

Macromolecular Nomenclature Note No. 12

[The Nomenclature Committee of the ACS Division of Polymer Chemistry
(W. V. Metanowski, chairman) presents a guest contribution on proposed nomenclature of
controlled and living polymerization]

NAMING OF CONTROLLED, LIVING AND "LIVING" POLYMERIZATIONS [1]

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Synthesis of well-defined polymers and copolymers with predetermined molecular weights, low polydispersities, precisely controlled end group functionalities and chain topologies is the ultimate target of preparative polymer chemistry [2]. In principle, such macromolecules can be made by living polymerization. *Living polymerization* was first defined by Szwarc [3] as a chain growth process without chain breaking reactions (transfer and termination). Such a polymerization provides endgroup control and enables the synthesis of macromolecules with important architectures such as block copolymers by sequential monomer addition. However, it does not necessarily provide polymers with control of molecular weights and narrow molecular weight distributions (MWD). Additional prerequisites to achieve these goals are that the rate of initiation is at least comparable to that of propagation and that exchange between species of various reactivities and lifetimes is fast in comparison with propagation [4-6]. Some additional prerequisites are given below.

If these additional criteria are met, a polymerization is proposed to be named *controlled*. It can also be regarded as controlled if side reactions occur but only to an extent which does not considerably disturb the control of the molecular structure of the polymer chain.

In the past decade many new polymerization mechanisms for the formation of controlled polymer structures have emerged and have been named "living", such as cationic, ring-opening metathesis, group transfer, and radical polymerizations [2]. The two terms *living* and *controlled* have been considerably confused (not to say abused) by many authors due to the lack of agreed definitions. Very often the lack of control (shown by broad MWD) is equalled with chain-breaking reactions, i.e. a non-living process. In addition, new terms such as *quasiliving*, *pseudoliving*, *apparently living*, *"living"*, and *immortal*, have led to increasing confusion. Thus, we first will repeat/extend existing definitions of these terms. Then we will give a more detailed discussion and examples.

DEFINITIONS:

1. *Living* polymerization is a chain polymerization without *irreversible* chain breaking reactions, i.e. transfer and termination.
2. *Living* polymerization may include:
 - slow initiation,
 - reversible formation of species with various activities and lifetimes,
 - reversible formation of inactive (dormant) species (*reversible deactivation*),
 - reversible transfer (in some cases).

Living polymerization must not include:

 - irreversible deactivation (i.e., termination),
 - irreversible transfer.
3. *Controlled* polymerization is a synthetic method to prepare polymers which
 - (a) are well-defined with respect to:
 - topology (e.g., linear, star-shaped, comb-shaped, dendritic, cyclic),
 - terminal functionality,
 - composition and arrangement of comonomers (e.g., statistical, periodic, block, graft, gradient),
 - (b) have molecular weights predetermined by the ratio of concentrations of reacted monomer to introduced initiator, as well as unimodal and narrow molecular weight distribution.
4. Controlled polymerization may include transfer and termination but at a proportion low enough not to significantly affect the control of molecular properties given in definition 3. This means the rate of these side reactions should be low enough in comparison with propagation rate to reach a given synthetic goal. In addition, the following features should be fulfilled:

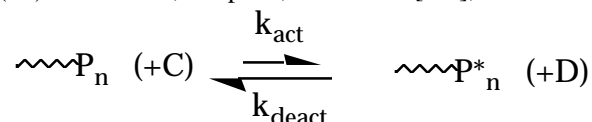
- a) the time of mixing reagents should be short compared to the half-life of the polymerization
 - b) the rate of initiation should be at least comparable to that of propagation
 - c) the rate of exchange between various active species should be faster than that of propagation of the fastest species
 - d) the rate of depropagation should be low in comparison to that of propagation.
5. *Living* polymerizations are *controlled* if conditions 4 are fulfilled. *Controlled* polymerizations are *living* if irreversible transfer and termination is below the detection limit using currently available instrumentation. It is suggested to determine the contribution of transfer and termination reactions in controlled polymerizations (e.g., by working at higher molecular weights or variable temperatures) to distinguish them from living polymerizations.
6. The term *controlled* is preferred to *apparently living* or "*living*" (with quotation marks) used to indicate synthesis of well-defined polymers under conditions in which chain breaking reactions undoubtedly occur, like in radical polymerization.

