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IUPAC Recommendation

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Terminology for chain polymerization (IUPAC Recommendations 2021)

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Abstract: Chain polymerizations are defined as chain reactions where the propagation steps occur by reaction between monomer(s) and active site(s) on the polymer chains with regeneration of the active site(s) at each step. Many forms of chain polymerization can be distinguished according to the mechanism of the propagation step (e.g., cyclopolymerization – when rings are formed, condensative chain polymerization – when propagation is a condensation reaction, group-transfer polymerization, polyinsertion, ring-opening polymerization – when rings are opened), whether they involve a termination step or not (e.g., living polymerization – when termination is absent, reversible-deactivation polymerization), whether a transfer step is involved (e.g., degenerative-transfer polymerization), and the type of chain carrier or active site (e.g., radical, ion, electrophile, nucleophile, coordination complex). The objective of this document is to provide a

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†Deceased (1939–2021).

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language for describing chain polymerizations that is both readily understandable and self-consistent, and which covers recent developments in this rapidly evolving field.

Keywords: anionic; catalyst-transfer; cationic; chain polymerization; controlled polymerization; coordination; coordination polymerization; group transfer polymerization; insertion polymerization; ionic polymerization; living polymerization; radical; radical polymerization; reverible deactivation polymerization.

CONTENTS

1 Introduction

The objective of this document is to provide a language for describing the many forms of chain polymerization that is both readily understandable and self-consistent. Many terms from the ‘Glossary of terms related to kinetics, thermodynamics, and mechanisms of polymerization’ [1] and the ‘Terminology for reversible-deactivation radical polymerization’ documents [2] are replicated here, sometimes with additional explanatory notes, for the purposes of endorsing their continued usage. It should be stressed that it is not the intention of this document to modify any of those terms except to correct minor errors and inconsistencies as noted.

The present term “chain polymerization” to describe processes for growth of a polymer chain that proceed by a chain reaction where the propagation steps are reaction(s) between monomer(s) and active site(s) with regeneration of the active site(s) after each monomer addition was introduced in 1994 [3] in response to the conflicting literature usage and contradictory explanations that prevailed at that time for the terms “chain-growth polymerization” and “step-growth polymerization”. The terms polyaddition and polycondensation were introduced at the same time [3] for the naming of polymerizations proceeding through reactions between molecules of all degrees of polymerization. The current IUPAC terminology describing overall polymerization mechanisms is summarized in Table 1. Note that there is no group term that embraces polyaddition and polycondensation. The terms “step polymerization” and “step-growth polymerization” are deprecated by IUPAC. This issue is being considered by a current IUPAC task group [4, 5].

This document does not specifically consider the additional terminology associated with the formation of copolymers or different polymer architectures. It also does not consider polymers that are synthesized as a series of discrete reaction steps. These steps may be chain reactions (as in RAFT single-unit monomer insertion), chain polymerizations (as in multi-block copolymer synthesis) or condensation reactions (as in solid-state peptide synthesis). These processes might be considered as interrupted chain polymerizations, to the extent that the overall process comprises the sequential addition of monomer units to an active site.

The terms appear in alphabetical order within each section and are consecutively numbered throughout the document.

Table 1: IUPAC terminology for polymerization mechanisms [3].

Propagation reaction type	**Polymerization reaction type**	**Polymerization mechanism**[a]	
		chain reaction; monomer units added one at a time to active site(s) with regeneration of the active site(s)	functional groups on bifunctional (or greater) molecules react with each other to form new bifunctional (or greater) molecules with same functionality
		chain (reaction) polymerization[b]	mostly non-chain (reaction) polymerization[c]
addition reaction [6] [without formation of small molecule(s)]	addition polymerization	(additive) chain (reaction) polymerization	polyaddition
condensation reaction [6] [with formation of small molecule(s)]	condensation polymerization	condensative chain (reaction) polymerization	polycondensation

[a] Words in parentheses are omitted in the recommended terms but are shown here to aid understanding. [b] Chain polymerization is both a group term and a specific term for those chain polymerizations where the discrete propagation steps are addition reactions, namely (additive) chain (reaction) polymerization. The adjective “chain” in chain polymerization, which is short for “chain reaction”, must not be confused with the noun “chain” in polymer chain, a synonym for macromolecule. [c] While deprecating the term “step polymerization” or “step-growth polymerization” in 1994 [3], IUPAC did not propose a group term for non-chain (reaction) polymerizations that encompasses both polyaddition and polycondensation. The term “non-chain (reaction) polymerization” used here does not have official status (see text).

2 Terms relevant to chain polymerization

This section provides definitions of *chain polymerization* and various classes of *chain polymerization* that differ according to what reactions constitute *propagation* (e.g., *cyclopolymerization* – when rings are formed, *condensative chain polymerization* – when propagation is a condensation reaction, ring-opening polymerization – when rings are opened), whether they involve a *termination* step (e.g., *living polymerization* – when *termination* is absent, *reversible-deactivation polymerization*), whether a *chain transfer* step is involved (e.g., degenerative-transfer polymerization). It also gives the IUPAC definition for *chain reaction*.

CP-1 activated-monomer polymerization (AMP)

Chain polymerization in which *propagation* involves reaction between a *growing chain-end* and an *activated monomer* [1].

Note 1: Examples include the anion-activated polymerization of lactams, the cation-activated polymerization of cyclic ethers, and the Lewis acid-activated polymerization of lactones.

Note 2: The *activator* in *activated-monomer polymerization* should not be referred to as a *catalyst* unless it is established that it is a *catalyst*.

See *activated-monomer*, *cation-activated-monomer polymerization, anion-activated-monomer polymerization.*

CP-2 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 [1].

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. 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 $P_x + M \rightarrow P_{x+1}$ (+L) $x \in \{1,2,\ldots\infty\}$ where P_x denotes a 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 *polymerizations* that proceed via *chain reactions* that are not chain polymerizations. For example, the polymerization $HS{-}X{-}SH + H_2C{=}CH{-}Y{-}CH{=}CH_2 \rightarrow ({-}S{-}X{-}S{-}CH_2{-}CH_2{-}Y{-}CH_2{-}CH_2{-})_n$ proceeds via a radical *chain reaction* with intermolecular transfer of the radical site. 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*.

Note 7: the term reactive sites, used in [7, 8], was replaced with the term *active sites* [1].

See also *condensative chain polymerization*.

CP-3 chain reaction

A reaction in which one or more reactive reaction intermediates (frequently radicals) are continuously regenerated, usually through a repetitive cycle of elementary steps (the propagation step) [9, 10]. For example, in the chlorination of methane by a radical mechanism, Cl· is continuously regenerated in the chain propagation steps:

$$\begin{array}{ll} Cl\bullet + CH_4 \rightarrow HCl + H_3C\bullet & \text{Propagation steps} \\ H_3C\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet & \end{array}$$

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

$$RCH_2\dot{C}HPh + H_2C{=}CHPh \rightarrow RCH_2CHPhCH_2\dot{C}HPh \qquad \text{Propogation steps}$$

CP-4 controlled polymerization

Term indicating control of a certain kinetic feature of a polymerization or structural aspect of the polymer molecules formed, or both [1, 2].

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, interrupting the 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), *aminoxyl-mediated radical polymerization (AMRP)*, 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.

See also *controlled radical polymerization, controlled ionic polymerization, controlled anionic polymerization, controlled cationic polymerization.*

CP-5 cyclopolymerization

A polymerization in which the number of cyclic structures in the constitutional units of the resulting macromolecules is larger than in the monomer molecules [1].

CP-6 degenerative-transfer polymerization (DTP)

degenerate-transfer polymerization

Reversible-deactivation polymerization in which the deactivation of the active species involves *degenerative chain transfer*.

Note: This term has often been specifically associated with *degenerative chain-transfer radical polymerization*. However, there are also degenerative chain-transfer processes involving non-radical mechanisms (e.g., *cationic, anionic, or coordination polymerization*).

See also *degenerative chain transfer, degenerative chain-transfer radical polymerization*.

CP-7 group-transfer polymerization (GTP)

Chain polymerization in which a specific atom or group is intramolecularly transferred to remain associated with the active chain-end during the course of polymerization.

Note 1: Group-transfer polymerization is most often a *reversible-deactivation polymerization* or a *coordination addition polymerization*.

Note 2: The term group-transfer polymerization is often specifically associated with polymerization of (meth)acrylates and acrylamides initiated by silyl ketene acetals such as 1-methoxy-2-methyl-1-(trimethylsiloxy)prop-1-ene (traditional name is methyl trimethylsilyl dimethylketene acetal) and catalysed by nucleophiles.

Note 3: Other forms of *chain polymerization* commonly referred to as group-transfer polymerizations include *catalyst-transfer polymerization* and *rare-earth-mediated* or *lanthanide-mediated coordination polymerization*.

See also *anionic group-transfer polymerization*, *catalyst-transfer polymerization, rare-earth-mediated coordination-addition polymerization.*

CP-8 insertion polymerization

polyinsertion

Chain polymerization in which monomer units are sequentially inserted into a specific site within a polymer structure with retention of chain-end functionality.

Note 1: The term insertion polymerization is most commonly used in the context of *coordination polymerization* but is occasionally also used to describe some forms of *reversible-deactivation radical polymerization* such as *RAFT polymerization* and *aminoxyl-mediated radical polymerization*.
Note 2: The term polyinsertion is almost exclusively used in the context of *coordination polymerization*

See also *coordination-insertion polymerization*.

CP-9 living polymerization

deprecated: pseudo-living polymerization
deprecated: quasi-living polymerization
deprecated: immortal polymerization
deprecated: “living polymerization”

Chain polymerization in which *chain termination* and irreversible *chain transfer* are absent [1, 2].

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. This is not a necessary condition for living polymerization.
Note 2: In a living polymerization, the reversible (temporary) deactivation of *active sites* 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 adjectives, such as pseudo-living, quasi-living or immortal, or the use of living polymerization within quotation marks, to describe a process that shows some living characteristics, but is not living, is deprecated.

See also *reversible-deactivation polymerization*. Note 1 modified from [1].

CP-10 reversible-deactivation polymerization (RDP)

controlled reversible-deactivation polymerization.

Chain polymerization, propagated by *chain carriers* that are deactivated reversibly, bringing them into active-dormant equilibria of which there might be more than one [2].

Note: An example of a reversible-deactivation polymerization is *group-transfer polymerization*.

See also *reversible-deactivation anionic polymerization, reversible-deactivation cationic polymerization, reversible-deactivation coordination polymerization, reversible-deactivation radical polymerization.*

CP-11 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 [1].

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

CP-12 polymerization

The process of converting a monomer or a mixture of monomers into a polymer [8].

3 Non-chain polymerization

The current definitions for *polyaddition* and *polycondensation* [1, 3, 7, 8], both non-chain polymerizations, are provided here.

CP-13 polyaddition

Polymerization in which the growth of polymer chains proceeds by addition reactions between molecules of all degrees of polymerization [1, 3, 7, 8].

Note 1: The growth steps are expressed by

$$\mathrm{P}_x + \mathrm{P}_y \rightarrow \mathrm{P}_{x+y} \qquad x, y \in \{1,2\ldots\infty\}$$

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

Note 2: The term “addition polymerization”, defined previously [11], embraced both the current concepts of *polyaddition* and *chain polymerization*, but did not include *condensative chain polymerization*. (See Note 3 under *chain polymerization*).

CP-14 polycondensation

Polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all degrees of polymerization [1, 3, 7, 8].

Note 1: The growth steps are expressed by:

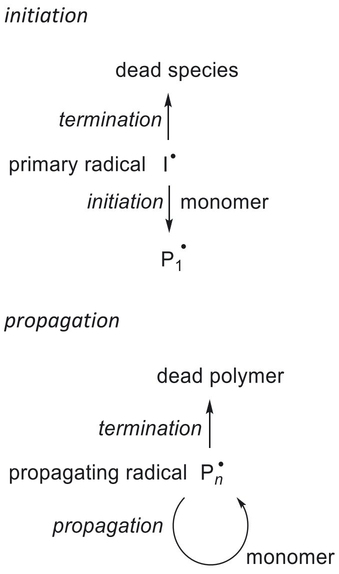
$$\mathrm{P}_x + \mathrm{P}_y \rightarrow \mathrm{P}_{x+y} + \mathrm{L} \qquad x, y \in \{1,2\ldots\infty\}$$

where P_x and P_y denote 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 [11], 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”.

4 Terms relevant to radical polymerization

A simplified mechanism for *radical polymerization* indicating some of the relevant terminology is presented in Scheme 1.



Scheme 1: Simplified mechanism for *radical polymerization*. $I^\bullet$ is a *primary radical*. $P_n^\bullet$ is an *active species*, a *propagating radical* of chain length *n*, and contains the *active centre*.

CP-15 controlled radical polymerization (CRP)

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

Note 1: The adjective "controlled" should not be used without specifying the particular kinetic or structural feature that is subject to control.

Note 2: The expression "controlled radical polymerization" is sometimes used as a synonym for *reversible-deactivation radical polymerization* (RDRP), e.g., *atom-transfer radical polymerization* (ATRP), *aminoxyl-mediated radical polymerization* (AMRP), or *reversible-addition-fragmentation chain-transfer* (RAFT) polymerization. This is acceptable subject to the proviso stated in Note 1.

Note 3: The term diffusion-controlled radical polymerization is sometimes used to indicate that the rate of termination is determined by the rate of diffusion of the active sites.

See also *controlled polymerization*.

CP-16 living radical polymerization

deprecated: pseudo-living radical polymerization
deprecated: quasi-living radical polymerization
deprecated: "living radical polymerization"

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

Note 1: *Radical polymerizations*, *controlled radical polymerizations* and *reversible-deactivation radical polymerizations* are not living radical polymerizations as there is a non-zero probability of *chain termination*.

Note 2: Examples of living radical polymerization may be certain polymerizations conducted in confined media which only allow reactions of individual *propagating radicals*.

Note 3: The term living radical polymerization can be used to refer to a hypothetical *radical polymerization* that occurs without *chain termination*.

Note 4: Use of the adjectives pseudo-living, quasi-living, "living" (within quotation marks) or other terms that containing the word living to describe a radical polymerization with only some living characteristics is deprecated [2].

See also *controlled radical polymerization*, *living polymerization, reversible-deactivation radical polymerization*.

