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General Kinetic Analysis and Comparison of Molecular Weight Distributions for Various Mechanisms of Activity Exchange in Living Polymerizations

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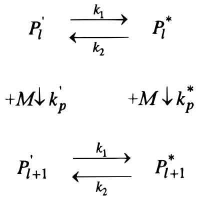
ABSTRACT: The molecular weight distributions in many living (e.g. anionic, group transfer, cationic, and radical) polymerizations strongly depend on the dynamics of various equilibria between chain ends of different reactivity. A very important special case is equilibria between active and dormant centers. Various mechanisms including uni- and bimolecular isomerization (or activation/deactivation), aggregation, and direct bimolecular activity exchange ("degenerative transfer") are discussed and compared. For all these mechanisms (and for both fast and slow monomer addition), the averages of the molecular weight distribution and the polydispersity index (DPI), $\bar{P}_w/\bar{P}_n$, are derived in a unified way. Their dependencies on three universal parameters are analyzed: (i) on the reactivity ratio of the two species, $\lambda = k'_p/k^*_p$, (ii) on the fraction of the more active species, $\alpha = P^*/I_0$, which is determined by the initial concentrations of reagents, and (iii) on a generalized exchange rate parameter, β, which quantifies the rate of exchange relative to that of propagation. The dependence of β on the initial concentrations of reagents is defined by the mechanism of exchange and can be used as a mechanistic criterion to distinguish between various possible mechanisms. For the typical case $\beta > 1$, the PDI decreases with monomer conversion, which is a common observation in many living polymerizations where $10 \le \beta \le 100$ was determined. At full conversion, a simple relation, $\bar{P}_w/\bar{P}_n \approx 1 + \Theta/\beta$, is valid, where Θ depends on α and λ. For the common case where one species is dormant this simplifies further to $\bar{P}_w/\bar{P}_n \approx 1 + 1/\beta$. Generally, the molecular weight distribution is narrower if monomer is added slowly.

Introduction

In many living polymerizations the coexistence of chain ends with different structures is observed ("two-state" or "multistate" mechanisms). Equilibria between species of different reactivity can lead to a considerable broadening of the molecular weight distribution (MWD) if the rate of interconversion is slow or comparable to the rates of propagation.

If exchange is very slow compared to propagation, we will find two narrow distributions generated independently by the two kinds of chain ends. On the other hand, if exchange is very fast or both centers have the same reactivity, the MWD formed will be similar to a single-state process, i.e. a Poisson distribution. Generally, the MWD will be broader than for a single-state mechanism. This was first shown independently by Figini[1,2] and by Coleman and Fox[3] for a unimolecular isomerization of chain ends as shown in Scheme 1, where P'_l and P^*_l denote polymer chains of chain length l and different reactivity. In the following it is assumed that species P′ are less active than species P*, i.e. $k'_p < k^*_p$.

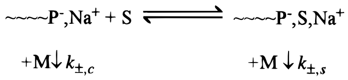
Scheme 1. Two-State Mechanism with Unimolecular Isomerization



$$\begin{tikzcd} P'_l \arrow[r, shift left, "k_1"] \arrow[d, "+M\ k'_p"'] & P^*_l \arrow[l, shift left, "k_2"] \arrow[d, "+M\ k^*_p"] \\ P'_{l+1} \arrow[r, shift left, "k_1"] & P^*_{l+1} \arrow[l, shift left, "k_2"] \end{tikzcd}$$

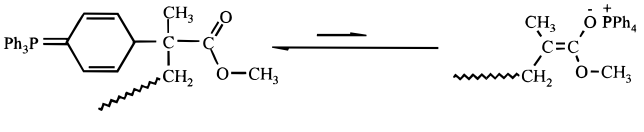
Figini's and Coleman's derivations are based on equilibrium (steady-state) initial conditions, i.e. it was assumed that the position of the equilibrium at time $t = 0$ is equal to that during polymerization. Especially if the chemical nature of the initiator is different from that of the living polymer and exchange is not very fast, this assumption may not be valid.

The results of Figini's calculations were first used by Schulz et al.[4,5] to calculate the rate constants of ion pair dissociation in the anionic polymerization of styrene in polar solvents (although the isomerization mechanism in Scheme 1 does not take into account the counterions formed, cf. Scheme 2b). The unimolecular isomerization of Scheme 1 is suitable for the interconversion of contact to solvent-separated ion pairs in anionic polymerization (which is pseudo-unimolecular because the solvent molecules, S, are in a large excess):



$$\begin{tikzcd} \sim\!\sim\!\sim P^-,Na^+ + S \arrow[r, shift left] \arrow[d, "+M\ k_{\pm,c}"'] & \sim\!\sim\!\sim P^-,S,Na^+ \arrow[l, shift left] \arrow[d, "+M\ k_{\pm,s}"] \\ {} & {} \end{tikzcd}$$

A very important special case of a two-state system is when species P′ is *inactive* or *"dormant"* ($k'_p = 0$, *reversible deactivation*). An example is the unimolecular isomerization between active enolate ion pairs and dormant phosphor ylides in the anionic polymerization of methyl methacrylates with tetraphenylphosphonium counterions in THF:[6,7]



Beside the unimolecular isomerization in Scheme 1, there are other possible mechanisms of activity ex-

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change which are shown in Schemes 2−4. In Scheme 2, the isomerization is bimolecular at least in one direction with one or two low-molecular weight species (C and/or E) involved.

Scheme 2

Scheme 2a: Bimolecular isomerization

$$P'_l + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P^*_l + E$$

Scheme 2b: Bi-/unimolecular isomerization

$$P'_l + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P^*_l$$

Scheme 2c: Uni-/bimolecular isomerization

$$P'_l \underset{k_2}{\overset{k_1}{\rightleftarrows}} P^*_l + E$$

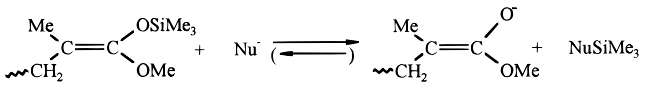
Examples for Scheme 2a are as follows:

anionic polymerization in the presence of alkoxides (both P′ and P* are active);

$$\sim\sim\sim\sim \mathrm{P^-,Li^+} + \mathrm{tBuOK} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^-,K^+} + \mathrm{tBuOLi}$$

however, in such a case typically mixed aggregates will be formed (cf. Scheme 4);

the “dissociative” mechanism of group transfer polymerization (GTP):[8] P′ is a dormant silyl ketene acetal, P* is an active enolate anion or ion pair, C is a nucleophilic catalyst, and E is a silyl ester of the catalyst or a fluorosilane (for $\mathrm{Nu^-} = \mathrm{HF_2^-}$);



the generation of free cations in cationic polymerization: P′ is a covalent species, P* is a free cation, C is a Lewis acid catalyst (“co-initiator”), and E is the counterion;

$$\sim\sim\sim\sim \mathrm{P\text{-}X} + \mathrm{MtX_n} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^+} + \mathrm{MtX^-_{n+1}}$$

however, it has to be taken into account that formation of free cations in general will be a two-step process (first generation of ion pairs, then dissociation). Such a three-state mechanism will not be dealt with here;

atom transfer radical polymerization (ATRP): P′ is a covalent species, P* is a radical, and C and E are a transition metal ion of lower and higher oxidation number, respectively.

$$\sim\sim\sim\sim \mathrm{P\text{-}X} + \mathrm{MtX_n} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^\bullet} + \mathrm{MtX_{n+1}}$$

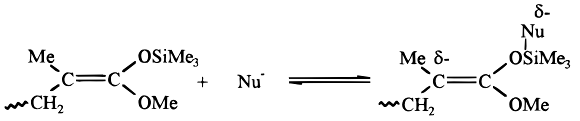
The MWD averages for a mechanism according to Scheme 2a (P′ dormant) were derived by Müller et al.[9] using nonequilibrium initial conditions.

