Hans-Georg Elias

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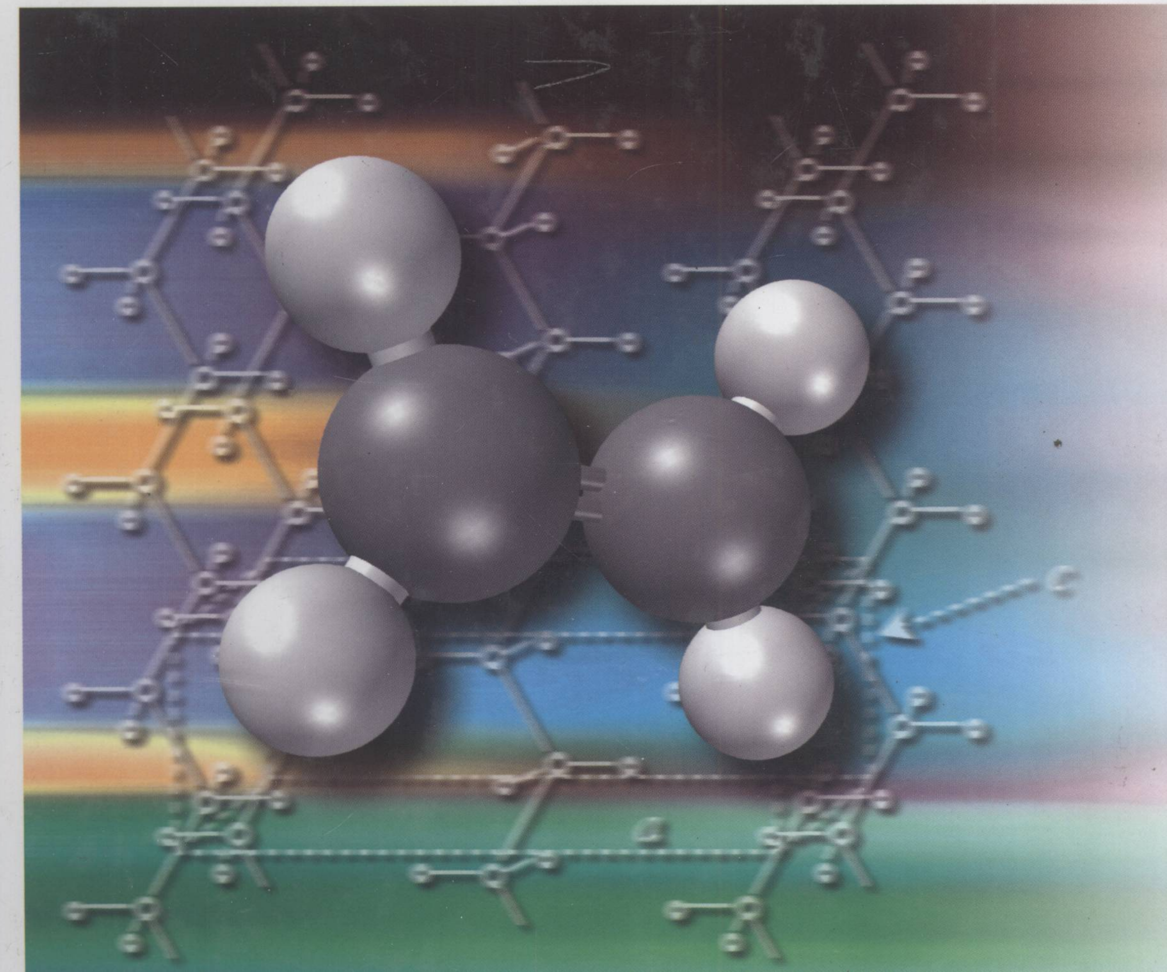
Macromolecules

Volume 3:
Physical Structures and Properties



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The Author

Prof. Dr. Hans-Georg Elias
Michigan Molecular Institute
1910 West St. Andrews Road
Midland, Michigan 48640
USA

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Daran erkenn' ich den gelehrten Herrn!
...
Was ihr nicht rechnet, glaubt ihr, sei nicht wahr;
Was ihr nicht wägt, hat für euch kein Gewicht; ...

Johann Wolfgang von Goethe,
Faust II, Act I (Mephistopheles)

Your words reveal to me a man of learning!
...
what you can't calculate, you don't believe is true;
what you can't weigh is of no weight to you ...

