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Ullmann's Polymers and Plastics

Products and Processes

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Preface

This handbook features selected articles from the 7th edition of *ULLMANN'S Encyclopedia of Industrial Chemistry*, including newly written articles that have not been published in a printed edition before. True to the tradition of the ULLMANN'S Encyclopedia, polymers and plastics are addressed from an industrial perspective, including production figures, quality standards and patent protection issues where appropriate. Safety and environmental aspects which are a key concern for modern process industries are likewise considered.

More content on related topics can be found in the complete edition of the ULLMANN'S Encyclopedia.

About ULLMANN'S

ULLMANN'S Encyclopedia is the world's largest reference in applied chemistry, industrial chemistry, and chemical engineering. In its current edition, the Encyclopedia contains more than 30,000 pages, 15,000 tables, 25,000 figures, and innumerable literature sources and cross-references, offering a wealth of comprehensive and well-structured information on all facets of industrial chemistry.

1,100 major articles cover the following main areas:

- Agrochemicals
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- Materials
- Metals and Alloys
- Organic Chemicals
- Pharmaceuticals
- Polymers and Plastics
- Processes and Process Engineering
- Renewable Resources
- Special Topics

First published in 1914 by Professor Fritz Ullmann in Berlin, the *Enzyklopädie der Technischen Chemie* (as the German title read) quickly became the standard reference work in industrial chemistry. Generations of chemists have since relied on ULLMANN'S as their prime reference source. Three further German editions followed in 1928–1932, 1951–1970, and in 1972–1984. From 1985 to 1996, the 5th edition of ULLMANN'S Encyclopedia of Industrial Chemistry was the first edition to be published in English rather than German language. So far, two more complete English editions have been published in print; the $6th$ edition of 40 volumes in 2002, and the $7th$ edition in 2011, again comprising 40 volumes. In addition, a number of smaller topic-oriented editions have been published.

Since 1997, *ULLMANN'S Encyclopedia of Industrial Chemistry* has also been available in electronic format, first in a CD-ROM edition and, since 2000, in an enhanced online edition. Both electronic editions feature powerful search and navigation functions as well as regular content updates.

Contents

Symbols and Units

Symbols and units agree with SI standards (for conversion factors see page XI). The following list gives the most important symbols used in the encyclopedia. Articles with many specific units and symbols have a similar list as front matter.

Symbols and Units (Continued from p. IX)

Symbol	Unit	Physical Quantity
U	J	internal energy
V	$m^3,$ L, mL, μL	volume
w		mass fraction
W	J	work
x_B		mole fraction of substance B
Z		proton number, atomic number
α		cubic expansion coefficient
α	$Wm^{-2}K^{-1}$	heat-transfer coefficient (heat-transfer number)
α		degree of dissociation of electrolyte
$[\alpha]$	10^{-2} deg cm ² g ⁻¹	specific rotation
η	Pa·s	dynamic viscosity
θ	C	temperature
χ		c_p/c_v
λ	$Wm^{-1}K^{-1}$	thermal conductivity
λ	nm, m	wavelength
μ		chemical potential
ν	$\text{Hz}, \text{ s}^{-1}$	frequency
$\boldsymbol{\nu}$	m^2/s	kinematic viscosity (η/ρ)
π	Pa	osmotic pressure
\mathbf{Q}	g/cm ³	density
σ	N/m	surface tension
τ	Pa $(N/m2)$	shear stress
φ		volume fraction
χ	Pa^{-1} (m ² /N)	compressibility

*** The official unit of pressure is the pascal (Pa).

Conversion Factors

Powers of Ten

Abbreviations

The following is a list of the abbreviations used in the text. Common terms, the names of publications and institutions, and legal agreements are included along with their full identities. Other abbreviations will be defined wherever they first occur in an article. For further abbreviations, see page IX, Symbols and Units; page XVII, Frequently Cited Companies (Abbreviations), and page XVIII, Country Codes in patent references. The names of periodical publications are abbreviated exactly as done by Chemical Abstracts Service.

Frequently Cited Companies (Abbreviations)

Country Codes

The following list contains a selection of standard country codes used in the patent references.

∗ For Europe, Federal Republic of Germany, Japan, and the Netherlands, the type of patent is specified: EP (patent), EP-A (application), DE (patent), DE-OS (Offenlegungsschrift), DE-AS (Auslegeschrift), JP (patent), JP-Kokai (Kokai tokkyo koho), NL (patent), and NL-A (application).

