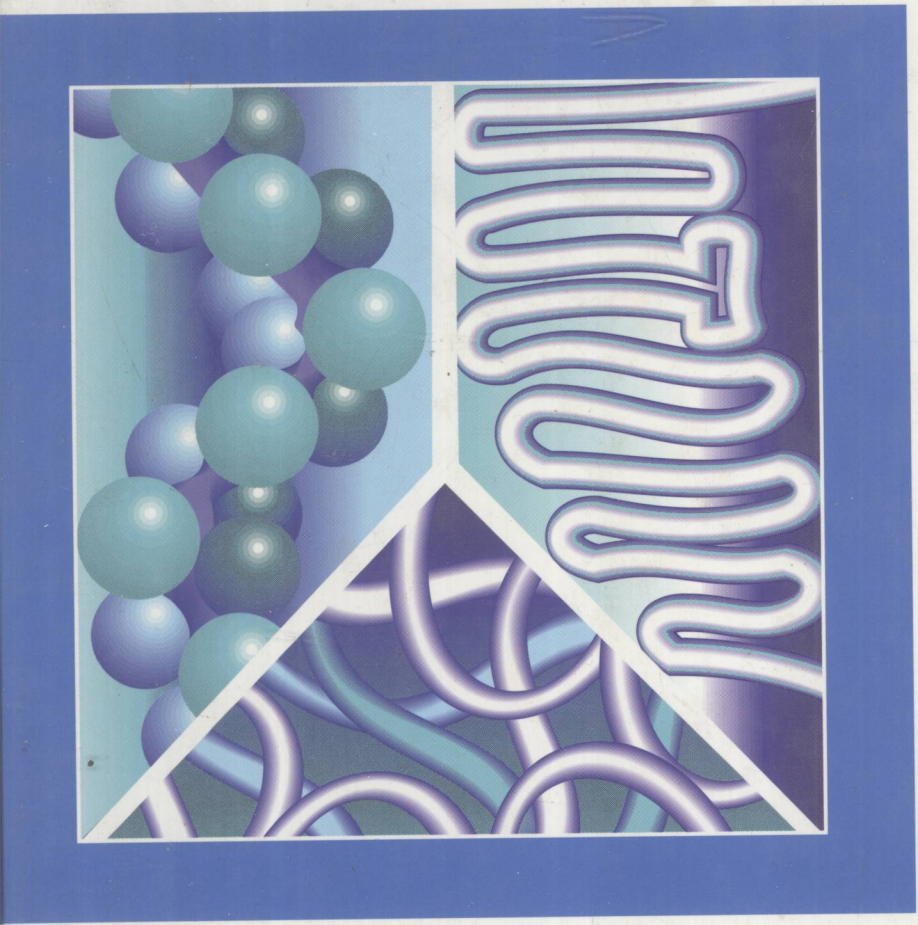
Hans-Georg Elias

An Introduction to Polymer Science



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Preface

Polymer science began with the discovery and synthesis of macromolecules. Physical methods were then employed to characterize these molecules and their applications as plastics, fibers, elastomers, coatings, adhesives, etc. Most introductory textbooks reflect this historical approach: they emphasize the chemistry of polymers and the characterization of polymers by physical methods.

My colleagues and I have long felt that this traditional approach does not do justice to the interdisciplinary nature of polymer science which is firmly rooted not only in the chemistry of macromolecules but also in their physical chemistry and physics. A modern book should furthermore provide the student with some information on the three most important uses of synthetic polymers as elastomers, fibers, and plastics but should not neglect biopolymers either.

This book is therefore divided into three approximately equal sized parts covering the chemistry, physical chemistry and physics of polymers, followed by a part on technology. The parts are preceded by an Introduction (Chapter 1) which defines the most important terms and reflects on the discovery of macromolecules.

