Pure Appl. Chem., Vol. 80, No. 10, pp. 2163–2193, 2008.
doi:10.1351/pac200880102163

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

POLYMER DIVISION
COMMISSION ON MACROMOLECULAR NOMENCLATURE*
SUBCOMMITTEE ON MACROMOLECULAR TERMINOLOGY**
and
SUBCOMMITTEE ON POLYMER TERMINOLOGY***

GLOSSARY OF TERMS RELATED TO KINETICS, THERMODYNAMICS, AND MECHANISMS OF POLYMERIZATION

(IUPAC Recommendations 2008)

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Glossary of terms related to kinetics, thermodynamics, and mechanisms of polymerization

(IUPAC Recommendations 2008)

Abstract: This document presents recommended definitions of basic terms related to polymerization processes. Recent developments relating to the kinetics, thermodynamics, and mechanisms of polymerization have necessitated the introduction of new terms and some revision or augmentation of terms previously defined in the *Compendium of Chemical Terminology* (the "Gold Book") or the IUPAC "Glossary of Basic Terms in Polymer Science".

Keywords: kinetics; polymerization; mechanisms; glossary; thermodynamics; IUPAC Polymer Division.

INTRODUCTION

This document presents recommended definitions of basic terms related to polymerization processes, principally to the kinetics, thermodynamics, and mechanisms of polymerization. Polymerization processes have specific features which dictate that the definitions of terms presented here differ, in some instances, from the general definitions provided in the *Compendium of Chemical Terminology* (the "Gold Book") [1]. Some terms defined in the present document were also included in previous IUPAC recommendations, particularly in the "Glossary of Basic Terms in Polymer Science" (the "Glossary") [2] and the "Basic Classification and Definitions of Polymerization Reactions" [3]. In most cases, the previously given definitions have been retained but, in a few cases, the development of the field has required changes. Those definitions from the Gold Book and the Glossary that have been changed are provided in appendices to the present document.

The terms defined in this document are presented in alphabetical order. Italic typeface is used for cross-references to terms defined elsewhere in the document.

RECOMMENDED DEFINITIONS

activated monomer
Reactive species generated reversibly from a monomer.

Note 1: Most frequently, the activated monomer is an anionic or cationic species

Note 2: Examples include a deprotonated lactam, a protonated cyclic ether, and a Lewis acid-coordinated lactone.

See also *activated-monomer polymerization.*

activated-monomer polymerization
Chain polymerization in which *propagation* involves reaction between a growing chain-end and an *activated monomer*.

Note: Examples include the base-catalyzed polymerization of lactams, the acid-catalyzed polymerization of cyclic ethers, and the Lewis acid-catalyzed polymerization of lactones.

See also *activated monomer.*

acyclic diene metathesis polymerization (ADMET)
Metathesis polymerization of an acylic diene monomer.

Note: An example is the metal-catalyzed polymerization of hexa-1,5-diene to form poly(buta-1,4-diene) [poly(buta-2-ene-1,4-diyl)] and ethene as a by-product.

active center (in a chain polymerization)
active site
kinetic-chain carrier
Site on a *chain carrier* at which reaction occurs.

Note: In [1], the terms "active center" and "active site" are defined with reference to heterogeneous catalysis and the term "reactive site" is used within the definition of *chain polymerization*.

active site (in a chain polymerization)
See *active center*.

alternating copolymerization
Copolymerization in which an alternating copolymer is formed [1,2].

Note 1: An alternating copolymer is a copolymer consisting of single-strand macromolecules comprising two species of monomer units in alternating sequence [2].

See also *periodic copolymerization*.

amide interchange
See *transamidation*.

anionic polymerization
Ionic polymerization in which the *active centers* are anions.

Note 1: The anions may be free, paired, or aggregated.

Modified from the definition in [1,2].

apparent rate constant of polymerization, k_p^{app}, SI unit: s^{-1} or dm^{-3} mol s^{-1}
Measured *rate of polymerization* divided by the concentration of the reactant (if there is only one) or the product of concentrations of the presumed reactants.

Note: The apparent rate constant of a *polymerization* should not be confused with the rate coefficients or the rate constants of the elementary reaction steps (compare the definitions of these in [1]).

auto-acceleration

Increase in the *rate of polymerization* with increasing conversion of the reactant(s).

Note: In a *polymerization*, auto-acceleration may be due to a variety of causes. An example of auto-acceleration in a *polymerization* is the Norrish–Trommsdorf effect (gel effect) which leads to a significant increase in the rate of *radical polymerization* with monomer conversion. The effect is due to the rate of termination decreasing with increasing viscosity of the system, causing an increase in the concentration of propagating *radicals*.

azeotropic copolymerization

Binary copolymerization in which the two *monomer reactivity ratios*, r_{12} and r_{21}, are not both equal to unity yet the copolymerization forms a copolymer with its molar ratio of monomer units equal to the molar ratio of monomers in the monomer feed.

Note 1: An *azeotropic polymerization* occurs at only one specific molar ratio of monomers in the feed.

Note 2: Although, in its equality of copolymer and monomer-feed compositions, an *azeotropic polymerization* has the same feature as an *ideal binary copolymerization* in which $r_{12} = r_{21} = 1$, it is not an *ideal copolymerization* as it has $r_{12}r_{21} \neq 1$.

backbiting

intramolecular chain transfer

Chain transfer from an *active center* on a macromolecule to another part of the same macromolecule.

Note 1: An *active center* may be located anywhere along a macromolecular chain.

Note 2: Often, branching occurs or cyclic structures are formed as a result of backbiting.

See also *chain transfer* and *intermolecular chain transfer*.

bead polymerization

See *suspension polymerization.*

binary copolymerization

Copolymerization involving two species of monomer.

bulk polymerization

Polymerization of an undiluted liquid monomer.

cage effect

Term referring to reactions between reactant molecules trapped transiently in a restricted volume of molecular dimensions.

Note 1: In polymerizations, the best-known result of the cage effect is the reduced efficiency of initiation of a *radical polymerization* due to a fast reaction between the two *radicals*, formed by the homolytic dissociation of initiator, within a transient cage of molecules. The reaction occurs before the radicals are able to diffuse apart.

Modified from the definition in [1].

cationic polymerization
Ionic polymerization in which the *active centers* are cations.

Note 1: The cations may be free, paired, or aggregated.

Modified from the definition in [1,2].

ceiling temperature, T_c, SI unit: K
Temperature above which, in a given *chain polymerization*, polymer of high molar mass is not formed.

Note 1: A ceiling temperature is only observed for enthalpy-driven *chain polymerizations* in which $\Delta H_m < 0$ and $\Delta S_m < 0$, where ΔH_m and ΔS_m are respectively the enthalpy and entropy change per mole of monomer reacted.

Note 2: For most *chain polymerizations*, $\Delta H_m < 0$ and $\Delta S_m < 0$.

Note 3: Below T_c, ΔG_m $(= \Delta H_m - T\Delta S_m) < 0$; at T_c, $\Delta G_m = 0$; and above T_c, $\Delta G_m > 0$.