Preface

The series "Macromolecules" consists of four volumes. Volume I discusses chemical structures and principles of syntheses of synthetic and some natural macromolecules. Volume II is concerned with raw materials and energy sorces for the polymer industry, monomer syntheses, industrial polymer manufacture, and general properties of individual polymers. The present Volume III treats physical structures and physical properties of both single macromolecules and macromolecular substances, i.e., polymers. The final Volume IV will be concerned with applications of polymers as plastics, fibers, elastomers, coating, thickeners, etc.

The very short first chapter of Volume III introduces a few chemical and technical terms. The subsequent Chapters 2-4 are concerned with structures and properties of *single macromolecules*. Chapter 2 discusses basic *chemical structures* (nomenclature, polymer architectures, chemical configurations) before it embarks on a detailed treatment of *molar mass averages* and *molar mass distributions*. The discussion of *microconformations* in Chapter 3 is followed in Chapter 4 by a treatment of *macroconformations* of single macromolecules (the polymer configurations of physics) which includes remarks on molecular modeling, chain flexibilities, molecule perturbations, and scaling. Because of their importance, *scattering methods* are discussed in a separate Chapter 5.

The next four chapters treat *physical structures in* the *solid state*: in the amorphous state (Chapter 6), in semicrystalline polymers (Chapter 7), in mesophases (Chapter 8), and of polymer molecules in and at interfaces (Chapter 9).

These chapters are followed by a group of three chapters that are concerned with properties of *polymers in solution*: thermodynamics of polymer solutions (Chapter 10); transport of polymer molecules by diffusion, sedimentation, and electrophoresis (Chapter 11); and rheology of dilute polymer solutions (Chapter 12).

The next three chapters are concerned with general properties of the *molten and bulk states* of polymers such as thermal properties including transitions and treansformations (Chapter 13), transport in and through polymers (Chapter 14), and melt viscosity (Chapter 15).

The final group of three chapters comprises *mechanical properties*: elasticity (Chapter 16), viscoelasticity (Chapter 17), and fracture (Chapter 18). Electrical and optical properties will be discussed in Volume IV.

This volume concludes with an Appendix (Chapter 19) that lists SI physical quantities and units, conversion factors for older units, terminologies of concentrations and ratios of physical quantities, and names and chemical constitutions of polymers that are discussed in this volume.

Volume III touches upon many aspects that are of interest to many scientific and technical disciplines ranging from pure and applied chemistry to pure and applied physics, including theoretical mechanics and the processing and use of plastics and other polymeric materials. Each of these fields has its own terminology, its own way of thinking, and its own idiosyncrasies. Chemists, for example, commonly use names of chemical compounds such as "benzene" without specifying whether they mean the molecule or the substance. The word "compound" itself has different meanings for chemists and technologists and words like "monomer," "configuration," "proton," and "density" signify different things for physicists and chemists. I have tried therefore to be consistent by using recommendations of IUPAC and IUPAP, especially when they deviate from common uses of words.

A book that discusses physical properties cannot restrict itself to rigorous physical theories since the necessary simplifications often do not do justice to the many different phenomena that are caused by widely varying chemical structures, and, often treated as nuisance, the sometimes strong effects of type and width of molar mass distributions on physical properties. Therefore, this volume contains not only many derivations of physical equations but also many experimentally observed properties that so far have eluded more rigorous theoretical approaches. Derivations of physical equations are given in detail if they are short and not too complex mathematically. Elaborate mathematical methods are discussed only qualitatively.

I am again indebted to my good friends and former colleagues at Michigan Molecular Institute, Professors Petar R. Dvornic and Steven E. Keinath, who read and checked the final draft of all chapters and made many helpful suggestions.

Midland, Michigan
Fall 2007

Hans-Georg Elias

List of Symbols

Symbols for physical units are strictly those of the International Standardization Organization (ISO). See Chapter 19 (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); exceptions are indicated. 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 (≡ physical quantity divided by mass) 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., see Appendix.

Indices are slanted if they refer to a 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 (example: $\overline{M}_\mathrm{n}$ = number-average molar mass).

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.

Symbols for Languages

D = German (deutsch),
F = French,
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: πολυς = polys (many)). For the same reason, χ was transliterated as "ch" and not as "kh."