The **chemistry** sections first introduce the constitution, configuration and microconformation of macromolecules (Chapter 2). Syntheses are then presented in Chapter 3 covering chain-growth polymerizations and Chapter 4 dealing with step-growth polymerizations and polymer reactions. This division seems natural since chain polymerizations are most expediently discussed via kinetics whereas non-chain polymerizations such as polycondensation and polyaddition are better treated according to their individual chemistry. Chapter 4 also contains information on biological macromolecules with special emphasis on industrially important ones.

The next three chapters are concerned with the **physical chemistry** of single macromolecules: size and shape (Chapter 5), thermodynamics of polymer solutions (Chapter 6), and polymer hydrodynamics (Chapter 7). Experimental methods are mentioned in the context of the corresponding physical phenomena; they are not listed in the usual handbook style according to the information they deliver. Prior knowledge is assumed for instrumental methods used in organic chemistry (NMR, IR, UV, etc.). Methods specific to polymer science are described but not in detail due to the prescribed size of the book. The reader should also bear in mind that experimental methods cannot be learned from books but need hands-on experience.

The chapters on single molecules are followed by three chapters on **polymer physics**. Chapter 8 discusses the structure of polymer assemblies, i.e., melts, amorphous solids, crystalline solids, liquid-crystalline polymers, domain formation, etc. Chapter 9 describes not only thermal transitions and relaxations but also diffusion and permeation phenomena. Mechanical, electrical and optical properties of solid polymers are treated in Chapter 10.

Chapters 1-10 are rounded off by four chapters on selected aspects of **polymer technology**. These chapters on the three most important applications of polymers intend to show that elastomers (Chapter 12), fibers (Chapter 13) and plastics (Chapter 14) are not simply polymers but polymer systems comprising additives (Chapter 11).

Chapter 14 also discusses reinforced and rubber-modified plastics. Chapters 11-14 have many cross-references to Chapters 1-10 which show the complexity of such polymer systems and the effect of processing on properties.

The book employs recommended IUPAC nomenclature and symbols and SI units. Since American industry continues to use Anglo-Saxon units, Chapter 15 therefore lists SI units and conversions of Anglo-Saxon units, as well as abbreviations and acronyms of polymer names and some important trade names.

Whenever possible, physical equations are not just presented but derived step by step from theories. Exceptions are those few equations that result from sophisticated theories requiring an elaborate mathematical apparatus. In many cases, numerical examples are given so that the student gets some feel for numerical values.

The book was envisioned for students with a basic knowledge of chemistry, physical chemistry and physics. Since it intends not only to acquaint the student with the basic terms, facts, methods, and theories but also to provide a bridge to an understanding of the primary literature, it uses a more formal, compact style than that commonly adopted by other introductory textbooks. Important terms are emphasized by bold type. Since the language of science is part of our heritage, explanations of the Greek, Latin, French, German, etc., linguistic roots of scientific terms are explained throughout the book.

The book is based on a short German-language text published in 1996 but it is not a cover-to-cover translation: sections have been rearranged and new paragraphs, tables and graphs have been added. The German language edition has been thoroughly worked over, keeping in mind the differences in background, knowledge, and cultural heritage of students in the United States and in German-speaking countries based on my experience with graduate students and postdoctoral fellows from 15 countries.

I am indebted to my former colleagues at Michigan Molecular Institute who read and checked the "final" drafts of several chapters: Professors Petar R. Dvornic (all Chapters), Steven A. Keinath (Chapters 1-7), Dale J. Meier (parts of Chapter 10), Robert L. Miller (Chapters 1, 2, 8, 9), and Karel Solc (Chapters 1, 2, 5, and 6 plus all chapters of the German version),

Midland, Michigan, Summer 1996 Hans-Georg Elias

List of Symbols for Physical Quantities

Abbreviations for languages:

E: English (American spelling) F: French
G: Greek L: Latin

Conventions for symbols of chemical entities (IUPAC) unless noted otherwise:

