INTRODUCTION TO LIVING POLYMERIZATION. LIVING AND/OR CONTROLLED POLYMERIZATION

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The effects of various imperfections such as slow initiation, termination, transfer and slow exchange on kinetics, molecular weights and polydispersities in chain growth polymerizations are simulated. The simulations demonstrate that well defined polymers can be prepared in systems with chain-breaking reactions. Thus, under carefully selected conditions, non-living polymerizations may provide controlled polymers. On the other hand, polymers with unpredictable molecular weights and broad and even polymodal molecular weight distributions can be formed in living systems without irreversible transfer and termination. In some living systems molecular weights may stay constant or even decrease with conversion. Therefore, a clear distinction should be made between living and controlled polymerizations.

INTRODUCTION

The term living polymerization was initially used to describe a chain polymerization in which chain-breaking reactions were absent.[1,2] In such an ideal system, after initiation is completed, chains only propagate and do not undergo transfer or termination. Thus, in the ideal living polymerization each chain should retain its ability to react with monomer infinitely. However, transfer and termination often occur in real systems.

The number of papers describing living polymers, living catalysts (?) and living polymerizations is growing exponentially. Some of these processes will be discussed in other papers in this issue; some have been summarized in a recent review[3] and will not be covered in this paper. Moreover, new terms such as quasi-living, semi-living, truly living, perfectly living, pseudo-living, apparently living and immortal have been used, often without defining the terms. Recently, some effort has been made[4–7] to classify these systems and to establish criteria for living polymerizations. These criteria can be generally separated into kinetic and synthetic.
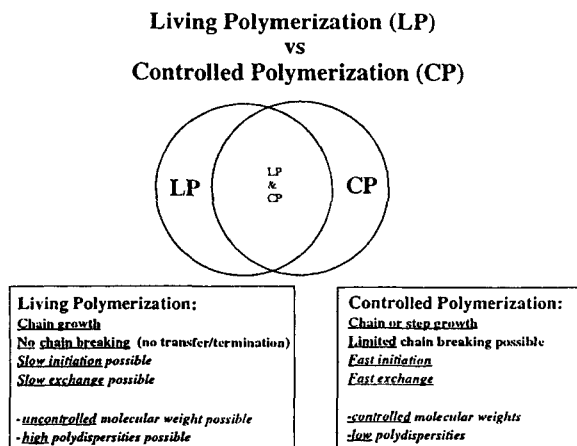
The intention of this paper is not to review existing and proclaimed living systems but to discuss the essence of a living polymerizations and to demonstrate that polymer properties are influenced by deviations from an ideal system. The importance of kinetics is stressed here and the effect of chain-breaking reactions and of slow initiation and slow exchange between species of different reactivities and lifetimes on rates, molecular weights and polydispersities is described quantitatively. These calculations show that well defined polymers can be prepared in the presence of chain-breaking reactions. Thus, living polymerizations (no chain-breaking reactions) and controlled polymerization (formation of well defined polymers) are two separate and not necessarily overlapping terms which should be distinguished and should not be confused. (Scheme 1)

A controlled polymerization is defined here as a synthetic method for preparing polymers with predetermined molecular weights ($DP_n = \Delta[M]/[I]_0$), low polydispersity and controlled functionality, and also block copolymers. Transfer and termination are allowed in a controlled polymerization if their contribution is sufficiently reduced by the proper choice of the reaction conditions such that polymer structure is not affected.

On the other hand, a living polymerization is defined as a chain polymerization without irreversible transfer and termination. Living polymerizations will lead to well defined polymers only if the following additional prerequisites are fulfilled: initiation is fast in comparison with propagation; exchange between species of different reactivities is fast in comparison with propagation; the rate of depropagation is low in comparison with propagation and the system is sufficiently homogeneous, in the sense of the availability of active centers and mixing. If these specifications are not met, living polymerizations will produce polymers with broader polydispersities and degrees of polymerization much higher than the $\Delta[M]/[I]_0$ ratio.

The proportion of chains affected by transfer and termination increases with the chain length. As discussed later, this may not cause much deviation from ideal behavior (linear increase in M_n with conversion,

Living Polymerization (LP)
vs
Controlled Polymerization (CP)

Living Polymerization:	Controlled Polymerization:
Chain growth	*Chain or step growth*
No chain breaking (no transfer/termination)	*Limited chain breaking possible*
Slow initiation possible	*Fast initiation*
Slow exchange possible	*Fast exchange*
-*uncontrolled molecular weight possible*	-*controlled molecular weights*
-*high polydispersities possible*	-*low polydispersities*

Scheme 1. Comparison between living and controlled polymerization

very narrow polydispersities) if the chains are sufficiently short. Such systems have often been called living. However, if attempts at preparing higher molecular weight polymers under otherwise identical conditions (initiator, additive, solvent, temperature, etc.) are unsuccessful, and if chain-breaking reactions are indicated by a non-linear evolution of molecular weights with conversion, and by variation of polydispersities and polymerization kinetics, then such a system should not be called living. The terms apparently living or 'living' polymerization have been used previously to name systems which produced well defined polymers of relatively low molecular weight but in which either transfer or termination is unambiguously present.[8,9] The term controlled polymerization is a more accurate description of these systems.
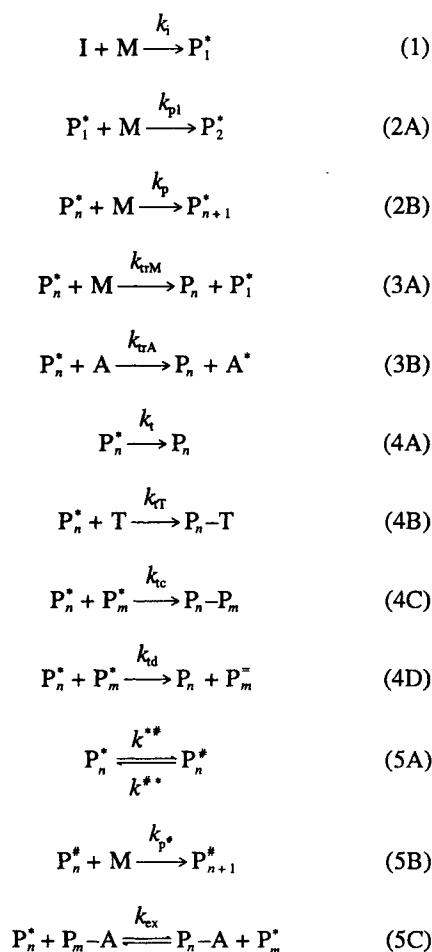
It has been proposed that the rate constants of transfer and termination or their ratios to that of propagation should be determined for polymerization systems which produce well defined polymers.[7] This will allow reproducible syntheses in which the limits for the preparation of well defined high polymers are set. The transfer/termination rate constants may be detectable only by working under 'difficult' reaction conditions which prevent preparation of well defined polymers (higher temperatures, lower $[I]_0$, longer chains, etc.). These results can then be extrapolated to the 'usual living' conditions.