Examples for Scheme 2b are as follows:

anionic polymerization in the presence of activating ligands, e.g. crown ether 12C4 (both P′ and P* are active);

$$\sim\sim\sim\sim \mathrm{P^-,Li^+} + \mathrm{12C4} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^-,Li^+,12C4}$$

the “associative” mechanism of GTP as proposed by Sogah and Webster[10,11] and modified by Mai and Müller:[12,13] P′ and P* are dormant and activated silyl ketene acetals, and C is a nucleophilic catalyst;



the generation of ion pairs in cationic polymerization: P′ is a covalent species, P* is an ion pair, and C is a Lewis acid catalyst (“co-initiator”).[14,15]

$$\sim\sim\sim\sim \mathrm{P\text{-}X} + \mathrm{MtX_n} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^+,MtX^-_{n+1}}$$

The MWD averages for a mechanism according to Scheme 2b (P′ dormant) were derived by Puskas et al.,[15] using equilibrium initial conditions, and by Müller et al.,[16] using nonequilibrium initial conditions.

Examples for Scheme 2c are as follows:

dissociation of ion pairs into free ions in anionic and cationic polymerization: P′ is the ion pair, P* is the free anion (cation), and E is the counterion;

$$\sim\sim\sim\sim \mathrm{P^+,MtX^-_{n+1}} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^+} + \mathrm{MtX^-_{n+1}}$$

again, it has to be taken into account that formation of free anions may occur via a two-step process (first formation of solvent-separated ion pairs, then dissociation). Such a three-state mechanism will not be dealt with here;

anionic polymerization in the presence of deactivating ligands, e.g. aluminum alkyls: P* is a lithiated chain end, P′ is an “ate” complex, and E is the Al alkyl;

$$[\sim\sim\sim\sim \mathrm{P\text{-}AlR_3}]^-,\mathrm{Li^+} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^-,Li^+} + \mathrm{AlR_3}$$

living/controlled radical polymerization: P* is the propagating radical, E is a stable radical, e.g. nitroxide or a thiocarbamate radical, and P′ is the inactive adduct of both.

$$\sim\sim\sim\sim \mathrm{P\text{-}O\text{-}NR_2} \rightleftharpoons \sim\sim\sim\sim \mathrm{P^\bullet} + {}^\bullet\mathrm{O\text{-}NR_2}$$

The MWD averages for a mechanism according to Scheme 2c (living radical polymerization, i.e. P′ inactive) were derived by Yan et al.[17] (no stable radical added) using nonequilibrium initial conditions and by Veregin et al.[18] (stable radical added) using equilibrium initial conditions.

In processes of Scheme 2 with dormant species (GTP and cationic and radical polymerizations), the fraction of active chain ends is much smaller than the total number of polymer chains, partly because the catalyst concentration is smaller than the initiator concentration (GTP with bifluoride catalyst), but more commonly because the equilibria are shifted to the left-hand side. Thus, exchange of activity between the chain ends is necessary in order for all the chains to grow.

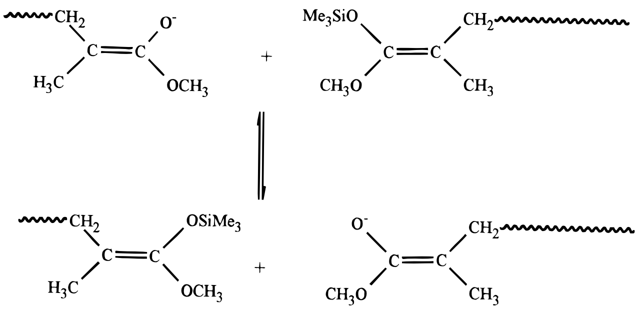
Beside the indirect mechanisms of Scheme 2, a direct bimolecular mechanism of activity exchange (“degenerative transfer”, Scheme 3) was recently proposed by us and the MWD moments were calculated.[19,20]

Scheme 3. Degenerative Transfer between Chain Ends of Different Activity

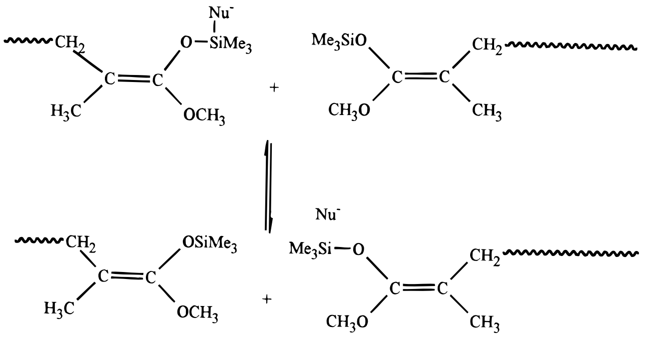
$$P'_l + P^*_m \underset{k_1}{\overset{k_1}{\rightleftarrows}} P'_m + P^*_l$$

In principle, such an exchange can occur for most living mechanisms:

in GTP via enolates (as generated by Scheme 2a):



in GTP via activated silyl ketene acetals (as generated by Scheme 2b):



in cationic polymerization it means the exchange of a halogen ion between a covalent species and a free cation:

$$\sim\sim\sim\sim\mathrm{P\text{-}X} + {}^{+}\mathrm{P}\sim\sim\sim\sim\sim\sim\sim \rightleftarrows \sim\sim\sim\sim\mathrm{P}^{+} + \mathrm{X\text{-}P}\sim\sim\sim\sim\sim\sim\sim$$

in living radical polymerization it means the exchange of a nonactive radical or a halogen atom between a covalent species and an active radical:

$$\sim\sim\sim\sim\mathrm{P\text{-}X} + {}^{\bullet}\mathrm{P}\sim\sim\sim\sim\sim\sim\sim \rightleftarrows \sim\sim\sim\sim\mathrm{P}^{\bullet} + \mathrm{X\text{-}P}\sim\sim\sim\sim\sim\sim\sim$$

in anionic polymerization in the presence of more than one counterion, where the different ion pairs have different activities,[21]

$$\sim\sim\sim\sim\mathrm{P}^{-},\mathrm{Na}^{+} + \mathrm{Li}^{+},\mathrm{P}^{-}\sim\sim\sim\sim\sim\sim\sim \rightleftarrows \sim\sim\sim\sim\mathrm{P}^{-},\mathrm{Na}^{+} + \mathrm{Li}^{+},\mathrm{P}^{-}\sim\sim\sim\sim\sim\sim\sim$$

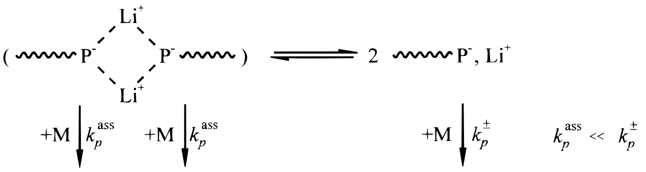
however, here the formation of mixed aggregates as intermediates has to be taken into account (cf. Scheme 4).

