

Terminology for reversible-deactivation radical polymerization previously called “controlled” radical or “living” radical polymerization (IUPAC Recommendations 2010)*

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Abstract: This document defines terms related to modern methods of radical polymerization, in which certain additives react reversibly with the radicals, thus enabling the reactions to take on much of the character of living polymerizations, even though some termination inevitably takes place. In recent technical literature, these reactions have often been loosely referred to as, inter alia, “controlled”, “controlled/living”, or “living” polymerizations. The use of these terms is discouraged. The use of “controlled” is permitted as long as the type of control is defined at its first occurrence, but the full name that is recommended for these polymerizations is “reversible-deactivation radical polymerization”.

Keywords: active-dormant equilibria; aminoxyl-mediated; AMRP; atom transfer; ATRP; chain polymerization; degenerative transfer; DTRP; controlled; IUPAC Polymer Division; living; nitroxide-mediated; NMRP; radical; RAFT; reversible-deactivation; reversible-addition-fragmentation chain transfer.

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1. INTRODUCTION

In conventional radical polymerization, the component steps in the process are chain initiation, chain propagation, chain termination, and sometimes also chain transfer. The process is a classical chain reaction, usually analyzed kinetically on the assumption of a stationary state with respect to the concentration of chain carriers (radicals). The lifetime of an individual radical is very short and equal to the

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period of chain growth for that chain, the termination step involves the mutual destruction of two chain carriers, and the distribution of molecular weights (molar masses) of the resulting polymers is rather broad.

Since the early 1980s, it has been found that certain additives are able to react reversibly with the chain carriers. Because the reaction is reversible, the period of chain growth of an individual propagating chain may be extended to the duration of the experiment. However, for most of the time, chains are in an inert (dormant) state, unable to participate in chain propagation or termination. Thus, polymerization conditions can be chosen such that the majority of chains are living. Most of these are in a dormant form, and at any given instant only a small fraction are active chains capable of chain growth. As long as the interconversion of active and dormant forms is rapid compared to propagation, all chains are able to grow at the same rate. As a result, with appropriate choice of reagents and reaction conditions, the process may take on much of the character of a living polymerization, i.e., a reaction from which chain termination and irreversible chain transfer are absent [1]. A consequence is that it becomes possible to synthesize block copolymers by the sequential addition of different monomers under conditions that support the interconversion of active and dormant chains. If, in addition, the initiating species are fully consumed prior to any appreciable chain growth, all chains grow at the same rate and the distribution of molar masses of the products can be much narrower than in the conventional radical polymerization and approach a Poisson distribution.

This type of radical polymerization has attracted a great deal of interest but the various authors have each tended to develop their own terminology, with the result that there is a confusing diversity of terms in use, some of which conflict with accepted definitions of terms. Among the terms that have been used are: controlled radical polymerization; living radical polymerization; controlled/living polymerization; but this selection is only indicative of the range of names that need to be considered. Other terms have been coined to describe specific types of polymerization. These include atom-transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP) (aminoxyl-mediated polymerization, AMP), reversible addition-fragmentation chain-transfer (RAFT) polymerization, and the list seems to grow steadily year on year.

An earlier attempt to address the attendant problems resulted in a paper [2] which, in recommending a revision of IUPAC terminology, rather than resolving the issue served to widen the discussion. The ensuing correspondence, as evidenced by a search of the Wiley Interscience web site [3], makes it clear that in essence there are two main schools of thought with neither willing to yield to the other's arguments such that parallel terminologies remain in use; this is a situation that IUPAC cannot ignore. For this reason, the Subcommittee on Polymer Terminology of IUPAC's Polymer Division (the SPT) has attempted to rationalize the situation by recommending definitions of the most important terms relating to reactions of this type.

At the commencement of the project, at a time when no definition had been agreed upon and the breadth of the subject was not clear, the phenomenon was coined as "radical polymerization with minimal termination—so-called 'living' and/or 'controlled' polymerization". Thus, central to much of the argument [2,3] underlying the need for this project is an understanding conveyed by two words, "living" and "controlled". As elaborated below, within chemistry, the use of the first of these is confined mainly to the present context, i.e., living polymerizations, whereas the second is used in many contexts.

