Fundamentals of
**POLYMER
ENGINEERING**

Fundamentals of

POLYMER ENGINEERING

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Book Designed by Reuven Solomon

To my beloved wife
SARA who patiently
did the hard work
on the hard disk

Preface

WE ALL ARE SURROUNDED by plastic materials and cannot imagine modern life and utilities without the synthetic polymers. And yet, how many of us can distinguish between polyethylene and PVC? After all, most people name any polymer as "Nylon." Is there any distinction between polymers and plastics?

This introductory textbook tries to answer these questions and many others. It endeavors to provide the basic information required in modern life about the best utilization of new materials in the plastics era; the chemical sources of synthetic polymers, and the processes in which small "simple" molecules are converted to giant macromolecules, namely, high polymers; and the understanding of the role of these unique structures, their behavior and performance, their mechanical and thermal properties, flow and deformation.

As we are mainly interested in the final product, the processing of plastics, through shaping and forming, presents a significant challenge to polymer engineering. All this is broadly discussed, ending with modern issues like composites, ecology and future prediction, followed by up-to-date information and data about old as well as novel high performance polymers.

The text is particularly targeted towards senior students of science and engineering (chemical, material, mechanical and others) who may use it as the first window to the world of polymers. At the same time many professionals who are involved in the resin or plastics industry may prefer this approach without elaborate math or overloading.

This book is mainly based on thirty-five years of teaching polymer engineering at the Technion, Haifa, Israel, and several universities in the United States.

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Last but not the least, I wish to thank my numerous students, from whom I learned the most.

— A.R.

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List of Symbols

SYMBOL	DEFINITION
a	exponent in eq. 3-5
A	area
AO	antioxidant
b	width
B	second virial coefficient (eqs. 3-11, 3-12)
C	concentration
CAD	computer aided design
CAM	computer aided manufacture
C _p	specific heat
d	thickness; diameter; density
D	diameter; diffusivity
De	Deborah number
DP	degree of polymerization (number of mers)
DSC	differential scanning calorimetry
E	energy of activation; Young's modulus; electrical potential
ESC	environmental stress cracking

f	initiator efficiency (eq. 2-42)
f_i	mole fraction of component i in feed mixture (for copolymerization)
F	force
F_i	mole fraction of component i in copolymer chain
G	shear modulus
G'	storage modulus
G''	loss modulus
G^*	complex modulus
GPC	gel permeation chromatography
h	depth of screw channel (extruder)
H	optical constant (eq. 3-12)
I	initiator concentration; current (electrical)
J	compliance
k	kinetic constant; heat conduction coefficient
k_d	initiator decomposition rate constant
k_i	rate constant of initiation
k_p	rate constant of propagation; rate constant of polymerization
k_t	rate constant of termination
$k_{t,c}$	rate constant of termination via combination
$k_{t,d}$	rate constant of termination via disproportionation
k_{tr}	rate of constant for transfer
ℓ	length
L	length
LCP	liquid crystal polymer
M	monomer concentration
M_o	monomer molecular weight
M^*	monomer radical concentration
$\overline{M}_n$	number-average molecular weight
$\overline{M}_v$	viscosity-average molecular weight
$\overline{M}_w$	weight-average molecular weight
$\overline{M}_z$	z average molecular weight

$\overline{M}_{z+1}$	$z + 1$ average molecular weight
MFI	melt flow index
MSW	municipal solid waste
MW	molecular weight
MWD	molecular weight distribution
n	number of moles; number of repeating units (mers); exponent in eq. 3-15 (Avrami); exponent in power law (eq. 4-3)
N	number of functional groups (in condensation), speed of rotation
N_0	initial number of functional groups
P	polymer concentration; pressure; load; permeability; degree of conversion
ppb	parts per billion
ppm	parts per million
q_d	drag flow rate
q_l	leakage flow rate
q_p	pressure flow rate
Q	flow rate (volumetric); electrical charge
r_i	rate of initiation
r_p	rate of propagation; rate of polymerization
r_t	rate of termination
R	gas constant; end-to-end distance; electrical resistivity
R^*	primary radical concentration
RIM	reactive injection concentration
S	tensile strength; solubility
S_B	tensile strength at break
S_y	tensile strength at yield
t	time; thickness; pitch (extruder)
t_c	cooling time (injection molding)
t_f	filling time (injection molding)
t_n	"dead" time (injection molding)
t_s	cycle time (injection molding)

T	temperature
T_c	temperature of crystallization
T_d	heat distortion temperature
T_f	temperature at opening of the mold
T_g	glass transition temperature
T_i	temperature of injection
T_m	melting temperature
T_s	surface temperature (mold)
u	velocity
U	velocity
UHMW	ultra high MW
UV	ultraviolet
UVA	ultraviolet absorber
V	velocity; volume; specific volume; elution volume
V_a	specific volume of amorphous phase
V_c	specific volume of crystalline phase
w_i	weight fraction of species i
W	weight
W_i	weight fraction
x_i	mole fraction of species i
X	mole ratio in the feed (copolymerization)
Y	mole ratio in the copolymer chain

Greek Symbols

SYMBOL	DEFINITION
α	thermal expansion coefficient; heat diffusivity
γ	strain; surface energy
$\dot{\gamma}$	rate of shear (velocity gradient)
δ	shift angle; depth of deformation
ϵ	dielectric constant
η	viscosity

η_o	low-shear viscosity (Newtonian)
η_{T_g}	viscosity at T_g
θ	dimensionless temperature, shift angle
λ	relaxation time, retardation time
μ	viscosity (Newtonian); micron
μ_e	effective viscosity
μ_r	relative viscosity
μ_s	viscosity of solvent
μ_{sp}	specific viscosity
$[\mu]$	intrinsic viscosity
ν	Poisson ratio
π	osmotic pressure
Π	power
ρ	resistivity (electrical); density
τ	turbidity; shear stress
ϕ	angle of inclination (extruder screw)
ϕ	shift angle
ω	frequency