Living Polymerization: Rationale for Uniform Terminology

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ABSTRACT: Polymer chemistry textbooks (e.g., B. Vollmert, Polymer Chemistry, Springer-Verlag: New York, 1973, p 37; G. Odian, Principles of Polymerization, 3rd ed., Wiley: New York, 1991, p 8; H. G. Elias, An Introduction to Polymer Science, VCH: Weinheim, 1997, p 51) classify polymerization reactions as chain, step, and living according to the dependence of their degree of polymerization ($\overline{DP}$) or molecular weight ($\bar{M}$) on conversion. This article discusses the rationale for uniform terminology in living polymerization. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 1706–1708, 2000

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Living radical polymerization is currently an area of intense research with many publications and presentations at technical meetings. We have noticed an odd trend in the discussion of these technologies. In private, practically all investigators use the term *living radical polymerization*, but when the subject is discussed publicly, the terminology multiplies. The terms *controlled polymerization*, *living*, *living/controlled*, *pseudo-living*, *living polymerization with reversible deactivation*, and others are scattered throughout the literature. Lack of a common language creates confusion, wastes time and journal space, and has the potential to inhibit computational literature searching.

To illustrate this point, a search of Chemical Abstracts (CAPLUS; accessed February 8, 1999) revealed 484 articles with the term *living (free) radical* (this group includes 11 articles with *quasi-living*, 13 with *psuedo-living*, and 38 with *controlled living*) and 149 articles with the term *controlled (free) radical* (28 of these were also indexed under *living (free) radical*; 20 articles on *diffusion controlled polymerization* have been excluded from this number). There were also articles in this area with technique-specific names, including *atom transfer radical* (or *ATRP*) with

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271 articles, *nitroxide-* (or *nitroxyl* or *N-oxyl*) *mediated* with 80 articles, *stable free radical polymerization* with 30 articles, and *iniferter* (including *photoiniferter*) with 164 articles. A significant fraction of the articles using technique-specific names were not indexed under either *living* or *controlled*.

These problems have been recognized by a number of authors, and some valiant attempts have been made to remedy the situation. We believe these attempts have also compounded this problem in nomenclature. It was recently suggested that the term *controlled radical polymerization* be used instead of *living radical polymerization* "when chain-breaking reactions undoubtedly occur, like in radical polymerization".[1] It was also suggested that the term *controlled/living* could be used for a transition period because researchers "are used to the term living".[1] The solution is problematical. It seeks to reserve the term *living* for an impossible ideal (immortality), thereby removing a valuable term from the vocabulary of the polymer scientist. It also requires that another word, *controlled*, be redefined to have a very specific meaning. This word already has a perfectly good meaning in the context of polymer science, a meaning not necessarily associated with living polymerization. For example, we find that the term *diffusion controlled polymerization* is widely used. *Controlled* or *control* is also used in connection with other mechanisms for controlling polymerization.[2c,d] These include chain transfer (which controls radical polymerizations no less effectively, but in a different sense), catalytic termination, template polymerization, and a number of other methods that control different features of radical polymerization. The art of polymer science is to control the polymerizations to achieve particular results. Thus, the term *controlled* is too broad to be monopolized by a single branch of polymer science or to be applied exclusively to any specific feature of polymerization.

The phenomenon of living polymerization will be observed whenever propagation and reversible termination are significantly faster than any process for irreversible termination.[3] The first reported example of this phenomenon was the anionic polymerization of styrene.[4] Since that time, living cationic and living covalent/coordination polymerizations have been reported.[5] Most recently, living radical polymerizations have been reported.[2] Examples of the latter include nitroxide-mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and polymerization with reversible addition fragmentation chain transfer (RAFT).[6] The attributes of living polymerization are well-known and include molecular weight control, narrow polydispersity, end-group control, and the ability to chain-extend.

Despite the fact that living polymerization has been known for more than 30 years, intensive investigation began relatively recently. As commonly happens for newly discovered reactions, initial attention focused on the reaction products.[5] Through the 1970s and 1980s, controversy arose as to whether polymerizations involving some form of reversible termination of the active intermediate (usually cationic or anionic) should be called *living*. This period also saw various criteria proposed to enable the worker to recognize living polymerization. They are not relisted here. A critical survey of these criteria has been published[5b,7] in which the deficiencies of many simple measures that are applied to establish livingness are pointed out. It was also recommended that the term *living* (as opposed to *quasi-living* or *pseudo-living*) should be used, irrespective of mechanism (allowing systems with reversible termination or chain transfer to be described as living), to describe processes that possess the attributes of a living polymerization, but it was also stressed that processes where chain-breaking reactions are detectable should not be called living polymerizations.[1,8] The more recent recommendation[1] goes one step further in proposing that processes should not be called living if (as in the case of radical polymerizations) it can be expected that some chain-breaking reactions should occur.

