International Union of Pure and Applied Chemistry
Polymer Division
Subcommittee on Polymer Terminology

A Brief Guide to Polymer Terminology (IUPAC Technical Report)

R. C. Hiorns* (France), J. Vohlídal* (Czech Republic), R. Boucher (UK), C. H. Chan‡ (Malaysia), C. M. Fellows (Australia), M. Hess (Germany), R. G. Jones‡ (UK), P. Kratochvíl‡ (Czech Republic), C. K. Luscombe (USA), J. B. Matson (USA), G. Moad (Australia), O. E. Philippova (Russia), S. Slomkowski (Poland), N. Stingelin (UK), P. Théato (Germany), J.-P. Vairon (France), M. Vert (France). ‡Deceased. *E-mails: roger-clive.hiorns@cnrs.fr and jiri.vohlidal@natur.cuni.cz

1) Introduction

The International Union of Pure and Applied Chemistry (IUPAC) publishes definitions of terms to enable communication of information worldwide. Definitions of terms commonly used in polymer chemistry are paraphrased here with hyperlinks and screen-tips to approved definitions in the Gold and Purple Books, or the original source documents. This document complements the Brief Guides to Polymer Nomenclature,[1] Polymerization Terminology,[2] and Polymer Characterization.[3]

2) Macromolecules and Polymers[4,5]

The terms macromolecule and polymer do not mean the same thing. A polymer is a substance composed of macromolecules of high molar mass (M). An oligomer molecule is of intermediate molar mass such that a change in the number of units will noticeably alter its properties. The degree of polymerization (X) indicates the number of monomeric units making up a macromolecule. Each sample normally contains a range of chain lengths. Dispersity ($Đ$) quantifies the breadth of this distribution and is defined by $Đ = M_m/M_n$.[6] The number-average molar mass (M_n) and mass-average molar mass (M_m or M_w) (unit g mol^{-1}), can be calculated using the equations, respectively:

$$M_n = \frac{1}{\sum_{M} (w_M / M)} \quad \text{and} \quad M_m \equiv M_w = \sum_{M} w_M M$$

in which w_M is the mass fraction of molar mass M.

A constitutional unit (CU) consists of one or more atoms and makes up an essential part of a macromolecular structure. A monomeric unit is the largest CU that can be identified as coming from a monomer molecule. Importantly, constitutional repeating units (CRUs) are the smallest CUs that can be used to identify the structure of the whole chain. A regular macromolecule can be described by a single CRU joined in the same way throughout, whereas an irregular macromolecule comprises more than one CU or a non-uniformly connected CU. Macromolecules can also be described using machine-readable IUPAC International Chemical Identifiers.

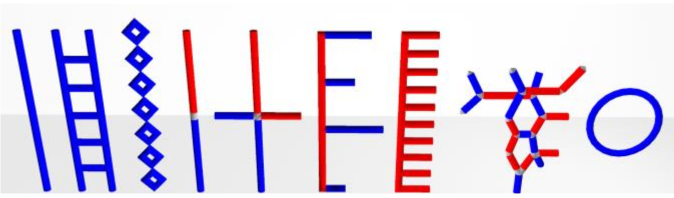

Fig. 1. Classes of macromolecular structures. Left to right: single-strand, ladder, spiro, block, star, graft, & comb macromolecules; a network & a macrocycle. Image: H. C. Piva.

Polymers are classified by their macromolecular skeletal structure, i.e., the sequence of atoms that defines their essential topological representation, as shown in Fig. 1. Those with CUs joined by two atoms are single-strand, and those with connected rings such as ladder and spiro macromolecules are double-strand. A block macromolecule is composed of linear sequences of blocks joined at a junction unit. A star macromolecule has at least three chains at the junction unit. The graft macromolecule has one or more side-chains connected to a main chain, with structural features from the main chain. However, a comb macromolecule typically has a higher density of side chains which do not need to be different from the main chain. A network polymer is highly interconnected, bonding each CU with many others. A macrocycle can be a cyclic macromolecule or just a cyclic part of a structure. Other structures include the branched polymer which has branch points. This structure is noticeably different from the dendritic macromolecule which is tree-like and carries one or more dendrons.[7] A related class is that of macromonomer which has an end-group allowing it to act as a monomer.

