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Polymer Division and the Subcommittee on Polymer Terminology

A Brief Guide to Polymerization Terminology (IUPAC Technical Report)

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1) Introduction. The use of self-consistent terminology to describe polymerizations is important for litigation, patents, research and education. Imprecision in these areas can be both costly and confusing. To address this situation the International Union of Pure and Applied Chemistry (IUPAC) has made recommendations, which are summarized below. References and hyperlinks lead to source documents. Screen tips contain definitions published in IUPAC recommendations. More details can also be found in the IUPAC Purple Book.[1] This guide is one of a series on terminology and nomenclature.[2]

2) Basic definitions.[3,4] A macromolecule is a molecule of high molar mass, consisting of constitutional repeating units, and is derived from low molar mass molecules called monomer molecules. A polymer is a substance comprised of macromolecules of varying molar masses. Dispersity ($Đ$), which is the ratio of the mass-average molar mass (M_m or M_w) to the number-average molar mass (M_n), i.e., $Đ = M_m/M_n$, is used to describe the breadth of the polymer molar mass distribution; for a uniform polymer there is no distribution of molar masses and $Đ = 1$, and polymers with higher molar mass dispersity have broader molar mass distributions. A polymerization is the process of converting monomers into macromolecules. When the polymerization involves reactions between molecules of all degrees of polymerization (DP) present, the process is known as a polyaddition or a polycondensation. When this involves sequential addition of monomer molecules to an active site, the process is known as chain polymerization.

3) Polyaddition and polycondensation.[5,6] For these polymerizations to occur, monomers must possess at least two reactive sites, i.e., they should have a functionality $\geq$ 2. In polyaddition, polymers are formed by addition reactions of molecules without making low molar mass by-products. In polycondensation, polymers are formed by condensation reactions, which produce small molecules during each reaction. Historically, polyaddition and polycondensation were collectively known as step-growth polymerization. The use of the latter term is discouraged.[5]

An example of polyaddition is the synthesis of polyurethane from a diisocyanate and a diol: n O=C=N–R–N=C=O + n HO–R'–OH → –[C(O)NH–R–NHC(O)O–R'–O]$_n$–. An example of polycondensation is polyester synthesis: n HO–R–OH + n HOOC–R'–COOH → –[O–R–O–C(O)–R'–C(O)]$_n$– + n H$_2$O.

Polyadditions and polycondensations can be performed either using two different monomers with mutually reactive functional groups (i.e., AA and BB type monomers) or with a single monomer that contains both functional groups (i.e., AB type monomer).

The molar mass of the polymer product can be controlled by adjusting the concentrations of the two monomers present or by introducing a monofunctional molecule as an end-group. The resulting DP can be predicted using the Carothers equation:

$$X_n = \frac{1+r}{1+r-2rp}$$

where X_n is the number-average DP; $r = N_{AA}/N_{BB}$ where N_{AA} and N_{BB} are the number of bifunctional monomer molecules with A functional groups and B functional groups, respectively, with B being the functional group in excess; and p is referred to as the extent of reaction (p represents the fraction of functional groups consumed with respect to their initial number). When $r = 1$, $X_n = 1/(1-p)$. In the case that a monofunctional molecule is being added to control the molar mass, $r = N_{AA}/(N_{BB} + 2N_B)$, where N_B is the number of monofunctional molecules. From X_n, the expected number-average molar mass can be calculated using $M_n = (X_n \times M_0)/n$, where M_0 is the molar mass of the repeating unit and n is the number of monomer units that make up the repeating unit.

4) Chain polymerization[6,7,8] is a chain reaction that comprises initiation, propagation and, in most instances, deactivation of chain carriers. If irreversible deactivation, by termination, chain transfer or inhibition, is absent, the process is a living polymerization. As long as the initiation in living polymerization is rapid with respect to the rate of propagation, then: X_n is close to the [monomer consumed]/[initiating species formed] value, the molar mass distribution approaches the breadth of a Poisson distribution, and end-groups and the ability to extend the chain are retained. When chain deactivation is reversible, the process is a reversible-deactivation polymerization (RDP). The same features for X_n and $Đ$ are displayed by RDP when the activation-deactivation equilibria are established rapidly with respect to the rate of propagation. Chain polymerizations can be called controlled polymerizations if particular kinetic (*e.g.*, rate of termination) or structural features (*e.g.*, M_n) are controlled. It is critical to define the aspects of the polymerization being controlled to avoid confusion when using this term.

Chain polymerizations are further divided according to what processes occur during propagation. In condensative chain polymerization (CCP), the propagation steps are condensation reactions. In ring-opening polymerization (ROP), the repeating units contain fewer rings than the monomer. In cyclopolymerization, the repeating units contain more rings than the monomer. In group transfer polymerization (GTP), a catalyst is transferred at each propagating step to remain associated with the active site. In polyinsertion, monomers are inserted into the active site.