Periodic Table of Elements

element symbol, atomic number, and relative atomic mass (atomic weight)

1A "European" group designation and old IUPAC recommendation
1 group designation to 1986 IUPAC proposal

^a provisional IUPAC symbol

* radioactive element; mass of most important isotope given.

Part 1

Fundamentals

Plastics, General Survey, 1. Definition, Molecular Structure and Properties

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1. Introduction

Plastics are commercially used materials that are based on polymers or prepolymers. The name plastics refers to their easy processibility and shaping (Greek: $plastein = to form, to shape)$. Plastics and polymers, also termed macromolecules (Greek: *macro* = large), are not synonyms. Polymers or prepolymers are raw materials for plastics; they become plastics only after processing. The same polymers may be used as plastics or as fibers, paints, rubbers, coatings, adhesives, thickeners, surfactants, and ionexchange membranes. Properties of polymers are engineered by varying the molecular architecture or the formulation, combining them with different materials in multicomponent and multiphase systems. Typically, plastics contain additives that are needed to enhance their stability and to tune their properties. Unparalleled by any other material, polymers are exceptional regarding their attractive combination of facile processing with low mass and high versatility in terms of properties, applications, flexible choice of feedstocks, and recycling. The system integration of functional polymers represents the key to the development of advanced technologies with applications ranging from lightweight engineering to packaging, construction, aerospace and automotive industries, as well as biomedical engineering. Whereas most plastics are passive, advanced functional

plastics are rendered interactive and capable of responding to environmental stimuli. Today, highly cost-, resource-, eco-, and energyefficient polymers play a prominent role in sustainable development of advanced materials and technologies.

1.1. Polymers

1.1.1. Fundamental Terms [1–16]

The term polymer refers to macromolecules composed of many units (Greek: *poly* = many, *meros* = parts). As first proposed by HERMANN STAUDINGER in 1920, who was awarded the Nobel Price of Chemistry for his groundbreaking concept in 1953, macromolecules consist of many atoms, usually a thousand or more, thereby having high molar masses. Prior to STAUDINGER, the term polymer was not related to high molar mass. For example, benzene was originally called a polymer which was "polymerized" from three acetylene molecules. What is now called a polymer consists of molecules with hundreds and thousands of such units; it was therefore termed "high polymer" in the ancient literature. The term polymer carries with it the connotation of molecules composed of many equal "mers", such as the ethylene units

in polyethylene, $R'(CH_2CH_2)_nR''$. The number *n* of monomer units in the polymer molecule is called the degree of polymerization *X*. There are, however, many polymer molecules (especially biopolymer molecules) with very different types of monomers per molecule, such as protein molecules H(NH–CHR– CO)*n*OH with up to 20 different R substituents. In accordance with STAUDINGER's view, a less constraining and more general term for polymer molecule is thus macromolecule. However, there is no sharp dividing line with respect to the number of units per molecule between macromolecules and low molar mass compounds. In principle, linear thermoplastic polymers are considered polymers when entanglement occurs, thus accounting for the viscoelastic properties typical for polymeric thermoplastics.

It was HERMANN STAUDINGER who recognized that polymers in industry and in nature are synthesized according to the same blueprint. Similar to pearls in a pearl necklace, monomer molecules are linked together by covalent bond formation. In the early days of polymer sciences and engineering, all polymers were biobased, because efficient synthetic polymerization processes were not at hand. Prominent examples of biopolymers include proteins, polynucleotides, *cis*-1,4-polyisoprene as natural rubber, polysaccharides (carbohydrates) with cellulose as the most abundant polymer and major component of biomass. Wood is a composite of two biopolymers, i.e., cellulose and lignin. As pointed out by STAUDINGER and others, most silicates are inorganic polymers derived by polymerization of silicic acid and its derivatives. Some of these naturally occurring polymers are used by man without further chemical transformation (e.g., cellulose for paper and cardboard). Yet, the chemical transformation of natural polymers with retention of their chain structures leads to solution and even melt processable semisynthetic materials, for example, cellulose acetates from cellulose. Chains of other natural polymers are crosslinked before commercial use. Examples are the hardening of casein (a protein) by formaldehyde to produce galalith (plastic) or the vulcanization of *cis*-1,4-polyisoprene (natural rubber) to afford an elastomer.