Systems with reversible transfer or reversible termination deserve special comment, since they have often been called pseudo-living or quasi-living. The first living systems were anionic polymerizations of non-polar monomers such as styrene and dienes in some hydrocarbon solvents. They showed perfectly living behavior, producing very high molecular weight polymers $(M_n \gg 100,000)$ with low polydispersities $(M_w/M_n < 1 \cdot 1)$ providing that initiation and mixing were fast

enough.[2,10-12] Polymerization resumes with the same rate after addition of a new portion of monomer with a linear increase in molecular weight with conversion. In addition, block copolymers form by consecutive polymerization of two comonomers. In these systems various active species coexist, including ions, ion pairs of various structures and reactivities and their aggregates. Reactivities of ions are sometimes much higher than those of ions pairs $(k_p^-/k_p^\pm \approx 10^5$ in polymerization of styrene with Li^+ counter ion in dioxane at 20 °C),[2,10-12] and in some cases ionic aggregates are much less reactive than ion pairs. Nevertheless, polymers with degrees of polymerization determined by the ratio of the concentration of reacted monomer to the overall concentration of active species or of introduced initiator $(DP_n = \Delta[M]/[I]_0)$ have been prepared with a narrow molecular weight distribution (MWD). This observation indicates that growing species with different reactivities exchange rapidly enough to give the same probability of growth for all chains. This also implies that the temporary decrease in activity (or temporary deactivation) does not interfere with the concept of a living polymerization. Thus, temporary deactivation is not considered as termination. The same reasoning can be applied to reversible transfer and it has been suggested that both systems can be simply called living.[6] The dynamics of the exchange reactions and the chain lengths are very important in both cases as discussed later.

DEVIATIONS FROM IDEAL SYSTEM

A general kinetic scheme for a typical chain polymerization is shown in Scheme 2. Initiation (1) usually proceeds by reaction of initiator (I) with monomer (M) to produce the first growing species (P_1^*). This species propagates (2A) with a rate constant which may be different from that of the macromolecular species (2B).

$$I + M \xrightarrow{k_i} P_1^* \tag{1}$$

$$P_1^* + M \xrightarrow{k_{p1}} P_2^* \tag{2A}$$

$$P_n^* + M \xrightarrow{k_p} P_{n+1}^* \tag{2B}$$

$$P_n^* + M \xrightarrow{k_{trM}} P_n + P_1^* \tag{3A}$$

$$P_n^* + A \xrightarrow{k_{trA}} P_n + A^* \tag{3B}$$

$$P_n^* \xrightarrow{k_t} P_n \tag{4A}$$

$$P_n^* + T \xrightarrow{k_{tT}} P_n\text{--}T \tag{4B}$$

$$P_n^* + P_m^* \xrightarrow{k_{tc}} P_n\text{--}P_m \tag{4C}$$

$$P_n^* + P_m^* \xrightarrow{k_{td}} P_n + P_m^= \tag{4D}$$

$$P_n^* \underset{k^{\#\bullet}}{\overset{k^{\bullet\#}}{\rightleftharpoons}} P_n^{\#} \tag{5A}$$

$$P_n^{\#} + M \xrightarrow{k_{p\#}} P_{n+1}^{\#} \tag{5B}$$

$$P_n^* + P_m\text{--}A \rightleftharpoons^{k_{ex}} P_n\text{--}A + P_m^* \tag{5C}$$

Scheme 2. Kinetic scheme for chain polymerization

Reaction of the growing species with monomer may also lead to transfer to monomer to generate new chains (3A). Transfer (3B) may also occur with a transfer agent (A). If the new species (A*) have a similar or higher reactivity than the growing species, there will be no effect on the kinetics. If the reactivity of A* is lower than P*, then degradative transfer occurs with retardation of the polymerization.

Growing species may lose reactivity by spontaneous unimolecular termination (4A) or by bimolecular termination (4B) with a terminating agent (T). In radical polymerization bimolecular termination occurs by coupling (4C) or by disproportionation (4D). Growing species (P*) may be in equilibrium (5A) with species P$^{\#}$ of different reactivity, which is also capable of reacting with monomer (5B). The last reaction (5C)

is a degenerative transfer in which both the total number of chains capable of growth $(P_n^* + P_m\text{--}A)$ and the concentration of active chains stay constant (P_n^*). This thermodynamically neutral process $(K = 1)$ may lead to polymers with a narrow molecular weight distribution.

The simplest system which is both living and controlled involves only reaction (2); reactions (3)–(5) should be absent. As shown later, well defined polymers still can be formed if the contribution of these reactions is small and the degree of polymerization is limited. However, living polymerization which involve slow initiation (1) will increase polydispersities and produce polymers of 'too high' molecular weights. If initiation is faster or comparable to propagation, then reaction (1) [and (2A)] can be omitted. Multiplicity of growing species with various reactivities and various lifetimes may produce polymers with broad and even polymodal molecular weight distributions. However, Poisson distributions result if exchange reactions (5A) are fast.

In the following sections, the quantitative deviations of the kinetics, molecular weights and polydispersities from those of ideal systems caused by reactions (1), (3), (4) and (5) will be presented. The magnitude of only one deviation will be varied at a time to demonstrate clearly the effect of slow initiation, termination, transfer and slow exchange on polymerization rates and properties of the produced polymers.

Slow initiation

The effect of slow initiation on kinetics is shown in Figure 1 for a hypothetical system in which only reactions (1) and (2B) (Scheme 2) participate and with the conditions $[M]_0 = 1 \text{ mol } l^{-1}$, $[I]_0 = 0.01 \text{ mol}^{-1}$ and $k_p = 1 \text{ mol}^{-1}\text{s}^{-1}$.