Note 4: Because $\Delta G_m = 0$ at the ceiling temperature, $T_c = \Delta H_m/\Delta S_m$. If ΔH°_m and ΔS°_m are the enthalpy and entropy changes in the standard state, and the monomer behaves ideally, then

$$T_c = \Delta H^\circ_m/\{\Delta S^\circ_m + R\ln([\mathrm{M}]_0/c^\circ)\}$$

where $c^\mathrm{o} = 1$ mol dm^{-3} is the standard concentration and $[\mathrm{M}]_0$ is the initial monomer concentration. Thus, T_c depends on the initial monomer concentration.

Note 5: The symbol $T_c(c^\circ)$ is used to denote the ceiling temperature when the initial monomer concentration, $[\mathrm{M}]_0$, is equal to c°.

Note 6: The symbol T_c(bulk) is used to denote the ceiling temperature when the initial monomer concentration is equal to its undiluted concentration.

See also *floor temperature.*

chain activation
See *chain reactivation*.

chain carrier
Intermediate species bearing an *active site* for the propagation of a chain reaction.

Note: If an *active site* is on the terminal monomer unit of a chain, the chain carrier is represented by the symbol …-m*.

Modified from the definition in [1].

chain copolymerization
Chain polymerization in which a copolymer is formed.

chain deactivation

Conversion of a *chain carrier* into an inactive species.

Note 1: Chain deactivation, unlike *chain termination*, may be reversible; see *reversible chain deactivation.*

Note 2: The reverse of chain deactivation is *chain reactivation.*

chain depropagation

depropagation

Chemical reaction that results in the formation of a monomer molecule at an *active center* on the terminal unit of a *chain carrier* and decreases the *degree of polymerization* of the chain carrier by one.

Note 1: *Chain depropagation* is the reverse of *chain propagation*.

See also *depolymerization* and *unzipping.*

chain-end reactivity ratio, s_1 and s_2

radical reactivity ratio

In a *binary copolymerization*, the ratio of two rate constants defining the relative activity of an *active center* on a given type of terminal unit of a *chain carrier* toward one type of monomer, in the two cases where the penultimate unit of the chain carrier is identical to and different from the terminal unit.

Note 1: The reactions involved are defined in accordance with the *penultimate-unit effect*, namely,

$$\ldots\text{-m}_{11}^* + \text{M}_1 \xrightarrow{k_{111}} \ldots\text{-m}_{11}^*$$
$$\ldots\text{-m}_{21}^* + \text{M}_1 \xrightarrow{k_{211}} \ldots\text{-m}_{11}^*$$
$$\ldots\text{-m}_{11}^* + \text{M}_2 \xrightarrow{k_{112}} \ldots\text{-m}_{12}^*$$
$$\ldots\text{-m}_{21}^* + \text{M}_2 \xrightarrow{k_{212}} \ldots\text{-m}_{12}^*$$
$$\ldots\text{-m}_{12}^* + \text{M}_1 \xrightarrow{k_{121}} \ldots\text{-m}_{21}^*$$
$$\ldots\text{-m}_{22}^* + \text{M}_1 \xrightarrow{k_{221}} \ldots\text{-m}_{21}^*$$
$$\ldots\text{-m}_{12}^* + \text{M}_2 \xrightarrow{k_{122}} \ldots\text{-m}_{22}^*$$
$$\ldots\text{-m}_{22}^* + \text{M}_2 \xrightarrow{k_{222}} \ldots\text{-m}_{22}^*,$$

where M_1 and M_2 are the two monomers involved in the binary copolymerization and $\ldots\text{-m}_{ij}^*$ ($i,j = 1,2$) denotes a *chain carrier* having an *active site* on its terminal monomer unit of type M_j and having the adjacent, penultimate monomer unit of type M_i (see *chain carrier*).

Note 2: The *chain-end reactivity ratios* are expressed mathematically by the equations

$$s_1 = k_{211}/k_{111};\ s_2 = k_{122}/k_{222}$$

Note 3: The *monomer reactivity ratios*, defined in accordance with the *penultimate-unit effect*, are

$$r_{112} = k_{111}/k_{112};\ r_{212} = k_{211}/k_{212};\ r_{221} = k_{222}/k_{221};\ r_{121} = k_{122}/k_{121}.$$

The symbols for the *monomer reactivity ratios* are often abbreviated to r_1, r_1', r_2 and r_2', respectively (see *monomer reactivity ratios* for the definitions of r_1 and r_2 ignoring the *penultimate-unit effect*).

chain initiation (in a chain polymerization)
initiation
Chemical reaction in which *initiating species* add to monomer to form *chain carriers*.

Note: The recommended symbol for the rate constant for chain initiation in a *polymerization* is k_i.

Modified from the definition in [1].

chain polymerization
Chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(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. However, cases exist where a low-molar-mass by-product is formed, as in the *polymerization* of oxazolidine-2,5-diones derived from amino acids (commonly termed amino acid *N*-carboxy anhydrides). When a low-molar-mass by-product is formed, the additional adjective condensative is recommended to form the term "condensative chain polymerization".

Note 4: The growth steps are expressed by

$$\mathrm{P}_x + \mathrm{M} \rightarrow \mathrm{P}_{x+1}\ (+\mathrm{L})\ x \in \{1,2,\ldots \infty\}$$

where P_x denotes the growing chain of *degree of polymerization* x, M a monomer, and L a low-molar-mass by-product formed 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 reactions involved in the growth step, e.g., ring-opening chain polymerization, cationic chain polymerization.

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

$$\mathrm{HS{-}X{-}SH + H_2C{=}CH{-}Y{-}CH{=}CH_2 \rightarrow ({-}S{-}X{-}S{-}CH_2{-}CH_2{-}Y{-}CH_2{-}CH_2{-})}_n$$

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

Modified from the definition in [1,2].

chain propagation (in a chain polymerization)
propagation
Chemical reaction between a *chain carrie*r and a monomer that results in the growth of a polymer chain and the regeneration of at least one chain carrier.

Note 1: The recommended symbol for the rate constant for chain propagation in a *homopolymerization* is k_p.

Note 2: For chain propagation in *copolymerization*, see *cross-propagation*.

Modified from the definition of chain-propagating reaction in [1].

chain reactivation
chain activation
Conversion of an inactive chain into a *chain carrier.*

Note 1: The term is usually used to refer to the reactivation of previously deactivated chains.

Note 2: Chain reactivation can be reversible or irreversible.

Note 3: The reverse of chain reactivation is *chain deactivation* or *reversible chain deactivation.*

chain scission
Chemical reaction resulting in the breaking of backbone bonds of a polymer chain.
Modified from the definition in [1,2].

chain termination (in a chain polymerization)
irreversible chain deactivation, termination
Chemical reaction in which a *chain carrier* is converted irreversibly into a non-propagating species without the formation of a new chain carrier.

Note 1: The recommended symbol for the rate constant or coefficient for chain termination in a *homopolymerization* is k_t.

Note 2: The term "chain deactivation" is often used to stress that, in contrast to chain termination, the formation of non-propagating species may be reversible; see *chain deactivation* and *reversible chain deactivation*.

Note 3: See also *combination*, *cross-termination*, *disproportionation*, and *spontaneous termination*.

Modified from the definition in [1].

chain transfer (in a chain polymerization)
Chemical reaction occurring during a *chain polymerization* in which an *active center* is transferred from a growing macromolecule or oligomer molecule to another molecule or to another site on the same molecule.

Note 1: See also *intermolecular chain transfer*, *intramolecular chain transfer*, and *backbiting*.

Note 2: The recommended symbol for the rate constant of chain transfer in a *homopolymerization* is k_{tr}.