Finally, the two species may differ in their state of aggregation (Scheme 4).

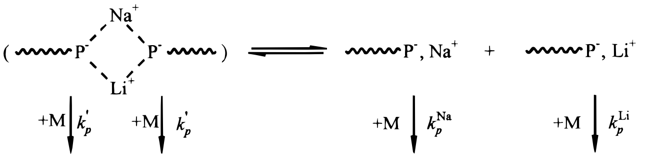
Scheme 4. Aggregation of Two Chain Ends

$$(P'_l \bullet P'_m) \underset{k_2}{\overset{k_1}{\rightleftarrows}} P^*_l + P^*_m$$

Aggregates are the predominant species in anionic polymerization in nonpolar solvents. It is assumed that propagation occurs predominantly[34,35] or exclusively[36] via nonaggregated species; i.e. aggregated polymers are much less active or even inactive. For polar monomers in polar solvents aggregates have a certain reactivity which is much lower than that of the nonaggregated species).[22]



Active bimetallic aggregates have been proposed in order to explain peculiar behavior in the anionic polymerization of dienes with mixed initiators:[21]



The MWD averages for the case of inactive aggregates were derived by Kunkel et al.[22] using equilibrium initial conditions and for active aggregates by Müller and Litvinenko using nonequilibrium initial conditions.[23]

Often, kinetic measurements are not sufficient in order to establish the true mechanism of a given polymerization. Additional information can be obtained from the MWD of the polymers formed. Thus, from the kinetic schemes given above, the dependence of the MWD averages can be derived as a function of conversion and initial concentrations. These dependences may serve as a mechanistic criterion in order to discriminate between two or more possible mechanisms. Based on such comparisons, we proposed that degenerative transfer may be the predominant mechanism of exchange in GTP and cationic polymerization.[9]

In this paper we wish to give a general treatment and unified view of the various mechanisms of exchange between various species and to compare the MWD averages obtained in these mechanisms and their dependences on monomer conversion and initial concentrations of reagents. Due to the complexity of the differential equations it is generally not possible to calculate the full MWD function, unless monomer concentration is kept constant (i.e. slow monomer addition or low conversion).

Kinetic Differential Equations

Independently of the particular mechanism of exchange, differential equations describing the conversion of the monomer and the evolution of concentrations of more and less active macromolecules, P^*_l and P'_l, respectively, containing l monomer units which add monomer with rate constants k^*_{p} and k'_{p} can be represented in a unified form:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -M(k^*_{\mathrm{p}}P^* + k'_{\mathrm{p}}P')$$

$$\frac{\mathrm{d}P^*_l}{\mathrm{d}t} = k^*_{\mathrm{p}}M(P^*_{l-1} - P^*_l) + k_1AP'_l - k_2BP^*_l \qquad (l \geq 0) \tag{1}$$

$$\frac{\mathrm{d}P'_l}{\mathrm{d}t} = k'_{\mathrm{p}}M(P^*_{l-1} - P^*_l) - k_1AP'_l + k_2BP^*_l \qquad (l \geq 0)$$

where $P^* = \sum_0^\infty P^*_l = \alpha I_0$ and $P' = \sum_0^\infty P'_l = (1 - \alpha)I_0$ are

Table 1. Equilibrium Concentrations of More Active Centers, α, and Parameters *A* and *B* in Eq 1 [$\epsilon = C_0/C_0$; $\eta = E_0/I_0$

Scheme No.	Mechanism of exchange	A	B	$\alpha = P^*/I_0$	K
1	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	1	1	$\frac{1}{K+1}$	$\frac{k_2}{k_1}$
2a	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	$C = I_0(\varepsilon - \alpha)$	$E = (\alpha + \eta)I_0$	$\frac{\sqrt{(\varepsilon + 1 + K\eta)^2 + 4\varepsilon(K-1)} - (\varepsilon + 1 + K\eta)}{2(K-1)}$	$\frac{k_2}{k_1}$
2b	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	$C = I_0(\varepsilon - \alpha)$	1	$\frac{\varepsilon}{K+1}$	$\frac{k_2}{k_1 I_0}$
2c	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	1	$E = (\alpha + \eta)I_0$	$\frac{\sqrt{(1 + K\eta)^2 + 4K} - (1 + K\eta)}{2K}$	$\frac{k_2 I_0}{k_1}$
3	$P_l' + P_m^* \underset{k_1}{\overset{k_1}{\rightleftarrows}} P_m' + P_l^*$	αJ_0	$(1-\alpha)I_0$	depends on the mechanism of generation of active centers	1
4	$(P_l' \bullet P_m') \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + P_m^*$	1	αJ_0	$\frac{\sqrt{1+4K} - 1}{2K}$	$\frac{k_2 I_0}{k_1}$

the total concentrations of the more and less active centers, respectively, and $\alpha = P^*/I_0$ is the equilibrium fraction of more active centers. Index $l = 0$ denotes initiator molecules. Parameters A and B are defined by the particular scheme of exchange (see Table 1).

For degenerative transfer (Scheme 3), α is given by the particular process which generates the active centers (if a mixture of two initiators is used, α can be chosen arbitrarily: $0 < \alpha < 1$). For all other mechanisms, α is defined from the equilibrium (steady-state) condition

$$k_1 A(1 - \alpha) = k_2 B\alpha \tag{2}$$

The dependence of α on the rate constants of exchange and reagent concentrations is also shown in Table 1.

Depending on the conditions of the experiment, two limiting type cases can be imagined: equilibrium and nonequilibrium initial conditions. In the latter, more general case, the equilibrium of eq 2 is not yet reached at $t = 0$. However, it was shown that the effect of initial conditions is significant only when the exchange is sufficiently slow compared to propagation.[9,16] This case will be discussed later. Thus, we first restrict the discussion to equilibrium initial conditions. Then, eq 2 is valid from $t = 0$, and

$$P_l^*|_{t=0} = \alpha I_0 \delta_{l,0} \qquad P_l'|_{t=0} = (1 - \alpha)I_0 \delta_{l,0}$$

where $\delta_{l,j}$ is the Kronecker symbol. This case corresponds to an experiment where initiator and polymer chain ends have the same chemical nature (and thus the same equilibrium constant) and reagents have enough time to establish the equilibrium before monomer is added. This treatment is less general and—except for the special treatment of unreacted initiator in the case of dormant polymers—is similar to that of Figini[1] for unimolecular isomerization of chain ends (Scheme 1).