The kinetics is first order in monomer and should provide a straight line in semilogarithmic coordinates if the concentration of active sites is constant (instantaneous initiation). The time-scale is defined by the product of the concentration of the propagating species and the rate constant of propagation, but the shape of the plot depends on the ratio of the rate constants of propagation to that of initiation. For the particular ratio $[M]_0/[I]_0 = 100$, no detectable deviation from the ideal law is found for $R_i = k_p/k_i = 1$. If $R_i = 10$, the initiator is nearly consumed at approximately 40% monomer conversion. On the other hand, at $R = 30$ and 100, the unreacted initiator remains even at complete monomer consumption. Thus, continuous acceleration in the semilogarithmic coordinates is observed.

It is even easier to notice the effect of slow initiation by analyzing the evolution of molecular weight with conversion in Figures 2 and 3. The small increase in the polymerization degree relative to the ideal case disappears at approximately 40% conversion when $R_i = 10$. However, it is necessary to add subsequent portions of monomer (conversions >100%) for ratios $R_i = 30$ and
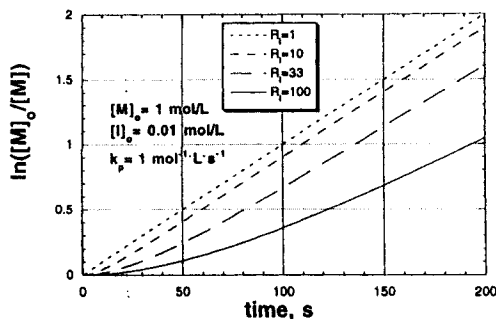
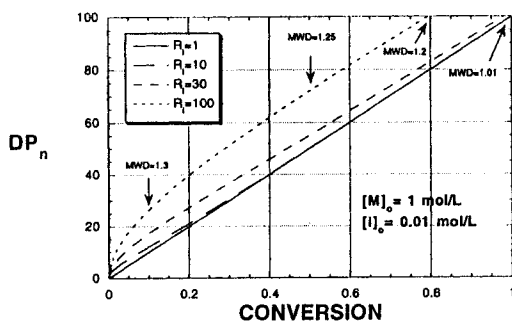Figure 1. Effect of various ratios $R_i = k_p/k_i$ on kinetics for slow initiation

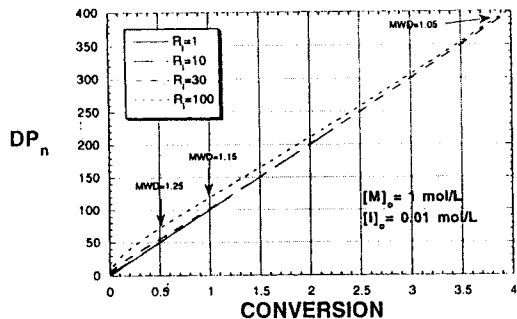Figure 2. Dependence of DP_n on conversion for various ratios $R_i = k_p/k_i$

Figure 3. Dependence of DP_n on conversion for various ratios $R_i = k_p/k_i$ during four consecutive monomer additions for slow initiation

100 to approach asymptotically ideal M_n values as shown in Figure 3.

Polydispersities in systems with slow initiation depend on the ratio $[M]_0/[I]_0$ and R_i, and are very narrow for $R_i = 1$ and 10 ($M_w/M_n < 1\cdot02$) but approach $M_w/M_n \approx 1\cdot15$ for the ratio $R_i = 100$. The highest polydispersity due to slow initiation is $M_w/M_n \approx 1\cdot3$.[13] The effect of slow initiation on kinetics, molecular weights and polydispersities has been discussed before in detail

for general systems[2,13-15] and for carbocationic polymerization.[16]

Termination

The effect of termination was studied for a hypothetical system in which only reactions (2B) and (4A) (Scheme 2) participate. Termination has no effect on the final number average molecular weights because it does not change the total number of chains. Of course, termination may lead to incomplete polymerization if the initiator concentration is too low. If termination is unimolecular the final monomer conversion ($[M]_\infty$) is set by

$$\ln([M]_0/[M]_\infty) = [I]_0(k_p/k_t) \qquad (6)$$

Thus, the effect of termination is mostly kinetic, as shown in Figure 4.

Figure 4 depicts the semilogarithmic plots for various ratios $R_t = k_p/k_t$, taking arbitrary values of $k_p = 1$ mol^{-1}s^{-1}, $[M]_0 = 1$ mol l^{-1}, $[I]_0 = 0.001$ mol^{-1} and assuming instantaneous initiation.

For the ratios $R_t = 100,000$ and 10,000 nearly no deviation from the ideal behavior is observed and complete conversions, predicted molecular weights and polydispersities lower than $M_w/M_n < 1\cdot03$ are calculated. On the other hand, if $R_t = 1000$, 63% conversion is expected at infinite time. Calculations predict $DP_n = 630$ and $M_w/M_n = 1\cdot45$ for the final product. The effect of termination on molecular weight distribution has been discussed thoroughly.[17-19] Bimolecular termination with a terminating agent T obeys pseudo-first-order kinetics if $[T] \gg [P^*]$.

Termination in radical polymerization

The growing species in radical polymerization terminate by either disproportionation or coupling. Most radical polymerization systems involve slow initiation and a very low stationary concentration of radicals in order to prepare polymers of sufficiently high molecular
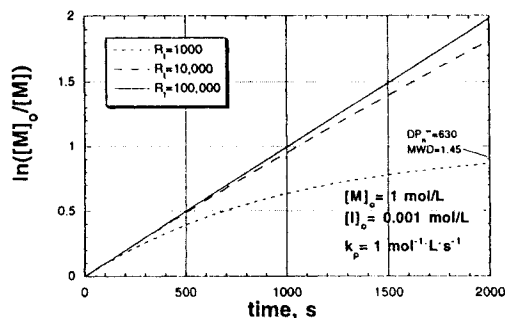

Figure 4. Effect of various ratios $R_t = k_p/k_t$ on kinetics

weights. Therefore, in most systems only a small fraction of the initiator is used, and the rate of initiation is approximately constant (decomposition of the initiator by light, heat or a redox process is usually the rate determining step, $r_i = k_d[I]_0$). The number-average degree of polymerization depends on the ratio of the rate of propagation to that of the initiation and termination. Both the propagation rate and the polymerization degree decrease with conversion as shown in Figure 5. The arbitrarily chosen conditions ($[M]_0 = 10$ mol l^{-1}, $r_i = 10^{-7}$ mol^{-1} l s^{-1}, $k_p = 10^2$ mol^{-1} l s^{-1} and $k_t = 10^7$ mol^{-1} l s^{-1}) are close to those for the bulk polymerization of styrene at 60 °C initiated by azo-bisisobutyronitrile (AIBN).