Modified from the definition in [1].

chain-transfer agent
Substance able to react with a *chain carrier* by a reaction in which the original chain carrier is deactivated and a new chain carrier is generated.

Note: In a *polymerization*, the common occurrence is that a new *chain carrier* of lower molar mass is generated.

chain-transfer constant, C_{tr}
In a *homopolymerization*, rate constant for *chain transfer*, k_{tr}, divided by the rate constant for *chain propagation*, k_p, i.e., $C_{tr} = k_{tr}/k_p$.

combination
Chain termination, in a *chain polymerization*, between two propagating macromolecules that gives rise to a single macromolecule of molar mass equal to the sum of the molar masses of the two macromolecules.

Note 1: Combination is often incorrectly called "recombination".

Note 2: Radical combination is also called colligation [1], although this terminology is not commonly used in the context of a *chain polymerization*.

comonomer
Monomer used in *copolymerization*.

connectivity (in polymer science)
See *functionality*.

controlled polymerization
Term indicating control of a certain kinetic feature of a *polymerization* or structural aspect of the polymer molecules formed, or both.

Note 1: The expression "controlled polymerization" is sometimes used to describe a *radical* or *ionic polymerization* in which *reversible deactivation* of the *chain carriers* is an essential component of the mechanism, increasing the time of propagation to secure control of one or more kinetic features of the *polymerization* or one or more structural aspects of the macromolecules formed, or both.

Note 2: The expression "controlled radical *polymerization*" is sometimes used to describe a *radical polymerization* conducted in the presence of reagents that lead to, e.g., atom-transfer *radical polymerization* (ATRP), nitroxide- [aminoxyl] mediated *polymerization* (NMP), or reversible-addition-fragmentation-*chain transfer* (RAFT) *polymerization*.

Note 3: Generally, the adjective "controlled" should not be used without specifying the particular kinetic or structural feature that is subject to control.

coordination polymerization
Chain polymerization that involves the preliminary coordination of a monomer molecule with a *chain carrier*.

Note: Coordination polymerization often occurs by *pseudo-ionic polymerization*.

copolymerization
Polymerization in which a copolymer is formed [1,2].

Note: A copolymer is a polymer derived from at least two species of monomer [1,2].

copolymerization composition equation
Equation relating the instantaneous composition of a binary copolymer to the *monomer reactivity ratios* and the ratio of instantaneous monomer concentrations.

Note 1: The instantaneous composition of copolymer generally changes during the course of a *copolymerization* due to the changing composition of the monomer mixture (but see *azeotropic polymerization*).

Note 2: See also *chain-end reactivity ratio*, *monomer reactivity ratios*.

Note 3: Integrated forms of the *copolymer composition equation* have been developed to relate polymer composition to *monomer reactivity ratios* and monomer conversions.

Note 4: The copolymer composition equation is known also as the Mayo–Lewis equation.

counterion (in polymer science)
Ion that carries a charge opposite to that carried by an ionized group of an ionic macromolecule (ionomer or polyelectrolyte) or by an ionized group of the *chain carrier* of an *ionic polymerization*, thus maintaining overall electrical neutrality.

Note: Definitions in other contexts appear under “counter-ions” in [1]

Augmentation of the definitions in [1].

coupling reaction (in polymer science)
Linking of two macromolecules through chemical reaction.

Note: The coupling may proceed with or without interaction with an added coupling agent.

cross-propagation
Propagation reaction in a *copolymerization* in which a *chain carrier*, bearing at its active end a monomer unit of one kind, reacts with a monomer molecule of another kind.

Note: The recommended symbol for the rate constant of cross-propagation in a *binary copolymerization* is k_{ij}, in which i and j refer to (a) the type of terminal monomer unit of the *chain carrier* and (b) the reacting monomer molecule, respectively.

cross-termination
Termination reaction in a *copolymerization* between two *chain carriers* with different chemical structures.

Note 1: Usually only the chemical structures of the units at the *active centers* are considered.

Note 2: Cross-termination may occur by *combination* or *disproportionation*.

cyclopolymerization
Polymerization in which the number of cyclic structures in the constitutional units of the resulting macromolecules is larger than that in the monomer molecules [1,2].

dead-end polymerization
Radical polymerization that stops, as a consequence of the depletion of the initiator, before the monomer has reacted fully.

degenerate chain transfer
See *degenerative chain transfer*.

degenerative chain transfer
degenerate chain transfer
Chain transfer reaction that generates a new *chain carrier* and a new *chain-transfer agent* with the same reactivity as the original chain carrier and chain-transfer agent.

degradative chain transfer
Chain-transfer reaction that generates a new *chain carrier* of much lower reactivity than that of the original chain carrier.

degree of polymerization (DP), X
Number of monomeric units in a macromolecule, an oligomer molecule, a block, or a chain [1,2].

depolymerization
Process of converting a polymer into a monomer or a mixture of monomers [1,2].
See also *chain depropagation* and *unzipping*.

depropagation
See *chain depropagation*.
See also *unzipping*.

diffusion-controlled termination
Chain termination in a *chain polymerization* in which the rate-determining step is a diffusion process.

disproportionation (in a chain polymerization)
Chain termination, in a *radical polymerization*, between two propagating macromolecules that results in two macromolecules, one carrying an unsaturated chain-end, the other carrying a saturated chain-end.
Different from the definition in [1].

emulsion polymerization
Process whereby monomer(s), initiator, dispersion medium (and possibly colloid stabilizer) are mixed, forming initially an inhomogeneous system conducive to the *polymerization* of the monomer(s), and resulting in particles of colloidal dimensions.

Note: The term "emulsion polymerization" is a misnomer because historically it was thought that the *polymerization* occurred within the droplets of a monomer emulsion.

end-capping
Reaction in which *end-groups* of a desired structure are intentionally formed.

end-group
Constitutional unit that is an extremity of a macromolecule or oligomer molecule [2].

ester interchange
See *transesterification.*

(molar) enthalpy of polymerization, ΔH_m or $\Delta_{ab}H_m$, SI unit: J mol^{-1}
Change of enthalpy, in a *chain polymerization* forming a homopolymer, associated with the conversion of one mole of monomer into polymer under isobaric and isothermal conditions.

Note 1: Under defined standard conditions the enthalpy of polymerization is designated ΔH^o_m.

Note 2: The subscripts in $\Delta_{ab}H_m$ denote (a) the state of the monomer and (b) the state of polymer, as follows:

- g: gaseous state (hypothetical in the case of polymer)
- l: liquid state (must be specified in the case of a mesophase)
- s: in solution (solvent and mesophases, if any, must be specified)
- c: (condensed) amorphous, glassy states
- c': crystalline or partly crystalline state

e.g., $\Delta_{lc}H_m$ means: from liquid state to amorphous or glassy state; $\Delta_{ss}H_m$ means: from monomer in solvent to polymer in solvent.

Note 3: The symbol ΔH_{ab}, in common usage in polymer chemistry, is discouraged as the IUPAC-recommended symbol is $\Delta_{ab}H_m$ [4].

(molar) entropy of polymerization, ΔS_m or $\Delta_{ab}S_m$, SI unit: J mol^{-1} K^{-1}
Change of entropy, in a *chain polymerization* forming a homopolymer, associated with the conversion of one mole of monomer into polymer under isobaric and isothermal conditions.