From the set of differential eqs 1 it follows that monomer conversion, $x = (M_0 - M)/M_0$, increases with time according to the same law as for a single-state living polymerization:

$$x = 1 - \exp(-\bar{k}_p I_0 t) \tag{3}$$

with the apparent rate constant of propagation, $\bar{k}_p$, which is related to the individual rate constants by

$$\bar{k}_p = \alpha k_p^* + (1 - \alpha)k_p' = k_p' + \alpha(k_p^* - k_p') \tag{4}$$

From set 1 it is easy to derive the corresponding equations for the nth moments of the MWD for the more and less active centers, respectively,

$$\mu_n^* = \sum_0^\infty l^n P_l^* \quad \text{and} \quad \mu_n' = \sum_0^\infty l^n P_l' \tag{5}$$

and for the total polymer formed, $\mu_n = \mu_n^* + \mu_n'$:

$$\frac{d\mu_n^*}{dt} = k_p^* M \sum_{i=0}^{n-1} \binom{n}{i} \mu_i^* + k_1 A \mu_n' - k_2 B \mu_n^*$$

$$\frac{d\mu_n'}{dt} = k_p' M \sum_{i=0}^{n-1} \binom{n}{i} \mu_i' - k_1 A \mu_n' + k_2 B \mu_n^* \tag{6}$$

$$\frac{d\mu_n}{dt} = M \sum_{i=0}^{n-1} \binom{n}{i} (k_p^* \mu_i^* + k_p' \mu_i')$$

where

$$\binom{n}{i} = \frac{n!}{i!(n-i)!}$$

According to the definition, the zeroth moment of the total polymer is the total number of polymer chains, and if initiation is fast for the both types of centers,

$$\mu_0 = \mu_0^* + \mu_0' = I_0 \tag{7}$$

The first moment is the amount of monomer converted into polymer,

$$\mu_1 = \mu_1^* + \mu_1' = M_0 x \tag{8}$$

If initiation is fast for the centers of both types, the number-average degree of polymerization is independent of the exchange rate

$$\bar{P}_n \equiv \mu_1/\mu_0 = \gamma x \tag{8a}$$

where $\gamma = M_0/I_0$ is the degree of polymerization of the polymer formed in a single-state living polymerization at full conversion.

Polydispersity Index for Two Active Centers

In order to calculate the second moment of the MWD it is convenient to rewrite eqs 6 using conversion, x, as the variable. Neglecting in the summations over l all terms with $l < n - 1$, which are responsible for the Poisson inhomogeneity, we obtain:

$$(1-x)\frac{d\mu_n^*}{dx} = n\gamma^*(1-x)\mu_{n-1}^* + \beta\left(\mu_n' - \frac{1-\alpha}{\alpha}\mu_n^*\right)$$

$$(1-x)\frac{d\mu_n'}{dx} = n\lambda\gamma^*(1-x)\mu_{n-1}' + \beta\left(\mu_n' - \frac{1-\alpha}{\alpha}\mu_n^*\right) \qquad (9)$$

$$\frac{d\mu_n}{dx} = n\gamma^*(\mu_{n-1}^* + \lambda\mu_{n-1}')$$

where $\lambda = k_p'/k_p^*$ is the ratio of rate constants of propagation of the less and more active species and $\gamma^* = \gamma/[\alpha + \lambda(1-\alpha)]$. Parameter

$$\beta = \frac{\chi B}{(1-\alpha)I_0}\,\frac{\alpha}{\alpha + \lambda(1-\alpha)}$$

is a generalized exchange rate, where $\chi = k_2/k_p^*$ is the ratio of rate constants of formation of less active species and of propagation of more active centers.

In order to calculate the weight-average degree of polymerization, $\bar{P}_w \equiv \mu_2/\mu_1$, it is necessary to calculate the second MWD moment, μ_2, and, consequently, as it follows from the last equation of set 9, the first moment of one of the species, e.g., μ_1^*.

From eqs 9 for $n = 1$ we obtain for μ_1^*

$$\mu_1^*/M_0 = \alpha x + \frac{\lambda\alpha(1-\alpha)}{\alpha + \lambda(1-\alpha)}\,\frac{(1-x) - (1-x)^\nu}{\nu - 1} \qquad (10)$$

where $\nu = \beta/\alpha > \beta$.

Substituting expression 10 into the last equation of set 9 and integrating over conversion at $n = 2$, we obtain the final expression for the weight-average degree of polymerization:

$$\bar{P}_w/\gamma = x + \frac{\Theta}{\alpha(\nu-1)}\left\{2 - x - 2\frac{1-(1-x)^{\nu+1}}{x(\nu+1)}\right\} \qquad (11)$$

where

$$\Theta = \frac{\alpha^2(1-\alpha)(1-\lambda)^2}{[\alpha + \lambda(1-\alpha)]^2} < 1 \qquad (12)$$

is a parameter which combines the effects of α and λ on the PDI and is always less than unity. Expression 11 is universal and valid for all mechanisms of exchange (Schemes 1−4) and all possible values of α, β, and λ.

Assuming fast initiation for both types of active centers (i.e., $\bar{P}_n = \gamma x$), we obtain for the polydispersity index (PDI)

$$\bar{P}_w/\bar{P}_n = 1 + \frac{\Theta}{\beta - \alpha}\left\{\frac{2}{x} - 1 - 2\,\frac{1-(1-x)^{\nu+1}}{x^2(\nu+1)}\right\} \qquad (13)$$

For full conversion, general expression 13 leads to

$$\bar{P}_w/\bar{P}_n = 1 + \frac{\Theta}{\beta + \alpha} < 1 + \frac{1}{\beta} \qquad (14)$$

The upper limit in eq 14 follows from eq 12 (i.e., $\Theta < 1$).

If exchange is sufficiently fast ($\nu \gg 1$, or $\beta \gg \alpha$), even at low conversion it is possible to neglect the last term in eqs 11 and 13. Then, the expressions for $\bar{P}_w$ and PDI simplify to

$$\bar{P}_w/\gamma \approx x + \frac{2-x}{\beta}\Theta \qquad (11a)$$

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{\Theta}{\beta}\left(\frac{2}{x} - 1\right) \qquad (13a)$$

As follows from eq 13a, PDI decreases with increasing conversion and at full conversion is

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{\Theta}{\beta} \qquad (14a)$$

Thus, if the exchange rate is sufficiently high ($\beta \gtrsim 10$), the PDI of the final polymer will be small irrespective of α and λ. For $\beta < 10$ the dependence of PDI on parameters α and λ is more complicated (see below). However, before we can discuss this point in detail, we have to take care of another important point.