Mathematical Symbols (IUPAC)

=	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
→	approaches, tends to	±	plus or minus
Δ	difference	sin	sine of
δ	differential	cos	cosine of
f	function of (IUPAC: *f*)	tan	tangent of
Σ	sum	cot	cotangent of
∫	integral	sinh	hyperbolic sine of
Π	product	arctan	inverse tangent

lg	logarithm to the base 10	(IUPAC: lg or $\log_{10}$)
ln	logarithm to the base e (natural logarithm)	(IUPAC: ln or $\log_\mathrm{e}$)

Symbols for Chemical Structures

A: symbol for a monomer or a leaving group (polycondensations)
B: symbol for a monomer or a leaving group (polycondensations)
L: symbol for a leaving molecule, for example, H_2O from the reaction of –COOH + HO–
R: symbol for a monovalent substituent, for example, CH_3– or C_6H_5–
Z: symbol for a divalent unit, for example, –CH_2– or –*p*-C_6H_4–
Y: symbol for a trivalent unit, for example, −C(R)< or −N<
X: symbol for a tetravalent unit, for example, >C< or >Si<
*: symbol for an active site: radical ($^{\bullet}$), anion ($^{\ominus}$), cation ($^{\oplus}$)
*p*Ph *para*-phenylene (in text)
p-C_6H_4 *para*-phenylene (in line formulas)

Averages and Other Markings

–	line above letter indicates common average, for example, $\overline{M}_{\mathrm{n}}$ = 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, $\tilde{v}_{\mathrm{A}}$ = 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, $\lvert q \rvert$ = magnitude of the scattering vector $\boldsymbol{q}$

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, $[\eta] = K_{\mathrm{v}} M^{\alpha}$.

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

Indices and Subscripts

Subscripts are slanted if they refer to physical properties that are held constant. Example: C_p = isobaric heat capacity.

o	standard or original state, for example, T_o = reference temperature
0	state at time zero
1	solvent
2	solute, usually polymer
3	additional component (salt, precipitant, etc.)
∞	final state
A	compound A, for example, M_A = molar mass of substance A
a	group or monomeric unit of A, for example, mass m_a of group a
am	amorphous
B	substance B
B	fracture
b	group, for example, monomeric unit from substance B
bd	bond, especially chain bond
be	effective bond length (= length of monomer unit projected onto the chain direction)
bl	blob
bp	boiling temperature (boiling point)
br	branch, branched
c	chain (L: *catena*), for example, in networks
cl	coil
comb	combination
cr	crystalline
crit	critical
crl	correlation, for example, L_{crl} = correlation length
cryst	crystallization
cu	chain unit, for example, $-CH_2-$ in $+O-CH_2+_n$
cycl	cyclic
D	related to diffusion
e	entanglement
el	elastic
eff	effective
end	endgroup
eq	equilibrium
exc	excess
F	filler
fl	flexural
G	glass transformation
g	any statistical weight, e.g., n, m, z or x, w, Z
H	hydrodynamically effective property or hydration
h	hydrodynamic average
I	Initiator molecule; I^* active initiator species, for example, a radical $I^\bullet$
i	ith component

i	isotactic diad (IUPAC recommends m = *meso*; see Chapter 4)
ii	isotactic triad (IUPAC: mm)
iii	isotactic tetrad (IUPAC: mmm)
inh	inherent (dilute solution viscosity)
is	heterotactic triad (IUPAC: mr)
$\lvert\text{is}\rvert$	sum of heterotactic triads, $\underline{\text{is}}$ = is + si
it	isotactic
j	variable
k	variable
k	chain unit
L	liquid, melt
l	liquid
M	melting
M	monomer molecule
M	matrix (in blends or reinforcd polymers)
Mt	metal
m	monomeric unit in macromolecules
m	molar (also as superscript)
mol	molecule
mon	monomer (if M is confusing)
mu	monomeric unit
n	number average (note: *not* in italics since it does not refer to a physical quantity that is held constant)
P	polymer
p	index for quantity at constant pressure
p	packing
pol	polymer (if P is confusing)
ps	persistence
q	index, defined differently for each section or chapter
q	number of electric charges
R	reactant
r	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 (with respect to the end-to-end distance)
red	reduced
rel	relative
rep	repeating unit
rlx	relaxation
S	solvating solvent
S	related to sedimentation
s	syndiotactic diad (IUPAC recommends r = *racemo*)
s	related to radius of gyration
seg	segment
si	heterotactic triad (IUPAC recommends rm)
sl	screening length
soln	solution

sph	sphere
ss	syndiotactic triad (IUPAC recommends rr)
T	index for quantity at constant temperature
t	termination
tr	transfer
u	monomeric unit in polymer
u	monomer conversion
V	quantity at constant volume
v	viscosity average (solutions)
w	mass average ("weight average"); note: *not* in italics since it does not refer to a physical quantity that is held constant
x	crosslink(ed)
y	yield (stress-strain)
z	z average
η	viscosity average (melts)

