

IUPAC Recommendations

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Basic classification and definitions of polymerization reactions (IUPAC Recommendations 2025)

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Abstract: This document provides recommendations addressing the long-standing dilemma of the wide variety of terms that are used to describe the two common classes of *polymerization* mechanisms in the scientific literature, which includes chemistry and polymer-science textbooks. It is an update of a 1994 IUPAC document on this topic and provides clarification and hierarchical structure regarding the basic classification and terminology describing polymerization reactions. The term *step polymerization* describes polymerizations in which growth occurs by reactions between monomer, oligomer, or polymer molecules of any length. We clearly denote here the two subclasses of step polymerization: *additive step polymerization* (synonym: *polyaddition*) and *condensative step polymerization* (synonym: *polycondensation*). The term *chain polymerization* describes polymerizations that proceed via a chain reaction with monomer molecules adding to active sites on polymer chains. Subclasses of *chain polymerization* include *additive chain polymerization* and *condensative chain polymerization*. The terms provide a logical and straightforward structure for describing the two common classes of polymerization mechanisms. Previously defined terms relevant to these two classes of polymerization reactions are also replicated in this Recommendation document.

Keywords: Chain polymerization; growth step; polymer chemistry; polymer synthesis; step polymerization.

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1 Introduction

Polymerization, which is the process of converting a monomer or mixture of monomers into a polymer,¹ takes place in nearly all cases through one of two common classes of polymerization mechanisms. These two common classes are: 1) reactions between one (or more) type(s) of multifunctional monomer(s) where at least bifunctionality is required, with growth occurring between monomer, oligomer, or polymer molecules of any length and 2) a chain reaction process of monomer molecules being added to polymeric active sites. The Subcommittee on Polymer Terminology recently detailed the current situation regarding terminology in this area, the historical evolution of these terms, and our concerns with them.² In short, our investigations revealed that a clear set of terms for these fundamental processes is lacking. In the scientific literature, as well as many textbooks, the terms “step-growth” and “chain-growth” or variations thereof often appear, but IUPAC has never endorsed either. Other terms are also used, including historical terms that do not accurately capture the distinctions between these two processes. Furthermore, authors seeking guidance from IUPAC were forced to rely on a 1994 Recommendations document from the predecessor of this subcommittee,³ which unfortunately failed to clearly recommend general terms for these two processes, recommending the term *chain polymerization* as both a general and a specific term, and suggesting only terms describing the subclasses *polyaddition* and *polycondensation* with no general term. We concluded that a new set of definitions is needed. Therefore, our goal in this project is to recommend terms that

are easy to implement, familiar, and efficiently describe the critical differences in the two classes of polymerization mechanisms. In addition, we strive for the recommended terms and their definitions to be logical and internally consistent with other terms defined by IUPAC in polymer science and organic chemistry.

This Recommendation updates the 1994 Recommendations document³ and addresses the confusion identified in our recent publication.² One issue that quickly became apparent during our work on this project was that the words “step” and “chain” create confusion because all polymerizations are a series of steps that result in a polymer chain. However, because terms containing the words “step” and “chain” remain widely embedded in the lexicon of the polymer science community, we elected to retain these words in our recommended terms with context in the notes explaining their use.

Given this backdrop, we recommend here the term *step polymerization* to describe polymerizations in which molecules of all molar masses react together, and we clarify that the term *chain polymerization* serves as a general term for all polymerizations that proceed through a series of chain reactions. Subclasses of each are then described using the modifiers “additive” or “condensative” to indicate whether the polymerization occurs through a series of *addition reactions* or *condensations*. The previously recommended terms *polyaddition* and *polycondensation* are retained as synonyms for *additive step polymerization* and *condensative step polymerization*, respectively. In contrast, the terms “addition polymerization” and “condensation polymerization” are not acceptable because their historical definitions encompass different sets of polymerizations to those of the similar-sounding terms *polyaddition* and *polycondensation*. Furthermore, the terms *step polymerization* and *chain polymerization* are preferred to the historical terms “step-growth polymerization” and “chain-growth polymerization,” which should be avoided for two reasons: 1) The new term *growth step* is defined here and applies in both *chain polymerizations* and *step polymerizations*, causing potential confusion with “chain-growth” and “step-growth” and 2) There can be no polymerization without growth; therefore, it is a tautology to say “-growth polymerization.” Sections 2 and 3 of this document describe the new recommended terms for these polymerization processes. Each term is numbered (e.g., BC-1, BC-2 with BC referring to ‘basic classification’).

