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Ranking Living Systems

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The term "living polymerization" has been coined by Szwarc for chain-growth polymerizations in which contribution of chain-breaking processes can be neglected.[1] Thus, initiation is followed by propagation, and neither transfer nor termination can be detected. This is the ideal case, but in real systems chain-breaking reactions do exist. Various criteria for living systems have been recently discussed in a qualitative way.[2-4] In this paper, the living systems are ranked more quantitatively based on the ratio of the rate constants of transfer and termination to that of propagation and also on the absolute values of the rate constants of the chain-breaking reactions. Although these criteria are kinetic in nature, they have extremely important synthetic implications. The ratio of the rate constants of transfer to propagation defines the limit of molecular weight which can be obtain under specified reaction conditions. The ratio of the termination to the propagation rate constants affects ultimate monomer conversions. The absolute values of the rate constants of transfer and termination determine the reaction time for various synthetic manipulations such as end functionalization and preparation of block copolymers. Thus, it is very important to know what the contribution of chain-breaking reactions is and how they affect polymer synthesis.

In some new "living" systems, the reported molecular weights are much lower than those obtainable in classic living systems. Transfer and termination may therefore be more difficult to detect. For example, a particular system may behave ideally for low molecular weight macromolecules such as those with DP $\approx$ 10, whereas high polymer with DP $\approx$ 1000 may never be obtained under otherwise identical conditions. Reports that a particular system is living may therefore be misleading, and it would instead be more beneficial to report the upper limits of molecular weights of polymers that are still well-defined under the reported conditions.

A system is living when all chains are active due to the absence of transfer and termination. If, additionally, initiation is fast, then the number of active chain ends will equal the initial number of initiator molecules. Monomer is continuously consumed under these conditions, and the degree of polymerization is defined by the ratio of the concentration of the reacted monomer to the initial initiator concentration ($DP_n = \Delta[M]/[I]_0$). If the polymerization is also irreversible and if the various active sites exchange at a rate faster than that of propagation, a Poisson molecular weight distribution will result.

The effect of transfer and termination on the polymerization rate, final conversion, molecular weight, and polydispersity depends on the chain length and thus on the initiator concentration. Equation 1 shows the ultimate

$$\ln([M]_0/[M]_\infty) = [I]_0(k_p/k_t) \tag{1}$$

conversion as a function of $[I]_0$ and k_p/k_t when termination is unimolecular. If termination agent X is used, then k_t should be substituted by $k_{tX}[X]$. This equation does not apply to bimolecular termination such as in the radical polymerization. The degree of polymerization is affected mostly by transfer. When only transfer to monomer occurs, the number-average degree of polymerization is defined by eq 2.[4] However, when a unimolecular transfer

$$DP_n^{\ M} = \Delta[M]/([I]_0 + \Delta[M](k_{tr(m)}/k_p)) \tag{2}$$

dominates, such as that to counterion or pseudounimolecular to solvent, the degree of polymerization is defined by eq 3.[4]

$$DP_n^{\ S} = \Delta[M]/\{[I]_0 + \ln([M]_0/[M])(k_{tr}/k_p)\} \tag{3}$$

As discussed by Szwarc,[5] another important synthetic criterion for a living system is that its shelf time be long enough to perform preparative manipulations. This parameter determines how many active sites survive after a certain time and is related to the absolute rate constant of any chain-breaking reaction ($k_{t/tr}$), as defined by eq 4.

$$\ln([P^*]_0/[P^*]) = k_{(t/tr)}t \tag{4}$$

An arbitrarily chosen 10% deviation from ideal behavior may be used as a limit for well-defined systems. 10% deactivation may not yet be detected by SEC or by end-group analysis. The time at which 10% of the chains have been deactivated is defined by eq 5.

$$\tau_{10\%} = \ln(1/0.9)/k_{(t/tr)} \tag{5}$$

We have ranked the "livingness" of polymerization systems from 1 to 6 according to the ratios k_{tr}/k_p and k_t/k_p. According to this definition, class 1 corresponds to $k_{trM}/k_p = 10^{-1}$, $k_{tr}/k_p = 10^{-1}$ mol L^{-1}, $k_t/k_p = 10^{-1}$ mol L^{-1}, and $k_{(t/tr)} = 10^{-1}$ s^{-1}. Class 4 corresponds to $k_{trM}/k_p = 10^{-4}$, $k_{tr}/k_p = 10^{-4}$ mol L^{-1}, $k_t/k_p = 10^{-4}$ mol L^{-1}, and $k_{(t/tr)} = 10^{-4}$ s^{-1}, etc. Table I tabulates the time for 10% deactivation of growing species, the final monomer concentrations, and the final degrees of polymerization for the different classes of livingness using $[M]_0$ = 1 mol/L and two initiator concentrations: $[I]_0 = 10^{-2}$ mol/L and $[I]_0 = 10^{-4}$ mol/L. In the absence of transfer and termination and with fast initiation, the former conditions correspond to a theoretical degree of polymerization DP = 100, which is often considered the lowest limit to call a macromolecule a polymer rather than an oligomer. The latter conditions correspond to very high polymer with a theoretical degree of polymerization DP = 10 000; in this case, $M_n \approx$ 1 000 000 for an average monomer with $M \approx$ 100 molecular weight.

Two final degrees of polymerization were calculated for each class, assuming that only one type of side reaction occurs at a time, i.e., either exclusive transfer to monomer in the absence of spontaneous transfer and termination or exclusive spontaneous transfer in the absence of transfer to monomer. Instantaneous initiation was assumed. Values of $DP_n^{\ M}$ for transfer to monomer were calculated at 100% monomer conversion. Values of $DP_n^{\ S}$ for spontaneous transfer were calculated for an arbitrarily chosen 98% monomer conversion. At higher conversions, the $DP_n^{\ S}$ would decrease due to the formation of shorter oligomers. Sometimes they may not be detected, especially if a polymer is separated by precipitation.