Note 1: Under defined standard conditions, the entropy of polymerization is designated ΔS°_m; thus, if the standard state refers to standard concentration, and the monomer behaves ideally, $\Delta S_m = \Delta S^\circ_m + R \ln ([M]_0/c^\circ)$, where $[M]_0$ denotes the starting monomer concentration and $c^\circ = 1$ mol dm^{-3} is the standard concentration.

Note 2: The subscripts in $\Delta_{ab}S_m$ denote the state of the monomer (a) and the state of polymer (b) (see Notes to *enthalpy of polymerization*).

floor temperature, T_f, SI unit: K
Temperature below which, in a given *chain polymerization*, polymer of high molar mass is not formed.

Note 1: A floor temperature is only observed for entropy-driven *chain polymerizations* in which $\Delta H_m > 0$ and $\Delta S_m > 0$, where ΔH_m and ΔS_m are respectively the enthalpy and entropy change per mole of monomer reacted.

Note 2: Examples of *chain polymerizations* for which $\Delta H_m > 0$ and $\Delta S_m > 0$ are polymerizations of larger cyclic monomers, e.g., elemental sulfur (S_8) and octamethylcyclotetrasiloxane [2,2,4,4,6,6,8,8-octamethyl-1,3,5,7,2,4,6,8-tetraoxatetrasilocane], proceeding via ring-opening mechanisms.

Note 3: Above T_f, ΔG_m (= $\Delta H_m - T\Delta S_m$) < 0; at T_f, $\Delta G_m = 0$; and below T_f, $\Delta G_m > 0$.

Note 4: Because $\Delta G_m = 0$ at the floor temperature, $T_f = \Delta H_m/\Delta S_m$. If ΔH°_m and ΔS°_m are the enthalpy and entropy changes in the standard state, and the monomer behaves ideally, then

$$T_f = \Delta H^\circ_m/\{\Delta S^\circ_m + R\ln([M]_0/c^\circ)\}$$

where $c^\circ = 1$ mol dm^{-3} is the standard concentration and $[M]_0$ is the initial monomer concentration. Thus, T_f depends on the initial monomer concentration

Note 5: The symbol T_f (c°) is used to denote the floor temperature when the initial monomer concentration, $[M]_0$, is equal to c°.

Note 6: The symbol T_f (bulk) is used to denote the floor temperature when the initial monomer concentration is equal to its undiluted concentration.

See also *ceiling temperature.*

free ion (in a condensed phase)
Ion whose behavior is independent of the influence of a *counterion*.

Note 1: A free ion is a distinct kinetic entity, and its reactivity is usually different from that of an *ion pair*.

Note 2: The behavior of a free ion may still be influenced by neighboring atoms or molecules.

functionality (in polymer science), f
connectivity (in polymer science)
Number of covalent bonds that a monomeric or polymeric reactant can form with other reactants in the course of a polymerization.

Note 1: There are no monofunctional monomers.

Note 2: If $f = 2$, a linear chain macromolecule or a macrocycle (see Definition 1.57 in [2]) can be formed.

Note 3: If $f > 2$, a branch point can be formed leading to a branched macromolecule, a network or a micro-network.

Note 4: Ethene and ethylene glycol [ethane-1,2-diol] are examples of difunctional monomers, glycerol [propane-1,2,3-triol] is an example of a trifunctional monomer, and divinylbenzene and pentaerythritol [2,2-bis(hydroxymethyl)propane-1,3-diol] are examples of tetrafunctional monomers.

gelation point
See *gel point*.

gel point
gelation point
Point of incipient network formation in a process forming a chemical or physical network [5].

Note 1: In both network-forming polymerization and the crosslinking of polymer chains, the gel point is expressed as an extent of chemical reaction.

Note 2: At the gel point, a solid (network) material spanning the entire system is formed.

Note 3: The gel point is often detected using rheological methods. Different methods can give different gel points because viscosity is tending to infinity at the gel point and a unique value cannot be measured directly.

heat of polymerization, Q
Heat absorbed or given off from the conversion of a specified amount of monomer into polymer.

Note 1: The molar heat of polymerization is denoted by the symbol Q_m and is the heat of polymerization of 1 mole of monomer. SI unit: J mol^{-1}

Note 2: The molar heat of polymerization is equal to the *enthalpy of polymerization* under isobaric and isothermal conditions.

homopolymerization
Polymerization in which a homopolymer is formed [1,2].

Note: A homopolymer is a polymer derived from one species of (real, implicit, or hypothetical) monomer [2].

homopropagation
Addition of a monomer to a *chain carrier* bearing a terminal group derived from the same monomer species.

ideal binary copolymerization
Binary copolymerization in which the relative rates of incorporation of the two types of monomer into the copolymer are independent of the nature of the monomer unit at the end of a propagating chain.

Note 1: See *monomer reactivity ratios*. In an *ideal binary copolymerization*, $k_{11}/k_{21} = k_{12}/k_{22}$ and $r_{12}r_{21} = 1$.

Note 2: In the special case of an ideal binary copolymerization in which $r_{12} = r_{21} = 1$, the two monomers show equal reactivities toward both types of propagating species. Thus, $k_{11} = k_{21}$ and $k_{12} = k_{22}$. Hence, *copolymerization* of a mixture of two monomers with any ratio of monomer concentrations in the monomer feed gives rise to a copolymer in which the molar ratio of monomer units is identical to that in the monomer feed. (See also *azeotropic copolymerization*.)

ideal copolymerization
Copolymerization in which all types of propagating species show the same relative reactivity toward the monomers present.

inhibitor (in polymer science)
Additive that reacts so rapidly with the *chain carriers* that it reduces the observed rate of *polymerization* to zero.

> *Note*: Long-chain macromolecules cannot be formed until virtually all the inhibitor is consumed.

Different from the definition in [1].

initiating species
Species to which monomer adds to start *chain polymerization*.

> *Note 1*: An initiating species may be formed from an *initiator* or be the initiator itself.

> *Note 2*: In radical polymerization, initiating species formed directly from an initiator are called *primary radicals* [2].

initiator
Substance introduced into a reaction system in order to cause *chain initiation*.

> *Note*: In contrast to a catalyst, an initiator is consumed in the reaction.

Modified from the definition in [1].

initiator efficiency, f
Number of growing chains initiated divided by the number of *active centers* generated from *initiator* molecules.

> *Note 1*: In a *radical polymerization*, the rate of radical production from an initiator that provides two similar radicals is $2k_d f$, where k_d is the rate constant for initiator decomposition.

> *Note 2*: In some texts, the initiator efficiency is defined as the fraction of radicals that escapes the cage (see *cage effect*).

initiation (in a chain polymerization)
See *chain initiation.*

interchange reaction
Reaction between two molecules that causes a redistribution of functional groups between the two molecules.

> *Note*: *Transamidation* (*amide interchange*) and *transesterification* (*ester interchange*) are examples of interchange reactions.

interfacial polycondensation
Polycondensation involving two monomers separately dissolved in immiscible solvents, forming a two-phase system, with polycondensation taking place at (or near) an interface between the two phases.

intermolecular chain transfer
Chain transfer from an *active center* on a macromolecule to a different macromolecule.

Note: An *active center* may be located anywhere along a macromolecular chain.

See also *chain transfer*, *backbiting*.

intramolecular chain transfer
See *backbiting*.

ionic copolymerization
Copolymerization that is an *ionic polymerization* [2].

ionic polymerization
Chain polymerization in which *active centers* are ions or ion pairs.