Polymers can also be synthesized using methods that are not strictly *chain polymerizations* or *step polymerizations*. Sometimes called “multistep growth polymerizations,”⁴ these methods build up polymers through iterative reactions. Solid-phase peptide synthesis is a classical example, and recent interest in sequence-defined polymers has led to development of other methods, both solid-phase and solution-phase, to synthesize polymers in this manner. This document does not recommend or discourage terms in this field because it is the topic of another ongoing IUPAC project.⁵

Finally, in Section 4 of this document, we replicate some terms that have been previously defined and appear within the definitions of *step polymerization*, *chain polymerization*, and their subclasses. In this document, we have not substantially modified any of these terms except to correct minor errors and inconsistencies or provide additional context as noted. As we already mentioned, we also introduce the term *growth step*, which has been used in definitions for decades but has never been explicitly defined until now. Terms are presented in bold typeface, and where applicable, synonyms are noted underneath the defined term. Cross-references to terms defined elsewhere in the document are indicated in *italic typeface*, but terms defined here and used widely throughout the document (e.g., polymerization) are only italicized at first use. Related terms are noted in cases where two terms have similar though not identical meanings and it is essential that the distinction be recognized.

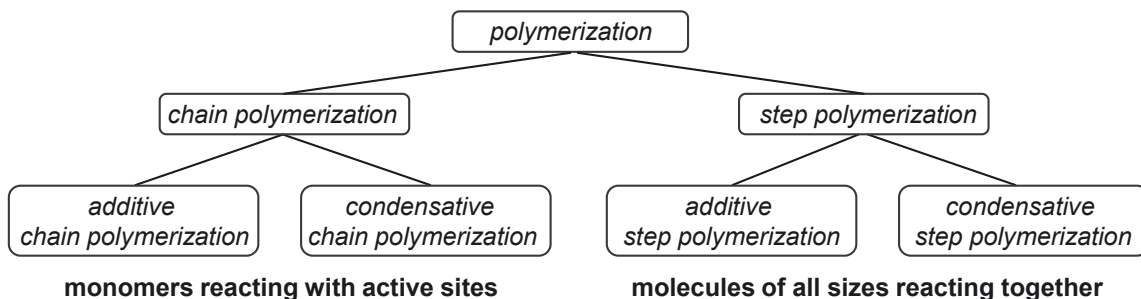
2 Terms describing the two common classes of polymerization mechanisms

This section provides definitions of *chain polymerization*, *step polymerization*, and their subclasses. Table 1 presents the hierarchy of terms, and Fig. 1 presents the terms graphically.

Table 1: Hierarchy of terms describing the two common classes of polymerization mechanisms.^a

Growth mechanism	Monomers reacting with active sites	Molecules of all sizes reacting together
General terms	<i>Chain polymerization</i>	<i>Step polymerization</i>
Specific terms	<i>Additive chain polymerization</i> <i>Condensative chain polymerization</i>	<i>Additive step polymerization</i> (synonym: <i>polyaddition</i>) <i>Condensative step polymerization</i> (synonym: <i>polycondensation</i>)

^aThis table is updated from Refs 1,3,6. The modifier “additive” refers to polymerizations that proceed through a series of *addition reactions*; similarly, the modifier “condensative” refers to polymerizations that proceed through a series of *condensations*. Definitions of these terms appear in Section 2. Use of the terms “addition polymerization” and “condensation polymerization” is not acceptable due to confusion created by their historical definitions, which encompass a different set of polymerizations.

**Fig. 1:** Graphical representation of hierarchy of terms describing the two common classes of polymerization mechanisms.

BC-1 chain polymerization

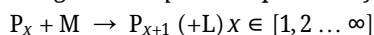
Chain reaction in which the growth of a polymer *chain* proceeds exclusively by reaction(s) between *monomer molecule(s)* and *active site(s)* on the polymer *chain* with regeneration of the *active site(s)* at the end of each *growth step*.

Note 1: A chain polymerization consists of chain initiation and chain propagation reactions, and may also include chain deactivation or chain-transfer reactions, or both.

