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Reconsidering terms for mechanisms of polymer growth: the “step-growth” and “chain-growth” dilemma

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The terms “step-growth polymerization” and “chain-growth polymerization” are used widely in both written and oral communications to describe the two main mechanisms of polymer growth. As members of the Subcommittee on Polymer Terminology (SPT) in the Polymer Division of the International Union of Pure and Applied Chemistry (IUPAC), we are concerned that these terms are confusing because they do not describe the fundamental differences in the growth of polymers by these methods. For example, both polymerization methods are comprised of a series of steps, and both produce polymer chains. In an effort to recommend comprehensive terms, a 1994 IUPAC Recommendation from the then version of SPT suggested *polycondensation* and *polyaddition* as terms for the two variants of “step-growth polymerization”, and similarly *chain polymerization* and *condensative chain polymerization* for the two variants of “chain-growth polymerization”. However, these terms also have shortcomings. Adding to the confusion, we have identified a wide variety of other terms that are used in textbooks for describing these basic methods of synthesizing polymers from monomers. Beyond these issues with “step-growth” and “chain-growth”, synthesis of polymers one monomer unit at a time presents a related dilemma in that this synthetic strategy is wholly encompassed by neither of the traditional growth mechanisms. One component of the mission of IUPAC is to develop tools for the clear communication of chemical knowledge around the world, of which recommending definitions for terms is an important element. Here we do not endorse specific terms or recommend new ones; instead, we aim to convey our concerns with the basic terms typically used for classifying methods of polymer synthesis, and in this context we welcome dialogue from the broader polymer community in a bid to resolve these issues.

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Introduction

Nearly all polymers that are chemically synthesized from monomers can be grouped into two classes based on their mechanism of polymer growth. The terms “step-growth” and “chain-

growth” are currently used widely by the polymer chemistry community to classify these mechanisms of polymer growth.¹ In brief, “step-growth” typically refers to polymers that are synthesized from one (or more) type(s) of multifunctional monomer(s) where at least bifunctionality is required,

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	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

Fig. 2 Recommendations on polymerization terminology made by SPT in 1994.⁴

between *polyaddition* and “addition polymerization” has created significant confusion because *addition* is employed quite differently in these two sets of terms, having migrated from meaning “chain-growth” under Carothers to “step-growth” under IUPAC.

(2) Furthermore, *polyaddition* is itself a questionable term. IUPAC has defined the term *addition reaction* to be a *chemical reaction of two or more reacting molecular entities, resulting in a single reaction product containing all atoms of all components with formation of two chemical bonds and a net reduction in bond multiplicity in at least one of the reactants.*⁷ Thus a *chain polymerization* (as defined in 1994) is a series of addition reactions, while *polyaddition* has a limited definition that excludes chain polymerization.

(3) In the 1994 document,⁴ *chain polymerization* was implicitly proposed as a term covering two situations: (i) a generic term encompassing all polymerizations that proceed via “chain growth”-type growth mechanisms, *i.e.*, 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*, and (ii) a specific subclass of chain polymerizations in which there is no condensate, which is the case in most chain polymerizations. The function of the term *chain polymerization* as both a generic term and a specific term has created some confusion. In contrast, in the case of “step-growth”-type growth mechanisms, no generic term was proposed, and filling this void is probably one reason why the term “step-growth” is still widely used. In internal SPT discussions we have used “non-chain polymerization” to cover polymerizations that proceed in a “step-growth” manner, but this is not ideal in that it defines these polymerizations by what they are not rather than providing a definition that alludes to their common characteristics.