A homopolymer is made from one real or apparent monomer, whereas a copolymer contains two or more. The monomeric units in statistical and random copolymers, respectively, are distributed following statistical laws or placed independently from the order of the adjacent units. A periodic copolymer has more than two monomeric units in a regular sequence, while an alternating copolymer has only two units in strict alternation.

An ionic polymer is made of macromolecules containing ionic or ionizable groups.[8] An ionomer and a polyelectrolyte are composed of macromolecules, respectively, with a small or a substantial number of CUs carrying ionic or ionizable groups or both. An ampholytic polymer contains both anionic and cationic groups, or corresponding ionizable groups. A zwitterionic polymer contains ionic groups of opposite signs, often on the same pendent group.

3) Configuration and Stereoisomerism[9,10,11]

Isomers have the same atomic composition but different line or stereochemical formulae. An isomerization is a reaction that yields a product that is isomeric to the reactant. Configuration is a spatial arrangement of atoms or groups about a stereoisomeric center. This can be a chiral center, a rigid group, or a cyclic moiety, as exemplified in Fig. 2. Rigid centers are described using the preferred stereodescriptors *Z* and *E*, respectively, denoting the lesser preferred terms, *cis* and *trans*. Asymmetric carbons are described using *R* and *S* in accordance with Cahn–Ingold–Prelog (CIP) priority rules. Diastereoisomers are stereoisomers that are not mirror images.

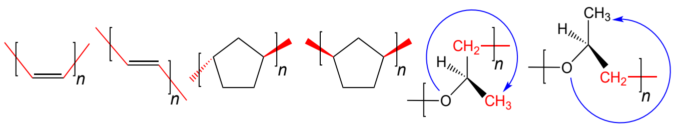

Fig. 2. Example stereodescriptors (left to right): poly[(*Z*)-ethene-1,2-diyl] and poly[(*E*)-ethene-1,2-diyl]; poly[(*Z*)-cyclopentane-1,3-diyl] and poly[(*E*)-cyclopentane-1,3-diyl]; and poly[(*R*)-oxy(1-methylethane-1,2-diyl)] and poly[(*S*)-oxy(1-methylethane-1,2-diyl)].

A CU having one or more stereoisomeric sites is termed a configurational unit, whereas a CRU with at least one stereoisomer is called a configurational base unit (CBU). The smallest series of CBUs that describe a configurational repetition of stereoisomerism in the main chain is a configurational repeating unit (CFRU). A CRU having stereoisomeric configurations at all main chain sites is a stereorepeating unit (SRU). The tacticity of a polymer defines the orderliness of CFRUs in the main chain (please see Fig. 3). A tactic macromolecule has identical CFRUs, while isotactic and syndiotactic macromolecules have CBUs with chiral atoms in the main chain uniquely or alternately arranged with respect to their adjacent CUs, respectively. An atactic macromolecule has CBUs in a random sequence. A diad comprises two stereoisomeric centers next to each other. When they are the same, *m* is used as a descriptor, and when they are different *r* is used.[12] Thus, syndiotactic chains have only *r* diads, isotactic chains are all *m* diads, while atactic chains have both *m* and *r* diads in a random sequence.

Fig. 3. The position of CBUs in stereoisomeric polymers.

[1] IUPAC. *Pure Appl. Chem.* **2012**, *84*, 2167.
[2] IUPAC. *Pure Appl. Chem.* **2022**, *94*, 1079.
[3] IUPAC. *Pure Appl. Chem.* **2023**, *95*, 1121.
[4] IUPAC. *Pure Appl. Chem.* **1996**, *68*, 2287.
[5] IUPAC. *Pure Appl. Chem.* **2009**, *81*, 1131.
[6] IUPAC. *Pure Appl. Chem.* **2009**, *81*, 351; Erratum ibid, **2009**, *81*, 779.
[7] IUPAC. *Pure Appl. Chem.* **2009**, *91*, 523.
[8] IUPAC. *Pure Appl. Chem.* **2006**, *78*, 2067.
[9] IUPAC. *Pure Appl. Chem.* **1996**, *68*, 2193.
[10] IUPAC. *Pure Appl. Chem.* **2002**, *74*, 915.
[11] IUPAC. *Pure Appl. Chem.* **1981**, *53*, 733.
[12] IUPAC. *Pure Appl. Chem.* **2020**, *92*, 1769.