According to Table I, class 4 of livingness should be sufficient to synthesize well-defined polymers with relatively low molecular weight (DP $\approx$ 100). The polymer reaches essentially complete conversion, the degrees of polymerization are within 4% of the theoretical value for both systems with either transfer to monomer or spon-

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Table I
Values of the Final Monomer Concentrations ($[M]_\infty$), Final Degrees of Polymerization Controlled by Transfer to Monomer ($DP_n{}^M$) and Spontaneous Transfer ($DP_n{}^S$), and Time for 10% Deactivation of the Growing Species for Different Classes of Livingness for $[M]_0$ = 1 mol/L and Two Initiator Concentrations $[I]_0 = 10^{-2}$ mol/L and $[I]_0 = 10^{-4}$ mol/L

class	$[I]_0$, mol/L	$[M]_\infty$, mol/L	$DP_n{}^M$	$DP_n{}^S$	$\tau_{10\%}$
1	10^{-2}	0.90	9	2.4	1 s
	10^{-4}	0.999	10	2.5	1 s
2	10^{-2}	0.37	50	20	10 s
	10^{-4}	0.99	99	25	10 s
3	10^{-2}	4×10^{-5}	91	70	≈2 min
	10^{-4}	0.90	909	240	≈2 min
4	10^{-2}		99	94	≈18 min
	10^{-4}	0.37	5000	2000	≈18 min
5	10^{-2}		99.9	97.6	≈3 h
	10^{-4}	4×10^{-5}	9091	7050	≈3 h
6	10^{-2}		99.99	98.0	≈1 day
	10^{-4}		9901	9430	≈1 day

taneous transfer, and there is sufficient time available for synthetic manipulations since it takes 18 min for 10% of the chains to be deactivated and 8 min for 5% deactivation. However, even class 5 is not sufficient to synthesize well-defined polymers with high molecular weight (DP ≈ 10 000). In this case, class 6 is required. If only class 5 livingness is achieved, the resulting molecular weight is expected to deviate from the theoretical value by 10% for systems with transfer to monomer and by 29% for those with spontaneous transfer. The molecular weight should deviate from the theoretical value by only 1–4% using class 6 systems. In principle, the synthesis of a well-defined polymer with $M_n \approx 10^x$ requires class x of livingness, assuming monomer molecular weight $M = 100$.

What information do we have on real living systems that will allow us to rank them? For example, how does group-transfer polymerization of methacrylates, living anionic or cationic polymerization of styrene, and other carbocationic polymerizations rank? In all cases, the class of livingness will be affected by the reaction conditions, including the solvent, temperature, and counterion. Although no precise data are available indicating that deactivation reactions occur in the anionic polymerization of styrene in THF and benzene (class >6), toluene certainly participates in transfer and limits the molecular weight to DP ~ 300 with sodium counterion,[6] corresponding to a class 3 polymerization. Lithium as a counterion increases livingness to class 4 (values of $[\text{toluene}](k_{tr}/k_p) \approx 5 \times 10^{-5}$ mol L^{-1} have been reported).[7] Similar values may be deduced from the results reported for polymerization of styrene in ethylbenzene with organolithium initiators.[8] Polymerization of butadiene is much more sensitive to transfer. Limited values of molecular weights obtained in toluene correspond to $M_n = 740$ and 1110 at 20 and 6 °C, respectively, which correspond to class 2 livingness.[9] Of course, high molecular weight polybutadiene can be prepared in aliphatic hydrocarbons and in benzene.

Success of group-transfer polymerization originates in the increase of the ratio of the rate constants of propagation to that of termination (via formation of cyclic ketone) with the counterion size. At 25 °C this ratio equals $k_t/k_p = 0.12$ mol/L for Li^+ (class 1) but $k_t/k_p = 0.0002$ mol/L for GTP (bulky tris(piperidino)sulfonium cation) (class 4); the latter value decreases down to $k_t/k_p = 10^{-5}$ mol/L at −40 °C (class 5).[10] Carbocationic polymerization of styrene enables formation of polymers with DP ≈ 10 at 70 °C (class 1) but DP ≈ 500 at −50 °C (class 3).[11] A more extensive collection of the data on chain-breaking reactions in the cationic polymerization of alkenes is summarized in ref 4. Thus, livingness determined by the selectivity of propagation and defined by the ratio of the corresponding rate constants depends not only on monomer and initiator but also on the reaction conditions (solvent, counterion, temperature).

This discussion should have demonstrated that there are no absolutely living systems and that, instead of simply stating that a polymerization is "living" under the reported conditions, it is preferable to determine the real values of the rate constants of propagation and transfer or termination, or at least the corresponding ratios. Although it may be difficult to determine the rate constants of transfer and termination under "living conditions", researchers can work at lower $[I]_0$ and/or at higher temperatures where side reactions are easier to detect. In this case, the desired rate constants can be obtained by extrapolating to the desired reaction conditions. The ratio k_{tr}/k_p is determined from simple plots of $1/DP$ vs $1/\Delta[M]$ and/or vs $\{\ln([M]_0/[M]\}/\Delta[M]$; k_t/k_p is determined by kinetic measurements at sufficiently low $[I]_0$. This information will enable more reproducible polymer synthesis by contributing to a better understanding of the chemistry and mechanism of the polymerization than will the ever-continuing discovery of new "living" systems. In order to further advance the field of polymer chemistry and to maintain or even improve its quality of research, it may be time for editors of major polymer journals to require that the absolute rate constants of transfer and termination are determined, as well as the corresponding ratios to the rate constant of propagation. This will set the synthetic limits for obtaining well-defined polymers.

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