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MACROMOLECULAR DIVISION
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BASIC CLASSIFICATION AND DEFINITIONS OF POLYMERIZATION REACTIONS

(IUPAC Recommendations 1994)

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Basic classification and definitions of polymerization reactions (IUPAC Recommendations 1994)

Synopsis

Polymerizations have traditionally been classified as addition polymerizations and condensation polymerizations. However, developments in chemical methods of polymerization and syntheses of new types of polymer have meant that more than two classes of polymerization need to be defined if a clear terminology is to be achieved. Several, alternative, two-fold terminologies have been introduced ad hoc into the literature. All have serious shortcomings in terms of comprehensiveness, unambiguity and scientific correctness.

The present document defines basically four categories of polymerization - chain polymerization, condensative chain polymerization, polycondensation and polyaddition - which cover unambiguously all presently known types of polymerization. The definitions also allow further qualification if desired e.g. cationic chain polymerization.

The present definitions are in accord with the recommended IUPAC Glossary of Terms for Physical Organic Chemistry (1983) and the IUPAC Basic Definitions of Terms Relating to Polymers (1974).

INTRODUCTION

In its report on "Basic Definitions of Terms Relating to Polymers" published in 1974 (ref. 1), the IUPAC Commission on Macromolecular Nomenclature defined the terms "addition polymerization" (polymerization by repeated addition processes) and "condensation polymerization" (polymerization by repeated condensation processes, i. e., with the elimination of small molecules). At that time, the terms were intended to classify polymerization reactions according to whether or not small molecules are formed in the growth reaction. Meanwhile, widespread use of the term addition polymerization for polymerizations with growth steps that are chain reactions has resulted in the introduction of alternative terms aimed at a clear distinction in terminology between the chain or non-chain nature of the growth reaction and the stoichiometry associated with the formation or not of a small molecule during that reaction (ref. 2). Most prominent amongst these are the terms "chain-growth polymerization" and "step-growth polymerization." However, conflicting usage in the literature and contradictory explanations of these terms in textbooks indicate the timeliness of a new set of definitions.

The definitions given in this document use a single term for polymerizations in which polymer chains grow via chain-reaction mechanisms, with the stoichiometry specified additionally, if so desired. "Polyaddition" and "polycondensation" are invoked only in the naming of polymerizations proceeding through reactions between molecules of all degrees of polymerization.

The definitions are in accord with the IUPAC terms for organic chemistry (ref. 3) and the basic definitions (ref. 1).

DEFINITIONS

1. chain polymerization

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

Notes:

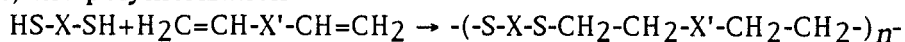
1. A chain polymerization consists of initiation and propagation reactions, and may also include termination and chain transfer reactions.
2. The adjective "chain" in "chain polymerization" denotes "chain reaction" rather than "polymer chain".
3. Propagation in chain polymerization often occurs without the formation of small molecules. However, cases exist where, at each propagation step, a low-molar-mass by-product is formed as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed amino-acid N-carboxyl anhydrides). When a low-molar-mass by-product is formed the adjective *condensative* is recommended to give the term "condensative chain polymerization".

4. The growth steps are expressed by



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

5. The term "chain polymerization" may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g., ring-opening chain polymerization and cationic chain polymerization.
6. There exist, exceptionally, some polymerizations that can proceed via chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization



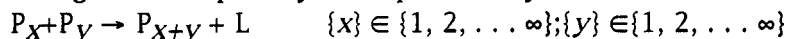
proceeds via a radical chain reaction with intermolecular transfer of the radical center. The growth step, however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition. If required, the classification can be made more precise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

2. polycondensation

A polymerization in which the growth of polymer chains proceeds by condensation reactions between molecules of all degrees of polymerization.

Notes:

1. The growth steps may be expressed by



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

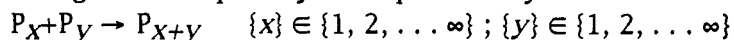
2. The earlier term "polycondensation" (as defined in ref. 1) was synonymous with "condensation polymerization". It should be noted that the current definitions of polycondensation and condensative chain polymerization were *both* embraced by the earlier term "polycondensation".

3. polyaddition

A polymerization in which the growth of polymer chains proceeds by addition reactions between molecules of all degrees of polymerization.

Notes:

1. The growth steps may be expressed by



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

2. The earlier term "addition polymerization" (as defined in ref. 1) embraced both the current concepts of "polyaddition" and "chain polymerization", but did not include "condensative chain polymerization".

SUMMARY

The classification of the types of polymerization resulting from the definitions, except for the polymerizations of definition 1, note 6, may be summarized in the following table:

	Growth Mechanism	Monomers reacting with active polymer chains	Molecules of all sizes reacting together
	Reaction Type	Chain reaction	Usually non-chain reaction
Stoichiometry	With low-molar-mass by-products	CONDENSATIVE CHAIN POLYMERIZATION	POLYCONDENSATION
	Without low-molar-mass by-products	CHAIN POLYMERIZATION	POLYADDITION

REFERENCES

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