Note 2: The adjective “chain” in chain polymerization denotes “chain reaction” rather than a “polymer *chain*.”

Note 3: Propagation in chain polymerization usually occurs without the formation of small molecules, in which case the polymerization is an *additive chain polymerization*. In chain polymerizations in which a low-molar-mass by-product is formed, which are relatively uncommon, the adjective “condensative” is added to form the term *condensative chain polymerization*.

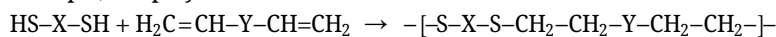
Note 4: The *growth steps* are expressed by the equation



where P_x denotes a growing chain of *degree of polymerization* x , M a monomer, and L a low-molar-mass by-product formed only in the case of *condensative chain polymerization*.

Note 5: The term “chain polymerization” may be qualified further, if necessary, to specify the type of chemical reaction involved in the *growth step*, e.g., ring-opening chain polymerization and cationic chain polymerization.

Note 6: There exist *polymerizations* that proceed via *chain reactions* that are not chain polymerizations. For example, the polymerization



proceeds via a radical chain reaction with intermolecular transfer of the radical site. The *growth step*, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as an *additive step polymerization* or a *polyaddition*. If required, the classification can be made more precise and the *polymerization* described as a chain-reaction *polyaddition*.

Note 7: Chain polymerizations may proceed by *addition reactions*, *condensations*, and other reaction types, such as substitution reactions, or sequences of reactions, such as addition-eliminations.

Note 8: The term “chain-growth polymerization” is a tautology because there can be no polymerization without growth and is therefore not recommended. However, the phrase “chain-growth” is acceptable when used adjectivally in other contexts; for example, “the chain-growth nature of the polymerization.”

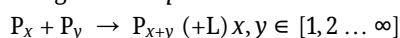
Source: Ref 6 entry CP-2 with updated notes to provide additional clarity and to demonstrate the hierarchy of terms.

BC-2 step polymerization

Polymerization in which the growth of polymer *chains* proceeds by reactions between molecules of all degrees of polymerization.

Note 1: A step polymerization that occurs without the formation of small molecules by-products is an *additive step polymerization*. In a *step polymerization* in which a low-molar-mass by-product is formed, the adjective “condensative” is used to form the term *condensative step polymerization*.

Note 2: The *growth steps* are reactions that can be expressed by the equation



where P_x and P_y denote chains of degrees of polymerization x and y , respectively, and L denotes a low-molar-mass by-product formed only in the case of *condensative step polymerization*. Each *growth step* involves a reaction between molecules (with degrees of polymerization x and y) to form a new molecule of increased molar mass (with *degree of polymerization* $x + y$).

Note 3: *Step polymerizations* may proceed by *addition reactions*, *condensations*, and other reaction types, such as substitution reactions, or a sequence of reactions such as addition-eliminations.

Note 4: The term “step-growth polymerization” is a tautology because there can be no polymerization without growth and is therefore not recommended. However, the phrase “step-growth” is acceptable when used adjectivally in other contexts; for example, “the step-growth nature of the polymerization.”

3 Terms describing subclasses of the two common classes of polymerization mechanisms

This section provides definitions of subclasses of *chain polymerization* and *step polymerization*.

BC-3 additive chain polymerization

Chain polymerization that proceeds without the generation of low-molar-mass by-product(s).

Note 1: Additive chain polymerization can be shortened to *chain polymerization* when the full term is specified at first use and when it is clear that there is no condensate.

Note 2: Additive chain polymerization may be qualified further, if necessary, to specify the type of chemical reaction involved in the *growth step*, e.g., ring-opening additive chain polymerization, cationic additive chain polymerization. In such cases, the modifier “additive” may be omitted provided that the full term is specified at first use.

Example 1: Polymerization of styrene to form polystyrene is an additive chain polymerization. Under cationic polymerization conditions, this polymerization is called a cationic additive chain polymerization or shortened to cationic chain polymerization.

Related terms: *condensative chain polymerization*.

BC-4 additive step polymerization

polyaddition

Step polymerization that proceeds without the generation of low-molar-mass by-products.

Note 1: Additive step polymerization can be shortened to step polymerization when the full term is specified at first use and when it is clear that there is no condensate. Alternatively, polyaddition can be used.