CP-17 radical polymerization

Chain polymerization in which the *active centres* are radicals [1].

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

CP-18 radical ring-opening polymerization

Radical polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

See *ring-opening polymerization.*

CP-19 reversible-deactivation radical polymerization (RDRP)

controlled reversible-deactivation radical polymerization

Chain polymerization, propagated by radicals that are deactivated reversibly, bringing them into active-dormant equilibria of which there might be more than one [2].

Note 1: The abbreviated term *controlled radical polymerization* shall be permitted, provided that its context (i.e., the nature of the control) is specified at the first occurrence.
Note 2: Names containing the word "living" are deprecated. Definition 84 in the kinetics document [1] stipulates that chain termination and irreversible *chain transfer* must be absent if a polymerization is to be regarded as living. Examples of deprecated terms include *living radical polymerization*, controlled/living polymerization and quasi-living polymerization.
Note 3: *Atom-transfer radical polymerization*, *reversible-addition-fragmentation chain-transfer polymerization*, and *stable-radical-mediated polymerization* all fall into this polymerization category.
Note 4: When the equilibria are established rapidly compared to the rate of propagation, the process may show many of the observable characteristics associated with *living polymerization*. One consequence of rapid equilibration is that it may become possible to exert control over the shape of the chain-length distribution, prepare polymers of low dispersity (i.e., polymers with a high degree of uniformity), and extend chains to form block copolymers, the block lengths of which are of low dispersity, by the sequential addition of monomers. Although some termination is inevitably taking place, the equilibrium between the remaining propagating radicals and *dormant species* is maintained.

Note 4 modified from [2].

5 Sub-classes of reversible-deactivation radical polymerization

Three classes of *RDRP* are distinguished according to the type *activation* mechanism. *RDRP* with *unimolecular activation* by dissociation of an *initiator* is known as *stable radical-mediated polymerization* (*SRMP*). *RDRP* with *bimolecular activation* by reaction of an *initiator* with an *activator* is known as *atom-transfer radical polymerization* (*ATRP*). *RDRP* with *activation* by *degenerative chain transfer* is known as *degenerative chain transfer radical polymerization* (DTRP).

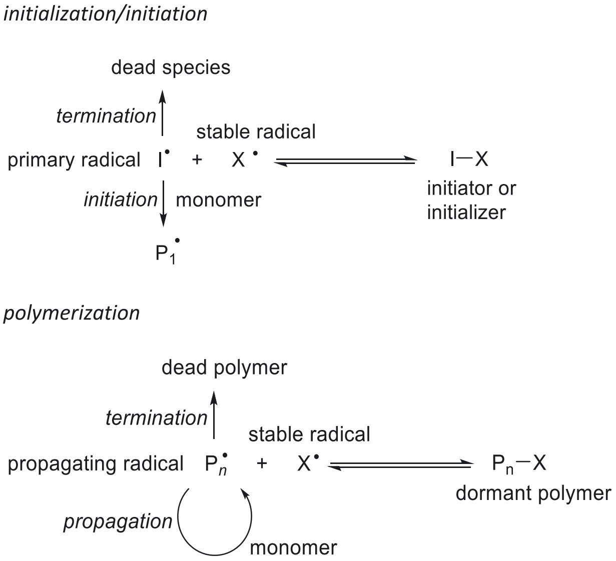
5.1 Reversible-deactivation radical polymerization with unimolecular activation

5.1.1 Stable-radical-mediated polymerization (SRMP)

A simplified mechanism and the terminology for *stable-radical-mediated radical polymerization* (*SRMP*) is presented in Scheme 2. The term *stable radical* (X• in Scheme 2) used in the context of *SRMP* embraces the organometallic complexes used in *cobalt-mediated radical polymerization* and other *organometallic-mediated radical polymerizations*.

The species referred to as "stable radicals" in the context of *SRMP* are not necessarily thermodynamically stable (storable-in-a-bottle) species, rather they are species that have sufficient "kinetic stability" such that they are largely unreactive towards addition to monomer under the conditions of the experiment.

Before *initialization*, the reaction medium for *SRMP* may comprise 1) a mixture of monomer(s) and the species I-X (the *initiator* or initializer); 2) a mixture of monomer(s), the *stable radical* (X·) and a source of radicals (I·); or 3) a mixture of monomer(s), a precursor to *stable radical* (X·) and a source of radicals (I·).



Scheme 2: Simplified mechanism for *stable-radical-mediated polymerization*. $I^\bullet$ is a *primary radical*. $X^\bullet$ is a *stable radical*. $P_n^\bullet$ is an *active species*, a *propagating radical* of chain length *n*.

CP-20 aminoxyl-mediated radical polymerization (AMRP)

aminoxyl-mediated polymerization
deprecated: nitroxide-mediated (radical) polymerization (NMP)

Stable-radical-mediated polymerization in which the deactivation of the radicals involves reversible coupling with aminoxyl radicals [2].

Note: The term "nitroxide" is deprecated in IUPAC nomenclature. The recommended term is "aminoxyl".

CP-21 cobalt-mediated radical polymerization (CMRP)

Reversible-deactivation radical polymerization mediated by a cobalt complex.

Note: The mechanism of cobalt-mediated radical polymerization may involve *stable-radical-mediated polymerization* (*SRMP*), *degenerative chain-transfer radical polymerization*, (*DTRP*), *atom-transfer radical polymerization* (*ATRP*) or some combination of these depending on the specific reagents and reaction conditions.

See also *organometallic-mediated radical polymerization*.

CP-22 iniferter process

Stable-radical-mediated polymerization where the *initiator* and *dormant species* are *iniferters*.

Note 1: Well-known examples of the iniferter process are polymerizations photoinitiated by bis(dialkylcarbamothioyl) disulfides with structure $(R_2NC(=S)S)_2$ (traditional name is tetraalkylthiuram disulfide) where the *mediating agents* are dialkylcarbamothioylsulfanyl radicals ($R_2NC(=S)S\bullet$) and the *dormant species* are dithiocarbamates. In this case, both the bis(dialkylcarbamothioyl) disulfide and the derived dithiocarbamates can be *iniferters*.

Note 2: In the iniferter process the dominant mechanism for control is *stable-radical mediated polymerization* (SRMP) but the control mechanism may also involve *degenerate chain transfer radical polymerization*.

CP-23 organometallic-mediated radical polymerization (OMRP)

Reversible-deactivation radical polymerization mediated by an organometallic reagent.

Note 1: The best-known example of OMRP is *cobalt-mediated radical polymerization*, CMRP.

Note 2: The term organometallic-meditated radical polymerization is not usually used in describing an *atom-transfer radical polymerization* process.

Note 3: The mechanism of organometallic-meditated radical polymerization may involve *stable-radical-mediated polymerization* (*SRMP*), *degenerative chain-transfer radical polymerization*, (*DTRP*), *atom-transfer radical polymerization* (*ATRP*) or some combination of these depending on the specific reagents and reaction conditions.

Modified from [2].

CP-24 stable-radical-mediated polymerization (SRMP)

deprecated: stable-free-radical-mediated polymerization (SFRMP)

Reversible-deactivation radical polymerization in which the deactivation involves reversible coupling with stable (persistent) radicals [2].

Note 1: Processes known to involve stable-radical-mediated polymerization include *aminoxyl-mediated radical polymerization* and some forms of *organometallic-mediated radical polymerization*.

Note 2: The use of the term “free radical” is deprecated in IUPAC terminology.

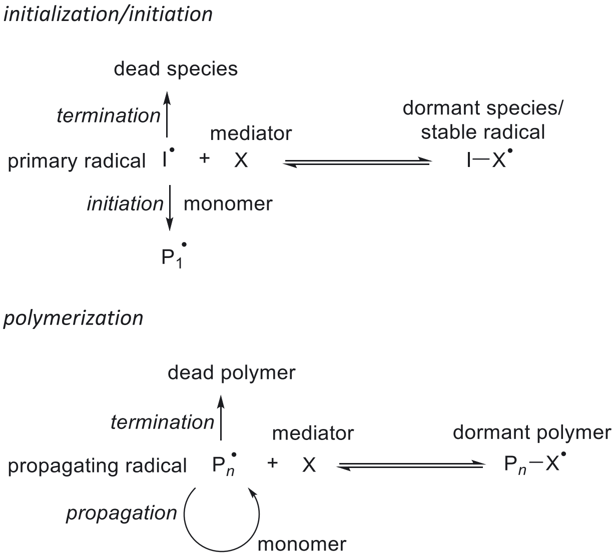
Note 3: *Initialization* may involve decomposition of an *initiator* in the presence of monomer and the *stable radical*. Polymerization then starts when there is complete consumption of the *stable radical*.

Note 4: The species identified as *stable radicals* in stable-radical-mediated polymerization are not necessarily stable in a thermodynamic sense.

Modified from [2].

5.1.2 Reversible-addition-fragmentation radical polymerization

The mechanism of *reversible-addition-fragmentation radical polymerization* (*RAFRP*) is, in overall terms, similar to *stable-radical-mediated radical polymerization*. However, in *RAFRP*, the *dormant species* is a *stable radical* and the *mediating agent* or *mediator* is an unsaturated compound. The mechanism and some of the relevant terminology is presented in Scheme 3. Examples of mediators include certain 1,1-diphenylethenes, captodative monomers (bearing both an electron-donating and an electron-withdrawing substituent), and some carbonothioyl compounds.



Scheme 3: *Reversible-addition-fragmentation radical polymerization*. $I^\bullet$ is a *primary radical*. $P_n^\bullet$ is an active species; a *propagating radical* on chain length *n*; X is the *mediator*; $I\text{-}X^\bullet$ is a *stable radical*.

CP-25 reversible-addition-fragmentation radical polymerization (RAFRP)

Reversible-deactivation radical polymerization in which the *dormant species* is a stable (persistent) radical and the deactivation step involves reversible fragmentation.

Note 1: Examples of mediators that are proposed to provide control by this mechanism are certain 1,1-diarylethylenes, so-called captodative monomers, and carbonothioyl compounds. This mechanism could also contribute to the degree of control observed in *RAFT polymerization*.

Note 2: In some cases, the dormant polymer may undergo reversible coupling.

Note 3: *Initialization* usually involves decomposition of an *initiator* in the presence of monomer and the reagent. Polymerization commences when there is complete consumption of the mediator by initiator-derived radicals.

CP-26 carbonothioyl-mediated radical polymerization

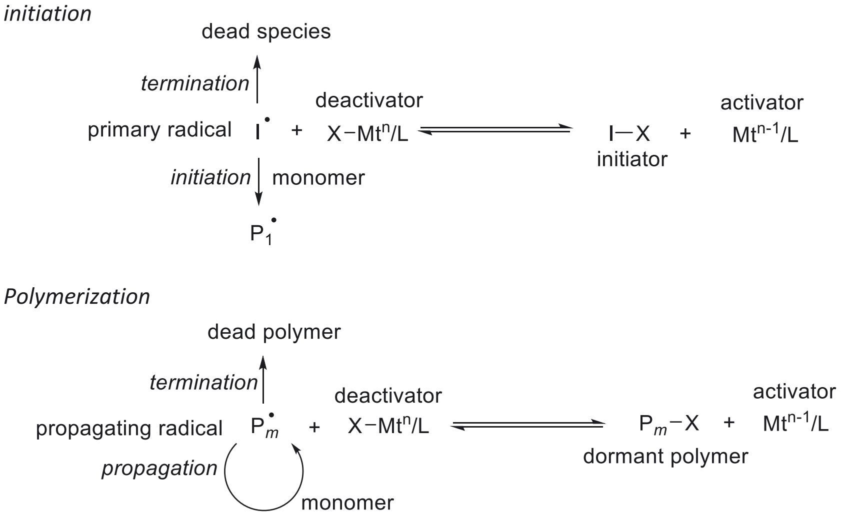
deprecated: thiocarbonyl-mediated radical polymerization

Reversible-addition-fragmentation radical polymerization mediated by a carbonothioyl compound.

Note: The commonly used term, thiocarbonyl, is not consistent with IUPAC nomenclature.

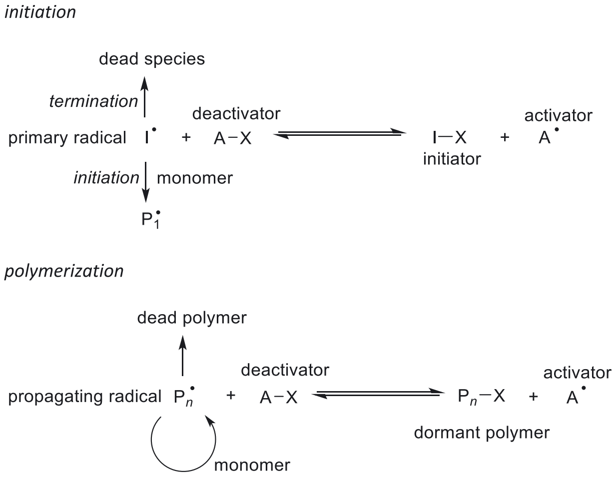
5.2 Reversible-deactivation radical polymerization with bimolecular activation

The overall process and some of the relevant terminology of *atom-transfer radical polymerization* (*ATRP*) is shown in Scheme 4. The term *ATRP* as defined herein is not intended not imply a specific mechanism for *reversible-deactivation radical polymerization* with *bimolecular activation*. It is recommended that terms that indicate a specific mechanism (e.g., *single-electron-transfer reversible-deactivation radical polymerization*, *SET-RDRP*) not be used in circumstances where the mechanism is unknown or uncertain. Specific forms of *ATRP* that differ in the method of implementation or the type of *activator* used are listed in the notes to the various terms. The abbreviations listed are those that are most commonly encountered in the literature. These terms do not have the status of IUPAC definitions.



Scheme 4: *Transition metal-mediated atom-transfer radical polymerization* (*TM-ATRP* or *ATRP*). $I^•$ is a *primary radical*. $P_m^•$ is an active species, a propagating radical of chain length *m*. $X–Mt^n/L$ is a *deactivator* (Mt^n is transition metal in a higher oxidation state, L is a ligand). $Mt^{n−1}/L$ is an *activator* ($Mt^{n−1}$ is a transition metal in a lower oxidation state).