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, l-branch = long chain branch, f-branch = branched with a branching point of functionality f
cis	cis configuration with respect to C–Cdouble bonds
co	joint (unspecified)
comb	comb
compl	polymer–polymer complex
cyclo	cyclic
ct	cis-tactic
eit	erythrodiisotactic
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
sl	screening length
st	syndiotactic
star	star-like. f-star, if the functionality f is known; f is then a number
stat	statistical (unspecified distribution)
tit	threodiisotactic
trans	trans configuration with respect to C-C double bonds
tt	trans-tactic

Other Abbreviations

AIBN	*N,N'*-azobisisobutyronitrile
BPO	dibenzoylperoxide
Bu	butyl group (*i*Bu = isobutyl group; *n*Bu = normal butyl group (according to IUPAC, the normal butyl group is not characterized by *n*, which rules out Bu as an unspecified butyl group); *s*Bu = secondary butyl group; *t*Bu = 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
I	initiator
IR	infrared
L	solvent (liquid)
LC	liquid-crystalline
LS	light scattering
MC	main chain
Me	methyl group
Mt	metal atom
Np	naphthalene
NMR	nuclear magnetic resonance
P	polymer
Ph	phenyl group
Pr	propyl group
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 19, Appendix)

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

A	absorption ($A = \lg (I_0/I) = \lg (1/\tau_i)$); formerly: extinction
A	area; A_c = cross-sectional area of a chain
A	Helmholtz energy ($A = U - TS$); formerly: free energy
$A^{\ddagger}$	pre-exponential constant (in $k = A^{\ddagger} \exp(-E^{\ddagger}/RT)$)

A_2	second thermodynamic virial coefficient
A_3	third thermodynamic virial coefficient
a	thermodynamic activity
a	linear absorption coefficient ($a = (1/L)\ \lg\ (I_0/I)$)
a_T	shift factor in the WLF equation
b	bond length; b_{eff} = effective bond length
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"
C	transfer constant (always with index, e.g., C_r of a regulator, C_s of a solvent)
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 capacity
C_N	Characteristic ratio in random coil statistics; C_∞ = characteristc ratio at infinitely high molecular weight
c	crystallographic bond length = crystallographic length of a repeating unit (usually crystallographic c axis)
c	specific heat capacity (usually in J/(g K)); c_p = isobaric specific heat capacity; c_V = isochoric specific heat capacity. Formerly: specific heat
c	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
D	tensile compliance
DP	often used in literature as 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_{bl} = diameter of a blob, d_{sph} = diameter of a sphere, etc.
d	dimensionality
E	energy
E	tensile modulus (= modulus of elasticity, Young's modulus); E_f = flexural modulus
$\boldsymbol{E}$	electric field strength (vectorial quantity)
e	elementary charge
e	cohesion energy density
$\boldsymbol{e}$	component of elongation or shearing (tensor)
$\boldsymbol{F}$	force (vectorial quantity)
f	fraction (unspecified); see also x = amount fraction ("mole fraction"), w = mass fraction ("weight fraction"), ϕ = volume fraction