Chain polymerizations are also classified according to the type of chain carrier or active site:

(a) Radical polymerization[6,7,8] is a chain polymerization where the chain carriers are radicals. Typical radical initiators are dialkyldiazenes and peroxides from which initiation is facilitated by heating or UV-visible irradiation. Termination occurs by combination of two propagating species ($P_x^\bullet$ and $P_y^\bullet$ with DP of x and y, respectively), to form a single macromolecule with DP = $x + y$, or by disproportionation to form two macromolecules with DP of x and y respectively, one with an unsaturated chain-end (e.g., -CH=CH$_2$) and the other with a saturated chain-end (e.g., -CH$_2$-CH$_3$). X_n and $Đ$ also depend on radical chain transfers to monomer, macromolecule, solvent and/or specific agent.

Reversible-deactivation radical polymerization (RDRP) denotes a chain polymerization in which propagating radicals are deactivated reversibly, thereby bringing them into active–dormant equilibria. Living polymer chains comprise dormant species and active propagating species. Major categories of RDRP include: stable-radical mediated polymerization (SRMP), including aminoxyl or nitroxide mediated (radical) polymerization (AMRP or NMP); atom transfer radical polymerization (ATRP); degenerate transfer radical polymerization (DTRP), including iodine transfer polymerization (ITP); and reversible-addition-fragmentation chain-transfer (RAFT) polymerization.

(b) Ionic polymerization,[6,8] which includes anionic polymerization and cationic polymerization, is a chain polymerization in which the chain carriers are ions or ion pairs. In living ionic polymerization, chain termination and irreversible chain transfer are absent. Reversible-deactivation ionic polymerization (RDIP) is an ionic polymerization in which chain carriers are deactivated reversibly, bringing them into an active-dormant equilibrium and thereby conferring living characteristics on the polymerization, typically a reversible-deactivation cationic polymerization (RDCP) involving reversible ion-pair formation. In contrast, anionic group-transfer polymerization is a form of reversible-deactivation anionic polymerization (RDAP), in which a specific atom or group is intramolecularly transferred to remain associated with the active chain-end during the course of the polymerization. An example is polymerization of methacrylate by a silyl-ketene acetal in the presence of a nucleophilic catalyst.

(c) Coordination polymerization[6,8] is a chain polymerization that involves the preliminary coordination of a monomer molecule and a chain carrier, which invariably is a metal complex. Depending on the structure of the complex and the reaction medium, both homogenous and heterogeneous catalysis are possible. Coordination polymerization is mostly used for the polymerization of olefins. Some catalysts allow for stereospecific coordination polymerization of alk-1-enes, leading to the formation of isotactic and/or syndiotactic polymers. Various subclasses of coordination polymerization are living coordination polymerization, reversible-deactivation coordination polymerization (RDCP), chain-shuttling polymerization (CSP), chain-walking polymerization (CWP) and rare-earth-metal-mediated coordination-addition polymerization (sometimes referred to as lanthanoid-mediated group-transfer polymerization).

(d) Ring-opening polymerization (ROP)[6,8] is the chain polymerization of a cyclic monomer to yield a repeating unit that is either acyclic or contains fewer rings than the cyclic monomer. Chain carriers can be any of the reactive species noted above. Examples include anionic ring-opening polymerization, cationic ring-opening polymerization, and coordination ring-opening polymerization. Ring-opening metathesis polymerization (ROMP) is a form of ROP in which polymerization of unsaturated cyclic monomers generates unsaturated macromolecules.

5) Copolymerization.[6,9] Chain copolymerization is the process of forming a polymer that contains more than one type of monomer, i.e. a copolymer, by chain polymerization. A copolymer consisting of macromolecules in which the sequential distribution of the monomeric units obeys known statistical laws is referred to as a statistical copolymer.

In a binary copolymerization of monomers M_1 and M_2, the reactivity ratios, r_1 and r_2, are ratios of the homopropagation (k_{11} or k_{22}) and cross-propagation (k_{12} or k_{21}) rate coefficients:

$\sim M_1^* + M_1 \rightarrow \sim M_1 M_1^*$ k_{11}	$r_1 = k_{11}/k_{12}$
$\sim M_2^* + M_2 \rightarrow \sim M_2 M_2^*$ k_{22}	$r_2 = k_{22}/k_{21}$
$\sim M_1^* + M_2 \rightarrow \sim M_1 M_2^*$ k_{12}	$\sim$ indicates polymer chain
$\sim M_2^* + M_1 \rightarrow \sim M_2 M_1^*$ k_{21}	* indicates active site
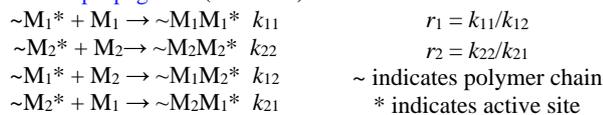
r_1 and r_2 can be used to predict both the composition and the instantaneous distribution of the monomer units within polymer chains. If the product of r_1 and r_2 is 1, then the probability of finding a given monomer unit at any given site in a macromolecule chain is independent of the nature of the adjacent units and the copolymer is called a random copolymer. If the values of both r_1 and r_2 are very close to 0, then monomers M_1 and M_2 will alternate along the macromolecule chain and the copolymer is called an alternating copolymer. Copolymerizations that form random or alternating copolymers are special cases; radical copolymerization typically delivers statistical copolymers.