The *inner-sphere electron transfer atom-transfer radical polymerization* (ISET-ATRP) process, sometimes known as reversible chain-transfer-catalyzed polymerization (RTCP), has an analogous mechanism to *atom-transfer radical polymerization* but involves a non-metallic *activator*/*deactivator*. It is referred to here as a form of *non-metal-mediated atom-transfer radical polymerization* (*NM-ATRP*). The overall process and some of the relevant terminology for *NM-ATRP* is shown in Scheme 5.



Scheme 5: Non-metal-mediated atom-transfer radical polymerization (NM-ATRP). $I^•$ is a primary radical. $P_n^•$ is an active species, a propagating radical of chain length *n*. A-X is a *deactivator*. $A^•$ is an activator.

CP-27 atom-transfer radical polymerization (ATRP)

Reversible-deactivation radical polymerization in which the *deactivation* of the radicals involves reversible atom-transfer or reversible group transfer to usually, though not exclusively, transition-metal complexes.

Note 1: The *activator* is often incorrectly termed a *catalyst*. The term *catalyst* should only be used when referring to a species which is not changed as a consequence of reaction.

Note 2: There are various forms of ATRP that differ in details of the intimate mechanism, the reaction conditions and/or the reagents used. These include:

i. Conventional, traditional or normal ATRP where the initial reaction mixture comprises an *initiator* (typically an alkyl halide) and an *activator* (the species on right-hand side of Scheme 4).
ii. Reverse ATRP where the initial reaction mixture comprises a conventional *initiator* as a source of radicals (e.g., a dialkyldiazene or a peroxide) and a *deactivator* (the species on left hand side of Scheme 4).
iii. AGET-ATRP (*Activator* Generated by Electron Transfer) where the *activator* is generated *in situ* by an electron transfer from a reducing agent at the commencement of the polymerization.
iv. ARGET-ATRP (*Activator* ReGenerated by Electron Transfer) where the *activator* is continuously regenerated by electron transfer from a reducing agent.
v. ICAR-ATRP (*Initiators* for Continuous Activator Regeneration) – ARGET-ATRP where the reducing agent is a radical derived from a conventional *initiator* (e.g., a dialkyldiazene).
vi. SARA-ATRP (Supplemental *Activators* and Reducing Agents) where the polymerization commences with the *activator* (e.g., a zero-valent metal or an inorganic sulfite) which is a both a supplemental *activator* and a reducing agent for the *deactivator*.
vii. eATRP (electrochemically-mediated ATRP) where the *activator* is continuously regenerated by electrical current.
viii. photoATRP (photochemically-mediated ATRP) where the *activator* is continuously regenerated by photoreduction. The reduction can be facilitated by the presence of electron donors.
ix. mechanoATRP (mechanically-mediated ATRP) where the *activator* is continuously regenerated by mechanical forces through the use of the piezoelectric effect or ultrasound.
x. PET-ATRP (photoinduced electron transfer ATRP) where *activation* involves electron-transfer from a photo-excited *activator* to an *initiator* which then dissociates to give an *initiating species*.
xi. O-ATRP (organic ATRP), a form of PET-ATRP where the *activator* is an organic photoredox *catalyst*.

Note 3: The term ATRP (unqualified) usually refers to copper-mediated ISET-ATRP.

Modified from [2].

See also *inner-sphere electron transfer atom-transfer radical polymerization (ISET-ATRP)*, *non-metal-mediated atom-transfer radical polymerization (NM-ATRP)*, *outer-sphere electron transfer ATRP (OSET-ATRP)*.

CP-28 inner-sphere electron transfer atom-transfer radical polymerization (ISET-ATRP)

Atom-transfer radical polymerization where the *activation* step involves direct atom or group transfer.

Note: *ATRP* is sometimes used as a synonym for ISET-ATRP. The term ISET-ATRP can be used to specify that the mechanism of *ATRP* involves direct atom or group transfer as distinct from single electron transfer followed by atom or group transfer or *OSET-ATRP*.

See also *atom-transfer radical polymerization (ATRP)*, *outer-sphere electron transfer ATRP* (*OSET-ATRP*).

CP-29 non-metal-mediated atom-transfer radical polymerization (NM-ATRP)

deprecated: reversible chain-transfer-catalyzed polymerization

Atom-transfer radical polymerization in which the *deactivation* of the radicals involves reversible atom transfer or reversible group transfer to a non-metallic reagent.

Note 1: The *activator* is often incorrectly termed a *catalyst*. The term *catalyst* should only be used when referring to a species which is not changed as a consequence of reaction being considered.

Note 2: NM-ATRP may be referred to as *ATRP*.

Note 3: There are various forms of NM-ATRP that differ in details of the intimate mechanism, the reaction conditions and/or the reagents used. These include:

  i. RCTP (reversible chain-transfer-catalyzed polymerization). The group transferred (X) is often iodine and examples of the *activator* (R-X) are certain nitrogen, phosphorus, germanium, or tin compounds, which include germanium tetraiodide and 1-iodopyrrolidine-2,5-dione (traditional name is *N*-iodosuccinimide). Use of the term RCTP is deprecated. The mechanism is proposed to involve *inner-sphere electron transfer atom-transfer radical polymerization* (ISET-ATRP).

  ii. RCMP (reversible-complexation-mediated radical polymerization) where the *activator* (typically an alkyl amine) reacts with an *initiator* (typically an alkyl iodide) by molecule-assisted homolysis to form the *initiating species* and an activator-complex.

  iii. O-ATRP (organocatalyzed atom-transfer radical polymerization). A photochemically-mediated *ATRP* in which an organic photoredox *catalyst* such as perylene, a 5,10-diaryl-5,10-dihydrophenazine or a 10-aryl-10*H*-phenoxazine is used as the *activator*. The mechanism is proposed to involve *outer-sphere electron transfer atom-transfer radical polymerization* (*OSET-ATRP*).

CP-30 outer-sphere electron transfer ATRP (OSET-ATRP)

single-electron-transfer RDRP (SET-RDRP)
deprecated: single-electron-transfer living radical polymerization (SET-LRP)

Atom-transfer radical polymerization where the *activation* step involves consecutive single electron transfer and atom or group transfer.

Note 1: The terms SET-RDRP (single-electron-transfer reversible-deactivation radical polymerization), SET-LRP (single-electron-transfer living radical polymerization), and zero-valent metal-mediated polymerization (e.g., Cu^0-mediated radical polymerization) are sometimes used to describe a process where the polymerization commences with the *activator* in the form of a zero-valent metal, e.g., Cu^0. The use of terms that might imply an outer sphere electron-transfer mechanism without evidence that the reaction proceeds by OSET-ATRP is deprecated.

Note 2: terms containing the phrase “living radical polymerization” are deprecated.

Note 3: OSET-ATRP may be referred to as *ATRP*.

See also *atom-transfer radical polymerization (ATRP), inner-sphere electron transfer ATRP* (*ISET-ATRP*)

CP-31 transition-metal-mediated radical polymerization

transition-metal-mediated reversible-deactivation radical polymerization
deprecated: transition-metal-mediated living radical polymerization

Reversible-deactivation radical polymerization mediated by transition-metal complexes or organometallic compounds.

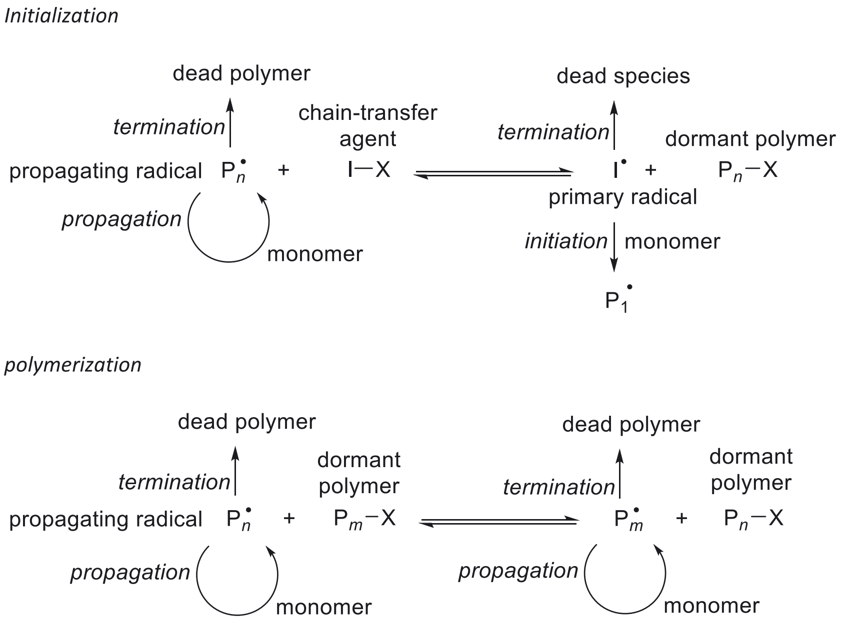
Note 1: Transition metal mediated polymerization is an overarching term for *atom-transfer radical polymerization (ATRP)* and *organometallic-mediated radical polymerization (OMRP)*. It is sometimes used as a synonym for transition-metal-mediated *atom-transfer radical polymerization*. This use of the term in that context without explanation is deprecated since it also includes *organometallic-mediated radical polymerization*.

Note 2: *Cobalt-mediated radical polymerization* is usually a form of *organometallic-mediated radical polymerization* (*OMRP*).

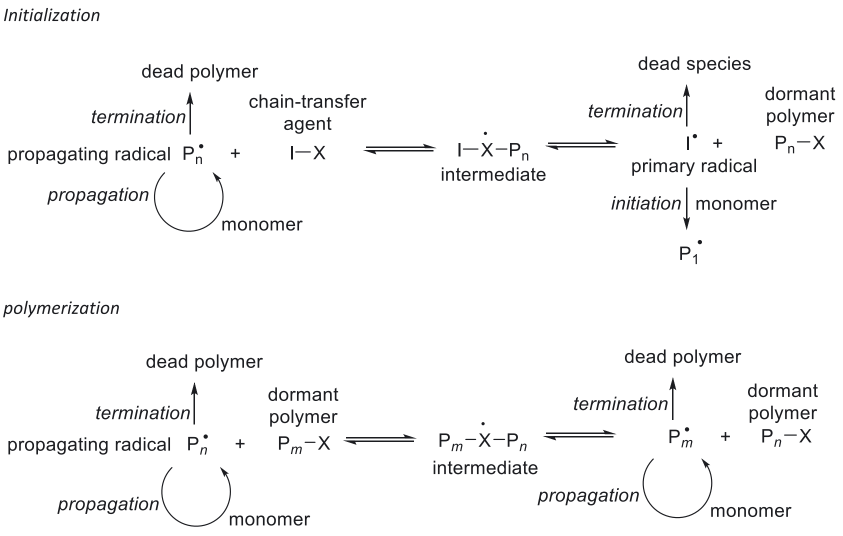
See *atom-transfer radical polymerization, organometallic-mediated radical polymerization.*

5.3 Reversible-deactivation radical polymerization with activation-deactivation by degenerative chain-transfer

The mechanism of *degenerate* or *degenerative chain-transfer radical polymerization* (*DTRP*) and some of the relevant terminology is provided in Scheme 6. The process is called degenerate because the species on each side of the equilibrium differ only in chain length. The mechanism of *reversible-addition-fragmentation chain-transfer* (*RAFT*) *polymerization* is shown in Scheme 7. It differs from the mechanism for *DTRP* shown in Scheme 6 in that the *transfer* step involves formation of a transient intermediate.



Scheme 6: *Degenerative chain-transfer radical polymerization.* $I^\bullet$ is a *primary radical*. $P_n^\bullet$ is an *active species*, a *propagating radical* of chain length n. I-X is a *chain-transfer agent*. The *dormant macromolecule*, P_n-X, is a *macro-chain-transfer agent*.



Scheme 7: Simplified mechanism for radical polymerization with *reversible-addition-fragmentation chain transfer* (RAFT polymerization). $I^•$ is a *primary radical*. $P_n^•$ is an *active species*, a *propagating radical* of chain length *n*. I-X is a *chain-transfer agent*. The *dormant species*, P_n-X, is a *macro-chain-transfer agent*. I-$\dot{X}$-P_n and P_m-$\dot{X}$-P_n are intermediate adducts formed by radical addition to the respective *chain-transfer agents*.

CP-32 degenerative chain-transfer radical polymerization (DTRP)

degenerate chain-transfer radical polymerization

Reversible-deactivation radical polymerization in which the deactivation of the radicals involves *degenerative transfer* (DT) of a group (or atom) [2].

Note 1: Examples of DT-active groups include those mentioned below under *reversible-addition-fragmentation chain-transfer polymerization* and certain derivatives of iodine (*iodine-transfer polymerization*, ITP), tellurium (*organotellurium-mediated radical polymerization,* TERP), antimony (*organostibane-mediated radical polymerization,* SBRP), or bismuth (*organobismuthane-mediated radical polymerization,* BIRP).

Note 2: Intermediate species may be present as, for example, in *reversible-addition-fragmentation chain-transfer polymerization* (RAFT polymerization).

CP-33 iodine-transfer polymerization (ITP)

Reversible-deactivation radical polymerization mediated by an iodo-compound.

Note: Where the initial polymerization mixture comprises a conventional *initiator* (e.g., a dialkyldiazene or a peroxide) and molecular iodine, the term RITP is commonly used.

See also *reverse iodine-transfer polymerization.*

CP-34 organobismuthane-mediated radical polymerization (BIRP)

Reversible-deactivation radical polymerization mediated by an organobismuthane compound.

CP-35 organostibane-mediated radical polymerization (SBRP)

Reversible-deactivation radical polymerization mediated by an organostibane compound.

CP-36 organotellurium-mediated radical polymerization (TERP)

Reversible-deactivation radical polymerization mediated by an organotellurium compound.

Note: The dominant mechanism of TERP thought to be *degenerative chain-transfer radical polymerization* (*DTRP*). However, at high temperature conditions or under photochemical irradiation the mechanism may involve *stable-radical-mediated polymerization* (*SRMP*).

CP-37 reverse iodine-transfer polymerization (RITP)

Iodine-transfer polymerization where the initial polymerization mixture comprises a conventional *initiator* (e.g., an azo-compound or a peroxide) and molecular iodine.