(4) Another problem of a similar nature is that all forms of polymerization generate polymer chains, but the term *chain polymerization* might be taken to imply that only such polymerizations do so, and that polyaddition and polycondensation do not. The issue here is that the word “chain” has multiple meanings (in this case *macromolecule* and *chain reaction*, respectively). As stated above, in the current IUPAC definition the chain in *chain polymerization* refers to polymerization

occurring through a *chain reaction* process; this may not be immediately obvious. This overlap in meaning creates ambiguity and therefore uncertainty, especially for non-native speakers of English. The current terminology also causes problems when considering reactions such as the polymerization of a dithiol and an α,ω -diene (a thiol-ene polymerization): the polymer forms in a “step-growth” type growth mechanism, but in a radical chain reaction process.

In addition to the specific points listed above, there are additional issues with the 1994 terms that have arisen in the intervening quarter century due to developments in polymer synthesis. For example, there are new polymerization growth mechanisms that fall outside the two traditional categories, and are therefore not covered by any current terminology, recommended by IUPAC or otherwise (detailed below). There are also methods to synthesize polymers from monomers that have been known for decades that do not fall cleanly into either of these traditional categories.

In view of the above situation, it is not surprising that the 1994 terms have not been widely adopted by the polymer community. In fact, we have found no textbooks that employ all four terms recommended in the 1994 document (see below). For this reason, many of us find ourselves using the terms “step-growth” and “chain-growth” in our publications and classes, even though IUPAC has never endorsed these terms, and despite the confusion this situation causes to students learning polymer chemistry. Here, we attempt to outline the dilemmas caused by the terms “step-growth” and “chain-growth” and their various synonyms and subclasses.

This contribution is not a recommendation of terms we think should be used; rather, we simply aim to make clear to the community why we think all present terminology is problematic. No set of terms is perfect, but we believe there must be a better system than the current options. Ideally, we would like to avoid the many shortfalls mentioned above, at the same time employing descriptive accuracy *and* finding simplicity that will be attractive to our diverse community. That this can be achieved is evidenced, for example, by the widespread replacement of the illogical term ‘polydispersity index’ by the more logical ‘dispersity’ in the decade since publication of IUPAC Recommendations (by SPT) on this matter in 2009.⁸

Discussion

Historical development of terms

Although Staudinger attempted to classify different types of polymerization processes,⁹ it was Wallace H. Carothers who first recognized the mechanistic distinction that would eventually lead to the “step-growth”/“chain-growth” classifications. Carothers was dealing with terms for polymers prepared by the two mechanisms in a pioneering period when even the definition of the general term “polymer” was still under discussion.¹⁰ At that time some definitions of polymer stated that a polymer and its monomer must have the same atoms in the same proportions.^{9,11} When introducing his theory of the



preparation of high-molar-mass polymers by reaction of monomers bearing functional groups, Carothers proposed the terms “addition or A polymers” for polymers in which the repeat unit has the same molecular formula as the monomer, and “condensation or C polymers” where the repeat unit is different from the monomer(s). Further, he defined two types of mechanisms of polymer growth: (i) “addition polymerizations” leading to A polymers, and (ii) “condensation polymerizations” leading to C polymers. The problem with these terms would soon become clear—by first classifying polymer structures as “A” or “C”, then deriving the terms “addition polymerization” and “condensation polymerization” for their growth mechanisms, a direct correspondence between polymer structure and mechanism of polymer growth was created. This system does not effectively capture polymers that can be synthesized in different ways. For example, poly(oxyethylene) is a C polymer when synthesized by polycondensation of ethane-1,2-diol, but an A polymer if it is prepared by ring-opening polymerization of oxirane (Fig. 3).