Note 1: Usually the chain-ends are ions, although ions can also be located on the monomer molecules, as in an *activated-monomer polymerization*.

Note 2: The ions may also be present in the form of higher aggregates that usually are less reactive than non-aggregated species.

Modified from the definition in [2].

ion pair (in polymer science)
Pair of oppositely charged ions, held together by Coulombic attraction.
Shortened from the definition in [1].

irreversible chain deactivation
See *chain termination.*

kinetic-chain carrier
See *active center.*

kinetic-chain length, ν
In a *chain polymerization*, the rate of *chain propagation* divided by the sum of the rates of all of the *chain-termination* processes.

Note 1: *Chain-termination* processes include termination by *combination* or *disproportionation* but do not include *chain transfer*.

Note 2: In the absence of *chain transfer*, the kinetic-chain length will be equal to the degree of polymerization.

living copolymerization
Copolymerization that is a *living polymerization* [1,2].

living polymerization
Chain polymerization in which *chain termination* and irreversible *chain transfer* are absent.

Note 1: In many cases, the rate of *chain initiation* is fast compared with the rate of *chain propagation*, so that the number of *kinetic-chain carriers* is essentially constant throughout the reaction.

Note 2: In a living polymerization, the reversible (temporary) deactivation of *active centers* can take place (see *reversible chain deactivation*).

Note 3: In a living polymerization, all the macromolecules formed possess the potential for further growth.

Note 4: Use of the adjectives "pseudo-living", "quasi-living", and "immortal" is discouraged.

Modified from the definition in [1,2].

macromonomer
Polymer or oligomer composed of molecules, each of which has at least one chain-end or other site bearing a functional group capable of undergoing polymerization.

Note: The *homopolymerization* or *copolymerization* of macromonomer molecules, each of which has a single functional group capable of undergoing polymerization, gives rise to graft copolymers.

Modified from the definition in [1,2].

metathesis polymerization
Polymerization in which unsaturated monomers are transformed into unsaturated polymers by a process of bond redistribution.

Note 1: Metathesis polymerization is most often metal-catalyzed and the *kinetic-chain carriers* alternate between metal carbene complexes and metallacyclobutanes or metal carbyne complexes and metallacyclobutenes.

Note 2: The two most common forms of metathesis polymerization are *ring-opening metathesis polymerization* (ROMP) and *acyclic diene metathesis polymerization* (ADMET).

monomer reactivity ratios, r_{12}, r_{21}
In *binary copolymerization*, (a) the ratio (r_{12}) of the rate constant (k_{11}) for the *homopropagation* of monomer M_1 to the rate constant (k_{12}) for the *cross-propagation* of the *chain carrier* ...-m_1* with the monomer M_2 and (b) the ratio (r_{21}) of the rate constant (k_{22}) for the *homopropagation* of monomer M_2 to the rate constant for the cross-propagation (k_{21}) of the chain carrier …-m_2* with monomer M_1. Thus, $r_{12} = k_{11}/k_{12}$, $r_{21} = k_{22}/k_{21}$.

Note 1: The reactions involved are

$$\ldots\text{-m}_1^* + \text{M}_1 \xrightarrow{k_{11}} \ldots\text{-m}_1^*$$

$$\ldots\text{-m}_1^* + \text{M}_2 \xrightarrow{k_{12}} \ldots\text{-m}_2^*$$

$$\ldots\text{-m}_2^* + \text{M}_2 \xrightarrow{k_{22}} \ldots\text{-m}_2^*$$

$$\ldots\text{-m}_2^* + \text{M}_1 \xrightarrow{k_{21}} \ldots\text{-m}_1^*$$

where M_1 and M_2 are the two monomers involved in the *binary copolymerization* and …-m_i* (i = 1,2) denotes a *chain carrier* having an *active site* on its terminal monomer unit of type M_i.

Note 2: The symbols r_{12} and r_{21} are often abbreviated to r_1 and r_2, respectively.

Note 3: The present definition ignores the *penultimate-unit effect*. For the definition of monomer reactivity ratios accounting for the penultimate-unit effect, see Note 3 of *chain-end reactivity ratios*.

See also *chain-end reactivity ratios*.

monomer reactivity scale
Relative scale defined by the values of the rate constants for the addition of monomers to a reference *active center*.
See also *patterns of reactivity scheme*, *Q-e scheme*.

oligomerization
Process of converting a monomer or a mixture of monomers into an oligomer [1,2].

Note: An oligomer is a substance composed of oligomer molecules, the structure of which essentially comprises a small number of units derived, actually or conceptually, from molecules of lower molar mass [1,2].

See also *telomerization*.

patterns of reactivity scheme (in polymer science)
Method for the prediction of monomer reactivity ratios in *binary copolymerization*, based exclusively on experimentally determined parameters.

Note 1: The parameters may be the monomer reactivity ratios for the separate *copolymerizations* of the monomers concerned, namely, 1 and 2, with a nonpolar monomer, e.g., styrene (S), and a polar monomer, e.g., acrylonitrile (A). The equations for the desired monomer reactivity ratios, r_{12} and r_{21}, are then as follows:

$$\ln r_{12} = \ln (r_{1S}r_{S2}) - [\ln (r_{AS}r_{S2}/r_{A2})][\ln (r_{SA}r_{1S}/r_{1A})]/\ln (r_{AS}r_{SA})$$

$$\ln r_{21} = \ln (r_{2S}r_{S1}) - [\ln (r_{AS}r_{S1}/r_{A1})][\ln (r_{SA}.r_{2S}/r_{2A})]/\ln (r_{AS}r_{SA})$$

Note 2: The patterns of reactivity scheme is known also as Jenkins' scheme.

pearl polymerization
See *suspension polymerization*.

penultimate-unit effect
Phenomenon that the penultimate monomer unit preceding the *active center* on the terminal unit of an active polymer chain affects the reactivity of that active center.
See also *chain-end reactivity ratio*.

periodic copolymerization
Copolymerization in which a periodic copolymer is formed [1,2].

Note: A periodic copolymer is a copolymer consisting of macromolecules comprising more than two species of monomeric units in regular sequence [1,2].

photoinitiator
Substance introduced into a reaction system in order to cause *chain initiation* upon irradiation of the system by visible or ultraviolet light.
See *initiator*.

photopolymerization
Polymerization initiated by visible or ultraviolet light, typically in the presence of a light-sensitive compound known as a *photoinitiator*.

Note: Depending on the mechanism of decomposition of the *photoinitiator* upon irradiation and the structure of the monomer, photopolymerization may proceed by either a radical or an ionic mechanism.

polyaddition
Polymerization in which the growth of polymer chains proceeds by addition reactions between molecules of all *degrees of polymerization* [1,2].

Note 1: The growth steps are expressed by

$$P_x + P_y \rightarrow P_{x+y} \qquad x \in \{1,2...\infty\};\ y \in \{1,2...\ \infty\}$$

where P_x and P_y denote chains of *degrees of polymerization* x and y, respectively.

Note 2: The earlier term "addition polymerization", defined previously [6], embraced both the current concepts of *polyaddition* and *chain polymerization*, but did not include condensative *chain polymerization*. (See Note 3 under *chain polymerization*.)

polycondensation
Polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all *degrees of polymerization* [1,2].

