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TERMINOLOGY FOR RADICAL POLYMERIZATIONS WITH MINIMAL TERMINATION – THE SO-CALLED 'LIVING' AND/OR 'CONTROLLED' RADICAL POLYMERIZATION

(IUPAC Recommendations 200X)

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Terminology for radical polymerizations with minimal termination – the so-called ‘living’ and/or ‘controlled’ radical polymerization

(IUPAC Recommendations 200X)

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 polymerisations. In recent technical literature, these reactions have often been referred to as, *inter alia*, ‘controlled’ or ‘controlled/living’ polymerizations. The phenomenon is defined, a name for it is recommended, and definitions are provided for the relevant basic terms.

Keywords: chain polymerisation; reversible deactivation; active-dormant equilibria; living; controlled, radical; atom transfer; degenerative transfer; reversible addition fragmentation chain transfer; nitroxide-mediated; IUPAC Polymer Division.

CONTENTS

1. INTRODUCTION
2. BASIC DEFINITIONS
3. SPECIFICATION OF THE RANGE OF REACTIONS TO BE CONSIDERED
4. THE NAME OF THIS TYPE OF RADICAL POLYMERIZATION
5. DEFINITIONS OF RELATED TERMS
6. MORE GENERAL CONSIDERATIONS
7. REFERENCES

1. INTRODUCTION

In traditional 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 analysed kinetically on the assumption of a stationary state with respect to the concentration of chain carriers (radicals). The life-time of a radical is very short, 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, comparable with a Gaussian distribution.

Within the last 20 years, it has been found that certain additives are able to react reversibly with the chain carriers to reduce the effective concentration of active chain carriers, and the probability of mutual chain termination. Because the reaction is reversible, the life-time of an individual propagating chain is extended but most of the time it is 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 rate of equilibration of active and dormant forms is rapid with respect to propagation, all chains are able to grow simultaneously. As a result, the process takes on much of the

RADICAL POLYMERIZATIONS WITH MINIMAL TERMINATION – THE SO-CALLED 'LIVING' AND/OR 'CONTROLLED' RADICAL POLYMERIZATION

character of a living polymerisation, *i.e.*, a reaction from which chain termination and irreversible chain transfer are absent [1].

One of the results is that the distribution of molar masses of the products can be much narrower than in the conventional case, and another is that it becomes possible to synthesise block copolymers by the sequential addition of monomers under conditions that support the equilibration of active and dormant chains.

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; atom transfer radical polymerization (ATRP); nitroxide-mediated polymerization (NMP); and reversible addition-fragmentation chain transfer (RAFT) polymerization, but this selection is only indicative of the range of names that need to be considered.

For this reason, the Sub-Committee for Polymer Terminology of Division IV of IUPAC (the SPT) has attempted to rationalise the situation by recommending definitions of the most important terms relating to reactions of this type. The terminology to be adopted must be consistent with that in existing IUPAC documents, so a list of definitions already included in the Glossary of Terms Related to Kinetics, Thermodynamics, and Mechanism of Polymerization (the 'Kinetics document') [2], 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 other cases, the definitions are adapted from definitions in the Kinetics document and are compatible with all the other definitions. In all cases, the number of the appropriate definition in the Kinetics document is added to the name in parentheses, and Notes relating to the terms will be found there.

2. BASIC DEFINITIONS

2.1 active centre (in a polymerization) (4)

Site on a chain carrier at which reaction occurs.

2.2 chain activation (18)

Conversion of an inactive chain into a chain carrier.

2.3 chain carrier (19)

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

2.4 chain deactivation (21)

Conversion of a chain carrier into an inactive species.

2.5 chain initiation (adapted from 24)

Chemical reaction in which primary radicals add to monomer molecules to form chain carriers.

A. D. JENKINS and G. MOAD

2.6 chain polymerization (25)

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.

2.7 chain propagation (in a polymerization) (adapted from 26)

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.

2.8 chain reactivation (27)

Conversion of an inactive chain into a chain carrier.

2.9 chain termination (29)

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

2.10 chain transfer (30)

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

2.11 degenerative chain transfer (48)

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.

2.12 dormant polymer chain (adapted from 112)

Temporarily deactivated polymer chain.

2.13 living polymerization (84)

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

2.14 radical polymerization (107)

Chain polymerization in which the active centres are radicals.

2.15 reversible chain deactivation (112)

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

3. SPECIFICATION OF THE RANGE OF REACTIONS TO BE CONSIDERED

The name of the phenomenon at the heading of this document was coined at the commencement of the project, at a time when no definition had been agreed and the breadth of the subject was not clear. The definition of the type of reaction has since been formulated as follows.

Chain polymerization, propagated by radicals that are deactivated reversibly, bringing them into active-dormant equilibria which may involve more than two states.

RADICAL POLYMERIZATIONS WITH MINIMAL TERMINATION – THE SO-CALLED 'LIVING' AND/OR 'CONTROLLED' RADICAL POLYMERIZATION

Note 1: Atom-transfer radical polymerization, reversible addition-fragmentation transfer, and polymerization mediated by a nitroxide (or similarly-acting substance) all fall into this category.

Note 2: 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 by the sequential addition of monomers.

4. THE NAME OF THIS TYPE OF RADICAL POLYMERIZATION

The name of this type of polymerization shall be
Controlled Reversible-Deactivation Radical Polymerization

Note 1: The abbreviated name **Controlled Radical Polymerization** shall be permitted, *provided that its context (i.e., the nature of the control) is specified at the first opportunity.*

Note 2: Names containing the word 'living' are discouraged. Definition 84 in the 'Kinetics document' [2] stipulates that chain termination and irreversible chain transfer must be absent if a reaction is to be regarded as living, and this is not usually the case.

5. DEFINITIONS OF RELATED TERMS

5.1 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 with transition-metal complexes.

Note: An alternative name for this process is Transition-Metal-Mediated Polymerization.

5.2 Degenerative 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). Examples of DT-active groups include dithioesters, dithiocarbamates, iodine, and certain derivatives of Te, As, Sb or Bi.

5.3 Reversible Addition-Fragmentation Chain-Transfer Polymerization (RAFT)

Controlled reversible-deactivation radical polymerization in which chain activation and chain deactivation involve a degenerate chain-transfer process which occurs by a two-step addition-fragmentation mechanism.

A. D. JENKINS and G. MOAD

5.4 Nitroxide-Mediated Polymerization (NMP) Aminoxyl-Mediated Polymerization (AMP)

Controlled reversible-deactivation radical polymerization in which the deactivation of the radicals involves reversible coupling with aminoxyl radicals.

Note: The term 'nitroxide' is not officially recognised in IUPAC nomenclature, which instead uses the term 'aminoxyl' [1].

6. MORE GENERAL CONSIDERATIONS

The essential characteristics of this type of polymerization mechanism are also displayed by reactions in which the chain carriers are not radicals. A general definition of the phenomenon of Controlled Reversible-Deactivation Polymerization might then be the following.

Chain polymerization, propagated by chain carriers that are deactivated reversibly, bringing them into active-dormant equilibria which may involve more than two states.

7. REFERENCES

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