The polydispersity increase with conversion from the value $M_w/M_n = 1\cdot5$ for termination by coupling to $M_w/M_n = 2\cdot5$ at 95% conversion. This is due to the change in the ratio of the rate of propagation to that of initiation, according to[17]

$$DP_n = \frac{2([M]_0 - [M])k_p}{\ln([M]_0/[M])(2r_ik_t)^{1/2}}$$

$$DP_w = \frac{3([M]_0 + [M])k_p}{2(2r_ik_t)^{1/2}} \tag{7}$$

A similar dependence is predicted for termination by disproportionation, although the initial polydispersities are higher ($M_w/M_n = 2$).

Transfer

Ideally, transfer has no effect on kinetics, but does have a pronounced effect on molecular weights and polydispersities.[17,18,20] Figure 6 shows the effect of transfer to monomer on the polymerization degree for various ratios $R_{trM} = k_p/k_{trM}$, using arbitrary concentrations $[M]_0 = 1$ mol l^{-1}, $[I]_0 = 0\cdot01$ mol l^{-1}, and assuming that initiation is instantaneous and termination is absent. Instead of the predicted final $DP_n = 100$, smaller values are computed ($DP = 91$, 75 and 50) when $R_{trM} = 1000$,
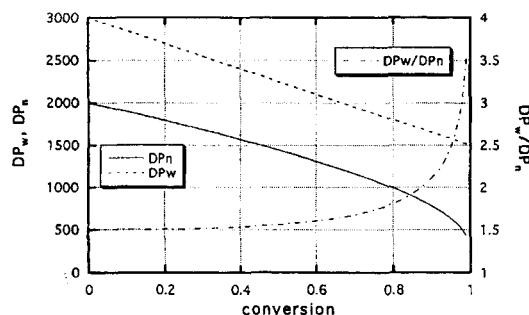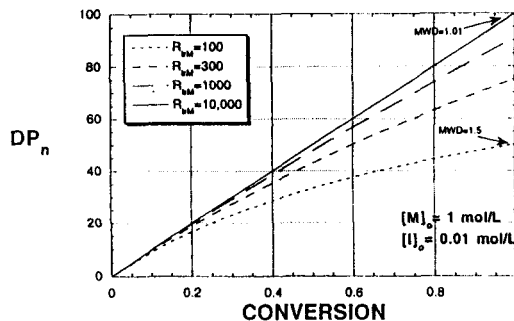

Figure 6. Dependence of DP_n on conversion for various ratios $R_{trM} = k_p/k_{trM}$ for transfer to monomer

300 and 100, respectively. Note that the deviation from $\Delta[M]/[I]$ is smaller at lower DP and increases at higher DP range for each R_{trM} value.

As shown in Figure 7, this deviation depends not only on R, but also on the ratio of the concentration of the monomer to that of the initiator, which can be expressed by the parameter $a = (k_{trM}/k_p) [M]_0/[I]_0$:

$$DP/DP^{id} = 1/\{1 + (k_{trM}/k_p) [M]_0/[I]_0p\} \tag{8}$$

The ratio of the degree of polymerization in the presence of transfer to that predicted for the ideal system without transfer ($DP^{id} = \Delta[M]/[I]_0$) decreases with conversion.[9]

For the initial conditions $[M]_0 = 1$ mol l^{-1}, $[I]_0 = 0\cdot01$ mol l^{-1} and $R_{trM} = k_p/k_{trM} = 1000$, a 10% deviation from ideal behavior is expected (case when $a = 0$ 1). At complete conversion a decrease in the initiator concentration to $[I]_0 = 0\cdot001$ mol l^{-1} ($a = 1$) leads to a DP that is half of the ideally predicted value, whereas $[I]_0 = 0\cdot0001$ mol l^{-1} ($a = 10$) leads to one tenth of that value. However, nearly ideal behavior can be reached with $[I]_0 = 0\cdot1$ mol l^{-1}. This shows that in systems dominated by transfer it is possible to improve polymerization control by simply manipulating (increasing) the initiator concentration.
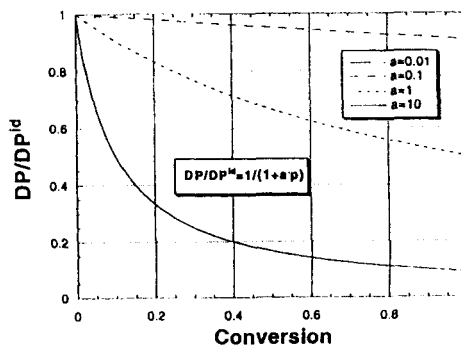

Figure 5. Dependence of DP_n, DP_w and DP_w/DP_n on conversion for termination by coupling in a radical polymerization with constant initiation rate

Figure 7. Effect of parameter $a = (k_{trM}/k_p)(\Delta[M]/[I]_0)$ on deviation from ideal behavior for transfer to monomer

Figure 8 depicts the predicted effect of the parameter a on the polydispersities.[20] Using $[M]_0 = 1$ mol l^{-1} and $[I]_0 = 0.01$ mol l^{-1}, a polydispersity of $M_w/M_n \approx 1.06$ is expected for the ratio $k_p/k_{trM} = 1000$. Decreasing the initiator concentration to $[I]_0 = 0.001$ mol l^{-1} leads to $M_w/M_n \approx 1.5$, whereas increasing $[I]_0$ to 0.1 mol l^{-1} should provide polymers with narrower polydispersities.

Figure 9 is similar to Figure 7, but it takes into account deviations caused by unimolecular transfer (e.g. transfer to counter ion). The plots in Figure 9 were calculated using the following equation:[21]

$$DP/DP^{id} = 1/\{1 + \ln[1/(1-p)](k_{tr}/k_p)/[I]_0\} \quad (9)$$

for various values of parameters $b = (k_{tr}/k_p)/[I]_0$.