DISCUSSION AND EXAMPLES:

In order to clarify points stated above we discuss some of them in more detail below, giving examples.

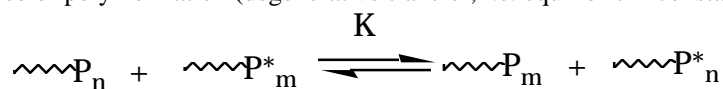
1 & 2. The term "*irreversible*" is important.

(a) *Reversible termination* (better: *reversible deactivation*) is a process where active species are in a dynamic equilibrium with inactive (dormant) species. These equilibria are part of nearly all modern controlled polymerizations, like cationic, group transfer, and radical polymerizations where the dormant species (P) are covalent and the active ones (P*) can be ions, ion pairs, or radicals [4-6],

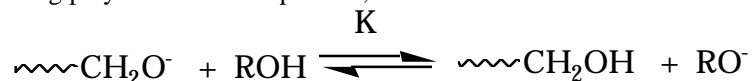


Here, C is a catalyst (co-initiator/activator) and D is a deactivator or product of the activation process. Such systems have been called *quasiliving* [7] or *pseudoliving* [8]. In order to avoid confusion, they should be called *living* or *living with reversible deactivation*.

(b) Reversible transfer can be a bimolecular reaction between a dormant and an active polymer chain which only differ in their degree of polymerization (degenerative transfer, i.e. equilibrium constant $K=1$) [6],



or a reaction with a low molecular compound with a structure similar to the chain end, e.g. addition of alcohols in the anionic ring-opening polymerization of epoxides,



If the rate of exchange is fast, the latter reaction will lead to molecules of identical structure where the molecular weight is given by the ratio of concentrations of reacted monomer over introduced initiator and transfer agent. If transfer is fast compared to propagation narrow MWD will be obtained although control of functionality may not be perfect. Such systems have been named *immortal* [9]. In order to avoid confusion they should be named *living with reversible transfer*.

3a. We discussed macromolecular control in terms of topology, functionalities and composition but refrain from discussing stereochemical microstructure. Control of the stereochemistry means, e.g., control of tacticity of polypropylene or of the various isomers in isoprene polymerization. It is best reached in coordination polymerization, and to a lesser extent in anionic polymerization. Most polymers obtained in other chain-growth processes exhibit none or poor stereocontrol. Since this is not always the synthetic aim, polymerizations without stereocontrol may still be named controlled.

3b. In case of reversible transfer with an added transfer agent the degree of polymerization is given by the ratio of the concentration of reacted monomer to that of initiator and transfer agent.

In case of very slow initiation (see 4b below) full conversion of initiator cannot be reached and DP_n will be higher than the ratio of concentrations of reacted monomer to introduced initiator.

For many reasons, it is experimentally difficult to reach and to experimentally determine the polydispersity index given by the Poisson distribution ($M_w/M_n = 1 + 1/DP_n$). It is not possible to define a limit where MWD should be named "narrow". The limit depends on the difficulty of the particular synthetic task. A value of $M_w/M_n \leq 1.1$ may be agreed on for anionic polymerization whereas $M_w/M_n \leq 1.2$ or 1.3 may be agreed on for other polymerization mechanisms.

4. In some systems relatively well-defined polymers can be prepared in spite of the presence of side reactions. Usually the effect of chain breaking reactions becomes more significant with the chain length. Therefore, some identical initiating/catalytic systems provide well-defined polymers with $M_n < 10,000$ but fail entirely for polymers with $M_n > 100,000$. Thus, the former can be considered as controlled whereas the latter not, although the only difference between them is the initiator concentration. In order to systematize such systems, we proposed a ranking which is based on the simple kinetic parameters such as ratios of transfer and termination rate constants to that of propagation [10]. See also point 5 for more details.

(a) If the time needed for mixing the reagents (monomer, initiator, catalysts), t_{mix} , is not short compared to the half-life of the polymerization, $t_{1/2}$, the MWD will not be given by the mechanism of polymerization but by the hydrodynamics of mixing. If $t_{mix} > t_{1/2}$, very broad MWD's can result. Sometimes these systems have been called non-living whereas they are uncontrolled.