See also *iodine-transfer polymerization.*

CP-38 reversible-addition-fragmentation chain-transfer polymerization (RAFT polymerization)

Degenerate-transfer radical polymerization in which *chain activation* and *chain deactivation* involve a *degenerative chain-transfer* process, which occurs by a two-step addition-fragmentation mechanism [2].

Note 1: The term RAFT polymerization (unqualified) usually refers to polymerization mediated by a carbonothioylsulfanyl *RAFT agent*.

Note 2: There are various forms of RAFT polymerization that differ in details of the initiation mechanism, the reaction conditions and/or the reagents used. These include:

i. Carbonothioylsulfanyl RAFT polymerization. The more commonly used term thiocarbonylthio RAFT polymerization is deprecated as it is inconsistent with IUPAC nomenclature. Examples of carbonothioylsulfanyl *RAFT agents* include certain dithioesters, trithiocarbonates, xanthates (dithiocarbonates), and dithiocarbamates with structure S=C(Z)–SR, where Z is aryl, alkylsulfanyl, alkyloxy, or dialkylamino, respectively, and R is a homolytic leaving group.
ii. Macromonomer RAFT polymerization where the RAFT agent is a “macromonomer” with structure $CH_2=C(Z)-CH_2R$, where Z is usually $-CO_2$alkyl or $-CO_2$aryl and R is a homolytic leaving group. This form of RAFT polymerization is also known as sulfur-free RAFT polymerization.
iii. MADIX (macromolecular design by interchange of xanthate) where the *RAFT agent* is a xanthate.
iv. PhotoRAFT polymerization where radical generation involves direct photolysis of a carbonothioylsulfanyl-*RAFT agent* to give an *initiating species* and a carbonothioylsulfanyl radical.
v. PET-RAFT (photo-induced energy or photo-electron-transfer RAFT) polymerization where radical generation involves photo-induced energy or electron transfer from a photoredox *catalyst* or a photosensitizer, respectively, to a carbonothioylsulfanyl-*RAFT agent* which then dissociates to give an *initiating species*.
vi. redoxRAFT where radical generation involves ISET or OSET between the *RAFT agent* and a reducing agent agent to give an *initiating species*.
vii. eRAFT polymerization where radical generation involves electrochemical reduction of the *RAFT agent* either directly or through a redox mediator.

6 Terms relating to species and processes in chain polymerization

Many of the terms in this section are taken from the Kinetics Document [1], without modification unless indicated. These definitions, in a few cases, differ from those in the current Gold [6] and Purple Books [7]. A full list of those modified definitions is provided in [1].

The word "species", that occurs in various terms, may be replaced by the type of species, e.g., radical, anion, cation, as appropriate for the context. Thus, the definition of *propagating species* is provided, and the definitions of propagating radical, anion, cation, etc. are implicit.

The use of the terms *activator* and *catalyst* in chain polymerization require brief discussion. A *catalyst* increases the rate of a reaction and is both a reactant and a product of that reaction; i.e., it is not consumed in the reaction. The *catalyst* or catalytic site in *coordination polymerization* and *ring-opening metathesis polymerization* (*ROMP*) is the coordination complex that comprises the *active site*. The precursors to those coordination complexes should not be called *catalysts*.

In *ATRP chain activation-deactivation* is accelerated by a redox reaction that, in some cases, may be part of a catalytic cycle. In most cases, the rate coefficient for *propagation* is unchanged from that in the absence of the *activator*. It is recommended that the term *catalyst* is not used to denote either the *activator* or *deactivator* in *ATRP*.

CP-39 activated monomer

Reactive species generated reversibly from a monomer [1].

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, cationic activated-monomer polymerization, anionic activated-monomer polymerization.*

CP-40 activator (in *activated-monomer polymerization*)

Species that coordinates with a monomer converting it to a more reactive species.

Note 1: Examples include a base in *anion-activated-monomer polymerization* of lactams and a proton in *cation-activated-monomer polymerization* of cyclic ethers.
Note 2: The definition of activator is different from that defined in the context of enzyme activation [9, 12].

CP-41 activator (in *ATRP*)

deprecated: catalyst (in *ATRP*)

Reagent that reacts reversibly with the *initiator* or *dormant chain* to form an *initiating* or *propagating species*, respectively, and a *deactivator*.

Note 1: An activator in *atom-transfer polymerization* (ATRP) is often incorrectly called a *catalyst*. The term *catalyst* should not be used to refer to a species that is consumed during the course of a reaction or to a species that is regenerated other than by deactivation.
Note 2: The definition of activator is different from that defined in the context of enzyme activation [9, 12].

CP-42 activator (in *coordination polymerization*)

cocatalyst (in *coordination polymerization*)

Species that reacts with a coordination compound converting it to an active *catalyst* during *initialization* of *coordination polymerization*.

Note 1: An example of a cocatalyst is methylaluminoxane (MAO).
Note 2: The definition of activator is different from that defined in the context of enzyme activation [9, 12].

CP-43 active centre (in a *chain polymerization*)

active site

Site on a *chain carrier* at which reaction occurs [1].

Note: In [7, 8] the term "reactive site" is used within the definition of *chain polymerization*. In [13], the terms "active center" and "active site" are defined in the context of heterogeneous catalysis

CP-44 active polymer chain

active macromolecule (in *RDP*)

See *propagating species*.

CP-45 addition-fragmentation chain transfer

Chain-transfer process that proceeds by a *propagating species* adding to a chain-transfer agent to form an intermediate that then fragments to provide an *initiating species*.

CP-46 bimolecular chain activation

bimolecular activation

See *chain activation* (in *ATRP*)

CP-47 cage effect

Term referring to reactions between reactant molecules trapped transiently in a restricted volume of molecular dimensions [1].

Note: 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.

CP-48 catalyst

Substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction; the process is called catalysis. The catalyst is both a reactant and product of the reaction [14].

CP-49 catalyst (in *coordination polymerization* or *ROMP*)

Coordination compound that comprises the active site.

Note: Often the precursor species to the active coordination complex are incorrectly referred to as the catalyst.

CP-50 catalyst precursor (in *coordination polymerization*)

precatalyst (in *coordination polymerization*)
initiator (in *coordination polymerization*)

Coordination compound that by reaction with an *activator* or *cocatalyst* provides an active *catalyst* during *initialization* of *coordination polymerization*.

Note: Examples of catalyst precursors are certain transition metal or rare-earth metal complexes, such as titanium tetrachloride or bis(cyclopentadienyl)titanium chloride.

CP-51 catalytic chain transfer (CCT)

Chain-transfer process involving transfer of an atom or group to a reagent (the *catalyst*) that in turn transfers that group to a monomer to reinitiate polymerization and regenerate the original reagent.

Note 1: An example of polymerization with catalytic chain transfer is *radical polymerization* in the presence of certain square-planar cobalt complexes.
Note 2: Catalytic chain transfer may be observed as a side reaction in certain *reversible-deactivation radical polymerizations* including *organometallic-mediated radical polymerization.*

CP-52 catalytic chain termination

Chain termination process involving transfer of a group to a reagent (the *catalyst*) that in turn transfers that group to a *propagating species* to terminate a chain and regenerate the original reagent.

Note: Catalytic chain termination may be observed as a side reaction in certain *reversible-deactivation radical polymerizations.*

CP-53 chain activation

activation (in chain polymerization)

See *chain reactivation.*

CP-54 chain activation (in *SRMP*)

activation (in *SRMP*)
unimolecular chain activation
unimolecular activation

Unimolecular dissociation of a *dormant species* to form a *mediating agent* and a *propagating species*.

Note 1: In *aminoxyl-mediated radical polymerization* [nitroxide-mediated polymerization (NMP)], the *dormant species* is an alkoxyamine and the *mediating agent* is an aminoxyl radical.
Note 2: In *organometallic-mediated radical polymerization* (OMRP), the *domant species* and the *mediating agent* are organometallic species.
Note 3: In *reversible addition-fragmentation polymerization* (RAFRP), the *dormant species* is a *stable radical* and the *mediating agent* is a non-propagating olefin, e.g., 1,1-diphenylethylene.
Note 4: *chain deactivation* (in *SRMP*) is the reverse of chain activation (in *SRMP*).

CP-55 chain activation (in *ATRP*)

activation (in *ATRP*)
bimolecular chain activation
bimolecular activation

Reaction of an *activator* with a *dormant species* to form a *deactivator* and a *propagating species*.

Note 1: The activation and deactivation process may form part of a catalytic cycle. However, in general, the activator should not be called a *catalyst*.
Note 2: *chain deactivation* (in *ATRP*) is the reverse of chain activation (in *ATRP*).

CP-56 chain activation (in *DTRP*)

activation (in *DTRP*)

See *degenerative chain transfer*.

CP-57 chain carrier (in polymerization)

kinetic-chain carrier

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

Note: The *propagating species* and *chain-transfer agent*-derived species are chain carriers in polymerization.

See *active centre, active polymer chain, propagating species*.
Modified from [1].

CP-58 chain deactivation

deactivation

Conversion of a *chain carrier* into an inactive species [1].

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

Note 2: The reverse of chain deactivation is *chain activation or chain reactivation.*
Note 3: The recommended symbol for the rate coefficient for chain deactivation in a polymerization is k_{deact}.

Note 3 added to the definition in [1].

CP-59 chain initiation

initiation

Chemical reaction in which *chain carriers* are generated [1].

Note: The recommended symbol for the rate coefficient for chain initiation in a polymerization is k_{i}.

Note modified from [1].

CP-60 chain propagation (in a *chain polymerization*)

propagation

Chemical reaction between a *chain carrier* and a monomer that results in the growth of a polymer chain and the regeneration of at least one *chain carrier* [1].

Note 1: The recommended symbol for the rate coefficient for chain propagation in a homopolymerization is k_{p}.

Note 1 modified from [1].

CP-61 chain reactivation

reactivation (in a *chain polymerization*)
chain activation
activation (in a *chain polymerization*)

Conversion of an *inactive chain* into a *chain carrier* [1].

Note 1: The term is usually used to refer to the reactivation of previously deactivated or *dormant chains*.
Note 2: Chain reactivation can be reversible or irreversible.
Note 3: The reverse of chain reactivation is *chain deactivation.*
Note 4: The recommended symbol for the rate coefficient for chain reactivation in a polymerization is k_{act}.

Note 4 added to the definition in [1].

CP-62 chain termination (in a *chain polymerization*)

termination
irreversible chain deactivation

Chemical reaction in which a *chain carrier* is converted irreversibly into a *non-propagating species* without the formation of a new *chain carrier* [1].

Note 1: The recommended symbol for the rate coefficient for chain termination in a polymerization 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*, *disproportionation*.

Note 1 modified from the definition in [1].

CP-63 chain transfer

transfer

Chemical reaction occurring during a *chain polymerization* in which an *active site* is transferred from a growing macromolecule or oligomer molecule to another molecule or to another site on the same molecule [1].

Note: The recommended symbol for the rate coefficient for chain transfer in a polymerization is k_{tr}.

CP-64 chain-transfer agent (CTA)

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 [1].

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

CP-65 cocatalyst (in *coordination polymerization*)

See *activator (in coordination polymerization)*.

CP-66 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 [1].

Note 1: Combination is often incorrectly called “recombination”. The term recombination should only be used to refer to the reaction, with each other, of two transient species produced from a common precursor [6].
Note 2: Combination is also called colligation [6], although this terminology is not commonly used in the context of *chain polymerization.*

CP-67 deactivator (in *ATRP*)

Reagent that reacts reversibly with the *initiating species* or *propagating species* to form an *initiator* or a *dormant chain,* respectively, and an *activator*.

CP-68 dead polymer chain

dead macromolecule (in *RDP*)

Polymer chain which plays no active role in the polymerization.

Note 1: A dead polymer chain is a chain unlikely to be activated or reactivated to form a *propagating species* under the polymerization conditions within the timescale of the polymerization.
Note 2: The products of *chain termination* and irreversible *chain transfer* comprise dead polymer chains.

CP-69 degenerate chain transfer

degenerate transfer

See *degenerative chain transfer*.

CP-70 degenerative chain transfer

degenerative transfer
degenerate chain transfer
degenerate 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* [1].

CP-71 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 [1].

CP-72 dormant species

dormant polymer chain
dormant macromolecule (in *RDP*)

Temporarily deactivated *chain carrier* [2].

Note 1: A dormant polymer chain can be reactivated to a propagating chain under the polymerization conditions within the timescale of the polymerization.
Note 2: Examples of dormant species are the *macroinitiator* in *AMRP* or *ATRP* and the *macroCTA* or *macro-RAFT agent* in *RAFT polymerization*.

CP-73 growing chain

See *propagating species*.

CP-74 inactive chain

non-propagating species
inactive macromolecule (in *RDP*)

Dead chains or *dormant chains*.

CP-75 inhibition (in polymer science)

Absence of polymerization brought about by the action of an inhibitor.

CP-76 inhibitor (in polymer science)

Additive that reacts so rapidly with the *chain carrier* that it reduces the observed rate of *polymerization* to zero [1].

Note 1: Long-chain macromolecules cannot be formed until virtually all the inhibitor is consumed.
Note 2: An ideal inhibitor causes a well-defined induction period during which time the inhibitor is consumed and there is no discernible polymerization, and after which polymerization proceeds at the same rate as in the absence of the inhibitor.
Note 3: In general chemical terminology, the term inhibitor is defined as a substance that diminishes the rate of a chemical reaction [1].

See also *retarder*.

CP-77 inifer

Substance that combines the properties of an *initiator* and a reversible *chain-transfer agent*.

Note: An example of an inifer in *cationic polymerization* is boron trichloride.

CP-78 iniferter

Substance that combines the properties of an *initiator*, a reversible *chain-transfer agent* and a chain terminator or reversible *deactivator*.

Note 1: Examples of iniferters in *radical polymerization* are bis(carbamothioylsulfanyl)disulfides with structure $(R_2NC(=S)S)_2$ (traditional name is thiuram disulfide).
Note 2: Some iniferters are also *RAFT agents*.
Note 3: A substance that combines the properties of a photoinitiator, a reversible *chain-transfer agent* and a chain terminator or reversible *deactivator* is known as a photoiniferter.

See *iniferter process*.

CP-79 initialization (in *RDP*)

Process for converting a starting *initiator* or *chain transfer agent* into a *macro-initiator* or *macro-chain-transfer agent* during *reversible-deactivation polymerization* (*RDP*).

