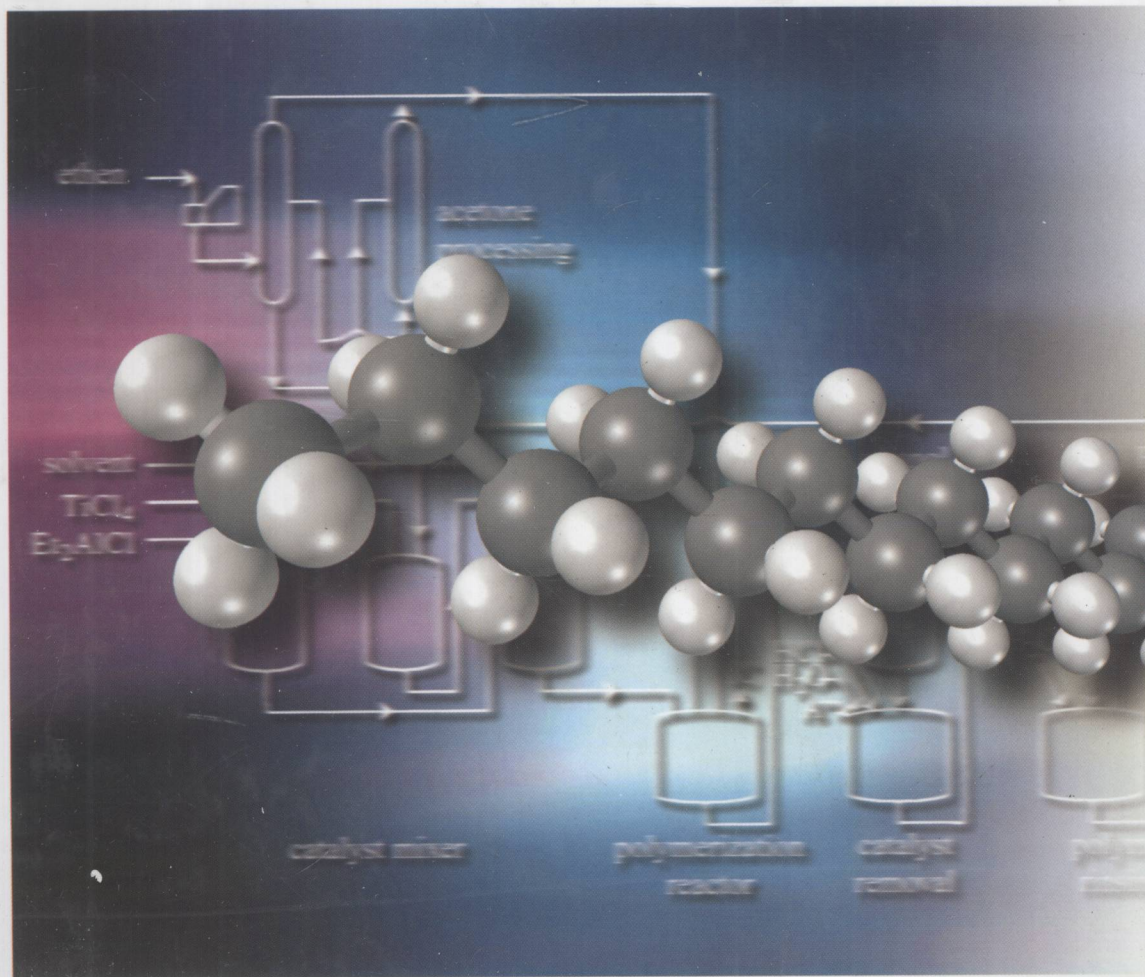


Hans-Georg Elias

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Macromolecules

Volume 2:
Industrial Polymers and Syntheses



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Volume 2: Industrial Polymers and Syntheses



E2010000084

WILEY-VCH Verlag GmbH & Co. KGaA

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- Volume 1 Chemical Structures and Syntheses
(Published in 2005)
- Volume 2 Industrial Polymers and Syntheses
- Volume 3 Physical Structures and Properties
- Volume 4 Processing and Application of Polymers

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Library of Congress Card No.:
applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available in the Internet at <http://dnb.d-nb.de>.

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Printed in the Federal Republic of Germany
Printed on acid-free paper

Printing Strauss GmbH, Mörlenbach

Binding Litges & Dopf Buchbinderei,
Heppenheim

Cover Design Gunther Schulz, Fußgönheim

ISBN: 978-3-527-31173-6

Hans-Georg Elias
Macromolecules

1807–2007 Knowledge for Generations

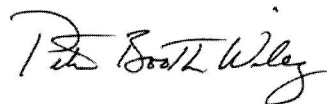
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The polymers, those giant molecules,
like starch and polyoxymethylene,
flesh out, as protein serfs and plastic fools,
the Kingdom with life's stuff.