Soon after Carothers there was the discovery by Otto Bayer at I. G. Farbenindustrie of the formation of polyurethanes from the reaction of diols and diisocyanates.^{6,12} This polymerization proceeds like a condensation polymerization, but no low-molar-mass by-product is released, meaning that technically it is an “addition polymerization” according to the terminology of Carothers. In view of this difficulty, Bayer named his process a “polyaddition”. This led to confusion because of the similarity of the terms “addition polymerization” and “polyaddition”.¹³

Despite these difficulties, the Carothers terminology was adopted for a long time, as reflected by it being the basis of the 1974 IUPAC recommendation,³ as already mentioned. Of greatest significance was this terminology being used in Flory's influential 1953 textbook.¹⁴

Flory continued to use the terms “addition polymers” and “condensation polymers”, as well as “addition polymerization” and “condensation polymerization”, but he was well aware of inescapable problems with them. For example, he wrote: “Whether or not the structural unit differs in composition from the monomer from which it is derived is of no particular significance. The principal justification for the differentiation between condensation and addition polymers (and polymerizations) lies in the marked contrast between the processes by which they are formed”. And elsewhere: “The original Carothers distinction between addition and condensation

polymers, if applied quite literally, oftentimes fails to serve the desired purpose”. Flory also recognized the problem posed by polyurethanes and the like, writing (his italics) “a *polymerization process* which proceeds by a reaction between pairs of functional groups with the formation of a type of interunit functional group not present in the monomer(s) will be regarded as a condensation polymerization”. In a polymerization sense this is reasonable, but in a broader chemistry sense it is not, because polyurethane formation does not involve “condensation” as it is generally understood by all chemists. [IUPAC defines the term *condensation reaction* as a (usually stepwise) reaction in which two or more reactants (or remote reactive sites within the same molecular entity) yield a single main product with accompanying formation of water or of some other small molecule, e.g. ammonia, ethanol, acetic acid, hydrogen sulfide.¹⁵]

Flory supported his recommendation as follows: “It is thus appropriate to broaden the definition of condensation polymers ... to include also those polymers which on chemical degradation (e.g., by hydrolysis) yield monomeric end products differing in composition from the structural units”. Flory does this because he wants to avoid “the confusion which would arise” if the one polymer were to be categorized in different ways depending on how it was made, e.g., the poly(oxyethylene) example above. This means that, for example, nylon-6 made by ring-opening polymerization of ϵ -caprolactam, a chain-polymerization process, would still be termed a condensation polymer by Flory. He recognized the incongruity of this, giving the example of poly(lactic acid), but nevertheless still felt compelled to have a classification primarily based on polymer structure rather than mechanism.

The mechanism of chain polymerization was elucidated by Norrish and Brookman in 1939.¹⁶ According to a search of the Chemical Abstracts Service database using SciFinder™, the term *chain polymerization* (not “chain-growth polymerization”) was first introduced to refer to these reactions by Hoshino and Iwakura in 1947.¹⁷ It is not clear when the term “step (-growth)” first appeared, but Elias writes that it was in response to the problems in the polymer-based classification of Carothers:¹³ “It turned out later that the true distinguishing factor was ... the growth steps. ...Organic chemists therefore started to refer to ‘condensation polymerizations’ as ‘step-growth polymerizations’ since the reaction products could be easily isolated and reacted again after several ‘steps’ whereas those of the known ‘addition polymerizations’ could not”. In other words, the slow rate of “step-growth” polymerizations usually allows for them to be easily stopped and their intermediates isolated, similar to “steps” in preparative synthesis of low-molar-mass organic compounds. Therefore, this use has nothing to do with steps in the mechanistic sense, a fact not widely appreciated today. In this sense this term is “an unlucky choice of words”.¹³

Unlucky or not, the term “step-growth” has stuck, becoming part of the dominant classification system of “step-growth polymerization” and “chain-growth polymerization”. According to a SciFinder™ search, these terms do not appear

Synthesis of poly(oxyethylene), a “C polymer”



Synthesis of poly(oxyethylene), an “A polymer”



Fig. 3 Synthesis of poly(oxyethylene) by two different routes.



in the abstracts of papers in the chemical literature before their use in a well-known 1967 textbook by Robert Lenz,¹⁸ although in the textbook the author makes no claim to be introducing a new terminology.