Note 1: The growth steps are expressed by

$$P_x + P_y \rightarrow P_{x+y} + L \quad x \in \{1,2...\infty\};\ y \in \{1,2...\ \infty\}$$

where P_x and P_y denote the chains of *degree of polymerization* x and y, respectively, and L a low-molar-mass by-product.

Note 2: The terms "polycondensation" and "condensation polymerization", defined previously [6], were synonymous. It should be noted that the current definitions of polycondensation and condensative *chain polymerization* (see Note 3 under *chain polymerization*) were both embraced by the previous term "polycondensation".

polymerization
Process of converting a monomer or a mixture of monomers into a polymer [1,2].

Note: A polymer is a substance composed of macromolecules [1,2].

primary radical (in a chain polymerization)
Radical that is formed from an *initiator* or monomer molecule and that is capable of initiating *polymerization.*

Note 1: A primary *radical* may be formed by the action of heat, irradiation or electrode charge transfer.

Note 2: The recombination of primary radicals and their reactions with other species may lead to reduced *initiator efficiency*.

Note 3: The term "primary radical" is also used to designate a radical centered on a primary carbon atom, for example, an ethyl radical [1].

See *secondary radical*.

primary-radical termination
Termination reaction involving a radical *chain carrier* and a *primary radical*.

propagation (in a chain polymerization)
See *chain propagation*.

pseudo-ionic polymerization
Polymerization proceeding by insertion of a monomer into a polar bond without the generation of ions.

Note: Most *pseudo-ionic polymerizations* involve concerted (e.g., four- or multi-center) mechanisms of propagation.

See also *coordination polymerization*.

pulsed-laser polymerization (PLP)
Polymerization initiated by successive pulses of laser light.

Note: In a *radical polymerization*, PLP allows determination of the propagation rate constants.

Q-e **scheme**
Empirical equations expressing the *monomer reactivity ratios* in a *binary radical copolymerization*, r_{12} and r_{21}, in terms of the empirical parameters Q and e for the two monomers, namely, Q_1, Q_2, e_1, and e_2, with

$$r_{12} = (Q_1/Q_2)\exp[-e_1(e_1 - e_2)] \text{ and } r_{21} = (Q_2/Q_1)\exp[-e_2(e_2 - e_1)]$$

Note 1: Although the parameters are empirically derived, the parameter Q is considered to be a measure of the stabilization by conjugation of a monomer and the radical derived from it, while the parameter e is considered to be a measure of the polar effects of substituents on the monomer and the radical derived from it.

Note 2: The *Q*-*e* scheme is known also as the Alfrey–Price scheme.

radical (in polymer science)
Molecular entity possessing an unpaired electron.

Note: The use of the term "free radical" is discouraged.

Shortened from the definition in [1].

radical copolymerization
Copolymerization that is a radical polymerization.
Modified from the definition in [1,2].

radical polymerization
Chain polymerization in which the *active centers* are radicals.

Note: Each active chain-end bears an unpaired electron.

Modified from the definition in [1,2].

radical reactivity ratio (in a chain polymerization)
See *chain-end reactivity ratio*.

radical reactivity scale (in a chain polymerization)
Scale of the values of the rate constants for the reaction of *radicals* with a reference monomer.

random copolymerization
Copolymerization in which a random copolymer is formed [1,2].

Note 1: A random copolymer is a copolymer consisting of macromolecules in which the probability of finding a given monomer unit at any given site in the chain is independent of the nature of the adjacent units [2].

Note 2: Random copolymerization should not be confused with *statistical copolymerization.*

rate of polymerization
Rate of consumption of monomers in a *chain polymerization*, or the rate of consumption of the functional groups in the reaction mixture of a *polycondensation* or *polyaddition*.

reversible chain deactivation
Deactivation of a *chain carrier* in a *chain polymerization*, reversibly converting an *active center* into an inactive one and then, within the average lifetime of a growing macromolecule, regenerating an active center on the same *original carrier*.

Note 1: The temporarily deactivated species created in this process are often described as dormant.

Note 2: Reversible deactivation often involves reversible *combination* or reversible *chain transfer*.

ring-opening copolymerization
Copolymerization that is a ring-opening polymerization with respect to at least one monomer [2].

ring-opening metathesis polymerization (ROMP)
Metathesis polymerization in which an unsaturated cyclic monomer is converted into an unsaturated monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

ring-opening polymerization (ROP)
Polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

Note: If the monomer is polycyclic, the opening of a single ring is sufficient to classify the polymerization as a ring-opening polymerization.

Modified from the definition in [1,2].

secondary radical (in a chain polymerization)
Radical formed by the rearrangement or fragmentation of a *primary radical* that is capable of initiating a *polymerization*.

Note: The term "secondary radical" is also used to designate a radical centered on a secondary carbon atom, e.g., a 2-propyl radical [1].

See *primary radical*.

self-initiated polymerization
Polymerization in which *initiating species* are formed exclusively from the monomer.

solid-state polymerization
Polymerization of a crystalline monomer.

Note 1: The *initiating species* can be formed by the action of heat, irradiation of the monomer with, e.g., ultraviolet light or γ-rays, or (less frequently) by chemical initiation.

Note 2: A solid-state polymerization may lead to a semi-crystalline polymer having a crystal structure different from that of the crystalline monomer, or alternatively it may proceed as a *topochemical polymerization*.

Note 3: Depending on the *initiation* mode and the structure of the monomer, a solid-state polymerization may proceed by a *radical* or an ionic mechanism.

Note 4: Use of the term "bulk polymerization" to describe solid-state polymerization is discouraged.

spontaneous termination
Chain termination proceeding as a unimolecular process.

statistical copolymerization
Copolymerization in which a statistical copolymer is formed [1,2].

Note 1: A statistical copolymer is a copolymer consisting of macromolecules in which the sequential distribution of the monomeric units obeys known statistical laws [1,2].

Note 2: Statistical copolymerization should not be confused with *random copolymerization.*

stereospecific polymerization
Polymerization in which a tactic polymer is formed [6].

Note 1: A tactic polymer is composed of tactic macromolecules [1,2].

Note 2: A tactic macromolecule is a regular macromolecule, in which essentially all the configurational repeating units are identical [1,2].

Modified from the definition in [1].

suspension polymerization
pearl polymerization, bead polymerization
Polymerization that takes place in particles that exceed colloidal dimensions dispersed in an inert liquid medium.

Note: The initiator of a suspension polymerization is soluble in the dispersed monomer phase and essentially insoluble in the inert-liquid dispersing phase.

telomerization (in polymer science)
Oligomerization by *chain polymerization* in the presence of a large amount of *chain-transfer agent*, so that end-groups are essentially fragments of the chain-transfer agent [2].

template polymerization
Polymerization of a monomer adsorbed or oriented, or both, (a) on a surface, (b) in a polymer lattice, or (c) on a polymer in solution, whereby the structure of the polymer chains formed is *controlled* by the orientation of the monomer molecules.

termination (in a chain polymerization)
See *chain termination.*

topochemical polymerization
Solid-state polymerization, resulting in the formation of a polymer having essentially the same crystal structure as that of the monomer.

Note 1: A topochemical polymerization is usually initiated by irradiation of the crystalline monomer with, e.g., ultraviolet light, γ-rays, or by chemical initiators.