John Updike
The Dance of the Solids
("Midpoint and Other Poems"
A. Knopf, New York 1968)

Preface

The preceding Volume I of the 4-volume work "Macromolecules" discusses chemical structures and syntheses of natural and synthetic macromolecules. It is mainly concerned with the principles of structures and polymerizations which by necessity involves ideal and idealized structures and processes. Industrial polymerizations are rarely ideal, however. Monomers are usually not pure by laboratory standards and reactions are often neither isothermal nor homogeneous. Variations in the type of initiator or catalyst, in the nature of the process (homogeneous versus heterogeneous, continuous versus discontinuous), deliberately introduced side reactions, or small proportions of comonomers produce very different *grades* of polymers from the same monomer.

The present Volume II is thus concerned with what can loosely be called the *chemical technology* of polymers. Like Volume I, it is based on a volume of the 6th German edition of this work, i.e., Volume III (2001). It is not a cover-to-cover translation, though, but an updated and expanded version as attested to by the size (635 versus 566 pages) and the fact that no less than 43 % of all of the figures are new.

Commodity polymers such as poly(ethylene), poly(propylene), poly(styrene), poly(vinyl chloride), poly(hexamethylene adipamide), etc., result from a few types of monomers that are especially simple to obtain from intermediates and raw materials. On the other hand, very many different types of monomers are used not only for specialty plastics, fibers, and rubbers but also for other polymer applications such as thickeners, in optoelectronics, for surface treatments, and the like. Information about such monomers and polymers can rarely be found in standard textbooks of polymer science. Monographs about specific polymers, on the other hand, usually concentrate on applications but not on syntheses, structures, and fundamental properties. The bulk of the chapters of this book thus discusses the *chemical technology* of industrially produced and/or used polymers, both synthetic ones and those based on natural sources.

Chemical technology is concerned with the delicate and complex interplay between the availability and chemistry of raw materials, base chemicals, intermediates, monomers, and polymers, the chemistry and technology of polymerization processes and plants, the properties and use of polymers, and the influence of economics, politics, and environmental concerns.

Chapter 1 of this book introduces the field. Chapter 2 reviews very briefly some of the chemical and physical polymeric terms that are used in later chapters of this volume. Although these aspects are discussed in great detail in the other three volumes of this series, it was deemed necessary to include such a chapter in order to make the book self-contained as much as possible.

Chapter 3 discusses raw materials for polymers (coal, natural gas, crude oil, wood, etc.) as well as their competing uses as energy sources, including economic and environmental aspects. Chapter 4 briefly outlines the sources of intermediates and monomers for polymers without detailing the chemistry of their syntheses, which is beyond the scope of this book.

Chapter 5 reviews basic polymerization mechanisms, processes, and techniques as well as polymerization reactors and their influence on polymer properties. The book does not venture into chemical engineering proper: hardware is treated in only a cursory manner and software such as process modeling and scale-up not at all.

Chapters 6–12 constitute the bulk of the book since they survey industrial syntheses and basic properties of the industrially and scientifically most important polymers. Each chapter comprises polymers of the same basic chain structure which usually coincides with an organization according to their syntheses and/or their intermediates and raw materials. Chapter 6 is therefore concerned with carbon-chain polymers, Chapter 7 with carbon-oxygen chains, Chapter 8 with polysaccharides, Chapter 9 with carbon-sulfur chains, Chapter 10 with carbon-nitrogen chains, Chapter 11 with peptides and proteins, and Chapter 12 with inorganic and semi-inorganic polymers.

Even a book of this size cannot discuss *all* polymers. It concentrates therefore on major industrial commodity and specialty polymers, including abandoned ones if they teach a lesson. Also included are some polymers that are not yet industrial but are interesting because their structures, syntheses, and/or properties are often not easy to generalize. "Polymer" is used in the widest meaning: it includes many biopolymers as well as several inorganic polymers that are of great economic importance but are usually not treated in polymer textbooks.

The book concentrates on industrial syntheses; physical properties and applications of resulting polymers are discussed in a qualitative manner but not in great detail (see Volume III for principles of general physical properties and structure–property relationships). This book does describe average properties of unmodified standard grades before processing, however; these data were taken from handbooks or company literature.

Compounding and processing of polymers to plastics, elastomers, fibers, coatings, etc., is not discussed here but in Volume IV of this work. Volume IV also contains data on filled and reinforced polymers as well as adjuvants for polymers.

Volume II is not an encyclopedia. Space requirements and the impossibility of reporting all available information restricts the treatment of individual polymers and processes to exemplary data. A complete list of all polymer properties, process variations, and applications is neither possible nor attempted. The volume should however provide a glimpse at the many possible syntheses of base chemicals, intermediates, monomers, and polymers and the almost infinite variations in the structures and properties of the resulting polymers. The content of Volume II is therefore much more descriptive and less quantitative than that of Volumes I (fundamental chemistry) and III (physical chemistry and physics).

The whole "Macromolecules" series can probably be best described as an expanded textbook: the four volumes are not monographs and therefore also not reference books. More in-depth information can be found in the extensive lists of monographs and review articles which includes some older books that I used as sources of information for historic data. Primary publications are usually too specialized for the scope of this work; they are therefore only cited as sources of graphs and tables.