f_o	functionality of a molecule
f_{or}	Hermans orientation factor
G	Gibbs energy ($G = H - TS$); formerly: free enthalpy
G	shear modulus, G' = shear storage modulus (real modulus, in-phase modulus, "elastic modulus"), G'' = shear loss modulus (imaginary modulus, 90° out-of-phase modulus, viscous modulus), $G_N{}^o$ = plateau modulus
G	statistical weight fraction ($G_i = g_i/\Sigma_i g_i$)
G	conductance
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.
g	parameter for the ratio of dimensions of branched macrmolecules to those of unbranched macromolecules of equal molecular weight (branching index); g_h = branching index from hydrodynamic measurements
H	height
H	enthalpy; ΔH_{mix} = enthalpy of mixing, $\Delta H_{mix,m}$ = molar enthalpy of mixing
h	Planck constant ($h = 6.626\ 075\ 5 \cdot 10^{-34}$ J s)
h	branching index in hydrodynamics
I	electric current
I	light intensity
i	radiation intensity of a molecule
i	variable (ith component, etc.)
J	flux (of mass, volume, energy, etc.)
J	shear compliance
K	general constant; equilibrium constant
K	compression modulus
k	rate constant (always with index); k_i = rate constant of initiation; k_p = rate constant of propagation, k_t = rate constant of termination, k_{tr} = rate constant of transfer
k_B	Boltzmann constant ($k_B = R/N_A = 1.380\ 658 \cdot 10^{-23}$ J K^{-1})
L	length (always geometric); L_{chain} = true (historic) contour length of a chain (= 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_K = length of a Kuhn segment (Kuhnian length); L_{ps} = persistence length; L_{seg} = segment length
L	phenomenological coefficient
l	length
$\mathbf{M}$	moment
M	molar mass of a molecule (= physical unit of mass of molecule divided by amount of molecule, for example, g/mol). $\overline{M}_n$ = number-average molar mass; $\overline{M}_w$ = mass-average molar mass; M_{crit} = critical molar mass; $\overline{M}_{R,n}$ = number-average molar mass of reactants (= polymer plus monomer)
M_e	entanglement molar mass from Newtonian viscosities ($M_{e,\eta}$) or the plateau modulus ($M_{e,G}$)

M_r	relative molar mass = relative molecule mass = molecular weight (physical unit of unity = "dimensionless"); $\overline{M}_{r,n}$ = number-average molecular weight
m	mass; m_{mol} = mass of molecule
N	number of entities
N_A	Avogadro constant ($N_A = 6.022\ 136\ 7 \cdot 10^{23}\ \mathrm{mol}^{-1}$)
n	amount of substance (in mol); formerly: mole number
n	refractive index in medium; n_1 = refrective index of solvent; n_2 = refractive index of solute
P	permeation coefficient ($P = DS$)
P	power
P	Perrin factor (ellipsoids)
$P(\mathrm{q})$	particle scattering factor
p	conditional probability
p	pressure
p	extent of reaction (fractional conversion); p_A = extent of reaction of A groups
p	number of conformational repeating units per completed helical turn
$\boldsymbol{p}$	dipole moment (vectorial quantity)
Q	electric charge = quantity of electricity
Q	heat
Q	parameter in the Q,e copolymerization equation
Q	polymolecularity index ("polydispersity index"), for example, $Q = \overline{M}_w/\overline{M}_n$
Q	intermediate variable or constant, usually a ratio; varies with section
q	intermediate variable or constant, usually a ratio; varies with section
q	charge of an ion
q	scattering parameter with a magnitude of $\lvert\boldsymbol{q}\rvert = q = (4\ \pi n_1/\lambda_o)\sin(\vartheta/2)$
R	molar gas constant ($R = 8.314\ 510\ \mathrm{J\ K^{-1}\ mol^{-1}}$)
R	electrical resistance
R	dichroic ratio
R	rate of reaction, for example, R_p = rate of propagation
R	radius: R_d = Stokes radius (from diffusion coefficient), R_{sph} = radius of equivalent sphere, R_v = Einstein radius (from dilute solution viscosity)
R_θ	Rayleigh ratio of scattering intensities
r	radius
r	spatial end-to-end distance of a chain, usually as $\langle r^2\rangle^{1/2}$ with various indices; r_{cont} = conventional contour length (= end-to-end distance of a chain in all-trans conformation)
r	copolymerization parameter
r_0	initial ratio of amounts of substances in copolymerizations
S	entropy; ΔS_{mix} = entropy of mixing, $\Delta S_{mix,m}$ = molar entropy of mixing
S	solubility coefficient
S	sedimentation coefficient (literature uses mainly s which is the IUPAC symbol for the radius of gyration)
S_{pq}	(elastic) compliance tensor (Reuss elasticity constant)
s	radius of gyration (IUPAC), shorthand for $\langle s^2\rangle^{1/2}$ (IUPAC); in the literature often as R_g
s	selectivity coefficient (osmotic pressure)