Terms used in current textbooks

Perhaps because of the problems with all existing terms, and despite the 1994 classification system proposed by SPT, terminology in textbooks continues to vary widely. It is largely pointless to suggest terminology if it is not adopted. We therefore investigated what terms people actually use for basic classification of polymerization reactions. We examined the terms used in approximately 40 textbooks, including multiple editions of some. This allowed us to gauge the influence of the definitions recommended by SPT in 1994 over time. We present our findings in two categories.

First, Table 1 gives terms used in a selection of textbooks on general chemistry and organic chemistry (as indicated in the Category column). The selection is not intended to be comprehensive but represents a range of textbooks that we use in our classes across the world. A careful look at these textbooks reveals that despite most of these books being published in the last decade, the terms recommended in 1994 are completely absent. Some authors discuss polymerization but do not categorize by specific types of polymerization methods, perhaps in part due to confusion over which terminology to use. In terms of book categories, it is evident that general chemistry textbooks almost all retain the 1930s “addition/condensation polymerization” classification. With organic chemistry textbooks there is a strong preference for “chain-growth” and “step-growth”.

Overall, it is clear that in undergraduate chemistry textbooks there exists a somewhat chaotic situation regarding classifications: there is no dominant terminology for basic mechanisms of polymer growth, and IUPAC-recommended ter-

minology is absent. This is unlikely to be because it is rejected, but almost certainly because it is not known. This situation is undesirable in several ways. First, it propagates the use of logically flawed terminology. Second, it means that students are confronted by different terms for the same thing, depending upon the textbook used. Finally, how should translators of books into languages other than English deal with a non-uniform situation like this?

It is reasonable to expect more uniform usage of terminology from authors of textbooks on polymer science. Here we examined a selection of these with respect to which basic polymerization terms are used. Our survey is presented in Table 2, again organized by author last name. Rather than attempting to categorize polymer science books, we instead have given their titles, and these cover a full spectrum from synthetic chemistry to engineering and processing.

The first and overwhelming conclusion from Table 2 is that there is no consensus among polymer science textbook writers regarding which terms should be used, nor are there any preferred sets of terms. Invariably the word “step” is used, but in a variety of different ways: “step-growth”, “stepwise”, “step-reaction” or just plain “step”. Sometimes it is partnered with the same variant of “chain” (e.g. “chainwise” with “stepwise”), but often it is paired with “addition”.

A few authors discuss the 1994 recommendations from SPT. For example, Elias includes a discussion of IUPAC-recommended terms, and he adopts all the terms of Fig. 2 aside from *condensative chain polymerization*, which he spurns on the grounds that “it is illogical to label one subclass with an adjective (*condensative chain polymerization*) but not the other (*chain polymerization*)”. We agree with Elias on this point, noted above as issue (3) in the introduction. Instead, Elias proposes “polyelimination”,^{13,35} which nicely complements polycondensation and polyaddition in a linguistic sense, but seems flawed in several ways: (1) such processes do not meet

Table 1 Terminology employed for basic polymerization growth mechanisms in various textbooks on general chemistry and organic chemistry

Author(s)	Year (edition)	Category	Terminology employed
Blackman <i>et al.</i> ¹⁹	2012 (2 nd)	General	Addition or chain-growth, condensation or step-growth
Burrows <i>et al.</i> ²⁰	2017 (3 rd)	General	Addition polymerization, condensation polymerization
Chang ²¹	2007 (7 th)	General	Addition reactions, condensation reactions
Housecroft & Constable ²²	2010 (4 th)	General	Addition polymerization
Kotz <i>et al.</i> ²³	2018 (10 th)	General	Addition polymers, condensation polymers
Mahaffy <i>et al.</i> ²⁴	2014 (2 nd)	General	Addition polymers, condensation polymers
McMurry <i>et al.</i> ²⁵	2015 (7 th)	General	None
Bruice ²⁶	2014 (7 th)	Organic	Chain-growth polymerization, step-growth polymerization
Bruice ²⁷	2016 (8 th)	Organic	Chain-growth polymerization, step-growth polymerization
Carey & Sundberg ^{28,29}	1990 (3 rd)	Organic	None
Clayden <i>et al.</i> ³⁰	2001 (1 st)	Organic	Polymerizations by carbonyl substitution reactions, polymerization by electrophilic aromatic substitution, polymerization by the S _N 2 reaction, polymerization by nucleophilic attack on isocyanates, polymerization of alkenes
Clayden <i>et al.</i> ³¹	2012 (2 nd)	Organic	None ^a
Karty ³²	2014	Organic	Chain-growth polymerization, step-growth polymerization
Okuyama & Maskill ³³	2013 (1 st)	Organic	None
Vollhardt & Schore ³⁴	2014 (7 th)	Organic	None