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. My profound thanks go also to Dr. Friedrich Schierbaum, Potsdam, for the fast and detailed help with the section "Starch."

List of Symbols

Symbols for physical quantities follow the recommendations of the International Union of Pure and Applied Chemistry (IUPAC), symbols for physical units those of the International Standardization Organization (ISO). Exceptions are indicated.

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 = (classic) Greek, L = (classic) 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: $\pi\omicron\lambda\upsilon\varsigma$ = polys (many)). For the same reason, χ was transliterated as "ch" and not as "kh."

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 $-\text{COOH} + \text{HO}-$

R: symbol for a monovalent substituent, for example, CH_3- or C_6H_5-

Z: symbol for a divalent unit, for example, $-\text{CH}_2-$ or $-p\text{-C}_6\text{H}_4-$

Y: symbol for a trivalent unit, for example, $-\text{C}(\text{R})<$ or $-\text{N}<$

X: symbol for a tetravalent unit, for example, $>\text{C}<$ or $>\text{Si}<$

*: symbol for an active site: radical (\bullet), anion (\ominus), cation (\oplus)

pPh *para*-phenylene (in text)

p-C₆H₄ *para*-phenylene (in line formulas)

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*

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
star	star-like; f-star, if the functionality f is known; f is then a number
st	syndiotactic
stat	statistical (unspecified distribution)
tit	threodiisotactic
tt	trans-tactic

Quantity Symbols (unit symbols, see Chapter 13, Appendix)

Quantity symbols follow in general the recommendations of IUPAC.

[C]	amount-of-substance concentration of substance C = amount of substance C per total volume = "mole concentration of C"
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
E	energy
f	fraction (unspecified), see also x , w , ϕ , etc.
f	functionality
G	Gibbs energy ($G = H - TS$); formerly: free enthalpy
H	enthalpy; ΔH_{mix} = enthalpy of mixing, $\Delta H_{\text{mix,m}}$ = molar enthalpy of mixing
i	variable (i th component, etc.)
K	general constant; K_{n} = equilibrium constant
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 ($k_{\text{B}} = R/N_{\text{A}} = 1.380\,658 \cdot 10^{-23} \text{ J K}^{-1}$)
L	length (always geometric)
M	molecular weight. In this volume used instead of the correct symbol M_{r} (= relative molar mass with physical unit 1). Note that most physical methods measure molar masses (physical unit: mass per amount-of-substance) and not molecular weights. Molar mass and molecular weight are numerically identical if the molar mass is given in g/mol. \overline{M}_{n} = number-average molecular weight; \overline{M}_{w} = weight-average molecular weight
m	mass
N	number of entities
N_{A}	Avogadro constant ($N_{\text{A}} = 6.022\,136\,7 \cdot 10^{23} \text{ mol}^{-1}$)
n	amount of substance (in mol); formerly: mole number
p	extent of reaction (fractional conversion); p_{A} = extent of reaction of A groups
Q	polymolecularity index (= "polydispersity index"), e.g., $Q = \overline{M}_{\text{w}}/\overline{M}_{\text{n}}$

R	molar gas constant ($R \approx 8.314\,510\,\text{J K}^{-1}\,\text{mol}^{-1}$)
R	rate of reaction
r	copolymerization parameter
r_0	initial ratio of amounts of substances in copolymerizations
S	entropy
T	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_c = ceiling temperature, T_G = glass temperature, T_M = melting temperature
t	time
u	fractional conversion of monomer molecules (p = fractional conversion of groups; y = yield of substance)
V	volume
w	mass fraction = weight fraction
X	degree of polymerization of a molecule with respect to monomeric units (not to repeating units); \bar{X}_n = number-average degree of polymerization of a substance; \bar{X}_w = mass-average degree of polymerization of a substance
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.
x_{br}	degree of branching
y	yield of substance
z	coordination number, number of neighbors
ϵ_r	relative permittivity (formerly: dielectric constant)
η	dynamic viscosity, e.g., η_0 = viscosity at rest (Newtonian viscosity), η_1 = viscosity of solvent
	$\eta_r = \eta/\eta_1$ = relative viscosity,
	$\eta_i = (\eta - \eta_1)/\eta_1$ = relative visc. increment (= specific viscosity, η_{sp}),
	$\eta_{inh} = (\ln \eta_r)/c$ = inherent viscosity (= logarithmic visc. number),
	$\eta_{red} = (\eta - \eta_1)/(\eta_1 c)$ = reduced viscosity (= viscosity number, η_{sp}/c),
	$[\eta] = \lim_{c \rightarrow 0} \eta_{red}$ = limiting visc. number (= intrinsic viscosity)
λ	wavelength (λ_0 = wavelength of incident light)
ν	kinetic chain length
ν	frequency
π	mathematical constant pi
ρ	density (= mass/volume of the same matter)
ϕ	volume fraction; ϕ_f = free volume fraction
ϕ	angle

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