Because the rate of transfer to counter ion is independent of monomer concentration, whereas the rate of propagation decreases with conversion, lower molecular weights and large increases in polydispersity are expected at high conversion.[8,22] This explains the pronounced deviation at the end of the polymerization. However, this is often experimentally undetected if the precipitated polymer is analyzed
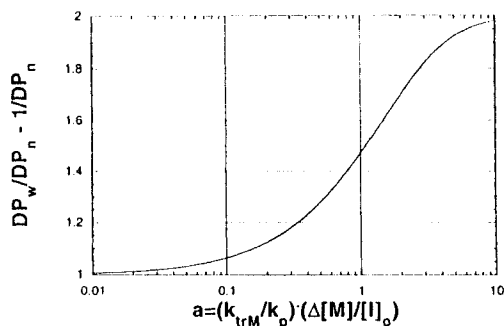

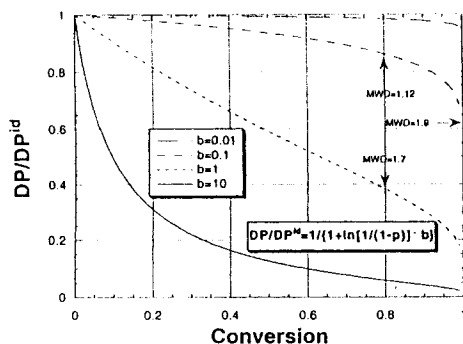Figure 8. Dependence of MWD on various ratios a for transfer to monomer

Figure 9. Effect of parameter $b = (k_{tr}/k_p)/[I]_0$ on deviation from ideal behavior for unimolecular transfer (e.g. to counter ion)

rather than the entire reaction mixture, which includes oligomeric products.

Slow exchange

Exchange between ions and ion pairs of different reactivities has been carefully analyzed in anionic systems and small broadening of polydispersities was used for the evaluation of the dynamics of the exchange.[10,23] When exchange becomes slower, as in the case of aggregation of ion pairs, then polydispersities are higher and the distribution may become bimodal.[24] Slow exchange is also one of the reasons for the high polydispersities obtained in coordination polymerizations, especially heterogeneous systems.

Figure 10 presents the results of Monte Carlo simulations for a binary system consisting of dynamically exchanging active (P^a) and dormant (P^d) species described by Scheme 3. Dormant species cannot react directly with monomer ($k_p{}^d = 0$) and they are present in a 1000-fold excess over active species ($K = 10^3$).

Figure 10 shows the effect of the dynamics of exchange on molecular weights and molecular weight distributions (the signal of the unreacted initiator was deleted from the simulated traces). Values of the equilibrium and rate constants were assumed to be equal for the initiator and macromolecular species. If the rate of conversion of active to dormant species is higher than or comparable to that of propagation [Figure (10(A), $k_p{}^a = 10^5$ M^{-1} s^{-1}, $k_{ad} = 10^7$ s^{-1}; Figure 10(B), $k_p{}^a = 10^5$ M^{-1} s^{-1}, $k_{ad} = 10^5$ s^{-1}], then narrow MWD and degrees of polymerization defined by the ratio of the reacted monomer to that of the introduced initiator are obtained. Using $[M]_0 = 1$ mol l^{-1} and $[I]_0 = 0.01$ mol l^{-1}, $DP_n = 10$, 50 and 90 are predicted at 10, 50 and 90% conversion, respectively. These values are indeed observed in Figure 10(A) and (B). Polydispersities are slightly broader. For example, $M_w/M_n = 1.12$, 1.02 and 1.01 in Figure 10(A) and 1.30, 1.05 and 1.025 in Figure 10(B) at 10, 50 and 90% conversion, respectively.

On the other hand, if the temporary deactivation of the growing species becomes slower than propagation [Figure 10(C), $k_p{}^a = 10^5$ M^{-1} s^{-1}, $k_{ad} = 10^3$ s^{-1}; Figure 10(D), $k_p{}^a = 10^5$ M^{-1} s^{-1}, $k_{ad} = 10^2$ s^{-1}], the molecular weights are higher than predicted (owing to incomplete initiation) and
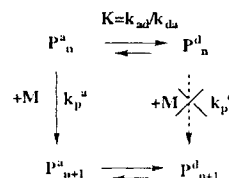
Scheme 3. Polymerization in systems with active and dormant species
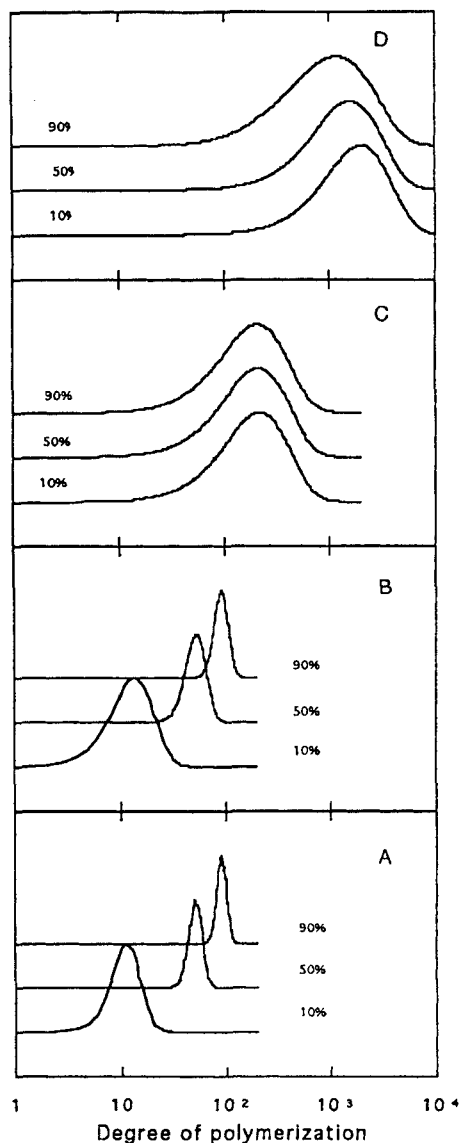
Figure 10. Effect of the dynamics of exchange between active and dormant species on the evolution of MW and MWD with conversion; $[M]_0 = 1$ M, $[I]_0 = 0.01$ M; $k_p^a = 10^5$ M^{-1} s^{-1}, $k_p^d = 0$ M^{-1} s^{-1}; $K = 10^{-3}$. (A) $k_{da} = 10^4$ s^{-1}, $k_{ad} = 10^7$ s^{-1}; (B) $k_{da} = 10^2$ s^{-1}, $k_{ad} = 10^5$ s^{-1}; (C) $k_{da} = 1$ s^{-1}, $k_{ad} = 10^3$ s^{-1}; (D) $k_{da} = 10^{-1}$ s^{-1}, $k_{ad} = 10^2$ s^{-1}

the polydispersities are also much broader. In Figure 10(C), $DP_n = 110$, 108 and 104 and $M_w/M_n = 1.99$, 2.00 and 2.04 were calculated for 10, 50 and 90% conversion, whereas in Figure 10(D), $DP_n = 1040$, 820 and 480 and $M_w/M_n = 2.00$, 2.08 and 2.73 were calculated for 10, 50 and 90% conversion, respectively.