Effect of Residual Initiator. Up to now, all results concerning PDI were obtained under the assumption of fast initiation, i.e., the number of polymer chains was assumed to be equal to the initiator concentration, I_0, from the very beginning of polymerization and, consequently, $\bar{P}_n = \gamma x$. However, when one type of center is dormant ($\lambda = 0$) or "nearly dormant" ($\lambda \ll 1$), the term "fast initiation" cannot be applied for it. If exchange is slow, there will be a considerable fraction of initiator which did not have the chance to add a single monomer molecule. This residual initiator cannot be considered as a polymer chain and it will not be measured in the experimental determination of the MWD.[19] Thus, it must be excluded from the calculations of the MWD moments by starting the summation from $l = 1$ instead of $l = 0$. It is obvious from eq 5 that inclusion or exclusion of the residual initiator, $P_0 = P_0' + P_0^*$, only comes into effect for the zeroth moment, μ_0, and, thus, only for the calculation of $\bar{P}_n$. Thus, the correct form of $\bar{P}_n$ must read:

$$\bar{P}_n = \frac{\mu_1}{\mu_0 - P_0} = \frac{M_0 x}{I_0 - P_0} = \frac{\gamma x}{1 - P_0/I_0} \qquad (9a)$$

Only in some special cases (e.g. dimeric or oligomeric initiator) it may be measured, and then, $\bar{P}_n = \gamma x$.

The concentration of unreacted initiator can be calculated directly from set 1 for $l = 0$. Rewritten in terms of conversion, these equations obtain the form

$$(1-x)\frac{dP_0^*}{dx} = -\gamma^*(1-x)P_0^* + \beta\left[P_0' - \frac{1-\alpha}{\alpha}P_0^*\right]$$

$$(1-x)\frac{dP_0'}{dx} = -\lambda\gamma^*(1-x)P_0' - \beta\left[P_0' - \frac{1-\alpha}{\alpha}P_0^*\right] \qquad (15)$$

Obviously, if exchange is very fast, P_0 will decrease very fast and can be neglected at low conversions. On the other hand, at very slow exchange the effect of P_0

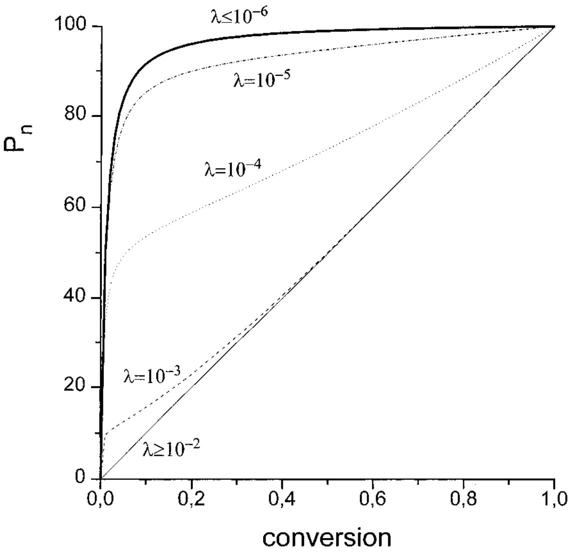


Figure 1. Dependence of the number-average degree of polymerization on conversion for different values of $\lambda = k_p'/k_p^*$. $\beta = 1$, $\alpha = 0.01$, $\gamma = 100$.

is significant till the end of polymerization. The approximate solution of eqs 15 was given for Schemes 2a,[9] 2b,[16] and 3[19] for the case of dormant species ($\lambda = 0$). The following simple considerations allow the upper limit for P_0 to be obtained, assuming instantaneous initiation by the more active initiator P_0^*. Then, the active initiator, P_0^*, formed from the less active one, P_0', will nearly exclusively add monomer instead of converting back to the dormant species. Since P_0^* directly reacts to form polymer, its actual concentration will be very low and the concentration of dormant initiator is approximately equal to the total concentration of residual initiator, $P_0' \approx P_0$. Thus, the second equation of set 15 can be simplified by neglecting the back-reaction

$$(1 - x)\frac{\mathrm{d}P_0'}{\mathrm{d}x} \approx -[\lambda\gamma^*(1 - x) + \beta]P_0' \qquad (15a)$$

The first term in square brackets relates to consumption of initiator by monomer addition, the second term to conversion to active initiator. This equation is easily integrated:

$$P_0/I_0 \approx P_0'/I_0 \approx (1 - \alpha)(1 - x)^{\beta} \exp(-\lambda\gamma^* x) \quad (16)$$

Equation 16 shows that the concentration of the residual initiator at full conversion ($x = 1$) vanishes. However, if both modes of disappearance of P_0' (due to exchange, β, and due to monomer addition, $\lambda\gamma^*$) are very slow, the consumption of initiator is very slow and is completed only in a very late stage of the polymerization that is hardly reached in a real polymerization.

Subtracting the concentration of unreacted initiator from the total number of polymer chains, we obtain for the number-average degree of polymerization

$$\bar{P}_n \approx \frac{\gamma x}{1 - (1 - \alpha)(1 - x)^{\beta} \exp(-\lambda\gamma^* x)} \qquad (17)$$

The character of the decrease in the concentration of unreacted initiator with conversion can be seen from Figure 1 for sufficiently slow exchange, $\beta = 1$. For low values of λ the deviation of $\bar{P}_n$ from the expected linear behavior becomes very pronounced. It can be concluded that species P′ can be considered as dormant if the rate of disappearance of P_0' due to propagation is negligible, i.e., $\lambda\gamma^* \ll 1$.

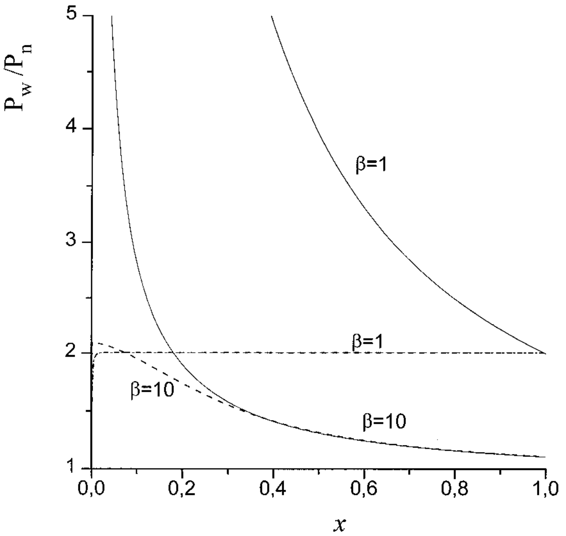


Figure 2. The effect of residual initiator on the polydispersity index for $\alpha = 0.01$ and $\lambda = 0$. Dashed lines: initiator is not considered as a polymer chain.

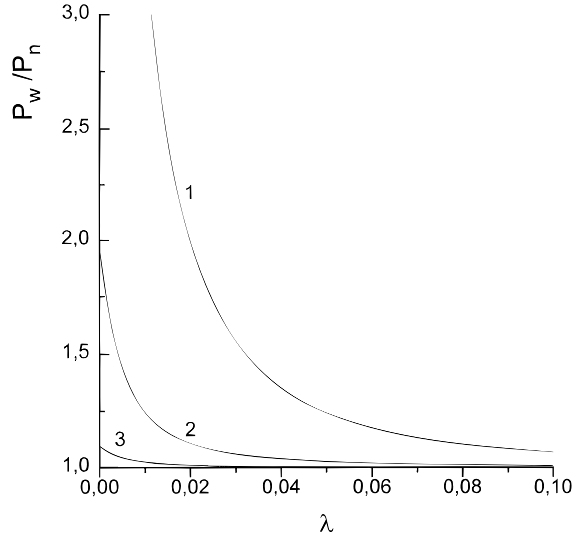


Figure 3. Dependence of the polydispersity index of the polymer obtained at full conversion on the reactivity ratio of centers, $\lambda = k_p'/k_p^*$. $\alpha = 0.01$. (1) $\beta = 0.1$, (2) $\beta = 1$, (3) $\beta = 10$.