Today, most polymers are synthesized chemically from synthetic monomers. Examples include the preparations of polyethylene from ethylene, poly(vinyl chloride) from vinyl chloride, nylon 6 from ε-caprolactam, or nylon 66 from adipic acid and hexamethylenediamine. Whereas the majority of monomers are derived from oil and gas in petrochemistry, the progress in biotechnology and the quest for green economy are stimulating the production of bio-based synthetic monomers, such as butadiene, ethylene, propene, acrylic acid, glycol, and lactic acid in biorefineries using biomass as feedstock. Some industrial polymers result from the chemical conversion of other synthetic polymers, for example, poly(vinyl alcohol) from poly(vinyl acetate). In contrast to natural polymer syntheses and biotechnology, most large scale commercial synthetic polymers are produced in the absence of water either in bulk or gas phase. Moreover, compared to biopolymers, synthetic polymers, including the synthetic bio-based polymers derived from renewable feedstocks, are much easier to tailor with respect to their molar mass distribution, short- and long-chain branching and stereochemistry, thus meeting the demands of polymer melt processing and polymer applications. In contrast to protein synthesis, where polypeptide chains are produced with identical molar mass and comonomer sequence distribution, is rather problematic to produce thermoplastics with shear thinning resulting from long chain branching and multimodal molar mass distribution with enzyme-catalyzed reactions.

1.1.2. Nomenclature [1, 5, 17–19]

The nomenclature of individual polymers and plastics is as confusing as their classification according to properties. Various systems of nomenclature are used simultaneously. Abbreviations and acronyms abound, sometimes with different meanings for the same letter combinations and other times without explanation. In addition, many thousands of trade names are used worldwide for plastics, fibers, elastomers, and polymeric additives. Furthermore, a polymer from a certain company may come in many different grades depending on the processibility and application, sometimes up to 100 per polymer type. Some of these grades may even bear different trade names for various applications. The following nomenclature systems are commonly used for polymers.

Long-known Natural Polymers often have Trivial Names. Examples are cellulose, the polymeric sugar (-ose) of the plant cell; casein, the most important protein of milk and cheese (Latin: *caseus* = cheese); nucleic acids, the acids found in the cell nucleus; catalase, a catalyzing enzyme.

Synthetic Polymers are often Named after Their Monomers. Polymers of ethylene thus lead to polyethylene, styrene to polystyrene, vinyl chloride to poly(vinyl chloride), and lactic acid to a polylactic acid. This "polymonomer" nomenclature has the disadvantage that the constitution of monomeric units of the polymer molecules is not identical with the constitution of the monomers themselves. For example, the polymerization of ethylene, $CH₂=CH₂$, leads to ~(CH_2 – CH_2)_n∼, a saturated compound and thus a polyalkane, not an unsaturated "ene" as the name polyethylene may suggest. The polymerization of lactams (cyclic amides) does not give macromolecules with intact lactam rings in the polymer chains but gives openchain polyamides, etc. This polymonomer scheme is also ambiguous if a monomer can lead to more than one characteristic unit in a polymer. An example is acrolein, $CH₂=CH$ (CHO), which can polymerize via the ethylenic double bond to give ∼[CH2–CH(CHO)]*n*∼, via the aldehyde group to $~\sim [O-CH(CH=CH₂)]_n$, or via both to give six-membered rings in polymer chains.

For trade purposes, certain polymer names may denote not only homopolymers but also copolymers, contrary to what the "chemical" names imply. For example, the copolymers of ethylene with up to 10% butene-1, hexene-1, or octene-1 are known as linear low-density polyethylenes (LLDPEs). The commonly used chemical names of plastics thus often do not indicate the true chemical structure of the monomeric units of the polymers on which they are based.

Polymers are often Named after Characteristic Groups in Their Repeating Units. Polyamides are thus polymers with amide groups –NHCO– in their repeating units; for example ∼[NHCO (CH2)5]*n*∼ = polyamide 6 = nylon 6 = poly (ε-caprolactam). Other examples are polyesters with ester groups –COO– or polyurethanes with urethane groups –NH–CO–O– in the chains. A disadvantage is that this naming scheme is identical with that of organic chemistry where a polyisocyanate denotes a low molar mass compound with more than one isocyanate group per molecule [e.g., $C_6H_3(NCO)_3$. A macromolecular polyisocyanate would thus be a polymer with many intact isocyanate groups per chain, for example, poly (vinyl isocyanate) ∼[CH2–CH(NCO)]*n*∼. The polyisocyanates of polymer chemistry, on the other hand, possess polymerized isocyanate groups as, for example, in ∼(NR–CO)*n*∼. Such compounds are unfortunately also often called polyisocyanates.

