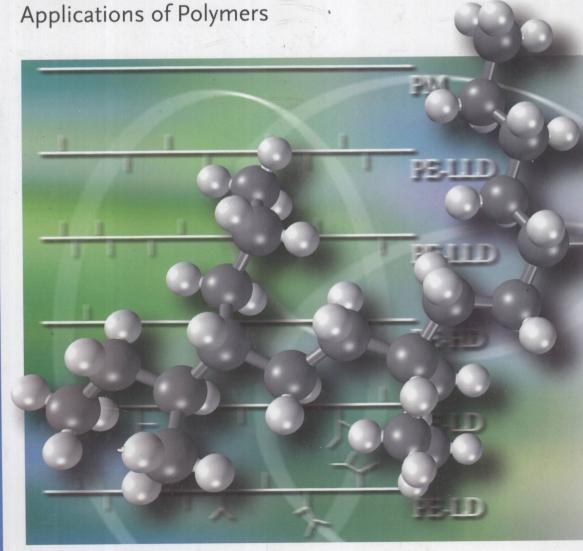
Macromolecules

Volume 4:



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Hans-Georg Elias

Macromolecules

Volume 4: Applications of Polymers







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What the gentlemen cannot prove, they call practice, and what they cannot disprove, they call theory.

L. Bamberger Speeches in the German Parliament

Preface

The four volumes of the series "Macromolecules" have a long history. After completing my doctoral thesis at the Technical University of Munich in 1957, I stayed on to work on my habilitation thesis (a kind of second doctorate) which was at that time (and still is at many German universities) required for all of those who wanted to pursue an academic career. Then, I received in the Fall of 1959 a surprise invitation to join the Swiss Federal Institute of Technology (ETH) in 1960 as Head Assistant in the Department of Organic-Chemical Technology. At ETH, I presented my habilitation thesis in 1961, was appointed Privatdozent, and started lecturing on the physical chemistry of polymers as my Department Head (H. Hopff) asked me to become his co-author.

Hopff, in turn, had been approached by a publisher because there was a need for a German language textbook on polymer chemistry which was just evolving as an independent academic discipline. As a young scientist, I was, of course, deeply honored to be asked to be the co-author of a respected researcher who had in his industrial (BASF) and academic (ETH) career amassed some 150 publications and 300 patents. However, after many months, Hopff lost interest in the venture while I had joined the professorial ranks (1963) and still had no textbook on polymer science for my lecture courses.

So I expanded my lecture notes, discussed details in seminars with my graduate students and postdoctoral workers, and injected some knowledge that I had gained as a consultant to industry in Switzerland and Germany. After I had spent some 6000 hours on drafting and writing, the first edition of the German-language book "Makromole-küle" (856 pp.) was published in the Fall of 1971. I never used the book as a back-up advanced textbook, though, because in the same month I became the founding president of what was to become the Michigan Molecular Institute in Midland, Michigan.

Over the years, while the field was growing and I gained more knowledge, the German-language editions grew from one volume (1st to 4th editions, 1971-1981) to two volumes (5th edition (1990, 1992)) and then to four volumes (1999-2003). It was only thereafter that I found the time to prepare the present English edition which follows in general the format of the 6th German edition but is not a cover-to-cover translation.

Volume I of this series discusses chemical structures and principles of syntheses of synthetic and some natural macromolecules. Volume II is concerned with raw materials and energy sources for the polymer industry, monomer syntheses, industrial polymer manufacture, and general properties of individual polymers. Volume III treats physical structures and physical properties of both single macromolecules and macromolecular substances, i.e., polymers. The present, final Volume IV is concerned with applications of polymers as plastics, fibers, elastomers, thickeners, adhesives, coatings, dielectrics, etc. Like Volumes I-III, Volume IV is basically rewritten and updated. It also contains many new subchapters, tables and graphs; 18 % of the latter are new.