Thus, a slow rate of initiation leads to higher values of $\bar{P}_n$ and, consequently, to PDI's lower than that predicted by eq 13. This is shown in Figure 2 for dormant species P′ ($\lambda = 0$). As can be seen, for $\beta < 10$ the difference is significant.

Consequently, the correct form of eqs 13 and 14 for the polydispersity index at incomplete conversion ($x < 1$) is obtained by multiplying with $1 - P_0/I_0$:

$$\left(\frac{\bar{P}_w}{\bar{P}_n}\right)_{\text{corr}} = \left(\frac{\bar{P}_w}{\bar{P}_n}\right)_{\text{with init}} [1 - (1 - \alpha)(1 - x)^{\beta} \times \exp(-\lambda\gamma^* x)] \quad (18)$$

Dependence of Polydispersity Index on the Fraction of More Active Species, α, the Reactivity Ratio, λ, and the Exchange Rate Parameter, β. For a given fraction of more active species, α, parameter Θ—and consequently, the PDI—decrease with increasing reactivity ratio, λ. The highest PDI is always obtained for $\lambda = 0$, i.e. for dormant species P′. For $\lambda = 1$ (both

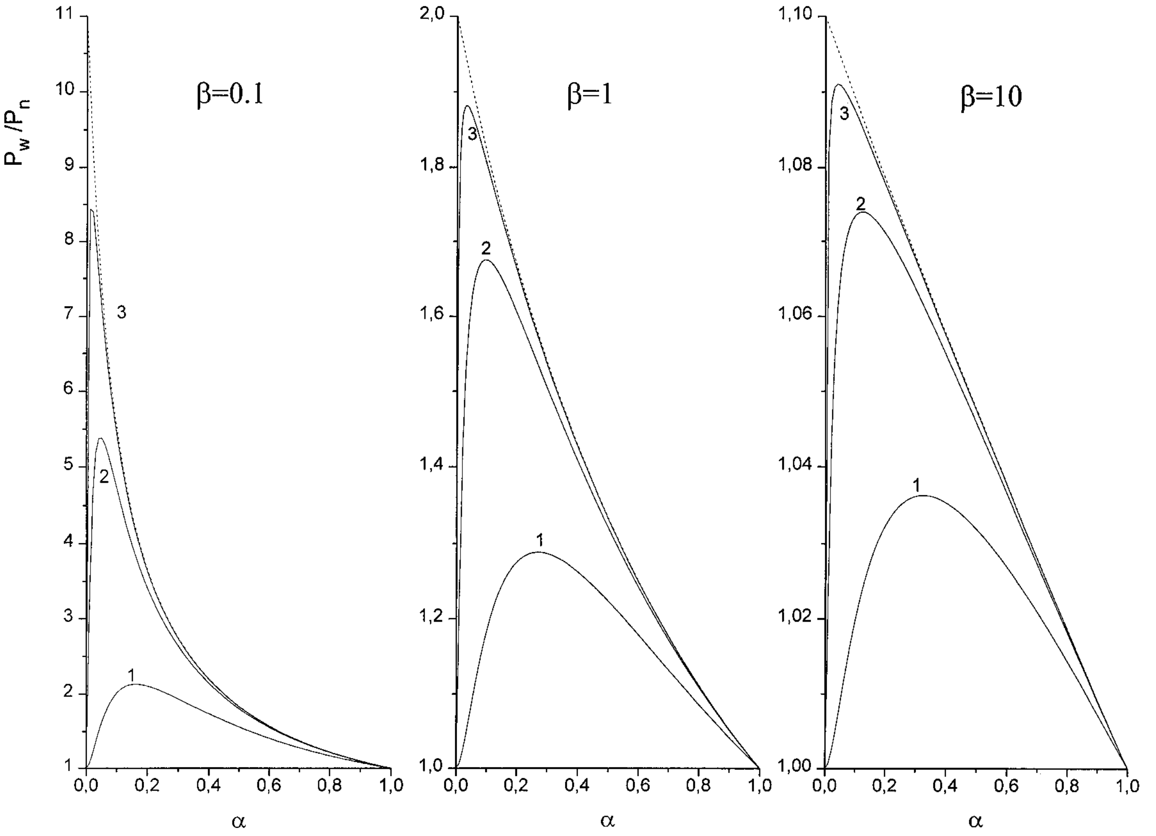


Figure 4. Dependence of the polydispersity index of the final polymer on the fraction of more active species $\lambda = k_p'/k_p^*$: (1) λ = 0.1, (2) λ = 0.01, (3) λ = 0.001, (dashed line) $\lambda \equiv 0$.

species are equally active) the PDI reaches unity, like in a single-state polymerization. This is shown in Figure 3 for the polymer obtained at full conversion.

In Figure 4 the polydispersity index is shown as a function of the fraction of more active species, α. Naturally, for the single-state cases α = 0 and α = 1, PDI is unity. Thus, $\bar{P}_w/\bar{P}_n$ passes a maximum. The position of the maximum and maximal value of $\bar{P}_w/\bar{P}_n$ depends on β and λ. In the limiting case of dormant species ($\lambda \equiv 0$), the PDI decreases with increasing α from $1 + 1/\beta$ (for $\alpha \ll 1$) to unity at α = 1.

The dependence of the PDI on conversion is rather complex. The results are shown in Figure 5 for $\beta = 1$. For this value of β, after an initial increase we always find a decrease of PDI with conversion, except for $\lambda \leq 10^{-6}$. Generally, the behavior depends on the relationship between α and λ and we can distinguish two limiting cases:

(i) For $\lambda \ll \alpha$, eq 12 leads to $\Theta \approx 1 - \alpha$, and $\bar{P}_w$ does not depend on λ (cf. eq 11). However, due to the effect of residual initiator, $\bar{P}_n$ decreases with increasing λ (cf. eq 16). Thus, at a given conversion, $x < 1$, the PDI increases with increasing λ.

(ii) On the other hand, for $\lambda \gtrsim \alpha$, species P′ are already sufficiently active and residual initiator can be neglected; thus, $\bar{P}_n \approx \gamma x$. However, now Θ begins to decrease with increasing λ and thus, for $\lambda \gtrsim \alpha$, the PDI at $x < 1$ decreases with increasing λ.

As follows from eq 14, for $x \equiv 1$, the PDI decreases with increasing β and reaches unity for $\beta \gg 1$. On the other hand, it can become very high for $\beta \ll \alpha$, i.e. $\bar{P}_w/\bar{P}_n \approx 1 + \Theta/\alpha$. However, it is clear that for a very slow exchange rate ($\beta \ll 1$) and very low reactivity of species P′ ($\lambda \ll 1$), even at conversions as high as $x = 0.999$, a sufficiently high fraction of initiator did not convert into polymer chains and thus only the more active species formed polymer. Consequently, the MWD will be very narrow. This can be seen from the dependence of polydispersity index on the exchange rate parameter, β, as shown in Figure 6 for 99% conversion. The character of the dependence of $\bar{P}_w/\bar{P}_n$ on λ is similar to that discussed above for Figure 5.