R: monovalent ligand, e.g. CH_3-, C_6H_5-
Z: bifunctional atom or group, e.g., -CH_2-, -(*p*-C_6H_4)-
Y: trifunctional atom or group, e.g., -N<
X: tetrafunctional atom or group

Other conventions in this book:

A, B: monomers leading to monomeric units -a- and -b- respectively, *or* leaving parts of functional groups (e.g., -OH from -COOH)
L = AB: symbol for a leaving molecule, e.g., H_2O from -OH + HOOC-;
p-C_6H_4, *p*Ph: in para position (1,4-position) substituted benzene ring (= *para*-phenylene)

Exponents

α exponent of the relationship between intrinsic viscosity and molar mass
ν exponent of the relationship between radius of gyration and molar mass (Flory exponent)

Indices:

1 solvent
2 solute (usually polymer)
a atom
c chain
crit critical (occasionally as c)
cryst crystalline
end end group
f free or functionality
G glass transformation
i *i*th component
i initiation
M melting
m molar quantity
mix mixing, mixture
mol molecule
mon monomer
n number-related quantity
p polymer, polymerization, or propagation
p quantity at constant pressure

r related to end-to-end distance
rel relative
s related to radius of gyration
T quantity at constant temperature
tr transfer
u monomeric unit
V quantity at constant volume
w mass-related quantity
η viscosity-related quantity

Physical quantities and units: Usually following IUPAC amd ISO recommendations, see I.Mills, T.Cvitas, K.Homann, N.Kallay, K.Kuchitsu, eds., (International Union of Pure and Applied Chemistry, Division of Physical Chemistry), "Quantities, Units and Symbols in Physical Chemistry", Blackwell Scientific Publications, Oxford 1988.

A area; A_c = cross-sectional area of a chain
A_2 second virial coefficient; A_3 = third virial coefficient
[A] molar concentration of chemical compound A
a persistence length
a_T shift factor in the WLF equation

B bulk compliance
b bond length; b_{eff} = effective bond length

C electric capacitance
C heat capacity; C_p (isobaric); C_V (isochoric)
C number concentration (number of entities per total volume)
[C] amount-of-substance concentration = amount of substance per total volume = molar concentration
C_j chain transfer constant (always with index, e.g., j = s (regulator))
C_N characteristic ratio; C_∞ = characteristic ratio at infinite molar mass

c concentration = mass concentration (= mass of substance per total volume)
c_p specific heat capacity at constant pressure

D diffusion coefficient
D tensile compliance
d diameter; d_{blob} = diameter of a blob, d_{sph} = diameter of a sphere

E energy, $E^\ddagger$ = activation energy
E tensile modulus (Young's modulus)

F force
f fraction (unless specified)

f functionality of a group or molecule

G Gibbs energy; e.g., $\Delta G_{mix,m}$ = molar Gibbs energy of mixing
G statistical weight fraction ($G_i \equiv g_i/\Sigma_i\, g_i$)
G shear modulus
G electrical conductance
g statistical weight
g branching parameter

H enthalpy; ΔH_{mix} = enthalpy of mixing, $\Delta H_{mix,m}$ = molar enthalpy of mixing
h Planck constant ($h \approx 6.626 \cdot 10^{-34}$ J s)

I intensity
I electric current

J shear compliance

K constant; K_n = equilibrium constant; K_ϑ = optical constant (scattering)
K bulk modulus
k rate constant (always with index); k_p = propagation rate constant, k_t = rate constant of termination, k_{tr} = rate constant of transfer
k_B Boltzmann constant ($k_B \approx 1.3805 \cdot 10^{-23}$ J K^{-1})

L length (always geometric); L_K = Kuhn length

M molar mass (mass per amount of substance); $\overline{M}_n$ = number-average molar mass, $\overline{M}_w$ = mass-average molar mass, M_{end} = molar mass of end group
M_r relative molecular mass (molecular weight; dimensionless); $\overline{M}_{r,n}$ = number-average molecular weight, $\overline{M}_{r,w}$ = weight-average molecular weight
m mass; m_{mol} = mass of a molecule