Note 2: A topochemical polymerization does not involve significant atomic or molecular motions.

transamidation (in polymer science)
amide interchange
Interchange reaction involving amide groups.

Note 1: The reactions of an amide group with an amine group to give a new amide group plus a new amine group (aminolysis), of an amide group with a carboxylic acid group to give a new amide group plus a new carboxylic acid group (acidolysis), and of an amide group with another amide group to interchange substituents are all examples of transamidation.

Note 2: Transamidations commonly occur during *polycondensations* to form polyamides.

transesterification (in polymer science)
ester interchange
Interchange reaction involving ester groups.

Note 1: The reactions of an ester group with a hydroxy group to give a new ester group plus a new hydroxy group (alcoholysis), of an ester group with a carboxylic acid group to give a new ester group plus a new carboxylic acid group (acidolysis), and of an ester group with another ester group to interchange substituents are all examples of transesterification.

Note 2: Transesterifications commonly occur during *polycondensations* to form polyesters.

unzipping (in polymer science)
Depolymerization occurring by a sequence of reactions, progressing along a macromolecule and yielding products, usually monomer molecules, at each reaction step, from which macromolecules similar to the original can be regenerated.
See also *chain depropagation*.

zwitterionic copolymerization
Copolymerization that is a *zwitterionic polymerization*.

Note: A zwitterionic copolymerization usually involves a nucleophilic monomer and an electrophilic monomer, and it may produce an alternating copolymer.

zwitterionic polymerization
Chain polymerization in which a growing macromolecule bears two ionic *chain carriers* of opposite signs, at one or both of its ends.

Note: Chains in a zwitterionic polymerization may grow from one or both of their ends.

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APPENDICES 1 AND 2

Changes to some of the terms in the "Gold Book" [1] and the IUPAC "Glossary of Basic Terms in Polymer Science" (the "Glossary") [2] have been necessitated by developments in polymer science and, in other cases, by the existing definitions not being specifically directed toward macromolecular terminology. In the latter instance, the new definitions are intended to augment the existing definition rather than be a replacement for it. Appendices 1 and 2 list the definitions in this document that have been modified or are different from those in the Gold Book [1] and from the Glossary [2]. These Appendices are enclosed so that interested readers have the information readily available without the need to cross-reference other documents.

APPENDIX 1

Relevant definitions from the "Gold Book" [1] that have been modified.

anionic polymerization
An *ionic polymerization* in which the *kinetic-chain carriers* are anions.

cage effect
When in a condensed phase, or in a dense gas, reactant molecules come together, or species are caged in by surrounding molecules, they may undergo a set of collisions known as an encounter: the term "cage effect" is then applied.

cationic polymerization
An *ionic polymerization* in which the *kinetic-chain carriers* are cations.

chain carrier
A species, such as an atom or free radical, which is involved in *chain-propagating reactions* is known as a chain carrier.

chain initiation
The process in a chain reaction that is responsible for the formation of a *chain carrier*.

chain polymerization
A chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.

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

Note 2: The adjective "chain" in "chain polymerization" denotes "chain reaction" rather than "polymer chain".

Note 3: Propagation in chain polymerization often occurs without the formation of small molecules. However, cases exist where, at each propagation step, a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed "amino acid *N*-carboxy anhydrides"). When a low-molar-mass by-product is formed, the adjective "condensative" is recommended to give the term "condensative chain polymerization".

Note 4: The growth steps are expressed by

$$P_x + M \rightarrow P_{x+1} \ (+ L) \quad \{x\} \in \{1, 2, ...\infty\}$$

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

The term "chain polymerization" may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g., ring-opening chain polymerization and cationic chain polymerization.

Note 5: There exist, exceptionally, some polymerizations that can proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization

$$\text{HS–X–SH} + H_2C\text{=CH–X'–CH=}CH_2 \rightarrow (\text{–S–X–S–}CH_2\text{–}CH_2\text{–Y–}CH_2\text{–}CH_2\text{–})_n$$

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

chain-propagating reaction
A chain-propagating reaction, or more simply a propagating reaction, is an elementary step in a chain reaction in which one *chain carrier* is converted into another. The conversion can be a unimolecular reaction or a bimolecular reaction with a reactant molecule.

chain scission (of a polymer)
A chemical reaction resulting in the breaking of skeletal bonds.

chain-termination reaction
See *termination*.

chain transfer
The abstraction, by the *radical* end of a growing chain-polymer, of an atom from another molecule. The growth of the polymer chain is thereby terminated but a new radical, capable of chain propagation and polymerization, is simultaneously created. For the example of alkylene polymerization cited for a chain reaction, the reaction

$$RCH_2\dot{C}HPh + CCl_4 \rightarrow RCH_2CHClPh + Cl_3C^{\bullet}$$

represents a chain transfer, the radical $Cl_3C^{\bullet}$ inducing further polymerization

$$CH_2\text{=CHPh} + Cl_3C^{\bullet} \rightarrow Cl_3CCH_2\dot{C}HPh$$

$$Cl_3CCH_2\dot{C}HPh + CH_2{=}CHPh \rightarrow Cl_3CCH_2CHPhCH_2\dot{C}HPh \text{ etc.}$$

The phenomenon occurs also in other chain reactions such as a cationic polymerization.

counter-ions

1. (in an ion exchanger): the mobile exchangeable ions.
2. (in colloid chemistry): ions of low relative molecular mass, with a charge opposite to that of the colloidal ion.

disproportionation

1. Any chemical reaction of the type A + A → A' + A", where A, A' and A" are different chemical species. For example:

   $$2ArH^+ \rightarrow ArH + ArH^{2+}$$

   The reverse of disproportionation is called comproportionation. A special case of disproportionation (or "dismutation") is "radical disproportionation", exemplified by

   $$^{\bullet}CH_2CH_3 + {}^{\bullet}CH_2CH_3 \rightarrow CH_2{=}CH_2 + CH_3CH_3$$

   Reactions of the more general type

   $$R\dot{C}HCH_3 + R'\dot{C}HCH_3 \rightarrow RCH{=}CH_2 + R'CH_2CH_3$$

   are also loosely described as radical disproportionations.
2. A reversible or irreversible transition in which species with the same oxidation state combine to yield one of higher oxidation state and one of lower oxidation state. Example: $3\ Au^+ \rightarrow Au^{3+} + 2\ Au$. The term also applies to an internal oxidation–reduction process as occurs, for example, among the iron atoms of $CaFeO_3$, where $2\ Fe^{4+} \rightarrow Fe^{(4-\delta)+} + Fe^{(4+\delta)+}$, at Fe subarrays on lowering the temperature.

inhibitor

A substance that diminishes the rate of a chemical reaction; the process is called inhibition. Inhibitors are sometimes called negative catalysts, but since the action of an inhibitor is fundamentally different from that of a catalyst, this terminology is discouraged. In contrast to a catalyst, an inhibitor may be consumed during the course of a reaction. In enzyme-catalyzed reactions, an inhibitor frequently acts by binding to the enzyme, in which case it may be called an enzyme inhibitor.

initiator

A substance introduced into a reaction system in order to bring about an *initiation* reaction.

initiation

A reaction or process generating free radicals (or some other reactive reaction intermediates) which then induce a chain reaction. For example, in the chlorination of alkanes by a radical mechanism the initiation step is the dissociation of molecular chlorine.

ionic polymerization

A *chain polymerization* in which the *kinetic-chain carriers* are ions or ion pairs. Usually, the growing chain ends are ions.

ion pair
A pair of oppositely charged ions held together by Coulomb attraction without formation of a covalent bond. Experimentally, an ion pair behaves as one unit in determining conductivity, kinetic behavior, osmotic properties, etc.