^a The relevant chapters from the first edition were removed for the second edition. They remain available as an electronic resource from the publisher.



Table 2 Terminology employed for basic polymerization growth mechanisms in various textbooks on polymer science

Author(s)	Year (edition)	Title	Terminology employed
Carraher ³⁹	2017 (4 th)	Introduction to polymer chemistry	Addition polymerization, step-reaction polymerization
Carraher ⁴⁰	2017(10 th)	Polymer chemistry	Addition polymerization, step-reaction polymerization
Cowie ⁴¹	1991 (2 nd)	Polymers: chemistry and physics of modern materials	Addition polymerization, step-growth polymerization; both together referred to as “chain growth mechanism”
Cowie ⁴²	2007 (3 rd)	Polymers: chemistry and physics of modern materials	Addition polymerization, step-growth polymerization; “chain growth” used to mean both forms together and addition individually
Dotson <i>et al.</i> ⁴³	1995 (1 st)	Polymerization process modeling	Chainwise, stepwise
Elias ³⁵	1997 (1 st)	An introduction to polymer science	Chain-growth polymerization, step-growth polymerization; polyelimination, chain polymerization, polycondensation, polyaddition
Elias ¹³	2005 (2 nd)	Macromolecules, vol. 1 – structure and properties	Chain-growth polymerization, step-growth polymerization; polyelimination, chain polymerization, polycondensation, polyaddition
Hiemenz & Lodge ⁴⁴	2007 (2 nd)	Polymer chemistry	Addition polymers/chain-growth polymerization, condensation polymers/step-growth polymerization
Koltzenburg <i>et al.</i> ⁴⁵	2017 (1 st)	Polymer chemistry	Chain-growth polymerization, step-growth polymerization
Nicholson ⁴⁶	2017 (5 th)	The chemistry of polymers	Chain polymerization, step polymerization
Novak ⁴⁷	1995 (1 st)	Organic polymer chemistry: a primer	Chain-growth, step-growth (said to be synonymous with condensation)
Odian ⁴⁸	1991 (3 rd)	Principles of polymerization	Chain, step (shortenings of chain-reaction, step-reaction)
Odian ³⁸	2004 (4 th)	Principles of polymerization	Chain polymerization, step polymerization
Painter & Coleman ⁴⁹	1994 (1 st)	Fundamentals of polymer science	Chain/addition polymerization, step-growth polymerization
Painter & Coleman ⁵⁰	2008 (1 st)	Essentials of polymer science and engineering	Chain/addition polymerization, step-growth polymerization
Ravve ⁵¹	2012 (3 rd)	Principles of polymer chemistry	Chain-growth polymerization, step-growth polymerization
Rudin ⁵²	1982 (1 st)	The elements of polymer science and engineering	Chain-growth polymerization, step-growth polymerization (polycondensation sometimes instead)
Rudin & Choi ⁵³	2012 (3 rd)	The elements of polymer science and engineering	Chain-growth polymerization, step-growth polymerization (polycondensation sometimes instead)
Stevens ⁵⁴	1999 (3 rd)	Polymer chemistry: an introduction	Chain-reaction condensation, chain-reaction polymerization, step-reaction polymerization, step-reaction addition
Walton & Lorimer ⁵⁵	2000 (1 st)	Polymers	Chain polymerization, step-growth polymers
Young & Lovell ³⁶	1991 (2 nd)	Introduction to polymers	Chain polymerization, step polymerization; polycondensation, polyaddition
Young & Lovell ³⁷	2011 (3 rd)	Introduction to polymers	Chain polymerization, step polymerization; polycondensation, polyaddition