Note: In *RAFT polymerization*, initialization is sometimes known as the pre-equilibrium step.

CP-80 initialization (in *coordination polymerization* or *ROMP*)

Process for converting a starting coordination complex or *precatalyst* into an *active catalyst*.

CP-81 initializer (in *RDP*)

Starting *initiator* or *transfer agent* in *reversible-deactivation polymerization* (*RDP*).

Note: Examples are a starting alkoxyamine *initiator* in *aminoxyl-mediated radical polymerization* (*AMRP*), a starting alkyl halide *initiator* in *atom-transfer radical polymerization* (*ATRP*) and a starting *RAFT agent* in *RAFT polymerization*.

CP-82 initialization efficiency (in *RDP*)

Efficiency of conversion of a starting *initiator* or *transfer agent* into a *macro-initiator* or *macro-chain-transfer agent*.

See also *initiator efficiency for initiation of polymerization* (f_i).

CP-83 initiating species

Species to which monomer adds or becomes inserted to start a *chain polymerization* [1].

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*.

CP-84 initiation (in a *chain polymerization*)

See *chain initiation*.

CP-85 initiator

Substance introduced into a reaction system in order to cause *chain initiation* [1].

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

CP-86 initiator efficiency (for initiation of polymerization) (f, f_i)

initiator efficiency

Number of *growing chains* initiated divided by the number of *active-centers* generated from initiator molecules [1].

Note 1: The number of *growing chains* initiated is the number of *initiating radicals* formed. The number of *active centers* generated is the number of *active centers* that could formed be in the absence of any *cage effect*.

Note 2: In a *radical polymerization*, the frequency of production of *propagating radicals* from an *initiator* that provides two similar radicals is $2k_d f_i$, where k_d is the rate coefficient for *initiator* decomposition.

Note 3: In RDP the efficiency of conversion of a starting *initiator* into a *macroinitiator* may be called the initiator efficiency (see *initialization efficiency*).

Note 4: The initiator efficiency for radical generation from initiators such as dialkyl diazenes and organic peroxides (common symbol f, recommended symbol f_g to distinguish from f_i) is defined as the fraction of radicals that escape the *cage* (see *cage effect*) and are potentially available for reaction with a substrate (e.g., monomer) [15]. The value of f_i will usually be less than f_g as depending on the monomer and the monomer concentration, initiator-derived radicals may react to form products other than *initiating radicals*.

See also *cage effect, initialization efficiency*.

Notes modified from [1].

CP-87 kinetic-chain carrier

See *chain carrier*.

CP-88 living polymer chain

living macromolecule (in *RDP*)

Polymer chains that possess the potential for chain growth under the polymerization conditions.

Note: Living polymer chains comprise all *active* and *dormant polymer chains*.

CP-89 macro-chain-transfer agent (macroCTA)

macroRAFT agent (in *RAFT polymerization*)

Macromolecule containing *chain-transfer-agent* functionality

Note: The *dormant species* in *RAFT polymerization* is often referred to as a macroCTA or macroRAFT agent.

CP-90 macroinitiator

Macromolecule containing *initiator* functionality

Note: The *dormant species* in *RDRP* such as *ATRP* or *SRMP* is often referred to as a macroinitiator.

CP-91 mediating agent

mediator

Species that mediates polymerization in *reversible-deactivation polymerization*.

Note: Examples of mediating agents are the aminoxyl radical in *aminoxyl-mediated radical polymerization* (*AMRP*) and the *RAFT agent* in *RAFT polymerization*.

CP-92 non-propagating species

See *inactive chain*.

CP-93 primary species (in a *chain polymerization*)

Species that is formed from an *initiator* or monomer molecule and that is capable of initiating *polymerization*.

Note 1: In *radical polymerization* a primary radical may be formed by the action of heat, irradiation or electron-transfer.
Note 2: In *radical polymerization*, recombination of primary radicals and their reactions with other radicals leads to reduced *initiator efficiency*.
Note 3: The term “primary species” is also used to designate a species centred on a primary carbon atom, for example, an ethyl radical [1].

See also *secondary species*. Adapted from the definition of primary radical in [1].

CP-94 propagating species (in a *chain polymerization*)

active polymer chain
active macromolecule (in *RDP*)
growing chain

Active species formed by addition to monomer that is capable of adding further monomer.

Note: The propagating species are *chain carriers* in *chain polymerization*.

See *chain carrier, active centre*.

CP-95 retardation (in polymer science)

Diminished rate of polymerization brought about by the action of a retarder.

CP-96 retarder (in polymer science)

Substance that decreases the rate of a reaction [16].

Note 1: A retarder is distinct from an inhibitor, which is a substance that stops a reaction [16]. A retarder does not cause an induction period.

Note 2: In general chemical terminology, the terms retarder and inhibitor are synonomous and defined as substances that diminish the rate of chemical reactions [1].

See also *inhibitor*.

CP-97 reversible-addition-fragmentation chain-transfer agent (RAFT agent)

chain-transfer agent (CTA) (in *RAFT polymerization*)

Chain-transfer agent that provides *chain transfer* by a reversible-addition-fragmentation mechanism.

Note 1: An example of a RAFT agent is 2-cyanopropan-2-yl dithiobenzoate in the polymerization of methyl methacrylate.
Note 2: RAFT agents are *mediating agents* in *RAFT polymerization*.

See also *RAFT polymerization*.

CP-98 secondary species (in a *chain polymerization*)

Species formed by the rearrangement or fragmentation of a *primary species* that is capable of initiating a *polymerization*.

Note: The term “secondary species” is also used to designate a species centred on a secondary carbon atom, e.g., a propan-2-yl radical.

See *primary species*. Adapted from the definition of secondary radical in [1].

CP-99 stable radical (in *SRMP* or *RAFRP*)

Mediating agent in *stable-radical-mediated radical polymerization* with sufficient kinetic stability such that it is essentially unreactive towards addition to monomer under the conditions of the experiment.

Note: The stable radical *mediating agent* need not be thermodynamically stable

See *stable-radical-mediated radical polymerization, chain activation* (in SRMP).

CP-100 unimer

Species comprising only one monomer unit.

Note: The term is commonly used to designate a *dormant species* in *reversible-deactivation radical polymerization* (RDRP) that contains only one monomer unit.

CP-101 unimolecular chain activation

unimolecular activation

See *chain activation* (in *SRMP*).

CP-102 substitution chain transfer

Chain-transfer process that proceeds by a one-step substitution reaction.

Note: In *radical polymerization* the process is called homolytic substitution chain transfer and reaction is by a S_H2 mechanism. An example of a *chain-transfer agent* that reacts by substitution chain transfer is a thiol.

7 Ionic polymerization

Ionic polymerization is an overarching term for *chain polymerization*s that involve ionic intermediates. Mechanisms for *anionic* and *cationic polymerization* are presented in Scheme 8 and Scheme 10, respectively. The definition for *activated-monomer polymerization* is also provided in this section because the activating species is most often, though not always, ionic.

CP-103 controlled ionic polymerization

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

Note 1: Generally, the adjective "controlled" should not be used without specifying the particular kinetic or structural feature that is subject to control.

Note 2: The term controlled ionic polymerization is sometimes used to indicate that the initiation is complete within a period that is short with respect to that for propagation such that dispersities are very low and the molar mass can be precisely predicted based on the initial reagent concentrations.

See *controlled polymerization*.

CP-104 ionic polymerization

ionic chain polymerization

Chain polymerization in which the *active centres* are ions or ion pairs [1].

CP-105 ionic ring-opening polymerization

Ionic polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

See *ring-opening polymerization*.

CP-106 living ionic polymerization

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

Note: *Ionic polymerizations*, *controlled ionic polymerizations* and *reversible-deactivation ionic polymerizations* should not be described as living if there is a non-zero probability of *chain termination* or irreversible *chain transfer*.

See *living polymerization*.

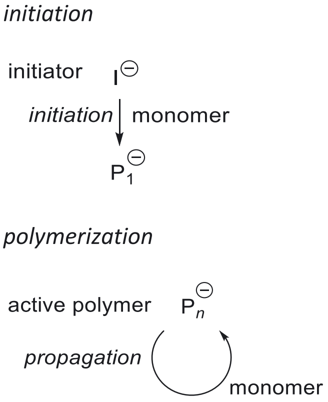
CP-107 reversible-deactivation ionic polymerization (RDIP)

Reversible-deactivation polymerization in which the *kinetic-chain carriers* are ions.

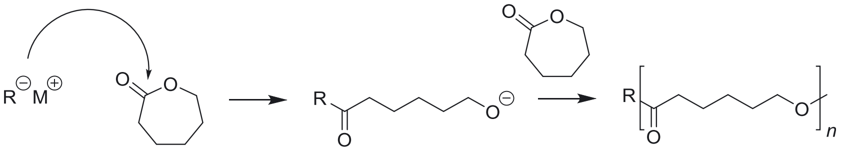
See *reversible-deactivation polymerization*.

8 Nucleophilic chain polymerization

In the propagation step of *nucleophilic chain polymerization* (Scheme 8), the *active centre* behaves as a nucleophile but does not necessarily possess a formal negative charge. For example, the nucleophile may be a nitrogen or sulfur lone-pair. *Anionic polymerization* is an example of both a *nucleophilic chain polymerization* and an *ionic polymerization*. An example is *anionic ring-opening polymerization* of caprolactone (Scheme 9).



Scheme 8: Simplified mechanism for *anionic polymerization*.



Scheme 9: *Chain-initiation* and *chain-propagation* steps in *anionic ring-opening polymerization of caprolactone*.

CP-108 anionic polymerization

Ionic polymerization in which the *active centres* are anions [1].

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

CP-109 anionic group-transfer polymerization

group-transfer polymerization (GTP)

Anionic polymerization in which a specific atom or group is intramolecularly transferred to remain associated with the active chain-end during the course of polymerization.

Note: An example is polymerization of methyl methacrylate initiated by 1-methoxy-2-methyl-1-(trimethylsiloxy)prop-1-ene (traditional name is methyl trimethylsilyl dimethylketene acetal) and catalysed by a nucleophile.

CP-110 anionic ring-opening polymerization

Anionic polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

Note: Some examples of monomers used in anionic ring-opening polymerization are intramolecular anhydrides of *N*-carboxy amino acids (commonly referred to as *N*-carboxy anhydrides or NCAs), epoxides and cyclic siloxanes.

See *ring-opening polymerization*.

CP-111 controlled anionic polymerization

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

Note 1: Generally, the adjective “controlled” should not be used without specifying the particular kinetic or structural feature that is subject to control.

Note 2: The term “controlled anionic polymerization” is sometimes used to indicate that the initiation is complete within in a period that is short with respect to the time for propagation such that dispersities are very low and the molar mass can be precisely predicted based on the initial reagent concentrations.

See *controlled polymerization*.

CP-112 living anionic polymerization

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

Note: *Anionic polymerizations*, *controlled anionic polymerizations* and *reversible-deactivation anionic polymerizations* should not be described as living if there is a non-zero probability of *chain termination* or irreversible *chain transfer*.

See *living polymerization*.

CP-113 reversible-deactivation anionic polymerization (RDAP)

Reversible-deactivation polymerization in which the *kinetic-chain carriers* are anions.

Note 1: An example of a *reversible-deactivation anionic polymerization* is *group-transfer polymerization* of methyl methacrylate initiated by 1-methoxy-2-methyl-1-(trimethylsiloxy)prop-1-ene (traditional name is methyl trimethylsilyl dimethylketene acetal) and catalysed by a nucleophile.
Note 2: Another example is *anionic polymerization* with reversible formation of an ion-pair or a different ion cluster size.

See *reversible-deactivation polymerization*.

CP-114 nucleophilic chain polymerization

Chain polymerization in which the *active centres* are nucleophilic species.

Note 1: *Anionic polymerization* is an example of nucleophilic chain polymerization.
Note 2: Some examples of non-ionic nucleophilic species are nitrogen and sulfur lone pairs.

See *anionic polymerization*.

CP-115 ring-opening nucleophilic chain polymerization

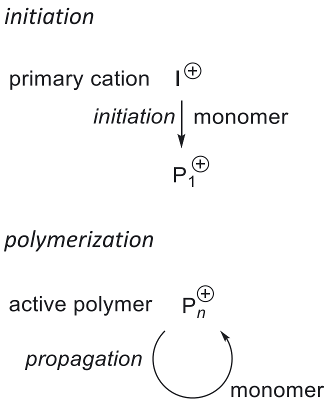
Nucleophilic chain polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

Note: Examples of non-ionic monomers used in ring-opening nucleophilic chain polymerization include intramolecular anhydrides of *N*-carboxy amino acids (commonly referred to as *N*-carboxy anhydrides or NCAs).

See *ring-opening polymerization*.

9 Electrophilic chain polymerization

In the *propagation* step of electrophilic chain polymerization, the *active centre* behaves as an electrophile but does not necessarily possess a formal positive charge. *Cationic polymerization* is an example of both an *electrophilic chain polymerization* and an *ionic polymerization*.



Scheme 10: Simplified mechanism for cationic polymerization.

CP-116 cationic polymerization

Ionic polymerization in which the *active centres* are cations [1].

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

CP-117 cationic ring-opening polymerization

Cationic polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

Note: Some examples of monomers used in cationic ring-opening polymerization are cyclic ethers, lactones and lactams.

See *ring-opening polymerization*.

CP-118 controlled cationic polymerization

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

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

See *controlled polymerization*.

CP-119 electrophilic chain polymerization

Chain polymerization in which the *active centres* are electrophilic species.

Note: *Cationic polymerization* is an example of electrophilic chain polymerization.

See *cationic polymerization*.

CP-120 living cationic polymerization

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

Note: *Cationic polymerizations*, *controlled cationic polymerizations* and *reversible deactivation cationic polymerizations* should not be described as living if there is a non-zero probability of *chain termination* or irreversible *chain transfer*.

See *living polymerization*.

CP-121 reversible-deactivation cationic polymerization (RDCP)

Reversible-deactivation polymerization in which the *chain carriers* are cations.

Note: An example of a reversible-deactivation cationic polymerization is reversible ion-pair formation.

See *reversible-deactivation polymerization*.