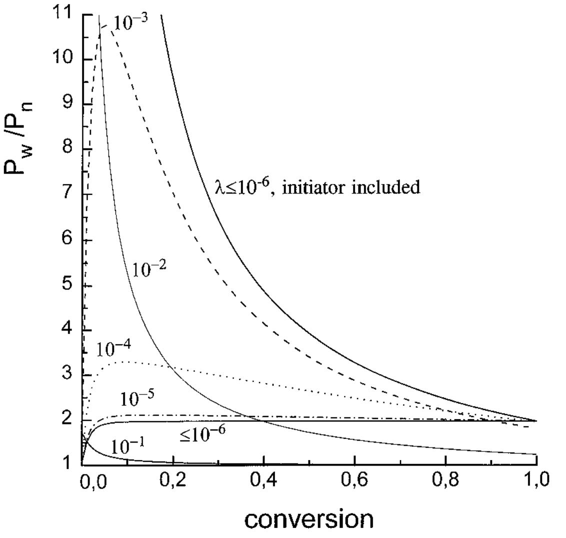


Figure 5. Dependence of polydispersity index on conversion for β = 1, α = 0.01, and different values of λ.

As can be seen from eqs 13 and 17, the dependence of PDI on conversion is independent of the mechanism. However, the dependence of the DPI on the concentrations of reagents is defined by the mechanism. This will be discussed below for the case in which one of the centers is dormant.

Table 2. Exchange Rate Parameter and Polydispersity Index at Full Monomer Conversion for Different Mechanisms of Activity Exchange Where P′ is Dormant ($\alpha \ll 1$)[$\epsilon = C_0/I_0$; $\eta = E_0/I_0$; $\chi = k_2/k_p$]

Scheme No	Mechanism of exchange	Relative exchange rate, β	Polydispersity index, $\bar{P}_w/\bar{P}_n$	
1	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	$\frac{\chi}{(1-\alpha)I_0} \approx \frac{\chi}{I_0}$	$1+\frac{k_p I_0}{k_2}$	
2a	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	$\chi(\alpha+\eta)$	equilibrium left $E_0 = 0; \chi >> 1$: $1+\frac{k_p}{\sqrt{k_1 k_2}} \cdot \sqrt{\frac{I_0}{C_0}}$ $E_0 \gtrsim C_0, \chi >> 1$: $1+\frac{k_p}{k_2}\frac{I_0}{E_0}$	equilibrium right, $\varepsilon << 1$ $E_0 = 0; \chi >> 1$. $1+\frac{k_p}{k_2} \cdot \frac{I_0}{C_0}$ $E_0 \gtrsim C_0, \chi >> 1$: $1+\frac{k_p}{k_2}\frac{I_0}{(C_0+E_0)}$
2b	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	$\frac{\chi}{I_0}$	$1+\frac{k_p I_0}{k_2}$	
2c	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	$\frac{\chi(\alpha+\eta)}{(1-\alpha)} \approx \chi(\alpha+\eta)$	$E_0 = 0$: $1+\frac{k_p}{\sqrt{k_1 k_2}} \cdot \sqrt{I_0}$	$E_0 > 0$: $1+\frac{k_p I_0}{k_2 E_0}$
3	$P_l' + P_m^* \underset{k_1}{\overset{k_1}{\rightleftarrows}} P_m' + P_l^*$	χ	$1+\frac{k_1}{k_p}$	
4	$(P_l' \bullet P_m') \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + P_m^*$	$\frac{\chi\alpha}{1-\alpha} \approx \chi\alpha$	$1+\frac{k_p}{\sqrt{k_1 k_2}} \cdot \sqrt{I_0}$	

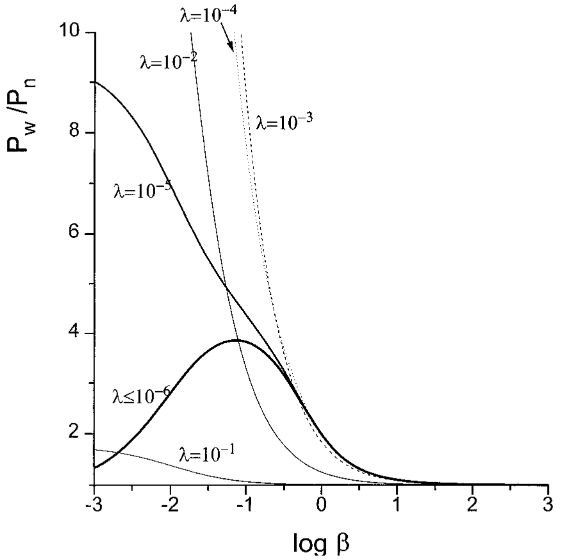


Figure 6. Dependence of polydispersity index on the exchange rate parameter, β, for $x = 0.99$. $\alpha = 0.01$.

Two-State Polymerization When One Type of Centers is Dormant

The most important limiting case is when one type of the centers, P′, is dormant, i.e. $k_p' \equiv 0$ or $\lambda = 0$. Since there is only one active species, we set $k_p^* \equiv k_p$. This case was discussed separately for Schemes 2a,[9] 2b,[16] 2c,[17] and 3.[19] We now will analyze this case in a more generalized form.

The expressions for the generalized exchange rate, β, for all schemes of exchange are given in Table 2. The expressions for $\bar{P}_w$ and $\bar{P}_n$ are obtained from eqs 11 and 16 for $\lambda = 0$. In this case parameter Θ simplifies to

$$\Theta = 1 - \alpha$$

and for full conversion expression 14 for the PDI takes the form

$$\bar{P}_w/\bar{P}_n = \frac{\beta + 1}{\beta + \alpha} \tag{19}$$

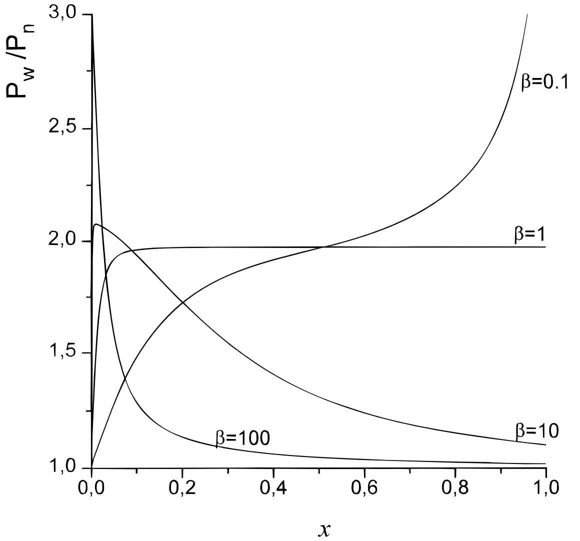


Figure 7. Dependence of polydispersity index on conversion for different values of β for the case of inactive P′ ($\lambda = 0$). $\alpha = 0.01$.