4) Polymerizations[13,14,15]

A polymerization converts monomers into polymer, whereas a depolymerization reverses this process. Unzipping occurs sequentially along the chain. A copolymerization converts two or more monomers to alternating, random, periodic or statistical copolymers. Four types of polymerization are shown in Table 1. In chain polymerizations, reactive sites are regenerated after each propagation step. The term living polymerization is specific to reactions where irreversible deactivation by termination or chain transfer do not happen. If chains are deactivated reversibly, the polymerization is a reversible-deactivation polymerization. A controlled polymerization indicates control of a kinetic feature of the reaction or a structural aspect of the resulting polymer. Polyadditions and polycondensations involve reactions of monomer, oligomer, and polymer molecules of all sizes, with the latter class of reaction eliminating small molecules.

Table 1. Four major classes of polymerization with example reactions.

growth mechanism	propagation stoichiometry	
	condensation reaction	addition reaction
monomers (M) react with reactive sites on polymer chains (PA*)	**condensative chain polymerization** $P_nA^* + M \rightarrow P_{n+1}A^* + X$	**chain polymerization** $P_nA^* + M \rightarrow P_{n+1}A^*$
monomers, oligomers and polymers react together	**polycondensation** $^*AP_nA^* + ^*BP_mB^* \rightarrow ^*AP_{n+m}B^* + X$	**polyaddition** $^*AP_nA^* + ^*BP_nB^* \rightarrow ^*AP_{n+m}B^*$

The rate of polymerization is a measure of the consumption of monomers or of a functional group in chain polymerizations and of functional groups in polyadditions and polycondensations. Radical, anionic and cationic polymerizations, respectively, have a radical, an anion or a cation as an active center. A ring-opening polymerization of a cyclic monomer yields a polymer that is acyclic or has fewer cycles. Conversely, a cyclopolymerization raises the number of cycles in the polymer with respect to the monomer molecule.

Polymerizations can also be classified as homogeneous, for example bulk or solution, and heterogenous, such as dispersion, precipitation, suspension, emulsion, or solid-state.[12,16]

5) Polymer Modifications and Degradations[17,18]

Chemical modification is a process by which a polymer's chemical constitution is changed. Examples of this include crosslinking between macromolecules which results in sites with at least four emanating chains, and amplification, where species that catalyze further reactions are generated. At surfaces, covalent bonds can be generated through surface grafting, while a polymer-supported reaction can occur *via* a range of polymer interactions.

Degradation results in the loss of desirable properties, while biodegradation arises from enzymatic processes.[19] Aging processes, such as photo-oxidative aging, occur over a specific period of time, and can give rise to, for example, abrasion, cracking and crazing. The durability of a polymer describes its ability to retain its initial properties. The use of an inhibitor stops a chemical reaction, while a retarder can decrease the rate.

6) Macromolecules in Solutions, Assemblies and Bulks[20,21]

A freely rotating chain is unhindered by a short- or long-range intramolecular interaction. Chain stiffness describes an unperturbed distance from end-to-end with respect to a model chain, and can be measured as a persistence length. In solution, a domain is the smallest volume containing a macromolecule in its average shape. A dilute solution of a polymer occurs when the total volume of occupied domains is much less than that of the solution. In contrast, a concentrated solution exists when the occupied domains overlap. When a solution is in a theta state, the polymer is an unperturbed random coil. Precipitation fractionation employs the changing solution power of a solvent to separate macromolecular species. Alternatively, the method of size-exclusion chromatography can be used to differentiate between macromolecules by their hydrodynamic size.

Miscibility is the capability of a mixture to form a single phase over certain ranges of temperature, pressure, and composition. The lower and upper critical solution temperature are, respectively, the points at which any composition of a mixture are immiscible or miscible. The reptation of chains in solutions or in the bulk is described using a model of a hypothetical tube created by neighboring chains.

A blend is a macroscopically homogeneous mixture, whereas a composite has phase domains of which at least one is continuous. A laminate consists of more than one layer and separates by delamination. Impregnation is a process of penetration of liquids into assembled fibers, and intercalation is where a substance is transferred into pre-existing spaces of molecular dimensions. Adhesion holds two bodies together by mechanical interlocking at sub-µm scales, while interfacial adhesion works through intermolecular forces or chain entanglement.