the usual definition of an *elimination reaction*;¹⁵ (2) “polyelimination” sounds like a degradation process, and indeed the different process of side-chain elimination from polymers is sometimes called polyelimination;¹³ (3) a polycondensation could for the same reason be termed a polyelimination. It is telling that Elias explains how the term “step-growth polymerization” is deeply defective, and yet he used it throughout his 1997 textbook due to lack of a better alternative, but then dropped it in his 2005 textbook, opting for the IUPAC-recommended terms *polyaddition* and *polycondensation* instead. Indeed, Elias long ago recognized the terminology dilemma we discuss here.

Young and Lovell also hint at IUPAC influence in two ways: (1) they write of a “modern preference” to use chain and step without “growth”, implying that this is a matter of taste; (2) they introduce the step-polymerization subclasses of polycondensation and polyaddition, in accordance with Fig. 2.^{36,37} However, they make no mention of IUPAC recommendations, and indeed their usage predates the 1994 recommendations.

Finally, Odian suggests in his latest edition, published in 2004,³⁸ that the 1994 recommendations from this subcommittee suggested “polycondensation” as a replacement for all types of “step polymerization”, neglecting to mention the rec-

ommended use of *polyaddition* in polymerizations that follow “step-growth” kinetics but lack a condensate (e.g., polyurethane synthesis). He uses the IUPAC-recommended term *chain polymerization* but does not mention *condensative chain polymerization*.

Several authors in Table 2 use “polycondensation” as a synonym for “step(-growth) polymerization”, and thereby fail to acknowledge that such polymerizations need not involve condensation. Ironically, nearly all textbooks do the one thing that SPT neglected to do in 1994—provide generic terms. The problem is that they have all used some combination of the old, flawed terms. We strive to remedy this problem.

Problems arising from translations of “step-growth” and “chain-growth” into other languages

The official language of IUPAC is English, so we focus here on terminology in English. However, it is worth noting that the terms “step-growth” and “chain-growth” present additional problems for non-native English speakers. While difficulties and ambiguities arise with translations of many technical terms, we find that a clear and precise definition in English tends to reduce problems in translation. In contrast, the lack of clarity and precision in “step-growth” and “chain-growth” in



terminology problem. We also aim to provide a similar structure, including an umbrella term, for *chain polymerizations* that encompasses those with and without condensates. Finally, we will suggest terms for reactions that generate polymers but currently cannot be classified using any of the existing polymerization terms. We welcome input from the community on this matter.

Conclusion

Here we have outlined our concerns with the terms “step-growth” and “chain-growth”, which remain in use, along with several related terms, despite their flaws and the deprecation of their use by IUPAC in 1994. An analysis of terms used historically and in current textbooks was particularly illuminating: despite a clear understanding for many decades of the two types of basic mechanisms of polymer growth, we as a community still have not agreed on terms to describe these two cases. The present use of similar-sounding terms with different meanings adds to the confusion, and this lack of clear and logical terminology causes problems in translating the terms from English into other languages. Furthermore, there are examples of reactions or processes in the field of polymer synthesis that produce polymers, but there are no terms that describe these polymerizations. As a group of polymer scientists, we are working to find a solution. We welcome input from the community as we attempt to remedy these dilemmas. Please let us know your thoughts by emailing us at polymer.terminology@iupac.org. Comments will be read until the end of 2022.

Conflicts of interest

There are no conflicts to declare.

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