This demonstrates the surprising result that molecular weights can decrease with conversion in a living polymerization! That is, no irreversible transfer or termination is present, and even the rate of initiation was considered equal to that of propagation. This strange and unexpected result is due to the slow reversible deactivation of the active species.

Figures 11 and 12 show the variation of MWD with conversion and as a function of the final polymerization degree for a system with exchanging active and dormant species. This could happen in cationic, anionic, radical, coordination and other polymerization systems. The MWD is unimodal but its breadth depends on the ratio of the rate constants of propagation and deactivation of active to dormant species (k_p^a/k_{ad}).

Polydispersities continuously decrease with conversion and with increasing chain length, in contrast to systems dominated by transfer. At faster exchange (lower value of k_p^a/k_{ad}) there is a higher number of exchange events during chain growth, leading to a more uniform distribution. Similarly, at lower concentration of growing species $([I]_0 - [I])$, longer chains with more narrow MWD are formed, according to

$$DP_w/DP_n = 1 + 1/DP_n + c(2-p)/p \qquad (10)$$

where $c = ([I]_0 - [I])(k_p^a/k_{ad})$.

Figure 12 demonstrates how the polymerization degree affects polydispersity at complete conversion according to

$$DP_w/DP_n = 1 + 1/DP_n + d/DP_n \qquad (11)$$

where $d = [M]_0 (k_p^a/k_{ad})$. For example, high polydispersity $(DP_w/DP_n = 3)$ is predicted for a system with $d = 20$ at $DP = 10$, but is reduced to $DP_w/DP_n = 1.2$ at $DP = 100$. This demonstrates that in order to obtain lower polydispersities, longer chain lengths must be reached in systems with slow deactivation. Of course, transfer may become significant at such high molecular weights and polydispersity may increase after its initial
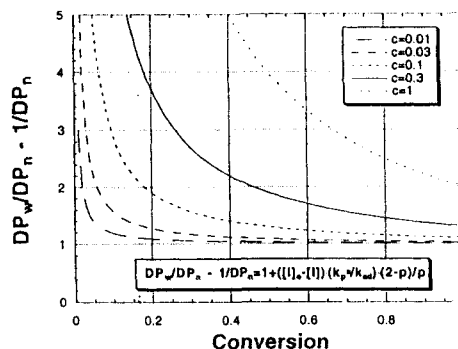

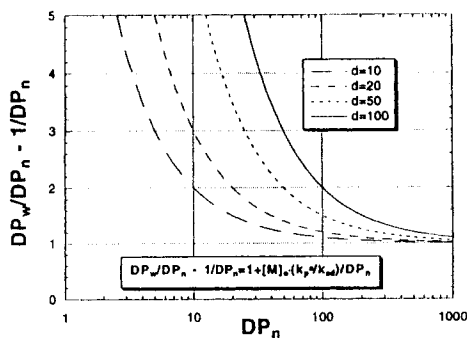Figure 11. Effect of parameter $c = ([I]_0 - [I])(k_p^a/k_{ad})$ on evolution of polydispersities with conversion

Figure 12. Effect of parameter $d = [M]_0(k_p^*/k_{td})$ on evolution of polydispersities with chain length at complete conversion

decrease. A typical feature of systems with slow exchange is that polydispersities decrease with conversion and with chain length in contrast to systems dominated by transfer.

Slow exchange in carbocationic systems

Slow exchange, in addition to transfer, is the most important parameter affecting polydispersity in carbocationic polymerizations.[25,26] It is the main reason for polymodal MWD. It is intuitively easy to imagine a bimodal MWD when two species of different reactivities do not exchange or exchange slowly in comparison with propagation, as clearly demonstrated for anionic systems. Kinetic studies of model and macromolecular systems show that the reactivities of ions and ion pairs are similar in carbocationic polymerization and dormant species are inactive.[27-30] The question remains, however, of whether or not a bimodal MWD is possible for two species with the same reactivities. The answer is 'yes', if their lifetimes are different.[31,32]

Figure 13 shows the evolution of molecular weights with conversion for a hypothetical system (Scheme 4), in which ions and ion pairs have the same reactivities $(k_p^+ = k_p^\pm = 10^5 \text{ mol}^{-1}\text{1 s}^{-1})$, covalent species are inactive $(k_p^c = 0)$, the ionization equilibrium constant is $K_I = 10^{-5} \text{ mol}^{-1}\text{1}$ and the dissociation constant is $K_D = 10^{-6} \text{ mol l}^{-1}$. K_I is defined by the ratio of the rate constant of ionization of covalent species by Lewis acid to that of recombination of ion pair $(K_I = k_i/k_r)$. K_D is defined by the ratio of the rate constant of dissociation of ion pair to that of association of free ions $(K_D = k_{dis}/k_{as})$.
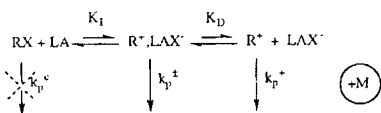
Scheme 4. Equilibria in carbocationic polymerizations

The initial conditions are $[M]_0 = 1 \text{ mol l}^{-1}$, $[I]_0 = 0.01 \text{ mol l}^{-1}$ and $[LA]_0 = 0.1 \text{ mol l}^{-1}$. These conditions, which are typical of the polymerization of styrene and some other alkenes,[33-35] should lead to average values of $DP_n = 10$, 50 and 90 at conversions 10, 5, and 90%, respectively, provided that initiation is quantitative.