A colloid exists in a state of dispersion of polymolecular particles of the order of 1 nm to 1 µm in scale.[22] A sol is a fluid colloidal system with two or more components, a gel is a network of connected macromolecular segments swollen by a liquid, and a xerogel is an open network cleared of a swelling agent. A hybrid polymer consists of inorganic and organic components.

In solids, domains are uniform in their chemical composition and physical states, and can be continuous, discontinuous or show dual phase domain continuity. Numerous definitions exist to describe their morphology such as core-shell, cylindrical, fibrillar, lamellar, rod-like, co-continuous double gyroid, and onion.

7) Crystalline *Versus* Amorphous Polymers[23]

A crystalline polymer has a significant fraction in a crystalline state i.e., a three-dimensional, long range order on an atomic scale. An amorphous polymer exhibits an absence of long-range molecular order. The two-phase model assumes that a polymer contains only crystalline and amorphous phase domains.

8) Thermal and Thermomechanical Properties[24,25]

A glass transition occurs when a polymer glass is heated and changes to a polymer melt, or on cooling, back to a polymer glass. In a semicrystalline polymer this only occurs in parts which are in the amorphous state. A characteristic temperature can be analyzed using a differential scanning calorimeter (DSC, see Fig. 4). Annealing performed by heating a polymer without melting it results in a desired change in its properties.

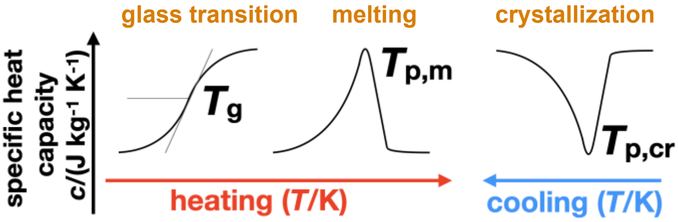

Fig. 4. Characteristic temperatures indicated by DSC: T_g, $T_{p,m}$ and $T_{p,cr}$ are the glass-transition temperature, the peak melting temperature and the peak crystallization temperature, respectively.

An elastomer displays rubber-like elasticity. A thermoplastic elastomer has a thermoreversible network. A thermosetting polymer is a prepolymer that irreversibly changes into an infusible, insoluble polymer network by curing. Viscoelasticity is the time-dependent response of a material to stress or strain, whereas creep is the time-dependent change in its dimensions due to a constant load.

9) Functional Polymers[17]

A functional polymer has uses arising from chemical groups. For examples, a compatibilizer modifies the interfaces of an immiscible polymer to stabilize a compatible polymer blend, while a polymer surfactant lowers the surface tension of a medium with another phase. Polymers can also be, for examples, conducting, electroluminescent, liquid-crystalline, piezoelectric, superabsorbent, impact-modified, resists and nonlinear optical materials, and can display shape-memory.

10) Biorelated Polymers[18]

A biopolymer consists of biomacromolecules formed by living organisms. A synthetic biopolymer is made using abiotic routes. A biobased polymer is derived from biological products. An artificial polymer is not a biopolymer while a green polymer conforms to concepts of green chemistry. Biocompatibility allows contact with living systems with acceptable effects.

13 IUPAC. *Pure Appl. Chem.* **1994**, *66*, 2483.
14 IUPAC. *Pure Appl. Chem.* **2008**, *80*, 2163.
15 IUPAC. *Pure Appl. Chem.* **2022**, *94*, 1093.
16 IUPAC. *Pure Appl. Chem.* **2011**, *83*, 2229.
17 IUPAC. *Pure Appl. Chem.* **2004**, *76*, 889.
18 IUPAC. *Pure Appl. Chem.* **1996**, *68*, 2313.
19 IUPAC. *Pure Appl. Chem.* **2012**, *84*, 377.
20 IUPAC. *Pure Appl. Chem.* **2015**, *87*, 71.
21 IUPAC. *Pure Appl. Chem.* **2004**, *76*, 1985.
22 IUPAC. *Pure Appl. Chem.* **2007**, *79*, 1801.
23 IUPAC. *Pure Appl. Chem.* **2011**, *83*, 1831.
24 IUPAC. *Pure Appl. Chem.* **1998**, *70*, 701.
25 IUPAC. *Pure Appl. Chem.* **2013**, *85*, 1017.

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