Note 2: Use of the term ‘addition polymerization’ as a synonym is not acceptable due to its historical definition, which encompasses a different set of polymerizations.⁷

Example 1: The polymerization of a diol with a diisocyanate to form a polyurethane is an additive step polymerization.

Source: Ref 6 entry CP-13 with updates to provide additional clarity, include the appropriate synonym, and to demonstrate the hierarchy of terms.

Related terms: *condensative step polymerization*.

BC-5 condensative chain polymerization

Chain polymerization in which the individual propagation steps are *condensations*.

Note 1: Condensative chain polymerization appears in the literature under a variety of names, which include chain-growth condensation polymerization, chain-growth polycondensation, catalyst-transfer polymerization, catalyst-transfer condensation polymerization, and catalyst-transfer polycondensation. Terms that indicate condensative chain polymerization to be a form of *polycondensation* are not acceptable because they are inconsistent with the IUPAC definition of *polycondensation*.

Note 2: Condensative chain polymerization can be shortened to *chain polymerization* when the full term is specified at first use and when the formation of a condensate is clear.

Note 3: Condensative chain polymerization may be qualified further, if necessary, to specify the type of chemical reaction involved in the *growth step*, e.g., ring-opening condensative chain polymerization and anionic condensative chain polymerization. In such cases, the modifier “condensative” may be omitted provided that the full term is specified at first use.

Example 1: Polymerization of an oxazolidine-2,5-dione (commonly termed an amino acid *N*-carboxyanhydride) to yield a polypeptide is a condensative chain polymerization, in which CO₂ is the condensate.

Example 2: Polymerization of potassium 5-cyano-4-methyl-2-propylphenolate initiated by (4-fluorophenyl)(4-(trifluoromethyl)phenyl)methanone to yield an aromatic polyether is a condensative chain polymerization, in which KF is the condensate.

Source: Ref 6 entry CP-142 with updated notes to provide additional clarity, highlight that *N*-carboxyanhydride polymerization is, in fact, a type of condensative chain polymerization, and to demonstrate the hierarchy of terms.

Related terms: *additive chain polymerization*.

BC-6 condensative step polymerization

polycondensation

Step polymerization that proceeds with the generation of low-molar-mass by-product(s).

Note 1: Condensative step polymerization can be shortened to *step polymerization* when the full term is specified at first use and when the formation of a condensate is clear. Alternatively, polycondensation can be used.

Example 1: The polymerization of a diol with a diester to form a polyester with elimination of an alcohol is a condensative step polymerization.

Example 2: The polymerization of a diol with a diacid to form a polyester with elimination of water is a condensative step polymerization.

Source: Ref 6 entry CP-14 with updated notes to provide additional clarity, include the appropriate synonym, and to demonstrate the hierarchy of terms.

Related terms: *additive step polymerization*.

4 Terms relevant to the two common classes of polymerization mechanisms

This section provides definitions of terms relevant to *chain polymerization*, *step polymerization*, and their subclasses. With the exception of *growth step*, which is a new term, these definitions replicate those in other documents and are not substantially modified except to correct minor errors and inconsistencies or to provide additional context as noted. The terms *addition reaction* and *condensation* have been defined by the IUPAC Subcommittee on Structural and Mechanistic Chemistry; all other terms have been defined by the Subcommittee on Polymer Terminology in specific references noted within the definitions.

BC-7 active center (in a chain polymerization)

active site

Site on a chain carrier at which reaction occurs.

Note 1: In 1,8, the term “reactive site” is used within the definition of *chain polymerization*. In,⁹ the terms “active center” and “active site” are defined in the context of heterogeneous catalysis

Source: Ref 10, page 2165.

BC-8 addition reaction

Chemical reaction of two or more reacting molecular entities, resulting in a product containing all atoms of all components, with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants.

Note 1: The addition to an entity may occur at only one site (1,1-addition, insertion), at two adjacent sites (1,2-addition), or at two non-adjacent sites (1,3- or 1,4-addition, etc.).

Examples

$R_3C-H + H_2C: \rightarrow R_3C-CH_3$ (1, 1-addition of a carbene)

$Br_2 + CH_2=CH-CH=CH_2 \rightarrow BrCH_2-CH(Br)-CH=CH_2$ (1,2-addition) +

$BrCH_2-CH=CH-CH_2Br$ (1, 4-addition)

Note 2: This is distinguished from adduct formation, which is less specific about bonding changes.