Volume IV consists of a very short introduction (Chapter 1; 6 pp.), three major parts (Fundamentals (4 chapters), Basic Polymer Applications (5 chapters), Special Polymer Applications (5 chapters)), and an Appendix. In all of the chapters, I have tried to relate scientific terminology to industrial practice, explain the history and driving forces behind industrial developments, and outline the scientific background of applications. The chapters contain, in part, information about specific syntheses and special physical properties but not detailed discussions about the scientific backgrounds because this informa-

VIII Preface

tion can be found in Volume I (principles of chemical syntheses), Volume II (industrial syntheses), and Volume III (principles of physical structure, solution behavior, and mechanical properties). With respect to company names and trademarks, no attempt was made to follow the recent series of company mergers, splittings, and name changes.

In Part I, Chapter 2 (12 pp.) reviews fundamental terms for the synthesis and structure of polymers in order to provide a common basis for the other chapters. Chapter 3 (56 pp.) discusses adjuvants (dyestuffs, fillers, plasticizers, processing agents, protecting agents, etc.) and their applications while Chapter 4 (56 pp.) is concerned with rheology and its effect on basic processing methods. Chapter 5 (22 pp.) contains information about important testing methods, many of which often produce data which do not translate easily to scientific properties. Of course, it is not possible to describe all or even most of the specialized tests that are in use in the various fields.

Part II outlines the basic applications of polymers as fibers (Chapter 6; 96 pp.), elastomers (Chapter 7; 53 pp.), and plastics (Chapters 8-10; 170 pp.). It may surprise the reader that I chose to present these applications in this order and not in the usual order plastics—elastomers—fibers. There are two reasons: (a) many technologies were first developed for fibers and rubbers before they were adopted for plastics and (b) fibers and rubbers are common adjuvants for plastics, which makes it expedient to treat them first.

Natural and synthetic fibers (Chapter 6; 96 pp.) are treated in greater detail, mainly because their application as textiles depends less on the chemical structure of their constituent polymers than on the physical after-treatment of fibers and the joining of fibers to fabrics. Rubbers and elastomers (Chapter 7; 53 pp.) describes not only the various types but also the economic and political factors leading to natural rubber production and the synthetic rubber industry. For convenience, plastics are discussed in three chapters: basic types in Chapter 8 (68 pp.), reinforcement in Chapter 9 (41 pp.), and polymer blends in Chapter 10 (61 pp.)

Part III discusses special applications of polymers: in Chapter 11 (39 pp.) solutions (exclusive of their role as vehicles), in Chapter 12 (40 pp) coatings and adhesives, in Chapter 13 (20 pp.) packaging materials, in Chapter 14 (40 pp.) applications as dielectrics and in the electronics industry, and in Chapter 15 (30 pp.) polymers in optics and optoelectronics. The work concludes with an Appendix (Chapter 16; 23 pp.) that lists SI quantities and units, conversion of outdated physical quantities, definitions of physical terms, and abbreviations and acronyms for fibers, rubbers, and plastics.

Industry is fond of using abbreviations, acronyms, and number and letter codes. Each field also has its own terminology. As a result, this volume contains a very large Subject Index. No attempt was made to follow name changes of companies and brands caused by recent mergers, splittings, and marketing considerations.

Like the preceding three volumes, this volume has again had the benefit of constant advice from my good friends and former colleagues at Michigan Molecular Institute (MMI), Professors Petar R. Dvornic and Steven E. Keinath, who read and checked the drafts of all 2788 pages of Volumes I-IV and made many helpful suggestions. I would also like to thank Professor Hans Schnecko, Hanau, Germany, for advice on Chapter 7 and Dr. Abhijit Sarkar, MMI, for comments on Section 15.3.

List of Symbols

Symbols for physical units are strictly those of the International Standardization Organization (ISO) (see Appendix).

Symbols for physical quantities follow the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) and the International Union of Pure and Applied Physics (IUPAP), except for those used in industrial practice. In particular, all symbols for physical quantities are slanted, two-letter symbols are used only for dimensionless quantities (for example, Reynolds number), and vectorial quantities are in bold letters. Specific quantities (\equiv physical quantity divided by mass m) are written in small letters, using the same symbol as for the quantity itself (for example, C_p = isobaric heat capacity, $c_p = C_p/m$ = specific isobaric heat capacity). For "normalized", "reduced", etc., quantities, see the Appendix.

Indices are slanted if they refer to a *physical* quantity that is held constant (for example, C_p = heat capacity at constant pressure). They are written upright if they do not indicate a constant quantity and are just indicators, for example, numbers.