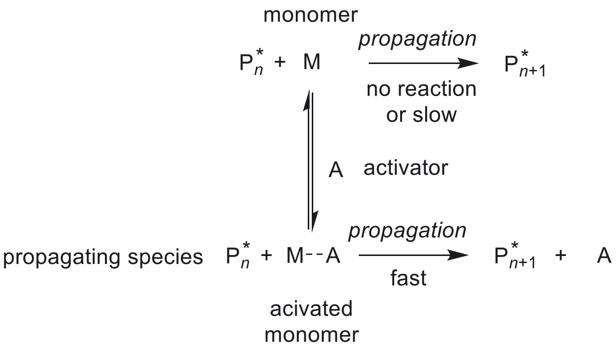
10 Activated-monomer polymerization

Activated-monomer polymerizations (see CP-1 and Scheme 11) are treated separately from *electrophilic chain polymerization* and *nucleophilic chain polymerization* even though most examples also belong to one of these categories. A distinction is also made between *activated-monomer polymerization,* where the monomer is activated by coordination with a *catalyst* or *activator*, and *coordination polymerization*, where both the monomer and the *propagating species* form part of a coordination complex.

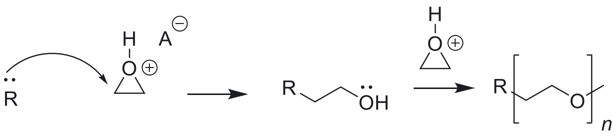
Radical polymerizations in the presence of certain Lewis acids, where the Lewis acid provides for substantial rate acceleration, might also be considered as *activated-monomer polymerizations*. However, the term is seldom used in this context.

The *propagation* reaction in *activated monomer polymerization* involves reaction between a *propagating species* and an *activated monomer* that is formed by coordination of an *activator* to a monomer.

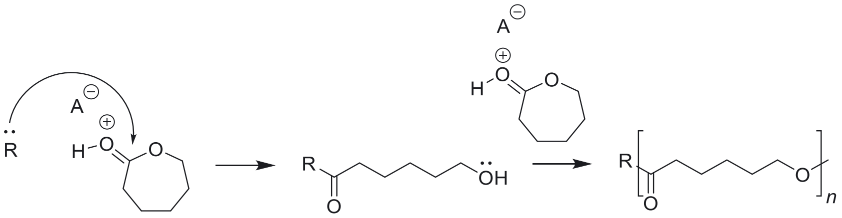
Examples of *activated monomer polymerization* are the *cation-activated-monomer polymerization* of oxirane (Scheme 12) and caprolactone (Scheme 13), and the *anion-activated-monomer polymerization* of an intramolecular anhydride of a *N*-carboxy amino acid (commonly referred to as an *N*-carboxy anhydrides or NCA) (Scheme 14).



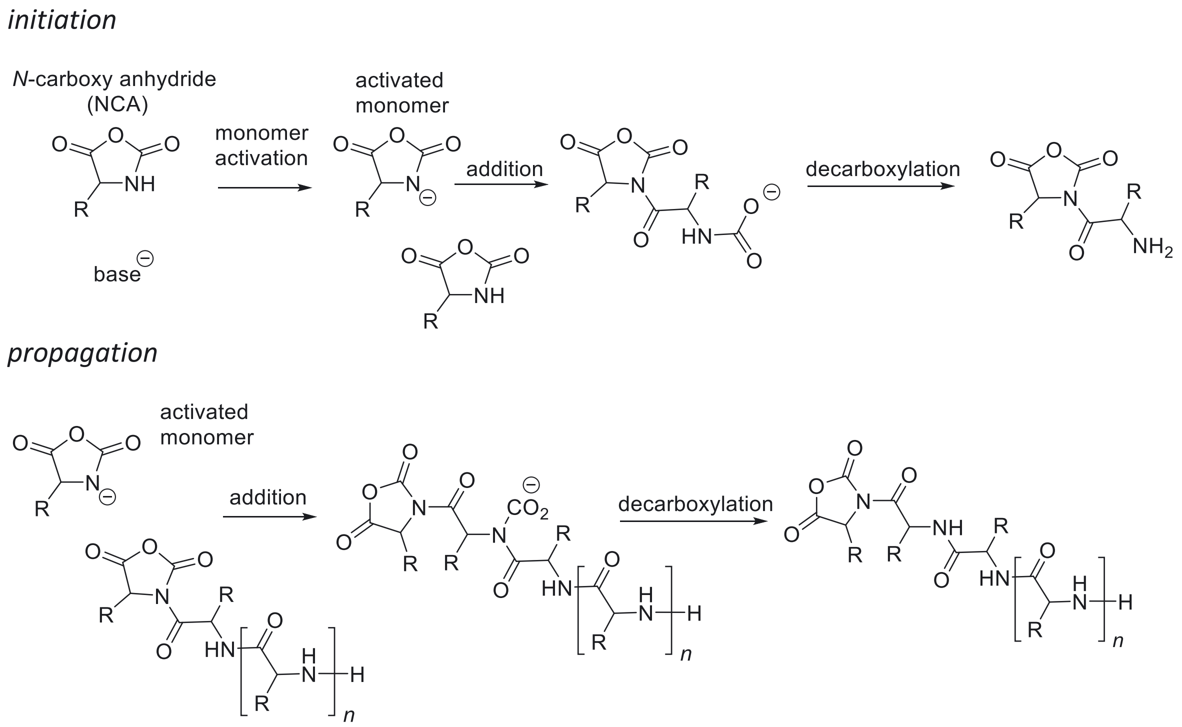
Scheme 11: Simplified mechanism for *activated-monomer polymerization*. P^*_n is a generic *propagating species*.



Scheme 12: *Chain-initiation* and *chain-propagation* steps in *cation-activated-monomer polymerization* of oxirane where the activator is a protic acid (AH).



Scheme 13: *Chain-initiation* and *chain-propagation* steps in *cation-activated-monomer polymerization* of caprolactone where the *activator* is a protic acid (AH).



Scheme 14: *Chain initiation* and *chain-propagation* steps in *anion-activated-monomer polymerization* of an *N*-carboxy anhydride (NCA) where the *activator* is a base. Note that *nucleophilic ring-opening polymerization* of *N*-carboxy anhydrides is not usually considered as a *condensative chain polymerization* because carbon dioxide is not eliminated in the *propagation* step, but rather in a separate step following *propagation*.

CP-122 anion-activated-monomer polymerization

anionic activated-monomer polymerization

Activated-monomer polymerization where the *propagating species* is an electrophile and activating species is anionic.

CP-123 cation-activated-monomer polymerization

cationic activated-monomer polymerization

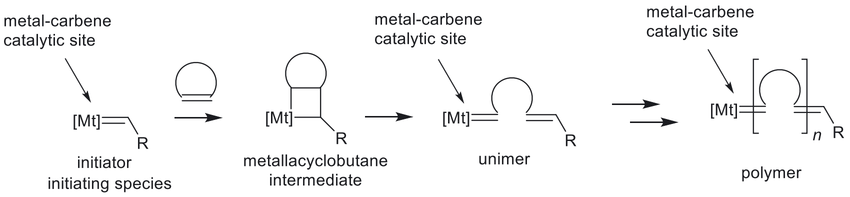
Activated-monomer polymerization where the *propagating species* is a nucleophile and the activating species is cationic.

11 Ring-opening metathesis polymerization

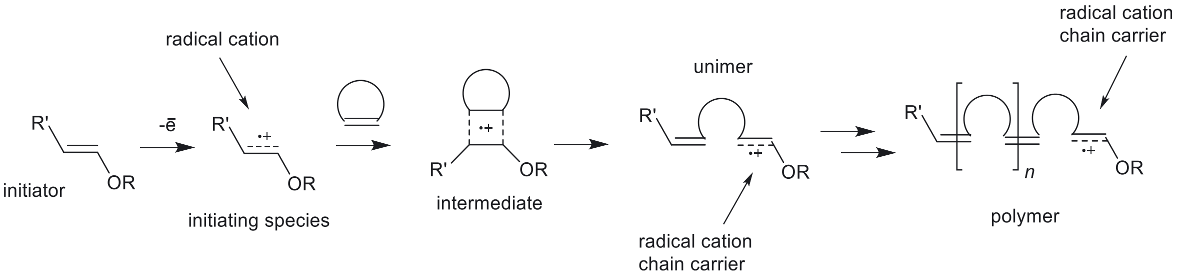
Metathesis polymerization is a process in which unsaturated monomers are transformed into unsaturated polymers by a process of bond redistribution. When the unsaturated monomer is contained in a ring, *ring-opening metathesis polymerization* (ROMP) is possible.

Ring-opening metathesis polymerization commonly involves cyclic olefin monomers and a metal-carbene complex as the *initiator*, which is the catalytic site (*catalyst*) in the polymerization (Scheme 15). In most cases, the initiating metal-carbene complex is formed *in situ*, in which case the precursor(s) to the complex are the *initiator* and the active catalyst is the *initiating species*.

In metal-free *electron-transfer ring-opening metathesis polymerization* (ET-ROMP) initiation is thought to involve single electron-transfer from a vinyl ether *initiator* with formation of a radical cation as the *initiating species* and *chain carrier* (Scheme 16).



Scheme 15: Simplified mechanism for *ring-opening metathesis polymerization* catalyzed by a metal-carbene complex. [Mt]= is a metal-carbene complex (ROMP).



Scheme 16: Simplified mechanism for *electron-transfer ring-opening metathesis polymerization* (*ET-ROMP*).

CP-124 living ring-opening metathesis polymerization

Ring-opening metathesis polymerization in which *chain termination* and irreversible *chain transfer* are absent.

Note: *Ring-opening metathesis polymerizations* should not be described as living if there is a non-zero probability of *chain termination* (e.g., due to side reactions consuming some part of the *catalyst*) or irreversible *chain transfer* (e.g., due to backbiting).

See *living polymerization.*

CP-125 metathesis polymerization

Polymerization in which unsaturated monomers are transformed into unsaturated polymers by a process of bond redistribution [1].

Note 1: Metathesis polymerization is most often metal-catalyzed and the *kinetic-chain carriers* alternate between metal-carbene complexes and metallacyclobutanes or between 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). ADMET is not a *chain polymerization*.

CP-126 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 [1].

Note: In general, ring-opening metathesis polymerizations that show some living characteristics should not be called *living ring-opening metathesis polymerization* when there are side reactions leading to loss of catalyst or irreversible *chain transfer*.

See *metathesis polymerization*, *ring-opening polymerization*.

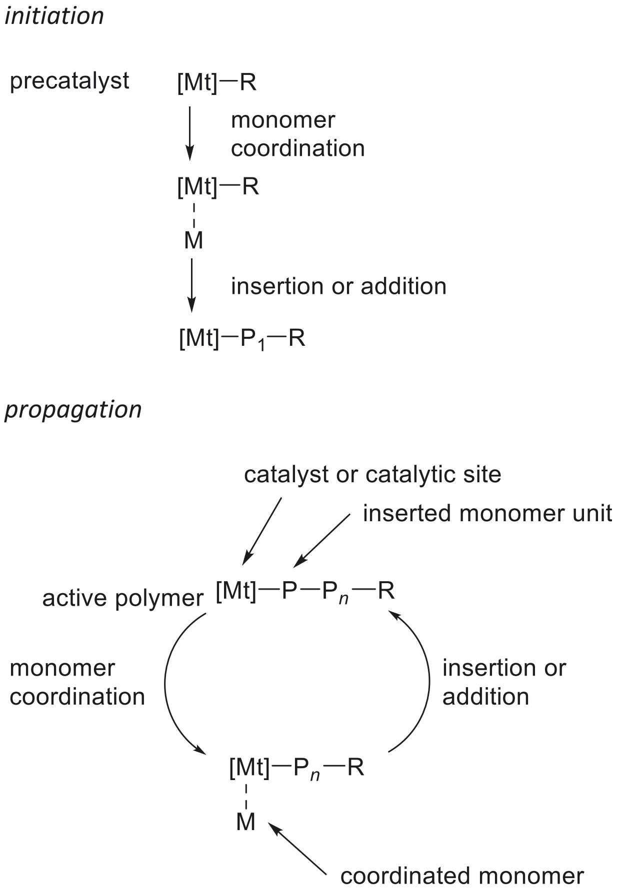
CP-127 electron-transfer ring-opening metathesis polymerization (ET-ROMP)

Ring opening metathesis polymerization (ROMP) proceeding through one-electron redox processes in the absence of a metal carbene *initiator*.

Note: ET-ROMP may be initiated by single electron-transfer to a vinyl ether from a photoredox catalyst or by electrochemical processes to create a radical cation as the *kinetic-chain carrier*.

12 Coordination polymerization

A simplified mechanism for coordination polymerization when it involves a metal complex as the catalyst is provided in Scheme 17.

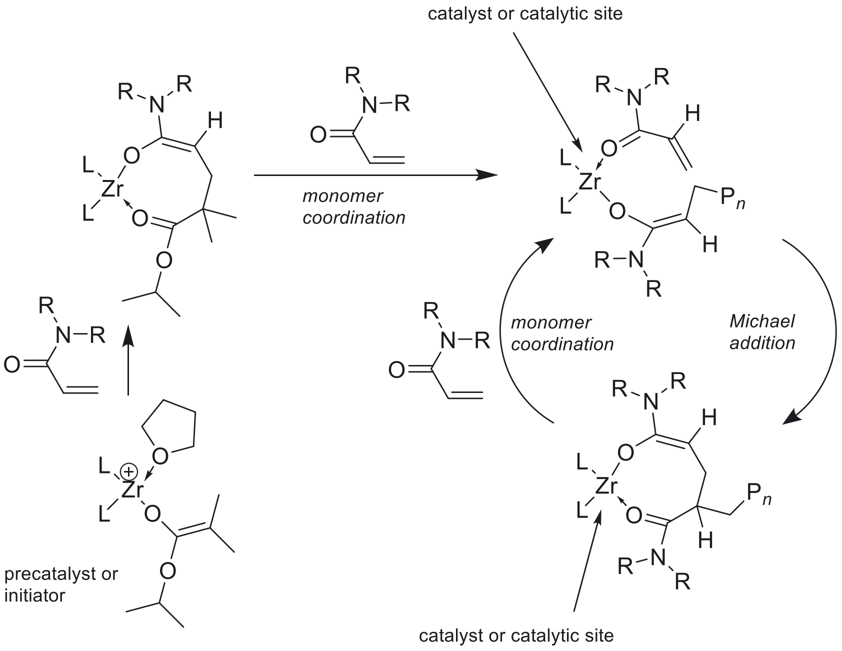


Scheme 17: Simplified mechanism for *coordination polymerization*. Monomer is sequentially coordinated and inserted into the [Mt]–P_n bond. [Mt] is a metal complex that comprises the catalytic site, M is a monomer, P is a monomer unit.