Figure 13 clearly demonstrates that although ions and ion pairs have the same reactivities, bimodal MWD is obtained when no common anion [Figure 13(A)] or when only a very small amount of the anion is added [10^{-6} M; Figure 13(B)]. The low molecular weight (LMW) peak increases progressively with conversion. The number-average degree of polymerization of the LMW peak increases for the case (A) from 1.5 to 4.6
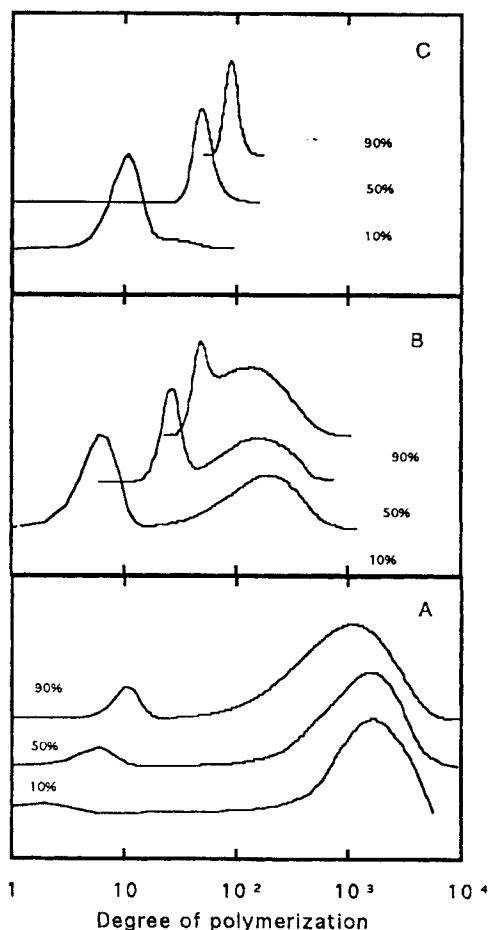

Figure 13. MWD in carbocationic polymerization as a function of conversion in the presence of common anion; $[M]_0 = 1$ M, $[I]_0 = 0.01$ M, $[LA]_0 = 0.1$ M; $k_p^+ = k_p^\pm = 10^5 \text{ M}^{-1}\text{s}^{-1}$; $K_D = 10^{-6}$ M; $K_I = 10^{-5} \text{ M}^{-1}$; $k_i = 10^2 \text{ M}^{-1}\text{s}^{-1}$; $k_r = 10^7 \text{ s}^{-1}$. (A) No salt; (B) $[A^-]_0 = 10^{-6}$ M: (C) $[A^-]_0 = 10^{-5}$ M

and to 9·8 and for case (B) from 5·1 to 25·8 and to 49·8 with conversion (10, 50 and 90%, respectively). The polydispersity of the LMW peak stays fairly narrow $[M_w/M_n = 1·26, 1·21$ and $1·09$ for (A) and $1·20, 1·05$ and $1·04$ for (B)].

The high molecular weight (HMW) peak varies much less than the LMW peak and its number average degree of polymerization decreases for case (A) from 1020 to 750 and to 460 and for case (B) it increases with conversion from 120 to 130 and 140. [The determination of DP_n for case (B) is less precise owing to peak overlap.] Polydispersities of the HMW peak increase for case (A) from $M_w/M_n = 2·2$ and $2·1$ to $2·54$, but decrease for case (B) from $M_w/M_n = 1·74$ and $1·43$ to $1·32$, respectively.

The overall number average degree of polymerization increases with conversion from 17 for (A) [11 for(B)] to 50 and 90 as expected for nearly complete initiation. The overall polydispersities decrease for case (A) from $M_w/M_n = 120$ to 30 and to 12 and for case (B) from $M_w/M_n = 11$ to 2·5 and to 1·6, respectively.

On the other hand, when the concentration of the common anion is increased tenfold to the concentration $[A^-] = 10^{-5} \, \mathrm{mol}\,\mathrm{l}^{-1}$, a nearly perfectly behaved system is found. This leads to degrees of polymerization corresponding exactly to those for the quantitative initiation (10, 50 and 90 at 10, 50 and 90% conversion, respectively). The polydispersities are also low: $M_w/M_n = 1·2, 1·05$ and $1·02$, respectively.

The dramatic effect of adding a common ion shown in Figure 13 is caused mainly by the reduction of the lifetime of free ions, since the rate of unimolecular deactivation of ion pairs is fast enough in this case $(k_r = 10^7 \, \mathrm{s}^{-1})$ compared to propagation $(k_p = 10^5 \, \mathrm{M}^{-1}\mathrm{s}^{-1})$. On the other hand, deactivation of free carbocations is bimolecular and depends on the concentration of the anion. Under the conditions simulated in Figure 13(A), the stationary concentration of ion pairs is $[P^\pm] \approx 10^{-8} \, \mathrm{mol}\,\mathrm{l}^{-1}$ and the stationary concentration of free ions $[P^+] = [A^-] \approx 10^{-7} \, \mathrm{mol}\,\mathrm{l}^{-1}$. Thus, providing that association is diffusion controlled $(k_{as} \approx 10^9 \, \mathrm{mol}\,\mathrm{l}^{-1})$, the lifetime of free cation is defined by

$$\tau^+ = 1/(k_{as}[A^-]) \approx 10^{-2} \, \mathrm{s} \qquad (12)$$

During that time a free carbocation can propagate 1000 times and form high molecular weight polymer:

$$DP^H = k_p^+[M]\tau^+ \approx 10^3 \qquad (13)$$

The lifetime of an ion pair is much shorter:

$$\tau^\pm = 1/(k_r) \approx 10^{-7} \, \mathrm{s} \qquad (14)$$

with less than one propagation step possible during one ionization period at $[M] = 1 \, \mathrm{mol}\,\mathrm{l}^{-1}$. Hence the population of ion pairs grows steadily and continuously, providing a polymer with narrow MWD.

Figure 14 shows the effect of both ionization and dissociation equilibria on the MWD of polymers
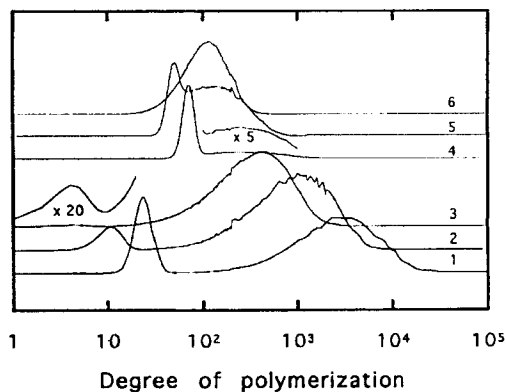