Symbols for Languages

D = German (Deutsch)
G = classical Greek
L = classical Latin

The Greek letter υ (upsilon) was transliterated as "y" (instead of the customary phonetic "u") in order to make an easier connection to written English (example: $\pi o \lambda \upsilon \varsigma = \text{polys (many)}$). For the same reason, χ was transliterated as "ch" and not as the customary phonetic "kh."

Mathematical Symbols (IUPAC; all mathematical symbols should be upright).

=	equal to	>	greater than
≠	not equal to	≥	greater than or equal to
=	identically equal to	>>	much greater than
≈	approximately equal to	<	less than
~	proportional to (IUPAC: ~ or ∞)	≤	less than or equal to
^	corresponds to	<<	much less than
\rightarrow	approaches, tends to	±	plus or minus
d	derivative		
9	partial derivative		
Δ	difference	sin	sine of
δ	differential	cos	cosine of
f	function of (IUPAC: f)	tan	tangent of
Σ	sum	cot	cotangent of
ſ	integral	sinh	hyperbolic sine of
П	product	arctan	inverse tangent
lg	logarithm to the base 10 (IUPAC: lg or log ₁₀)		

logarithm to the base e (natural logarithm) (IUPAC: ln or loge)

: identical with

ln

List of Symbols X

Symbols for Chemical Structures

```
symbol for a monovalent substituent, for example, CH<sub>3</sub>- or C<sub>6</sub>H<sub>5</sub>-
R
            symbol for a divalent unit, for example, -CH2- or -p-C6H4-
7.
            symbol for a trivalent unit, for example, -C(R)< or -N<
Y
            symbol for a tetravalent unit, for example, >C< or >Si<
X
            symbol for an active site: radical (^{\bullet}), anion (^{\ominus}), or cation (^{\oplus})
            para-phenylene (in text)
pPh
            para-phenylene = 1,4-phenylene (in line formulas)
p-C_6H_4
```

Averages and Other Markings

- line above letter indicates common average, for example, \overline{M}_n = number-average of molar mass (note: subscript is not italicized since it does not represent a physical quantity that is kept constant)
- tilde indicates a partial quantity, for example, \tilde{v}_A = partial specific volume of component A
- square brackets surrounding the symbol of the substance indicates the amount (of [] substance) concentration ("mole concentration"), usually in mol/L
- angled brackets surrounding a letter indicate spatial averages, for example, $\langle s^2 \rangle$ = () mean-square average of radius of gyration (IUPAC)
- two vertical lines enclosing the symbol for a vectorial quantity indicate the magnitude of that quantity. Example, |q| = magnitude of the scattering vector q

Exponents and Superscripts

Symbols for exponents are slanted if they indicate physical quantities but upright if the symbol indicates a number. Example: exponent α in the intrinsic viscosity = f(molar mass) relationship, $[\eta] = K_v M^{\alpha}$.

- degree of plane angle [= $(\pi/180)$ rad] minute of plane angle [= $(\pi/10 800)$ rad] second of plane angle [= $(\pi/648\ 000)$ rad] pure substance 0 infinite, for example, dilution or molecular weight 00 amount-of-substance related quantity if a subscript is inexpedient. According to m IUPAC, m can be used as either a superscript or a subscript qth order of a moment (always in parentheses since it does not represent a power) (q) activated quantity, for example, E^{\ddagger} = activation energy 1 general exponent in $P = K_P M^a$ (P = property) a general exponent q exponent in $[\eta] = K_v M^{\alpha}$ α exponent in $\langle s^2 \rangle^{1/2} = K_s M^v$ ν
- exponent in $\eta_0 = K_{\eta} M^{\varepsilon}$
- 3