Following Bjerrum, oppositely charged ions with their centers closer together than a distance

$$q = 8.36 \to 10^6 z^+ z^- / (\varepsilon_r T) \text{ pm}$$

are considered to constitute an ion pair (“Bjerrum ion pair”). [z^+ and z^- are the charge numbers of the ions, and ε_r is the relative permittivity (or dielectric constant) of the medium].

An ion pair, the constituent ions of which are in direct contact (and not separated by an intervening solvent or other neutral molecule) is designated as a “tight ion pair” (or “intimate” or “contact ion pair”). A tight ion pair of X^+ and Y^- is symbolically represented as X^+Y^-.

By contrast, an ion pair whose constituent ions are separated by one or several solvent or other neutral molecules is described as a “loose ion pair”, symbolically represented as $X^+ || Y^-$. The members of a loose ion pair can readily interchange with other free or loosely paired ions in the solution. This interchange may be detectable (e.g., by isotopic labeling) and thus afford an experimental distinction between tight and loose ion pairs.

A further conceptual distinction has sometimes been made between two types of loose ion pairs. In “solvent-shared ion pairs”, the ionic constituents of the pair are separated by only a single solvent molecule, whereas in “solvent-separated ion pairs”, more than one solvent molecule intervenes. However, the term “solvent-separated ion pair” must be used and interpreted with care since it has also widely been used as a less specific term for “loose” ion pair.

living polymerization
A *chain polymerization* from which *chain transfer* and *chain termination* are absent.

In many cases, the rate of *chain initiation* is fast compared with the rate of *chain propagation*, so that the number of *kinetic-chain carriers* is essentially constant throughout the reaction.

macromonomer
A polymer composed of macromonomer molecules.

macromonomer molecule
A macromolecule that has one *end-group* which enables it to act as a monomer molecule, contributing only a single monomeric unit to a chain of the final macromolecule.

oligomerization
The process of converting a monomer or a mixture of monomer into an oligomer.

An oligomerization by chain reaction carried out in the presence of a large amount of *chain-transfer agent*, so that the *end-groups* are essentially fragments of the chain-transfer agent, is termed “telomerization”.

radical
A molecular entity such as $^\bullet CH_3$, $^\bullet SnH_3$, $Cl^\bullet$ possessing an unpaired electron. (In these formulae the dot, symbolizing the unpaired electron, should be placed so as to indicate the atom of highest spin density, if this is possible). Paramagnetic metal ions are not normally regarded as radicals. However, in the “isolobal analogy” the similarity between certain paramagnetic metal ions and radicals becomes apparent.

At least in the context of physical organic chemistry, it seems desirable to cease using the adjective “free” in the general name of this type of chemical species and molecular entity, so that the term “free radical” may in future be restricted to those radicals which do not form parts of radical pairs.

Depending upon the core atom that possesses the unpaired electron, the radicals can be described as carbon-, oxygen-, nitrogen-, metal-centered radicals. If the unpaired electron occupies an orbital having considerable s or more less pure p character, the respective radicals are termed σ- or π-radicals.

In the past, the term “radical” was used to designate a substituent group bound to a molecular entity, as opposed to “free radical”, which nowadays is simply called radical. The bound entities may be called groups or substituents, but should no longer be called radicals.

radical polymerization
A *chain polymerization* in which the *kinetic-chain carriers* are *radicals*. Usually, the growing chain end bears an unpaired electron.

stereospecific polymerization
Polymerization in which a tactic polymer is formed. However, polymerization in which stereoisomerism present in the monomer is merely retained in the polymer is not to be regarded as stereospecific. For example, the polymerization of a chiral monomer, e.g., (*R*)-propylene oxide [(*R*)-methyloxirane], with retention of configuration is not considered to be a stereospecific reaction; however, selective polymerization, with retention, of one of the enantiomers present in a mixture of (*R*)- and (*S*)-propylene oxide molecules is so classified.

termination
The steps in a chain reaction in which reactive intermediates are destroyed or rendered inactive, thus ending the chain.

APPENDIX 2

Relevant definitions from the IUPAC “Glossary of Basic Terms in Polymer Science” [2] that have been changed or modified.

3.19 anionic polymerization
An *ionic polymerization* in which the *kinetic-chain carriers* are anions.

3.20 cationic polymerization
An *ionic polymerization* in which the *kinetic-chain carriers* are cations.

3.6 chain polymerization
A chain reaction in which the growth of a polymer chain proceeds exclusively by reaction(s) between monomer(s) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.

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

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

Note 3: Propagation in chain polymerization often occurs without the formation of small molecules. However, cases exist where, at each propagation step, a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed "amino acid *N*-carboxy anhydrides").

When a low-molar-mass by-product is formed, the adjective "condensative" is recommended to give the term "condensative chain polymerization".

Note 4: The growth steps are expressed by

$$\mathrm{P}_x + \mathrm{M} \rightarrow \mathrm{P}_{x+1}\ (+\ \mathrm{L}) \quad \{x\} \in \{1, 2, \ldots\infty\}$$

where P_x denotes the growing chain of degree of polymerization x, M a monomer, and L a low-molar-mass by-product formed 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 reactions involved in the growth step, e.g., ring-opening chain polymerization and cationic chain polymerization.

Note 6: There exist, exceptionally, some polymerizations that can proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization

$$\mathrm{HS{-}X{-}SH} + \mathrm{H_2C{=}CH{-}X'{-}CH{=}CH_2} \rightarrow (\mathrm{{-}S{-}X{-}S{-}CH_2{-}CH_2{-}Y{-}CH_2{-}CH_2{-}})_n$$

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

3.24 chain scission

A chemical reaction resulting in the breaking of skeletal bonds.

3.17 ionic polymerization

A *chain polymerization* in which the *kinetic-chain carriers* are ions or ion pairs.

Note: Usually, the growing chain ends are ions.

3.21 living polymerization

A *chain polymerization* from which *chain transfer* and *chain termination* are absent.

Note: In many cases, the rate of *chain initiation* is fast compared with the rate of *chain propagation*, so that the number of *kinetic-chain carriers* is essentially constant throughout the polymerization.

2.35 macromonomer

A polymer composed of macromonomer molecules.

1.9 macromonomer molecule

A macromolecule that has one *end-group* which enables it to act as a monomer molecule, contributing only a single monomeric unit to a chain of the final macromolecule.

3.2 oligomerization

The process of converting a monomer or a mixture of monomers into an oligomer.

Note: An oligomerization by chain reaction carried out in the presence of a large amount of *chain-transfer agent*, so that the *end-groups* are essentially fragments of the chain-transfer agent, is termed “telomerization”.

3.15 radical polymerization

A *chain polymerization* in which the *kinetic-chain carriers* are radicals.

Note: Usually, the growing chain end bears an unpaired electron.

3.13 ring-opening polymerization

A polymerization in which a cyclic monomer yields a monomeric unit which is acyclic or contains fewer cycles than the monomer.

Note: If the monomer is polycyclic, the opening of a single ring is sufficient to classify the reaction as a ring-opening polymerization.