumulated polymer
t	2–7	time
T_g	1, 7	glass transition temperature
T_m	1, 7	crystalline melting temperature
V	6	reactor volume
W	2, 3	normalization constant for molecular weight distribution
w_{Af}	2, 5	weight fraction of A_f monomers ($f = 2$ in Chapter 2)
W_i	1–4	molecular weight distribution
$w_{pendant}$	5	weight fraction of material with only one arm to the network
w_{sol}	5	weight fraction of soluble material
x	5	mass conversion of monomer to polymer in long-chain branching polymerizations
α	5	branching probability
	5	elongation ratio
θ	6, 7	residence time; average residence time = V/Q
λ_k	3, 5	kth moment of the intermediate chain length distribution $H(s)$
μ	7	volumetric growth rate of polymer particles

Variable	*Chapters*	*Meaning*
μ_k	1–6	kth moment of the chain length distribution $G(s)$
ν	3, 7	kinetic chain length; the number of monomers a radical adds to during its lifetime
ξ	3, 5, 6	fraction of chain-ending steps which are by combination
ρ_a	7	rate of absorption of radicals into a polymer particle
ρ_i	7	rate of initiation of radicals absorbed into polymer particles
τ	2	rescaled time, $d\tau = k\,dt$ (for AB step polymerization, or AB + XB step polymerization); $d\tau = 2k\,dt$ (for $A_2 + B_2$ step polymerization)
	3, 5, 6	rescaled time, eigenzeit variable, $d\tau = kM\,dt$
v_2	5	volume fraction of polymer (species 2) in a swelling experiment
ϕ_m	7	volume fraction of monomer in swollen polymer particle
χ	5, 7	Flory–Huggins polymer–solvent interaction parameter

Acronym	*Chapters*	*Meaning*
ABS	1, 6, 7	acrylonitrile–butadiene–styrene resin
cmc	7	critical micelle concentration
CSTR	7	continuous stirred tank reactor
GPC	1	gel permeation chromatography
HCSTR	6	homogeneous continuous stirred tank reactor
HIPS	1, 7	high impact polystyrene
IR	1, 7	infrared (spectroscopy)
LFTR	6	laminar flow tubular reactor
NMR	1	nuclear magnetic resonance (spectroscopy)
PFR	6, 7	plug flow reactor
PVC	1, 6	poly(vinyl chloride)
SBR	1, 7	styrene–butadiene rubber
SCSTR	6	segregated continuous stirred tank reactor

CONTENTS