List of Symbols XI

Indices and Subscripts

Subscripts are slanted if they refer to physical properties that are held constant. Example: C_p = isobaric heat capacity. Letters indicating variable physical quantities or numbers of physical entities are upright (example: N_i (with i = 1, 2 or 3)).

```
0
         standard or original state, for example, T_0 = reference temperature
0
         state at time zero
1
         solvent
2
         solute, usually polymer
3
         additional component (salt, precipitant, etc.)
         final state
\infty
A
         substance A, for example, M_A = molar mass of substance A
         group or monomeric unit of A, for example, mass m_a of group a
a
         amorphous
am
B
         fracture
В
         substance B
         boiling temperature (boiling point)
bp
         branch, branched
br
         chain (L: catena), for example, in networks
С
cr
         crystalline
         critical
crit
         cyclic
cycl
         entanglement
e
e1
         elastic
eff
         effective
end
         endgroup
         equilibrium
eq
exc
         excess
F
         filler, fiber
f1
         flexural
G
         glass transformation
         any statistical weight or statistical weight fraction, e.g., n, m, z or x, w, Z
g
H
         hydrodynamically effective property or hydration
h
         hydrodynamic average
ht
         heterotactic
i
         ith component
         isotactic diad (IUPAC recommends m = meso)
         inherent (dilute solution viscosity)
inh
is
         heterotactic triad (IUPAC: mr)
lisl
         sum of heterotactic triads, lisl = is + si
        isotactic
it
        ith component
```

XII List of Symbols

variable kliquid, melt L M melting matrix (in blends or reinforcd polymers) M monomeric unit in macromolecules m molar (also as superscript) m molecule mol monomer mon monomeric unit mu number average n P polymer index for quantity at constant pressure p polymer (if P is confusing) pol index, defined differently for each section or chapter q number of electric charges q relative (only in M_r = relative molecular mass = molecular weight) r based on end-to-end distance, e.g., α_r = linear expansion coefficient of a coil r (with respect to the end-to-end distance) red reduced relative rel repeating unit rep relaxation rlx S solvating solvent syndiotactic diad (IUPAC recommends r = racemo) S related to radius of gyration segment seg heterotactic triad (IUPAC recommends rm) si soln solution sph sphere Tindex for quantity at constant temperature monomeric unit in polymer u quantity at constant volume Vviscosity average (solutions) V mass average (weight average if dimensionless) W crosslink(ed) Х yield (stress-strain) У z average Z

viscosity average (melts)

η

List of Symbols XIII

Prefixes of Words (in systematic polymer names in italics)

alt alternating at atactic

blend polymer blend

block block (large constitutionally uniform segment)

br branched. IUPAC recommends sh-branch = short chain branch, 1-branch = long

chain branch, f-branch = branched with a branching point of functionality f

cis cis configuration with respect to C=C double bonds

co joint (unspecified)

comb comb

compl polymer-polymer complex

cyclo cyclic
ct cis-tactic
g graft
ht heterotactic

ipn interpenetrating network

it isotactic

net network; μ-net = micro network

per periodic

r random (Bernoulli distribution) sipn semi-interpenetrating network

st syndiotactic

star star-like. f-star, if the functionality f is known; f is then a number

stat statistical (unspecified distribution)

trans trans configuration with respect to C=C double bonds

tt trans-tactic

Other Abbreviations

AIBN N,N'-azobisisobutyronitrile

BPO dibenzoylperoxide

Bu butyl group (iBu = isobutyl group; nBu = normal butyl group (according to IUPAC, the normal butyl group is not characterized by n, which rules out Bu as an unspecified butyl group); sBu = secondary butyl group; tBu = tertiary butyl

group)

Bz benzene or benzyl

C catalyst; C^* = active catalyst or active catalytic center

cell cellulose residue

Cp cyclopentadienyl group DMF *N,N*-dimethylformamide

DMSO dimethylsulfoxide

Et ethyl group

G gauche conformation

Glc glucose

GPC gel permeation chromatography

XIV List of Symbols

I initiator IR infrared

L solvent (liquid)
LC liquid-crystalline
LS light scattering
MC main chain
Me methyl group
Mt metal atom

naphthalene

NMR nuclear magnetic resonance

P polymer
Ph phenyl group
Pr propyl group

Np

SANS small-angle neutron scattring SAXS small-angle X-ray scattering

SC side chain

SEC size exclusion chromatography

THF tetrahydrofuran
UV ultraviolet

Quantity Symbols (unit symbols: see Chapter 16, Appendix)

Quantity symbols follow in general the recommendations of IUPAC: quantity symbols are always slanted, and vectorial quantities are given in bold letters.