If r_1 and r_2 are not the same value, one monomer will be consumed more rapidly than the other, leading to a drift in composition of the monomer feed with extent of reaction and therefore of the copolymer composition. In a living copolymerization all chains are identical and the product is a spontaneous gradient copolymer, composed of macromolecules that are gradually more enriched in one monomer from one end to the other. For copolymerizations that do not possess attributes of living polymerizations, compositional drift in the monomer feed results in compositional heterogeneity in the copolymer molecules (i.e., richer in monomer M_1 or monomer M_2) depending on whether they were formed earlier or later in the process.

Copolymers can also be synthesized using polyadditions and polycondensations: in place of at least one of the monomers, two or more species are used, e.g., two diacids in polyamide synthesis.

6) Average molar mass versus extent of reaction. There are three basic paradigms for the variation of average polymer molar masses with conversion: (1) In polyaddition and polycondensation polymerizations, the polymer molar mass increases hyperbolically with extent of reaction – as described by the Carothers equation – due to the repeated reaction of mutually reactive groups that is necessary to build up macromolecules with a high degree of polymerization. (2) By contrast, individual macromolecules grow extremely quickly in chain polymerizations that are not living or RDP. (3) In polymerizations that are living or have living characteristics (e.g., RDRP), the average molar mass builds up progressively, ideally following a linear variation in which the final DP is equal to the initial concentration ratio of monomer to chain-initiating species.

7) Homogeneous and heterogeneous polymerizations.[6,10] Polymerizations can be homogeneous (bulk or solution) or heterogeneous (emulsion, dispersion, precipitation, or suspension). A bulk polymerization feed consists of only the monomer(s) and initiator or catalyst as needed. A solution polymerization comprises the monomer(s) and solvent with initiator or catalyst as needed. In precipitation polymerization, the medium is initially homogeneous but the polymer is insoluble in the medium and precipitates during polymerization. Dispersion polymerizations are similar to precipitation polymerizations but occur in the presence of colloid stabilizers leading to polymer particles of colloidal dimensions. Examples of heterogeneous polymerization with an aqueous continuous phase are suspension, emulsion, mini-emulsion and micro-emulsion polymerization. If the continuous phase is an organic solvent the adjective 'inverse' precedes the term.

8) Polymer architecture.[11,12,13,14,15] The molecular shape of macromolecules is often referred to as polymer architecture (the term polymer topology is also used). Commonly encountered types of polymer architecture include linear, branched, graft, cyclic, star and network, and are observed for both homo- and copolymers. Where a polymer is made up of discrete blocks that differ in composition, or in compositional or stereosequence distribution, the polymer is referred to as a block copolymer. A polymer comprised of hyperbranched macromolecules, where a substantial number of the constitutional repeating units are branched and terminal with some linear constitutional repeating units present, is known as a hyperbranched polymer. A dendrimer is composed of identical dendrimer molecules which consist of one or more dendrons that are composed exclusively of dendritic and terminal constitutional repeating units emanating from a single constitutional unit. Star polymers are comprised of macromolecules containing a single branch point, from which linear chains (arms) emanate. A network polymer can be 2D or 3D and is composed of macromolecule(s) consisting of a large number of conjoined macrocycles, each having at least three subchains in common with neighboring macrocycles.

References [1]IUPAC. The "Purple Book", RSC Publishing, Cambridge, UK (2008); [2]IUPAC. *Pure Appl. Chem.* **84**, 2167 (2012); [3]IUPAC. *Pure Appl. Chem.* **81**, 351 (2009); [4]IUPAC. *Pure Appl. Chem.* **87**, 71 (2015); [5]IUPAC. *Pure Appl. Chem.* **66**, 2483 (1994); [6]IUPAC. *Pure Appl. Chem.* **80**, 2163 (2008); [7]IUPAC. *Pure Appl. Chem.* **82**, 483 (2010); [8]IUPAC. *Pure Appl. Chem.* **94**, (2022); [9]IUPAC. *Pure Appl. Chem.* **68**, 149 (1996); [10]IUPAC. *Pure Appl. Chem.* **83**, 2229 (2011); [11]IUPAC. *Pure Appl. Chem.* **81**, 1131 (2009); [12]IUPAC. *Pure Appl. Chem.* **88**, 1073 (2016); [13]IUPAC. *Pure Appl. Chem.* **91**, 523 (2019); [14]IUPAC. *Pure Appl. Chem.* **80**, 201 (2008); [15]IUPAC. *Pure Appl. Chem.* **68**, 2287 (1996).