IUPAC Names. IUPAC recommends the use of constitutive names, similar to those used in inorganic and organic chemistry. The nomenclature of low and high molar mass inorganic molecules follows the additivity principle; those of low molar mass organic molecules the substitution principle. The nomenclature of organic macromolecules is a hybrid of both principles: The smallest repeating units are thought of as biradicals according to the substitution principle; then their names are added according to the additivity principle, put in parentheses, and prefixed with "poly." Names of repeating units are written without spaces between words. The polymer ∼[O–CH2]*n*∼ from formaldehyde, $H_2C=O$, is thus called poly(oxymethylene), abbreviated as POM. The polycondensation of ethylene glycol HO–CH₂–CH₂–OH with terephthalic acid HOOC–(*p*-C6H4)–COOH leads to a polymer ∼[O–CH2CH2–O–OC(*p*-C6H⁴)CO]*n*∼ with the systematic name poly(oxyethyleneoxyterephthaloyl). The trivial names of this polymer are poly (ethylene terephthalate) and poly(ethylene glycol terephthalate). It is also known as PET

(an acronym) or PETP (an abbreviation) in the plastics literature, by the acronym PES in thefiber literature, and as PETE for recycling purposes.

With exception of POM, IUPAC names are rarely used in the plastics literature. They are however important for systematic searches in *Chemical Abstracts* and other literature services.

1.2. Plastics

1.2.1. Fundamental Terms [20–56]

Early plastics resembled natural resins. Natural resin refers mainly to oleoresins from tree sap but is also used for shellac, insect exudations, and mineral hydrocarbons $(\rightarrow$ Resins, Natural). Early plastics were thus sometimes called synthetic resins. The word resin is today occasionally used for any organic chemical compound with medium to high molar mass that serves as a raw material for plastics (for a definition of the term resin according to current standards, see \rightarrow Resins, Synthetic). Resin is not to be confused with rosin, which refers to mixtures of C_{20} fused-ring monocarboxylic acids, such as pine oil, tall oil, and kauri resin. Rosin is the main component of naval stores $(\rightarrow$ Resins, Natural).

Plastics are usually divided into two groups according to their hardening processes. Those that yield solid materials by simple cooling of a polymer melt (a physical process) and soften while being heated are called *thermoplastics*. *Thermosets*, on the other hand, harden through chemical cross-linking reactions between polymer molecules; when heated, they do not soften but decompose chemically $(\rightarrow$ Thermosets). The shaping of a thermoplastic is thus a reversible process: The same material can be melted and processed again. A thermoset cannot be remelted and reshaped; its formation is irreversible.

Thermoplastics are normally composed of fairly high molar mass molecules because many physical properties effectively become molar mass independent only above a certain molar mass enabling chain entanglement. Examples are melting temperatures and the moduli of elasticity. Other properties, however,

increase with increasing molar mass and entanglement (e.g., melt viscosities).

Thermosets are usually generated from fairly low molar mass polymers, called oligomers (science) or prepolymers (industry). Oligomers containing functional endgroups are named telechelics, and telechelics containing polymerizable endgroups are termed macromonomers. High molar masses are unnecessary here because chemical reactions between prepolymer molecules lead to an interconnection of these molecules (cross-linking or advancement, respectively) and thus to a giant molecule with 100% conversion of the prepolymer. Prepolymers are thus thermosetting materials and become true thermosets only after the hardening reaction.

Plastics are usually divided into four groups: Commodity plastics (also called standard plastics or bulk plastics), engineering plastics (sometimes referred to as technical plastics or technoplastics), high-performance plastics, and functional plastics (or specialty plastics). A commodity, engineering, or high-performance plastic may have many different applications, whereas a functional plastic has one very specific application. Polyethylene, a commodity plastic, may according to its type or grade be used for containers, as packaging film, as agricultural mulch, etc. Poly(ethylene–co–vinyl alcohol) with a high content of vinyl alcohol units, on the other hand, is a functional plastic that is used only as an oxygen barrier resin. Other functional plastics are employed in optoelectronics, as resists, as piezoelectric materials, etc. Functional plastic is not synonymous with functional polymer or functionalized polymer, because the latter terms refer to polymers with functional chemical groups (i.e., groups with specific chemical reactivities).

Commodity plastics are manufactured in great amounts at low cost; hence, the terms bulk plastics or standard plastics. Engineering plastics possess improved mechanical properties and improved dimensional stability as compared to commodity plastics. Such improved properties may be higher moduli of elasticity, higher heat distortion temperature, smaller cold flows, higher impact strengths, etc. Engineering plastics are also often defined as those thermoplastics that maintain dimensional stability and