A area; A_c = cross-sectional area of a chain

A numerical aperture

 A^{\ddagger} pre-exponential constant (in $k = A^{\ddagger} \exp(-E^{\ddagger}/RT)$)

a specific surface area (in $m^2 g^{-1}$)

a thermodynamic activity

a areal fraction

a_T shift factor in the WLF equation

b bond length; $b_{\text{eff}} = \text{effective bond length}$

bbl barrel petroleum (= 42 US gallons = $0.158 987 \text{ m}^3$)

C number concentration (number of entities per total volume, $C = cN_A/M$)

[C] amount-of-substance concentration of substance C = amount of substance C per total volume = "molar concentration of C"

heat capacity (usually in J/K); C_p = isobaric heat capacity (heat capacity at constant pressure p); C_V = isochoric heat capacity (heat capacity at constant volume V); C_m = molar heat capacity (heat capacity per amount-of-substance n)

C electrical capacitance (C = Q/U)

c crystallographic bond length = crystallographic length of a repeating unit (usually crystallographic c axis)

specific heat capacity (usually in J/(g K)); c_p = isobaric specific heat capacity; c_V = isochoric specific heat capacity. Formerly: specific heat

List of Symbols X V

concentration = mass concentration (= mass-of-substance per total volume) = "weight concentration." IUPAC calls this quantity "mass density" (quantity symbol ρ). The quantity symbol c has, however, traditionally been used for a special case of mass concentration, i.e., mass-of-substance per volume of solution and the quantity symbol ρ for another special case, the mass density ("density") = mass-of-substance per volume of substance.

The mass concentration of a solute 2 is related to its density ρ and volume fraction by $c_2 = \rho_2 \phi_2$ if volumes are additive.

- \hat{c} velocity of light or sound (depends on chapter)
- D diffusion coefficient; $D_{rot} = rotatory$ diffusion coefficient
- DP often used in literature as the symbol for "degree of polymerization". This book uses *X* instead since slanted (!) two-letter symbols of physical quantities are reserved for dimensionless *transport* quantities (ISO).
- d diameter
- d dimensionality
- E energy
- E tensile modulus (= modulus of elasticity, Young's modulus); E_f = flexural modulus
- *E* electric field strength (vectorial quantity)
- e elementary charge
- e cohesion energy density
- e component of elongation or shearing (tensor)
- **F** force (vectorial quantity)
- F electrical field (vectorial quantity)
- f fraction (unspecified); see also x = amount fraction ("mole fraction"), w = mass fraction ("weight fraction"), $\phi =$ volume fraction
- f fineness = linear density = $m/L = \rho/A$
- f_0 functionality of a molecule
- Gibbs energy (G = H TS); formerly: free enthalpy
- shear modulus (in J m⁻³), G' = shear storage modulus (real modulus, in-phase modulus, "elastic modulus"), G'' = shear loss modulus (imaginary modulus, 90° out-of-phase modulus, viscous modulus), G_N° = plateau modulus
- G statistical weight fraction $(G_i = g_i/\sum_i g_i)$
- G electrical conductance
- G gloss
- $G_{\rm IC}$ fracture toughness (in J m⁻²)
- g acceleration (due to gravity)
- g statistical weight (for example: n, x, w). IUPAC recommends k for this quantity which is problematic because of the many other uses of k. Similarly, K cannot be used for the statistical weight fraction because of the many other meanings of K.
- H height
- H enthalpy; ΔH_{mix} = enthalpy of mixing, $\Delta H_{\text{mix,m}}$ = molar enthalpy of mixing
- H haze