The IUPAC-recommended definition of living polymerization first appeared in the "Glossary of basic terms in polymer science" in 1996 [4]. It is essentially the same as the one given below as Definition 2.20, which is identical to that in the recently published "Glossary of terms related to kinetics, thermodynamics, and mechanism of polymerization (the so-called "Kinetics document") [5] and predates the arguments surrounding its application to radical polymerizations. It was advanced against the background of its long use in the field of anionic polymerization and a ready grasp of the features of such polymerizations that confer livingness upon them. In essence, the understanding was that though termination and transfer reactions, as defined in Section 2, are extremely difficult to eliminate from any polymerization owing to residual impurities, at least conceptually they can be eliminated from

some anionic polymerizations. Furthermore, in the hands of the most experienced practitioners, their elimination can to all intents and purposes be achieved. In contrast, for a radical polymerization, even when such processes are undetectable using state-of-the-art techniques, they can never be eliminated, even conceptually, for the reason that termination by radical-radical reactions will always occur. Likewise, given the facility that propagating radicals have to abstract atoms, chain-transfer reactions are also commonplace. As a consequence, IUPAC cannot undertake to relax the present definition of a living polymerization in order to accommodate present usage in the context of radical polymerizations. By the same token, it cannot accept the continued and ubiquitous application of the word “living” to radical polymerizations, no matter how minimal the termination might be within such systems.

The word “controlled” is not defined by IUPAC except in specified contexts. Nonetheless, its use is frequent and is most commonly applied to the conditions for a synthesis or under which a measurement is carried out, i.e., in relation to the imposition of some external influence. In polymer chemistry, the term “diffusion-controlled termination” is used to describe a *chain termination* in a *chain polymerization* in which the rate-determining step is limited only by diffusion [5]. It is also applied to the consequences of following one particular methodology as opposed to another, and that is the sense in which it is being used in the present context. Whether or not the feature that is controlled is, for example, the near constancy of an average radical lifetime over the course of a polymerization or the quality of the polymeric product that results (see Definition 2.13), the reactions that are the subjects of this project, by their very nature, are exercising a control which is not offered by other reactions that yield the same polymer. It might be argued that all polymerization reactions exercise a control of sorts, but here it is implicit that superior product attributes are to be expected, typically, molecular weight control, a narrow molecular weight distribution, end-group control, or the ability to chain extend and thereby facilitate the synthesis of a block copolymer the block lengths of which are controlled. That is the sense in which the word “controlled” has crept into the language of polymer synthesis in recent years, and it is hard to fault. It is not a misnomer, and *controlled polymerization* has now been defined by IUPAC [5]. Furthermore, by now, anyone working as a polymer scientist understands and accepts what is implied by its extended usage within a compound adjective that characterizes a polymerization. It remains, however, unacceptable to use the term “controlled” by itself to imply a specific form of control without specifying what is being controlled, and the term “controlled polymerization” cannot by itself be used as a class name for polymerizations where the outcome is controlled by reversible-deactivation.

The terminology to be adopted must be consistent with that in existing IUPAC documents, so in Section 2 a list of definitions already included in the Kinetics document [5], and which are of particular relevance in the present context, precedes the new recommendations. For the most part, identical wording has been adopted for these definitions. In one instance, the definition has been adapted from the definition in the Kinetics document and is compatible with all the other definitions, and a possible ambiguity in Note 1 of Definition 2.13 has been eliminated. In some cases, additional notes relating to the terms will be found in the Kinetics document [5]. Throughout, cross-references to terms defined elsewhere in the present document are denoted in italic typeface.

2. BASIC DEFINITIONS

2.1 active center (in a polymerization)

active site

kinetic-chain carrier

Site on a *chain carrier* at which reaction occurs.

2.2 active site (in a polymerization)

See *active center*.

2.3 chain activation

See *chain reactivation*.

2.4 chain carrier

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

2.5 chain deactivation

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

2.6 chain initiation (in chain polymerization)
initiation

Chemical reaction in which *initiating species* add to monomer molecules to form chain carriers.

2.7 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.