N number of entities (molecules, segments, groups, atoms, etc.)); N_{end} = number of end groups; N_g = number of lattice sites
N_A Avogadro constant ($N_A \approx 6.023 \cdot 10^{23}$ mol^{-1})
n amount of substance (in mol)
n refractive index

P permeability coefficient
P power
$P(\vartheta)$ scattering function
p extent of reaction; p_A = extent of reaction of group A
p conditional probability
p pressure

Q intermediate variable or constant, usually a ratio
Q electric charge (quantity of electricity)
$Q(\vartheta)$ parameter in the scattering function
q order of a moment
q intermediate variable or constant

R molar gas constant ($R \approx 8.314$ J K^{-1} mol^{-1})
R radius; R_d = Stokes radius, R_v = Einstein radius
R rate of reaction
R electrical surface resistance
R_0 Rayleigh constant at angle zero; R_ϑ = Rayleigh constant at angle ϑ
r spatial end-to-end distance of a chain, usually as $\langle r^2 \rangle^{1/2}$ with various indices; r_{cont} = physical contour length of a chain
r_0 initial ratio of amounts of substances
r_A copolymerization parameter of chemical compound A

S entropy; ΔS_{mix} = entropy of mixing, $\Delta S_{mix,m}$ = molar entropy of mixing
S solubility coefficient
s radius of gyration (IUPAC)
s sedimentation coefficient
s Staverman coefficient

T thermodynamic temperature (in K); T_c = ceiling temperature, T_G = glass temperature, T_M = melting temperature
t time

U electric potential
u excluded volume

V volume; V_m = molar volume, $^*V_m$ = partial molar volume
v specific volume; $^*v$ = partial specific volume

w mass fraction (weight fraction)

X degree of polymerization; X_u = degree of polymerization of a unit (e.g., monomeric unit, repeating unit, etc.); $\overline{X}_n$ = number-average degree of polymerization; $\overline{X}_w$ = mass-average degree of polymerization
x mole fraction (amount-of-substance fraction); x_u = mole fractions of units, x_i = mole fraction of isotactic diads, x_{ii} = mole fraction of isotactic triads, etc.

y yield of substance

z number of immediate neighbors
z dissymmetry (light scattering)

α polarizability
α linear expansion coefficient of materials or coils (α_s if radius of gyration, α_r if end-to-end distance, α_h if hydrodynamic dimensions)
β cubic expansion coefficient
γ shear deformation; $\dot{\gamma}$ = shear rate
γ surface tension
Γ_s degree of solvation
δ solubility parameter
ε elongation
ε cohesion energy
ε_r relative permittivity (formerly: dielectric constant)
η viscosity; η_o = Newtonian viscosity, η_e = extensional viscosity, η_r = relative viscosity, η_{sp} = specific viscosity, $[\eta]$ = intrinsic viscosity
ϑ angle, especially scattering angle
θ torsional angle (conformational angle)
θ temperature in °C (T if in K)
Θ theta temperature
κ isothermal (cubic) compressibility
λ wavelength (λ_o = wavelength of incident light)
λ heat conductivity
λ draw ratio
Λ aspect ratio
μ moment of a distribution
μ chemical potential
μ Poisson ratio
ξ frictional coefficient
Ξ zip length
Π osmotic pressure
ρ density
ρ volume resistivity
σ tensile stress (= σ_{11})
σ steric factor
σ electrical conductance
σ_n standard deviation with respect to numbers or amounts
ς degree of coupling of chains
τ bond angle, valence angle
τ shear stress (= σ_{21})
Y cohesion energy density
ϕ volume fraction; ϕ_f = free volume fraction
Φ Flory parameter; Φ_Θ = Flory constant
χ Flory–Huggins interaction parameter
ψ parameter in an entropy quantity
ω angular velocity
Ω thermodynamic probability

Contents

Physical Chemistry