Figure 14. MWD in carbocationic polymerization as a function of the dissociation and ionization equilibrium constants; $[M]_0 = 1 \, \mathrm{M},$ $[I]_0 = 0·01 \, \mathrm{M},$ $[LA]_0 = 0·1 \, \mathrm{M};$ $kp^+ = k_p^\pm = 10^5 \, \mathrm{M}^{-1}\mathrm{s}^{-1};$ $k_r = 10^7 \, \mathrm{s}^{-1}.$ (1) $K_D = 10^{-7} \, \mathrm{M},$ $K_I = 10^{-5} \, \mathrm{M}^{-1};$ (2) $K_D = 10^{-6} \, \mathrm{M},$ $K_I = 10^{-5} \, \mathrm{M}^{-1};$ (3) $K_D = 10^{-5} \, \mathrm{M},$ $K_I = 10^{-5} \, \mathrm{M}^{-1};$ (4) $K_D = 10^{-7} \, \mathrm{M},$ $K_I = 10^{-3} \, \mathrm{M}^{-1};$ (5) $K_D = 10^{-6} \, \mathrm{M},$ $K_I = 10^{-3} \, \mathrm{M}^{-1};$ (6) $K_D = 10^{-5} \, \mathrm{M},$ $K_I = 10^{-3} \, \mathrm{M}^{-1}$

without added salts with common anions at 90% conversion with a standard recombination rate constant $k_r = 10^7 \, \mathrm{mol}^{-1}\mathrm{l}^{-1}\mathrm{s}^{-1}$. The bottom three traces and top three traces depict the change in K_D from 10^{-5} to $10^{-7} \, \mathrm{mol}\,\mathrm{l}^{-1}$ for two different ionization equilibrium constants, $K_I = 10^{-5} \, \mathrm{mol}^{-1}\mathrm{l}$ (bottom) and $10^{-3} \, \mathrm{mol}^{-1}\mathrm{l}$ (top), respectively.

When ionization is weak, a clear bimodal MWD is observed. The concentration of ion pairs is $[C^\pm] = 10^{-8} \, \mathrm{mol}\,\mathrm{l}^{-1}$, whereas the concentration of free ions changes from $[C^+] = 0·3 \times 10^{-7}$ to 1×10^{-7} and to $3 \times 10^{-7} \, \mathrm{mol}\,\mathrm{l}^{-1}$. This means that the proportion of monomer consumed by ions increases from ca 76 to 90 and to 97%, respectively. This is seen in the relative proportions of HMW and LMW peaks.

For the stronger ionization $(K_I = 10^{-3} \, \mathrm{mol}^{-1}\mathrm{l})$, the concentration of ion pairs is $[C^\pm] = 10^{-6} \, \mathrm{mol}\,\mathrm{l}^{-1}$, and the concentration of free ions varies from $[C^+] = 0·3 \times 10^{-6}$ to 1×10^{-6} and to $3 \times 10^{-6} \, \mathrm{mol}\,\mathrm{l}^{-1}$. This means that the contribution of free ions increases from approximately 25 to 50 and then to 75%, respectively. In trace 4, the 25% contribution of free ions can hardly be seen without magnification (broad MWD). In trace 5, nearly equal proportions of both peaks are seen, whereas in trace 6, free ions dominate but differences between polymerization degrees are so small that peaks cannot be separated.

The fraction of the LMW peak is determined by the proportion of ion pairs among all carbocations. However, if they exchange very rapidly with covalent species, they cannot be distinguished from dormant species and the average DP_n of LMW is in that case defined by the ratio of concentrations of the monomer reacted with growing ion pairs to the concentration of

Table 1. Effects of k_i, k_t, k_{tr} and k_{ex} on kinetics and molecular weights in comparison with an ideal living system (ILS)

	Rate	MW	MWD
Slow initiation	Slower than ILS (but with acceleration)	Initially higher, but approaches ILS	<1·3
Termination	Slower than ILS (with deceleration)	No effect (limited conversion)	Broader than ILS
Transfer	No effect	Lower than ILS	Broader than ILS
Slow exchange	No effect	? (may be polymodal)	Very broad, may be polymodal

covalent species (approximately equal to that of the initiator, provided that initiation is complete). Thus, DP_n of LMW is determined by

$$DP_n^L = \Delta[M]/([I]_0 - [I])\{[C^+]/([C^+] + [C^{\pm}])\} \quad (15)$$

The molecular weight of this fraction grows progressively with conversion and MWD is rather narrow ($M_W/M_n < 1·2$), but depends on the dynamics of exchange as discussed previously.

DP_n of the HMW fraction is more difficult to estimate. DP formed during one activation period depends on the relative rates of propagation and deactivation of free ions (the association process)

$$
\begin{aligned}
DP_n^H &= R_p/R_{ass}\{[C^+]/([C^+] + [C^{\pm}])\} \\
&= k_p[M]/k_{as}[C^+]\{[C^+]/([C^+] + [C^{\pm}])\} \quad (16) \\
&= k_p[M]/\{k_{as}([C^+] + [C^{\pm}])\}
\end{aligned}
$$

Surprisingly, the DP_n of the HMW peak does not depend on the concentration of ions rather than on the total amount of ionic species, as shown clearly in Figure 14. The decrease in DP_n^H in traces 1, 2 and 3 is due to increasing total concentration of carbocations from 4×10^{-8} to $1·1 \times 10^{-7}$ and to $3·3 \times 10^{-7}$ mol l^{-1}. The values of DP_n^H in traces 1, 2 and 3 in Figure 14 agree well with those predicted from equation (16), assuming a single activation process for this fraction: $DP_n^H = 1200$, 500 and 200. On the other hand, the values of DP_n^H in traces 4, 5 and 6 are in the range 100–200 and are much higher than those predicted for a single activation process for this population: $DP_n^H = 80$, 20 and 12, respectively. This indicates that this population must grow with conversion, in contrast to the changes shown in traces 1, 2 and 3. The repetitive activation processes also lead to a narrower MWD for this fraction which in traces 6 is $M_w/M_n = 1·30$ for both free ions (75%) and ion pairs (25%).

CONCLUSIONS

Table 1 summarizes the effects of various imperfections such as slow initiation, termination, transfer and slow

exchange on kinetics, molecular weights and polydispersities.

The simulations presented in this paper demonstrate that well defined polymers can be prepared in systems with chain breaking reactions present. Thus, non-living polymerizations may provide controlled polymers under carefully selected conditions. On the other hand, polymers with unpredictable molecular weights and broad or even polymodal molecular weight distributions may form in living systems without irreversible transfer and termination. As shown in Figure 10, the molecular weights may stay constant or even decrease with conversion in some living systems. Therefore, the differences between living and controlled polymerization outlined in Scheme 1 must be stressed.

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