XVI List of Symbols

```
Planck constant (h = 6.626\ 075\ 5\cdot10^{-34}\ J\ s)
h
         height
h
         electric current
         light intensity
         radiation intensity of a molecule
         variable (ith component, etc.)
         flux (of mass, volume, energy, etc.)
J
J
         shear compliance
         general constant; equilibrium constant
K
K
         compression modulus
         Boltzmann constant (k_B = R/N_A = 1.380 658 \cdot 10^{-23} \text{ J K}^{-1})
k_{\rm B}
         length (always geometric); L<sub>chain</sub> = true (historic) contour length of a chain
L
         (= number of chain bonds times length of valence bonds); L_{cont} = conventional
         contour length of a chain (= length of chain in all-trans macroconformation);
         L_{\rm K} = length of a Kuhn segment (Kuhnian length); L_{\rm ns} = persistence length;
         L_{\text{seg}} = \text{segment length}
         molar mass of a molecule in g mol-1 (= physical unit of mass of molecule di-
M
         vided by amount of molecule). \overline{M}_n = number-average molar mass; \overline{M}_w = mass-
         average molar mass. Physical methods (osmometry, light scattering, etc., deter-
         mine molar masses whereas chemical methods (end-group determinations, etc.,
         usually lead to molecular weights, i.e., relative molar masses M_r (dimensionless,
          physical unit "1").
             This book uses the same symbol for molar mass and molecular weight since
         M is used mostly in a descriptive manner and literature data usually do not dis-
          tinguish between molar mass and molecular weight.
          milkiness
 M
          mass; m_{\text{mol}} = \text{mass of molecule}
 m
          number of entities
 N
          Avogadro constant (N_A = 6.022 \ 136 \ 7 \cdot 10^{23} \ \text{mol}^{-1})
 N_{\mathsf{A}}
          amount of substance (in mol); formerly: mole number
          refractive index in medium; n_1 = refractive index of solvent; n_2 = refractive
 n
          index of solute
          permeability coefficient (P = DS)
 P
          power, electric power
 P
          dielectric polarization (= electric dipole moment per volume) (vector)
 P
          pressure
 p
          dipole moment (vectorial quantity)
 p
          electric charge = quantity of electricity
 Q
 Q
```

intermediate variable or constant, usually a ratio; varies with section

intermediate variable or constant, usually a ratio; varies with section

Q

q

9

charge of an ion

List of Symbols XVII

- R molar gas constant ($R = 8.314510 \text{ J K}^{-1} \text{ mol}^{-1}$)
- R electrical resistance
- R Pockels coefficient (electrooptics)
- R reflectivity
- R radius: R_d = Stokes radius (from diffusion coefficient), R_{sph} = radius of equivalent sphere, R_v = Einstein radius (from dilute solution viscosity)
- RH relative humidity
- r radius
- r shift of electrons (vectorial quantity)
- S entropy; ΔS_{mix} = entropy of mixing, $\Delta S_{\text{mix,m}}$ = molar entropy of mixing
- S solubility coefficient
- S electric strength
- S Kerr coefficient (electrooptics)
- s radius of gyration (IUPAC), shorthand for $\langle s^2 \rangle^{1/2}$ (IUPAC); in the literature often as R_g
- temperature (always with units). In physical equations always as thermodynamic temperature with unit kelvin; in descriptions, either as thermodynamic temperature (unit: kelvin) or as Celsius temperature (unit: degree Celsius). Mix-ups can be ruled out because the physical unit is always given. IUPAC recommends for the Celsius temperature either t as a quantity symbol (which can be confused with t for time) or θ (which can be confused with θ for the theta temperature). $T_{\rm C}$ = ceiling temperature, $T_{\rm d}$ = decomposition temperature, $T_{\rm G}$ = glass temperature, $T_{\rm M}$ = melting temperature
- T transparency
- t time
- U internal energy
- U electric potential difference (voltage drop, voltage)
- U tracking force
- *u* fractional conversion of monomer molecules (p = fractional conversion of groups; y = yield of substance)
- u excluded volume
- V volume; $V_{\rm h}$ = hydrodynamic volume, $V_{\rm m}$ = molar volume; $\tilde{V}_{\rm m}$ = partial molar volume
- V electrical potential difference (voltage drop, voltage)
- v specific volume; \tilde{v} = partial specific volume
- v linear velocity (v = dL/dt)
- W work
- w mass fraction = weight fraction. For example, mass fraction of component 2 in a mixture with component 1: $w_2 = m_2/m = x_2/[x_2 + x_1(M_1/M_2)]$
- X degree of polymerization of a molecule with respect to monomeric units (not to repeating units!); \overline{X}_n = number-average degree of polymerization of a substance; \overline{X}_w = mass-average degree of polymerization of a substance
- x mole fraction (amount-of-substance fraction)