Note 3: The reverse process is called an elimination reaction.

Source: Ref [11](#) page 357.

BC-9 apparent monomer

Monomer which from the name of a polymer appears to have been used in the synthesis of the latter when it has actually been prepared from different precursor(s).

Note 1: The formerly used terms ‘hypothetical monomer’ and ‘implicit monomer’ are obsolete.

Source: Ref [12](#) entry SB-1.1.

BC-10 chain, *noun*

Whole or part of a *macromolecule*, an *oligomer molecule*, or a block, comprising a linear or branched sequence of constitutional units between two boundary constitutional units, each of which may be either an end-group, a branch point, or an otherwise designated characteristic feature of the *macromolecule*, *oligomer molecule*, or block.

Note 1: Except in linear single-strand *macromolecules*, the definition of a chain may be somewhat arbitrary.

Note 2: A cyclic *macromolecule* has no end-groups but may nevertheless be regarded as a chain.

Note 3: Any number of branch points may be present between the boundary units.

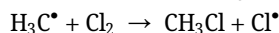
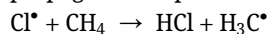
Note 4: Where appropriate, definitions relating to *macromolecule* may also be applied to chain.

Source: Ref [12](#) entry SB-1.4 updated to improve clarity and include the part of speech (noun, *n.*) because ‘chain’ can also be used adjectivally when referring to processes involving a chain reaction, e.g., *chain polymerization*.

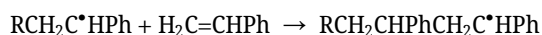
BC-11 chain reaction

Reaction in which one or more reactive intermediates (frequently radicals) are continuously regenerated through a repetitive cycle of elementary steps (“propagation steps”).

Example: Chlorination of methane by a radical mechanism, where $\text{Cl}^\bullet$ is continuously regenerated in the chain propagation steps:



Note: In chain polymerization reactions, reactive intermediates of the same types, generated in successive steps or cycles of steps, differ in molecular mass, as in:



Source: Ref [11](#), page 381.

BC-12 condensation

Reaction (usually stepwise) in which two or more reactants (or remote reactive sites within the same molecular entity) yield a product with accompanying formation of water or some other small molecule, e.g., ammonia, ethanol, acetic acid, and hydrogen sulfide.

Note 1: The mechanism of many condensation reactions has been shown to comprise consecutive addition and elimination reactions, as in the base-catalyzed formation of (*E*)-but-2-enal (crotonaldehyde) from

acetaldehyde, via dehydration of 3-hydroxybutanal (aldol). The overall reaction in this example is known as the aldol condensation.

Note 2: The term is sometimes also applied to cases where the formation of water or other simple molecule does not occur, as in “benzoin condensation.”

Source: Ref 11, page 389.

BC-13 degree of polymerization (DP), X

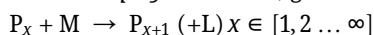
Number of monomeric units in a *macromolecule*, an *oligomer molecule*, a *block*, or a *chain*.

Source: Ref 13, entry 1.2.

BC-14 growth step

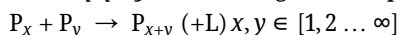
Reaction in a *polymerization* that leads to an increase in the molar mass of a *macromolecule* or *polymer chain* while regenerating *active sites* or maintaining active functional groups that are capable of further growth steps.

Note 1: In a *chain polymerization*, growth steps are expressed by the equation.



where P_x denotes a growing chain of *degree of polymerization* x , M a monomer, and L a low-molar-mass by-product formed only in the case of *condensative chain polymerization*.

Note 2: In a *step polymerization*, growth steps are discrete reactions that can be expressed by the equation.



where P_x and P_y denote chains of degrees of polymerization x and y , respectively, and L a low-molar-mass by-product formed only in the case of *condensative step polymerization*. Each growth step involves a reaction between molecules (with degrees of polymerization x and y) to form a new molecule of increased molar mass (with *degree of polymerization* $x + y$).

Each individual growth step in a *step polymerization* reduces the total number of active functional groups present by exactly two.