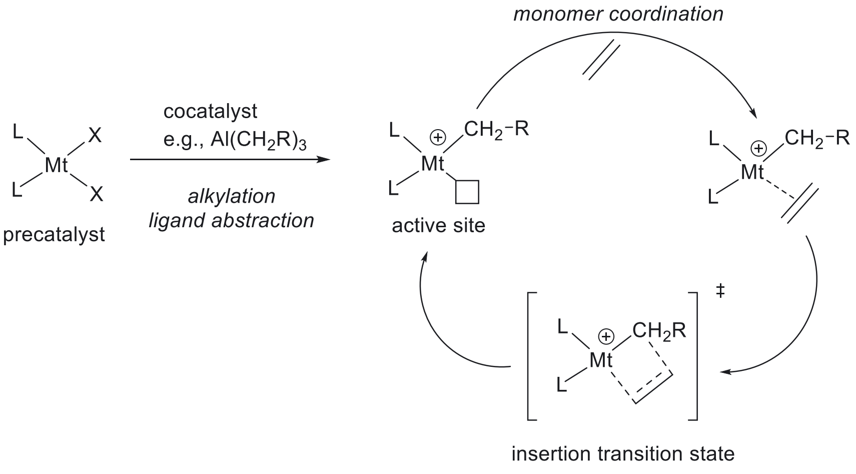
A distinction is made between *activated-monomer polymerization*, where the monomer is activated by coordination with a catalyst or activator, and coordination polymerization, where both the monomer and the *propagating species* form part of a coordination complex.

Coordination polymerization applied to olefins is often known as Ziegler-Natta polymerization. However, Ziegler-Natta polymerization is not a clearly defined term in the literature. Some use this to refer only to those polymerizations which make use of a heterogeneous catalyst. Others use the term only to refer to those polymerizations that make use of the particular form of heterogeneous *catalyst* defined in the early work of Ziegler and Natta. Named polymerization reactions are deprecated in IUPAC terminology.

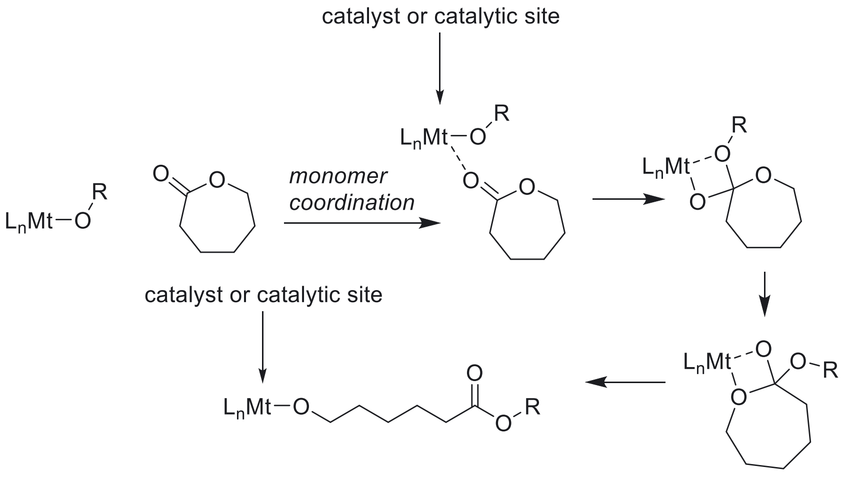
The *catalyst* in *coordination polymerization* is the species that comprises the *active site*. The precursor to that species (often called a *precatalyst*) is often also incorrectly called a *catalyst*. The catalyst precursor could be called an *initiator*. The mechanisms of *coordination-addition polymerization* and *coordination-insertion polymerization* and *ring-opening coordination polymerization* are shown in Schemes 18, 19, and 20, respectively. In *coordination-insertion polymerization* (Scheme 19), the *active site* is a coordinatively unsaturated metal complex containing a metal-carbon or metal-hydride bond into which monomer is inserted through a metallacyclobutane transition state, thereby regenerating the *active site*.



Scheme 18: Mechanism for coordination-addition polymerization of an acrylamide with a zirconium complex. L are ligands, R are alkyl substituents.



Scheme 19: Mechanism for catalyst formation in *coordination-insertion polymerization* of ethylene by the reaction of *catalyst precursor* (*precatalyst*) and *cocatalyst*. Mt is a metal, L are ligands, X is typically a halogen, R is alkyl or the growing chain, and □ is an empty orbital for alkene coordination.



Scheme 20: *Chain-propagation* step in *ring-opening coordination polymerization* of caprolactone.

CP-128 coordination polymerization

Chain polymerization that involves the preliminary coordination of a monomer molecule with a *chain carrier* [1].

Note 1: Coordination polymerization often occurs by *pseudo-ionic polymerization*.
Note 2: The term "metal-catalyzed polymerization" without explanation to designate coordination polymerization is deprecated.

CP-129 coordination-addition polymerization

Coordination polymerization of α,β-unsaturated amides or esters that proceeds by sequential monomer coordination and Michael addition events.

CP-130 coordination-insertion polymerization

insertion polymerization
polyinsertion

Coordination polymerization of olefins that proceeds by insertion of the olefin into a metal–carbon bond

See also *insertion polymerization*.

CP-131 living coordination polymerization

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

Note 1: *Coordination polymerizations*, *controlled coordination polymerizations* and *reversible-deactivation coordination polymerizations* should not be described as living if there is a non-zero probability of *chain termination* or irreversible *chain transfer*.
Note 2: The use of the adjective living to denote systems with an extended catalyst lifetime is deprecated.

See *living polymerization*.

CP-132 reversible-deactivation coordination polymerization (RDCP)

Reversible-deactivation polymerization in which the *chain carriers* are coordination complexes.

Note: Examples of reversible-deactivation coordination polymerization are *coordinative chain-transfer polymerization* (CCTP) and *chain-shuttling polymerization* (CSP).

See *reversible-deactivation polymerization*.

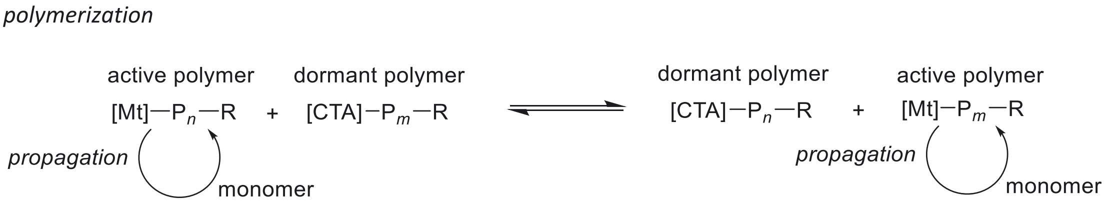
CP-133 coordination ring-opening polymerization

Coordination polymerization in which a cyclic monomer yields a monomeric unit that is either acyclic or contains fewer rings than the cyclic monomer.

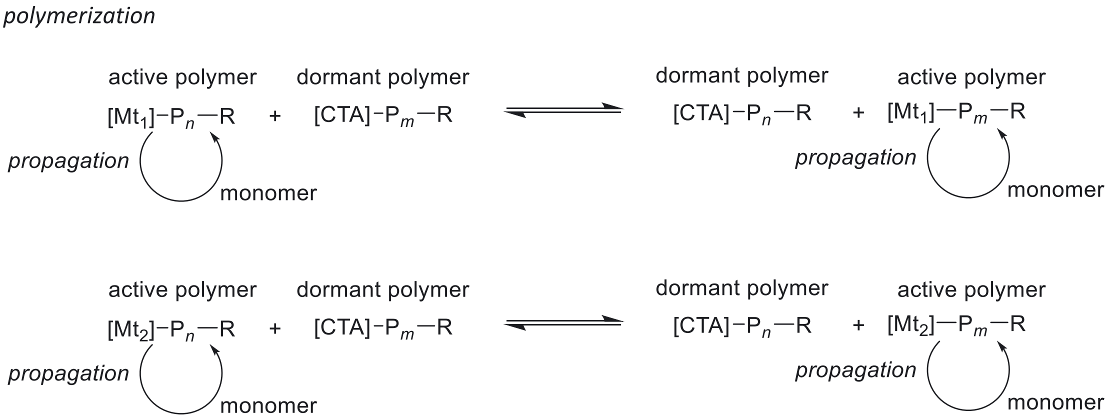
See *ring-opening polymerization*.

13 Sub-classes of coordination polymerization

A variety of forms of coordination polymerization have been described. Reversible *coordinative chain-transfer polymerization* (Scheme 21) and *chain-shuttling polymerization* (Scheme 22) are *degenerative chain-transfer polymerizations*, forms of *reversible-deactivation polymerization*.



Scheme 21: Simplified mechanism for reversible *coordinative chain-transfer polymerization*. [Mt] is a metal complex and [CTA] is a chain-transfer agent. Monomer units are sequentially inserted into the [M]–P_n bond.



Scheme 22: Simplified mechanism for *chain-shuttling polymerization* (*CSP*). [Mt_1] and [Mt_2] are metal complexes and [CTA] is a chain-transfer agent. The propagating chain is "shuttled" between the two catalysts by way of the CTA.

CP-134 chain-shuttling polymerization (CSP)

Coordinative chain-transfer polymerization that involves two different catalysts showing different specificity, where *chain propagation* occurs sequentially on the two catalysts, allowing for the formation of segmented or multiblock copolymers.

Note: chain-shuttling polymerization is a form of *degenerative chain-transfer polymerization* (DTP).

See also *coordinative chain-transfer polymerization*, *degenerative chain-transfer polymerization*.

CP-135 chain-walking polymerization (CWP)

Coordination polymerization in which the *chain carrier* migrates along the formed polymer chain through a series of β-hydrogen eliminations and reinsertions with inversion of stereochemistry.

Note 1: In contrast to classical *coordination polymerizations*, which provide linear polyethylene, CWP of ethylene leads to a branched polymer.
Note 2: CWP of α-olefins generally leads to less branched polymers than those formed by classical *coordination polymerization*.
Note 3: Examples of CWP catalysts are aryl-substituted α-diimine-palladium(II) complexes [17].

CP-136 coordinative chain-transfer polymerization (CCTP)

Coordination polymerization in which a propagating chain is able to transfer reversibly between the catalyst and a *chain-transfer agent*, thereby converting the *active species* into a *dormant species*.

Note: coordinative chain-transfer polymerization is a form of *degenerative chain-transfer polymerization* (DTP).

See also *chain-shuttling polymerization, degenerative chain-transfer polymerization*.

CP-137 heterogeneous catalysis coordination polymerization

heterogeneous coordination polymerization
deprecated: Ziegler-Natta polymerization

Coordination polymerization making use of a heterogeneous catalyst.

Note 1: Heterogeneous catalysis coordination polymerization of polyolefins is sometimes known as Ziegler-Natta polymerization. Named reactions are deprecated in IUPAC terminology.
Note 2: When using the term heterogeneous coordination polymerization, the context must allow distinction from a *coordination polymerization* in a heterogeneous medium.

CP-138 homogeneous catalysis coordination polymerization

homogeneous coordination polymerization

Coordination polymerization making use of a homogeneous catalyst.

Note 1: *Metallocene polymerization* is one form of homogeneous coordination polymerization.
Note 2: When using the term homogeneous coordination polymerization, the context must allow distinction from a *coordination polymerization* in a homogeneous medium.

CP-139 metallocene polymerization

Coordination polymerization making use of a metallocene catalyst.

CP-140 pseudo-ionic polymerization

Polymerization proceeding by insertion of a monomer into a polar bond without the generation of ions [1].

Note 1: Most pseudo-ionic polymerizations involve concerted (e.g., four- or multi-centre) mechanisms of propagation.
Note 2: The term pseudo-ionic polymerization has been most often used in connection with *ring-opening polymerization*.

See also *coordination polymerization*.

CP-141 rare-earth-metal-mediated coordination-addition polymerization

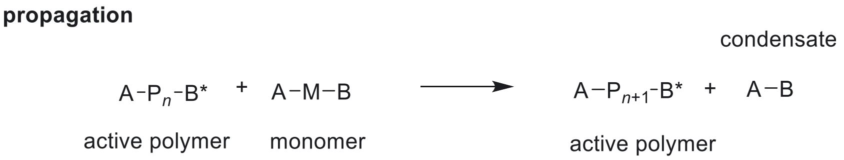
rare-earth-metal-mediated coordination polymerization
rare-earth-metal-mediated group-transfer polymerization
lanthanide-mediated group-transfer polymerization

Coordination-addition polymerization with propagation occurring within the coordination sphere of a rare-earth metal complex.

Note: The process may also involve non-rare-earth metal complexes with a sufficiently large coordination sphere (e.g., zirconium).

14 Condensative chain polymerization

Condensative chain polymerization was previously only defined within a note to the term *chain polymerization* [1, 3]. A general mechanism for the *propagation* step in *condensative chain polymerization* is shown in Scheme 23. Note that nucleophilic *ring-opening polymerization* of intramolecular anhydrides of *N*-carboxy amino acids (amino acid *N*-carboxy anhydrides) mentioned in [1, 3] is not usually considered as a *condensative chain polymerization* because carbon dioxide is not eliminated in the *propagation* step, but rather in a separate step following *propagation*.



Scheme 23: Simplified mechanism for *condensative chain polymerization*.

CP-142 condensative chain polymerization (CCP)

Chain polymerization in which the individual propagation steps are condensation reactions.