A definition should not be dependent on the limitations of current technology (a detection limit) or be based on subjective argument (an expectation). Let us return to the basics. One of the basic principles of chemistry is to name reactions on the basis of their mechanisms, not their yields. A new name should not be defined when it is realized that some side reaction also occurs. Thus, there is little precedent for assigning reaction names on the basis of a perceived absence or presence of side reactions. The Diels–Alder reaction is the Diels–Alder reaction whether the yield is 99.99% or 50%, or even 20%, when it is clear that some other reactions predominate in the reaction pot. Look at any handbook on named reactions; no warnings are provided that the names should only be applied once the absence of side reactions is proven. The name Diels–Alder is also applied, although not always without controversy, irrespective of mechanism (whether the process is a concerted cycloaddition, involves biradical intermediates, or requires transition-metal catalysis), as long as the product is that expected from a Diels–Alder reaction. Another of the basic principles of chemistry is to not introduce new terminology when there is no necessity for it, as is the case when existing terminology or theory still explains the experimental observations. This principle calls for simplicity, the application of Occam's razor to terminology.[9]

Living polymers are distinguished from dead polymers by being "able to grow whenever additional monomer is supplied." Szwarc,[4a] one of the pioneers in the field of living polymerization, in restating this definition in a recent article, recognized that nothing is perfect and that the rigorous exclusion of all termination processes was an ideal for which to strive, rather than an actual situation. He suggested a rider to his definition to the effect that living polymers "grow to a desired maximum size while their degree of termination or chain transfer is still negligible".[4b] We propose that the meaning of the term *living polymerization* be relaxed and defined as those processes that yield living polymers (or their dormant precursors). The term *living polymerization* should be used regardless of the yield of the process. It should, however, also be recognized that the various characteristics associated with livingness (i.e., narrow polydispersity, molecular weight control, end-group or block purity) will be maximized when irreversible termination processes such as chain transfer or self-reaction (in the case of radical polymerization) are negligible.

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3. In the classic picture of an ideal living polymerization, the growth has all chains being initiated simultaneously at the beginning of the process, with the rate constant for initiation greater than that for propagation and with no termination (i.e., processes such as transfer and self-reaction are rigorously excluded). Under these conditions, it is possible to obtain a very narrow Poisson molecular weight distribution. However, it must be recognized that slow initiation does not by itself cause chain death.
4. (a) Szwarc, M. Nature 1956, 178, 1168; (b) Szwarc, M. J Polym Sci Part A: Polym Chem 1998, 36, ix.
5. There are numerous surveys of living polymerization. See, for example, (a) Webster, O. W. Science 1991, 251, 887; (b) Hsieh, H. L.; Quirk, R. P. Anionic Polymerization: Principles and Practical Applications; Marcel Dekker: New York, 1996; p 71.
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8. MensOne criterion that has been suggested is that the polydispersity of living polymerization should be less than 1.1. The 1.1. limit was introduced when the determination of polydispersities less than 1.1 was not possible by the analytical tools then available (Fetters, L. J. In Encyclopedia of Polymer Science and Engineering, 2nd ed.; Kroschwitz, J. I., Ed.; Wiley Interscience: New York, 1987; Vol. 10, p 19). More accurate methods of determining true molecular weight distributions are emerging and undoubtedly will continue to emerge. Methods such as soft-ionization mass spectrometry, 2D chromatography, and new size exclusion chromatography columns/detectors all permit a more detailed characterization of a polymer sample. Should we now push the polydispersity criteria down to less than 1.01? One could find that no polymerizations fit the criteria, thus rendering living polymerization nothing more than a mental construct. Therefore, it is unwise to use such analytical measures to define a reaction class.
9. William of Occam (1300–1349) stated that "entities are not to be multiplied beyond necessity." From Cohen, J.; Stewart, I. The Collapse of Chaos; Viking: New York, 1994.