Reactions of chain-end active functional groups with backbone functional groups on the same or another polymer chain, which are often called chain exchange reactions, interchange reactions, or trans reactions, are not considered growth steps in a *step polymerization*. For example, transesterification in the synthesis of a polyester via *condensative step polymerization*, occurring between a chain-end alcohol and a backbone ester, is not a growth step because there is no net change in number-average *degree of polymerization*.

BC-15 macromolecule

polymer molecule

Molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

Note 1: In many cases, especially for synthetic *polymers*, a molecule can be regarded as having a high relative molecular mass if the addition or removal of one or a few of the units has a negligible effect on the molecular properties. This statement fails in the case of certain *macromolecules* for which the properties may be critically dependent on fine details of the molecular structure, e.g., the enzymatic properties of polypeptides.

Note 2: If a part or the whole of the molecule has a high relative molecular mass and essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass, it may be described as either macromolecular or polymeric, or by polymer used adjectivally.

Note 3: In most cases, the *polymer* is made by direct *polymerization* of the respective *monomer*, but in other cases, the description ‘conceptual’ denotes an *apparent monomer*, which indicates that the polymer has been prepared from different precursor(s). For example, poly (vinyl alcohol) is commonly prepared by polymerization of vinyl acetate followed by deacetylation.

Source: Ref 1 entry 1.1.

BC-16 monomer

Substance composed of *monomer molecules*.

Source: Ref 12 entry SB-1.15.

BC-17 monomer molecule

Molecule that contributes constitutional units to the essential structure of a *macromolecule*.

Source: Ref 12 entry SB-1.17.

BC-18 oligomer

Substance composed of oligomer molecules.

Note: An oligomer obtained by telomerization is often termed a telomer.¹⁴

Source: Ref 1 entry 2.3.

BC-19 oligomer molecule

Molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.

Note 1: A molecule is regarded as having an intermediate relative molecular mass if it has properties which do vary significantly with the removal of one or a few of the units.

Note 2: If a part or the whole of the molecule has an intermediate relative molecular mass and essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass, it may be described as oligomeric, or by ‘oligomer’ used adjectivally.

Source: ref 12 entry SB-1.18.

BC-20 polymer

Substance composed of *macromolecules*.

Source: Ref 1 entry 2.2.

BC-21 polymerization

Process of converting a *monomer* or a mixture of *monomers* into a *polymer*.

Source: Ref 1 entry 3.1.

Table 2: Alphabetical index of terms.

Term	Term number
active center (in a chain polymerization)	BC-7
active site	BC-7
addition reaction	BC-8
additive chain polymerization	BC-3
additive step polymerization	BC-4
apparent monomer	BC-9
chain	BC-10
chain polymerization	BC-1
chain reaction	BC-11
condensative chain polymerization	BC-5
condensative step polymerization	BC-6
condensation	BC-12
degree of polymerization	BC-13
growth step	BC-14
macromolecule	BC-15
monomer	BC-16
monomer molecule	BC-17
oligomer	BC-18
oligomer molecule	BC-19
polyaddition	BC-4
polycondensation	BC-6
polymer	BC-20
polymer molecule	BC-15
polymerization	BC-21
step polymerization	BC-2

4 Alphabetical index of terms

Table 2 lists all terms defined in this document in alphabetical order. Additional terms mentioned in Notes are not included in this list. The Term Number indicated for synonyms, where these have a separate Term Number, is that of the synonym for which the term is defined.

5 Memberships of sponsoring bodies

Membership of the IUPAC Polymer Division Committee for the period 2024–2025 is as follows:

President: Igor Lacik (Slovakia); Vice President: Peter E. Mallon (South Africa); Secretary: Paul D. Topham (UK); Past President: Christine K. Luscombe (Japan).

Titular Members: Tanja Junkers (Australia), Yongfeng Men (China/Beijing), Marloes Peeters (UK), Lydia Sosa-Vargas (France), Patrick Théato (Germany).

Associate Members: Dirk J. Dijkstra (Netherlands), Simon Harrisson (France), Akihiro Kishimura (Japan), John Matson (USA), Guido Raos (Italy), Anthony J. Ryan (UK).

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Membership of the Subcommittee on Polymer Terminology during the preparation of these Recommendations (2019–2025) was as follows:

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