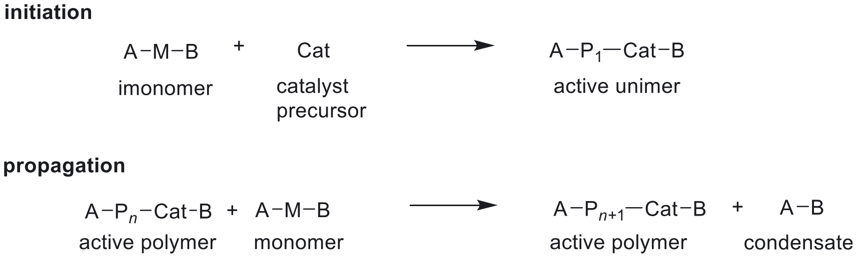
Note 1: *Condensative chain polymerization* appears under a variety of names, which include: chain-growth condensation polymerization, chain-growth polycondensation, *catalyst-transfer polymerization*, catalyst-transfer condensation polymerization, catalyst-transfer polycondensation. The use of terms that indicate CCP to be a form of *polycondensation* is deprecated as being inconsistent with the IUPAC definition of that term [1, 3].

Note 2: An example is the polymerization of potassium 5-cyano-4-methyl-2-propylphenolate initiated by (4-fluorophenyl)(4-(trifluoromethyl)phenyl)methanone to make an aromatic polyether, in which KF is the condensate.

See also *catalyst-transfer polymerization*.

15 Forms of condensative chain polymerization

A mechanism for *catalyst-transfer polymerization* is shown in Scheme 24. The process is a *condensative chain polymerization* and can show living characteristics when reaction of the *propagating species*, an active polymer (A-P_n-B*), with monomer (A-M-B) is much faster that the self-reaction of monomer (A-M-B with A-M-B) or the active polymer (A-P_n-B* with A-P_m-B*). The process should not be called a *living polymerization* if it is complicated by side reactions.



Scheme 24: Simplified mechanism for *catalyst-transfer polymerization*. -Cat-is a catalyst.

CP-143 catalyst-transfer polymerization (CTP)

catalyst-transfer chain polymerization

Catalysed *condensative chain polymerization* where the catalyst is transferred from reactant polymer to product polymer with high efficiency.

Note 1: Examples of catalyst-transfer polymerization include *catalyst-transfer cross-coupling polymerization* and enzyme-catalyzed polymerizations to form, for example, polypeptides, DNA, and RNA.

Note 2: It is recommended that the adjective “chain” be included in the term *catalyst-transfer chain polymerization* in circumstances where there may be confusion with respect to whether a chain mechanism is involved.

CP-144 catalyst-transfer cross-coupling polymerization

Catalyst-transfer polymerization where the propagation steps comprise cross-coupling reactions.

Note: Examples of catalyst-transfer cross-coupling polymerization are:

i. Kumada *catalyst-transfer cross-coupling polymerization* (KCTP), where the propagation steps comprise metal-catalyzed cross-coupling reactions of a Grignard reagent with an organic halide. The process is also known as Grignard metathesis (GRIM) polymerization.
ii. Suzuki–Miyaura *catalyst-transfer cross-coupling polymerization*, where the propagation steps comprise Pd-catalyzed cross-coupling reactions between an organoboron compound and an organic halide.
Named polymerization reactions are deprecated in IUPAC terminology.

CP-145 living condensative chain polymerization

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

Note: *Condensative chain polymerizations* should not be described as living if *chain termination* or irreversible *chain transfer* are evident.

16 Alphabetical index of terms

An alphabetical list of terms defined in this document is provided in Table 2. Deprecated terms are indicated. 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.

Table 2: Alphabetical Index of Terms.

Table 2: (continued)

Term	Term Number
catalyst precursor (in coordination polymerization)	CP-50
catalyst-transfer chain polymerization	CP-143
catalyst-transfer cross-coupling polymerization	CP-144
catalyst-transfer polymerization (CTP)	CP-143
catalytic chain termination	CP-52
catalytic chain transfer (CCT)	CP-51
cation-activated-monomer polymerization	CP-123
cationic activated-monomer polymerization	CP-123
cationic polymerization	CP-116
cationic ring-opening polymerization	CP-117
chain activation	CP-53
chain activation (in ATRP)	CP-55
chain activation (in DTRP)	CP-56
chain activation (in SRMP)	CP-54
chain carrier (in polymerization)	CP-57
chain deactivation	CP-58
chain initiation	CP-59
chain polymerization	CP-2
chain propagation (in a chain polymerization)	CP-60
chain reaction	CP-3
chain reactivation	CP-61
chain termination (in a chain polymerization)	CP-62
chain transfer	CP-63
chain-shuttling polymerization (CSP)	CP-134
chain-transfer agent (CTA)	CP-64
chain-transfer agent (CTA) (in RAFT polymerization)	CP-97
chain-walking polymerization (CWP)	CP-135
cobalt-mediated radical polymerization (CMRP)	CP-21
cocatalyst (in coordination polymerization)	CP-42
combination	CP-66
condensative chain polymerization (CCP)	CP-142
controlled anionic polymerization	CP-111
controlled cationic polymerization	CP-118
controlled ionic polymerization	CP-103
controlled polymerization	CP-4
controlled radical polymerization (CRP)	CP-15
controlled reversible-deactivation polymerization	CP-10
coordination polymerization	CP-128
coordination ring-opening polymerization	CP-133
coordination-addition polymerization	CP-129
coordination-insertion polymerization	CP-130
coordinative chain-transfer polymerization (CCTP)	CP-136
cyclopolymerization	CP-5
deactivator (in ATRP)	CP-67
dead polymer chain	CP-68
degenerate chain transfer	CP-69
degenerate chain-transfer radical polymerization	CP-32
degenerate transfer	CP-70
degenerate-transfer polymerization	CP-6
degenerative chain transfer	CP-70
degenerative chain-transfer radical polymerization (DTRP)	CP-32
degenerative transfer	CP-70
degenerative-transfer polymerization (DTP)	CP-6
disproportionation (in a chain polymerization)	CP-71
dormant macromolecule (in RDP)	CP-72
dormant polymer chain	CP-72

Table 2: (continued)

Term	Term Number
dormant species	CP-72
electron-transfer ring-opening metathesis polymerization (ET-ROMP)	CP-127
electrophilic chain polymerization	CP-119
group-transfer polymerization (GTP)	CP-7
growing chain	CP-73
heterogeneous catalysis coordination polymerization	CP-137
heterogeneous coordination polymerization	CP-137
homogeneous catalysis coordination polymerization	CP-138
homogeneous coordination polymerization	CP-138
immortal polymerization (deprecated term)	CP-9
inactive chain	CP-74
inactive macromolecule (in RDP)	CP-74
inhibition (in polymer science)	CP-75
inhibitor (in polymer science)	CP-76
inifer	CP-77
iniferter	CP-78
iniferter process	CP-22
initialization (in coordination polymerization or ROMP)	CP-80
initialization (in RDP)	CP-79
initialization efficiency (in RDP)	CP-82
initializer (in RDP)	CP-81
initiating species	CP-83
initiation	CP-59
initiation (in a chain polymerization)	CP-84
initiator	CP-85
initiator (in coordination polymerization)	CP-50
initiator efficiency (for initiation of polymerization) (f, f_i)	CP-86
inner-sphere electron transfer atom-transfer radical polymerization (ISET-ATRP)	CP-28
insertion polymerization	CP-8
iodine-transfer polymerization (ITP)	CP-33
ionic chain polymerization	CP-104
ionic polymerization	CP-104
ionic ring-opening polymerization	CP-105
irreversible chain deactivation	CP-62
kinetic-chain carrier	CP-87
living anionic polymerization	CP-112
living cationic polymerization	CP-120
living condensative chain polymerization	CP-145
living coordination polymerization	CP-131
living ionic polymerization	CP-106
living polymer chain	CP-88
living polymerization	CP-9
“living polymerization” (deprecated term when quotation marks used)	CP-9
living radical polymerization	CP-16
“living radical polymerization” (deprecated term when quotation marks used)	CP-16
living ring-opening metathesis polymerization	CP-124
macro-chain-transfer agent (macroCTA)	CP-89
macroinitiator	CP-90
macroRAFT agent (in RAFT polymerization)	CP-89
mediating agent	CP-91
mediator	CP-91
metallocene polymerization	CP-139
metathesis polymerization	CP-125
nitroxide-mediated (radical) polymerization (NMP) (deprecated term)	CP-20
non-metal-mediated atom-transfer radical polymerization (NM-ATRP)	CP-29
non-propagating species	CP-74

Table 2: (continued)

Term	Term Number
non-propagating species	CP-92
nucleophilic chain polymerization	CP-114
organobismuthane-mediated radical polymerization (BIRP)	CP-34
organometallic-mediated radical polymerization (OMRP)	CP-23
organostibane-mediated radical polymerization (SBRP)	CP-35
organotellurium-mediated radical polymerization (TERP)	CP-36
outer-sphere electron transfer ATRP (OSET-ATRP)	CP-30
polyaddition	CP-13
polycondensation	CP-14
polyinsertion	CP-8
polymerization	CP-12
precatalyst (in coordination polymerization)	CP-50
primary species (in a chain polymerization)	CP-93
propagating species (in a chain polymerization)	CP-94
propagation	CP-60
pseudo-ionic polymerization	CP-140
pseudo-living polymerization (deprecated term)	CP-9
pseudo-living radical polymerization (deprecated term)	CP-16
quasi-living polymerization (deprecated term)	CP-9
quasi-living radical polymerization (deprecated term)	CP-16
radical polymerization	CP-17
radical ring-opening polymerization	CP-18
rare-earth-metal-mediated coordination-addition polymerization	CP-141
reactivation (in a chain polymerization)	CP-61
retardation (in polymer science)	CP-95
retarder (in polymer science)	CP-96
reverse iodine-transfer polymerization (RITP)	CP-37
reversible-addition-fragmentation chain-transfer agent (RAFT agent)	CP-97
reversible-addition-fragmentation chain-transfer polymerization (RAFT polymerization)	CP-38
reversible-addition-fragmentation radical polymerization (RAFRP)	CP-25
reversible-deactivation anionic polymerization (RDAP)	CP-113
reversible-deactivation cationic polymerization (RDCP)	CP-121
reversible-deactivation coordination polymerization (RDCP)	CP-132
reversible-deactivation ionic polymerization (RDIP)	CP-107
reversible-deactivation polymerization (RDP)	CP-10
reversible-deactivation radical polymerization (RDRP)	CP-19
ring-opening metathesis polymerization (ROMP)	CP-126
ring-opening nucleophilic chain polymerization	CP-115
ring-opening polymerization (ROP)	CP-11
secondary species (in a chain polymerization)	CP-98
single-electron-transfer living radical polymerization (SET-LRP) (deprecated term)	CP-30
single-electron-transfer RDRP (SET-RDRP)	CP-30
stable radical (in SRMP or RAFRP)	CP-99
stable-free-radical-mediated polymerization (SFRMP) (deprecated term)	CP-24
stable-radical-mediated polymerization (SRMP)	CP-24
substitution chain transfer	CP-102
termination	CP-62
transfer	CP-63
transfer agent	CP-64
transition-metal-mediated living radical polymerization (deprecated term)	CP-31
transition-metal-mediated radical polymerization	CP-31
transition-metal-mediated reversible-deactivation radical polymerization	CP-31
unimer	CP-100
unimolecular activation	CP-54
unimolecular chain activation	CP-54
Ziegler-Natta polymerization (deprecated term)	CP-137

17 Acronyms, initialisms, abbreviations, and symbols

Table 3 provides a summary of acronyms, initialisms, abbreviations, and symbols for terms defined in this document.

Table 3: Acronyms, Initialisms, abbreviations, and symbols.

Acronym[a]	**Term**	**Term Number**
AMP	activated-monomer polymerization	CP-1
AMRP	aminoxyl-mediated radical polymerization	CP-20
ATRP	atom-transfer radical polymerization	CP-27
BIRP	organobismuthane-mediated radical polymerization	CP-34
CCP	condensative chain polymerization	CP-142
CCT	catalytic chain transfer	CP-51
CCTP	coordinative chain-transfer polymerization	CP-136
CMRP	cobalt-mediated radical polymerization	CP-21
CRP	controlled radical polymerization	CP-15
CSP	chain-shuttling polymerization	CP-134
CTA	chain-transfer agent	CP-64
CTP	catalyst-transfer polymerization	CP-143
CWP	chain-walking polymerization	CP-135
DTP	degenerative-transfer polymerization	CP-6
DTRP	degenerative chain-transfer radical polymerization	CP-32
ET-ROMP	electron-transfer ring-opening metathesis polymerization	CP-127
f	initiator efficiency	CP-86
f_i	initiator efficiency for initiation of polymerization	CP-86
GTP	group-transfer polymerization	CP-7
ISET-ATRP	inner-sphere electron transfer atom-transfer radical polymerization	CP-28
ITP	iodine-transfer polymerization	CP-33
macroCTA	macro-chain-transfer agent	CP-89
NM-ATRP	non-metal-mediated atom-transfer radical polymerization	CP-29
NMP	nitroxide-mediated radical polymerization (deprecated term)	CP-20
OMRP	organometallic-mediated radical polymerization	CP-23
OSET-ATRP	outer-sphere electron transfer ATRP	CP-30
RAFRP	reversible-addition-fragmentation radical polymerization	CP-25
RAFT agent	reversible-addition-fragmentation chain-transfer agent	CP-97
RAFT polymerization	reversible-addition-fragmentation chain-transfer polymerization	CP-38
RDAP	reversible-deactivation anionic polymerization	CP-113
RDCP	reversible-deactivation cationic polymerization	CP-121
RDCP	reversible-deactivation coordination polymerization	CP-132
RDIP	reversible-deactivation ionic polymerization	CP-107
RDP	reversible-deactivation polymerization	CP-10
RDRP	reversible-deactivation radical polymerization	CP-19
RITP	reverse iodine-transfer polymerization	CP-37
ROMP	ring-opening metathesis polymerization	CP-126
ROP	ring-opening polymerization	CP-11
SBRP	organostibane-mediated radical polymerization	CP-35
SET-LRP	single-electron-transfer living-radical polymerization (deprecated term)	CP-30
SET-RDRP	single-electron-transfer RDRP	CP-30
SFRMP	stable-free-radical-mediated polymerization (deprecated term)	CP-24
SRMP	stable-radical-mediated polymerization	CP-24
TERP	organotellurium-mediated radical polymerization	CP-36

[a] Acronyms, initialism, abbreviation, or symbol.

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