(b) If the ratio of rate constants of polymerization and initiation is $k_p/k_i < DP_n/4$, the effect of initiation on DP_n and MWD is negligible [11]. If $k_p/k_i \gg DP_n$, the maximum polydispersity index is $M_w/M_n = 1.35$ [12].

(c) For equilibria between active and dormant species (see 1a), the rate of deactivation should be much higher than the rate of polymerization, $R_{deact} \gg R_p$. The polydispersity index at full conversion is given as $M_w/M_n = 1 + 1/\beta$, where β is proportional to the ratio of the rate constants of deactivation and propagation, k_{deact}/k_p , and further depends on the mechanism of exchange [6,13,14]. If deactivation is slow, very broad MWD is observed. Here again, many such systems have been called non-living whereas they are uncontrolled.

In many processes we find equilibria between species of different activity, e.g., between free ions and ion pairs in anionic polymerization. The polydispersity index depends on the relative reactivities, the proportion of the species and rates of exchange [13].

(d) If the rate of depropagation becomes comparable to that of propagation full conversion cannot be reached, $x_{max} = 1 - 1/(K_p[M]_0)$ or $[M]_{eq} = 1/K_p$, where K_p is the equilibrium constant of polymerization. Thus we need $K_p [M]_0 \gg 1$. For styrene at 25 °C, $K_p = 5 \times 10^6$ mol/L, and this prerequisite is fulfilled. However, for α -methylstyrene at 25 °C, $K_p = 0.8$ mol/L and it is necessary to work at low temperature and/or high monomer concentration in order to have a controlled polymerization. Moreover, at prolonged standing of the polymerizing system, the chains will redistribute and finally lead to a most probable distribution ($M_w/M_n = 2$) in a time which is proportional to DP_n^2 over the rate constant of depolymerization, k_d . [11].

5. Irreversible chain breaking reactions result in deactivated chains the proportion of which progressively increases with conversion and chain length. Let us calculate the effects of (pseudo)unimolecular termination and transfer to monomer for $[M]_0 = 1$ mol/L and $[I]_0 = 10^{-3}$ mol/L, assuming fast initiation. If the ratios of termination/monomer transfer to propagation rate constant are $k_t/k_p = 10^{-3}$ mol/L and $k_{tr}M/k_p = 10^{-3}$, respectively, 20% of chains are deactivated when polymers with polymerization degree $DP_n = 200$ are targeted. However, at $DP_n = 500$, 50% of chains are deactivated by transfer and 70% by termination. For the ratios of rate constants 10^{-4} , $\approx 2\%$ of chains are deactivated when polymers with $DP_n = 200$ are targeted. At the stage of $DP_n = 500$, 5% of chains are deactivated, whereas at the stage of $DP_n = 900$, 10% of chains are deactivated by transfer and 20% by termination. At the very end of the polymerization, the rate of termination does not change but propagation slows down leading to the rapid increase of proportion of the deactivated chains, e. g. 50% at 99% monomer conversion or at $DP_n = 990$. Such analysis helps to define some limits for the synthesis of well-defined systems including functional polymers and block copolymers, e.g. [15].

6. According to the above definitions, systems like controlled radical polymerization [10] cannot be called living because two radicals always terminate by coupling or disproportionation. Since chain breaking reactions are detected and quantitatively determined it was proposed to name these systems as *apparently living* or "*living*" (quotation marks refer to systems which were called *living* although chain breaking reactions were detected) [16,17] or *controlled* [5].

CONCLUSIONS

Quantitative initiation and fast exchange are additional requirements for the synthesis of well-defined polymers. Slow initiation and slow exchange broaden polydispersities significantly, sometimes above values found in conventional systems, even if the proportion of terminated chains is low. Thus, polydispersities cannot

be used as the only criterion of livingness. Additionally, the time effect is important, termination will continue even after all monomer is consumed and polymers with polydispersities $M_w/M_n < 1.1$ may contain more than half of chains deactivated and fail to efficiently produce block copolymers.

In summary, the terms *living* and *controlled polymerizations* should be carefully distinguished. It is proposed to use the term *controlled* rather than *living* for polymerization systems which provide well-defined polymers but are not completely free of termination or transfer, like radical polymerizations. Since many researchers are used to the term *living*, the combination *controlled/"living"* may be used for a transition period.

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