2.8 chain propagation (in a chain polymerization)
propagation

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

2.9 chain reactivation
chain activation

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

2.10 chain termination (in a chain polymerization)
irreversible chain deactivation
termination

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

2.11 chain transfer (in a chain polymerization)

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

2.12 chain-transfer agent

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

2.13 controlled polymerization

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

Note 1: The expression “controlled polymerization” is sometimes used to describe a *radical* or *ionic polymerization* in which *reversible-deactivation* of the *chain carriers* is an essential component of the mechanism, 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), nitroxide- [aminoxyl] mediated polymerization (NMP), or *reversible-addition-fragmentation chain transfer* (RAFT) polymerization.

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

2.14 degenerate chain transfer

See *degenerative chain transfer*.

2.15 degenerative chain transfer

degenerate chain transfer

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

2.16 dormant polymer chain (adapted from the definition in [5])

Temporarily deactivated *chain carrier*.

2.17 initiating species

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

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

Note 2: In radical polymerization, initiating species formed directly from an initiator are called “primary radicals”.

2.18 initiation (in a chain polymerization)

See *chain initiation*.

2.19 irreversible chain deactivation

See *chain termination*.

2.20 kinetic-chain carrier

See *active center*.

2.21 living polymerization

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

2.22 propagation (in a chain polymerization)

See *chain propagation*.

2.23 radical polymerization

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

2.24 reversible chain deactivation

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

2.25 termination (in a chain polymerization)

See *chain termination*.

3. DEFINITIONS OF THE TYPES OF POLYMERIZATION TO BE CONSIDERED

3.1 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.

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 discouraged. Definition 84 in the Kinetics document [5] stipulates that chain termination and irreversible chain transfer must be absent if a polymerization is to be regarded as living. Examples of discouraged 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 polymerization mediated by an aminoxyl (or similarly acting substance) all fall into this polymerization category.

Note 4: When the equilibria are established rapidly compared to the lifetime of the majority of the polymer chains, 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.

The essential characteristics of reversible-deactivation radical polymerization are also displayed by reactions in which the *chain carriers* are not radicals. Hence, a more general definition is:

3.2 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.

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

4. DEFINITIONS OF RELATED TERMS

4.1 stable-radical-mediated polymerization, SRMP

stable-free-radical-mediated polymerization, SFRP

Controlled reversible-deactivation radical polymerization in which the deactivation involves reversible coupling with stable (persistent) free radicals.

Note 1: This term embraces *aminoxyl-mediated radical polymerization* and *organometallic-mediated radical polymerization*.

Note 2: The use of the term “free radical” is discouraged in IUPAC terminology [5].

4.2 aminoxyl-mediated radical polymerization, AMRP

nitroxide-mediated (radical) polymerization, NMP, NMRP

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

Note: The term “nitroxide” is discouraged in IUPAC nomenclature, which instead uses the term “aminoxyl” [1].

4.3 organometallic-mediated radical polymerization, OMRP

Stable-free-radical-mediated polymerization in which the deactivation of the radicals involves reversible cleavage of a metal-carbon bond.

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

4.4 atom-transfer radical polymerization, ATRP

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

4.5 transition-metal-mediated radical polymerization

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

Note: The term “transition-metal-mediated radical polymerization” is sometimes used as a synonym for *atom-transfer radical polymerization*. This use of the term is discouraged since it also includes *organometallic-mediated radical polymerization*.

4.6 degenerate-transfer radical polymerization, DTRP

Controlled reversible-deactivation radical polymerization in which the deactivation of the radicals involves degenerative transfer (DT) of a group (or atom).

Note: Examples of DT-active groups include those mentioned below under *reversible-addition-fragmentation chain-transfer polymerization*, iodine (iodine transfer polymerization, ITP) and certain derivatives of Te, As, Sb, or Bi.

4.7 reversible-addition-fragmentation chain-transfer polymerization, RAFT polymerization, RAFT

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.

Note 1: Examples of RAFT agents include certain dithioesters, trithiocarbonates, xanthates (dithiocarbonates), and dithiocarbamates.

Note 2: RAFT with xanthates is also known as MADIX (macromolecular design by interchange of xanthate).

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