If exchange is not very slow ($\beta \gg \alpha$), this expression transforms into eq 14.

The character of the dependence of polydispersity index on conversion can be seen from Figure 7. Three different forms of the dependence can be distinguished:

(i) $\beta < 1$ (slow exchange): $\bar{P}_w/\bar{P}_n$ continuously increases to the final value defined by eq 19 at $x = 1$. The rather strong increase for $x > 0.8$ shown in Figure 7 for $\beta = 0.1$ stems from the fact that, up to $x = 0.8$, only ca. 10% of the initiator molecules have been activated, thus enabling them to form polymer. The remaining initiator molecules become consecutively activated between $x = 0.8$ and $x = 1$, leading to the formation of many oligomer molecules, thus broadening the MWD.

(ii) $\beta = 1$: The polydispersity index rapidly increases up to a limiting value of $\bar{P}_w/\bar{P}_n \approx 2$.

(iii) $\beta > 1$ (moderately fast exchange): After a fast marked increase at very small conversions, $\bar{P}_w/\bar{P}_n$ continuously decreases to the final value defined by eq 19 at $x = 1$.

Typically, for many living polymerizations, values of $10 \le \beta \le 100$ are found.[16,19] Thus, the case $\beta \le 1$ need not be considered in too much detail.

Let us apply now the results obtained for the analysis of the PDI of the polymer formed at full conversion for particular mechanisms of exchange (Schemes 1–4). It will be seen that the PDI depends on the initial concentrations of reagents in a different way for most mechanisms. Thus, this dependence can be used as a mechanistic criterion.

Application to Particular Mechanisms of Exchange. Scheme 1 (Unimolecular Isomerization). For this scheme, the fraction of active centers is

$$\alpha = \frac{1}{K+1} = \frac{k_1}{k_1 + k_2}$$

with $K = k_2/k_1$, and the exchange parameter is

$$\beta = \frac{k_1 + k_2}{k_p I_0} = \frac{k_1}{\alpha k_p I_0} = \frac{k_2}{(1-\alpha) k_p I_0} = \frac{\chi}{(1-\alpha) I_0} \qquad (20)$$

If the equilibrium is shifted to the side of the dormant centers ($\alpha \ll 1$), this leads to

$$\beta \approx \frac{\chi}{I_0}$$

The general expression for the PDI is

$$\bar{P}_w/\bar{P}_n = \frac{\beta + 1}{\beta + \alpha} = \frac{\chi/I_0 + 1 - \alpha}{\chi/I_0 + \alpha(1-\alpha)} \qquad (21)$$

When $\beta \gg \alpha$, this equation simplifies to

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\beta} = 1 + \frac{I_0}{\chi} = 1 + \frac{k_p I_0}{k_2} \qquad (22)$$

Hence, the PDI linearly increases with increasing initiator concentration.

Scheme 2a (Bimolecular Isomerization). This case applies to GTP ("dissociative" mechanism), cationic polymerization via free ions, and ATRP (see Introduction). The fraction of active centers is given as

$$\alpha = \frac{\sqrt{(\epsilon + 1 + K\eta)^2 + 4\epsilon(K-1)} - (\epsilon + 1 + K\eta)}{2(K-1)} \qquad (23)$$

with $K = k_2/k_1$, $\epsilon = C_0/I_0$, and $\eta = E_0/I_0$.

The exchange parameter is given as[9]

$$\beta = \chi(\alpha + \eta)$$

leading to the following expression for the PDI:

$$\bar{P}_w/\bar{P}_n = \frac{\beta + 1}{\beta + \alpha} = \frac{\chi(\alpha + \eta) + 1}{\chi(\alpha + \eta) + \alpha} \qquad (24)$$

Since α depends on K and η, the effects of χ and K should be analyzed separately and we have to distinguish two cases.

(a) No *E* Added Prior to Polymerization ($\eta = 0$). E is the byproduct of active center formation. In GTP, it corresponds to a silyl ester, in cationic polymerization it is the free counteranion, and in ATRP it is a transition metal ion of higher oxidation state. Then,

$$\alpha = \frac{\sqrt{(\epsilon + 1)^2 + 4\epsilon(K-1)} - (\epsilon + 1)}{2(K-1)} \quad \text{and} \quad \beta = \chi\alpha \qquad (25)$$

Thus, eq 24 simplifies into

$$\bar{P}_w/\bar{P}_n = \frac{\chi\alpha + 1}{\chi\alpha + \alpha} \qquad (26)$$

(i) If the equilibrium in Scheme 2a is shifted to the right-hand side (i.e., $4\epsilon K \ll 1$, typical for GTP with strongly nucleophilic catalysts, where $\epsilon \ll 1$), eq 24 simplifies to $\alpha \approx \epsilon$ and

$$\bar{P}_w/\bar{P}_n = \frac{\chi\epsilon + 1}{\chi\epsilon + \epsilon} \qquad (26)$$

This value depends on the magnitude of χ. If exchange is not extremely slow, so that $\chi \gg 1$,

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\chi\epsilon} = 1 + \frac{1}{\chi}\frac{I_0}{C_0} = 1 + \frac{k_p}{k_2}\frac{I_0}{C_0} \qquad (27)$$

The polydispersity index linearly increases with the ratio of initial concentrations of initiator and catalyst.

(ii) When the equilibrium is shifted to the left hand side (i.e., $4\epsilon K \gg 1$, typical for all other cases),

$$\alpha \approx \sqrt{\epsilon/K} \ll \epsilon \quad \text{and} \quad \bar{P}_w/\bar{P}_n \approx \frac{\chi + (K/\epsilon)^{1/2}}{\chi + 1} \qquad (28)$$

For $\chi \gg 1$, the polydispersity is

$$\bar{P}_w/\bar{P}_n = 1 + \frac{1}{\chi}\sqrt{\frac{K}{\epsilon}} = 1 + \frac{k_p}{\sqrt{k_1 k_2}}\sqrt{\frac{I_0}{C_0}} \qquad (29)$$

In this limiting case the polydispersity index increases with the square root of the ratio of initial concentrations of initiator and catalyst. In both limiting cases the dependence is different from the one for Scheme 1.

(b) Product E Added ($\eta > 0$). As becomes clear from Scheme 2a, addition of product E (e.g. silyl ester, common ion salt, or transition metal salt of higher oxidation state) will decrease the fraction of active chain ends, α. The effect on kinetics was already analyzed earlier.[13] As a consequence, the relative rate of propagation over exchange will decrease and the MWD is expected to become narrower. This is demonstrated below.

(i) For the limiting case $K\eta \ll 1$, eq 25 can be approximated as $\alpha \approx \epsilon$, and eq 24 leads to

$$\bar{P}_w/\bar{P}_n = \frac{\chi(\epsilon + \eta) + 1}{\chi(\epsilon + \eta) + \epsilon} \qquad (30)$$

For a sufficiently fast exchange ($\chi \gg 1$), eq 30 simplifies to

$$\bar{P}_w/\bar{P}_n = 1 + \frac{1}{\chi(\eta + \epsilon)} = 1 + \frac{I_0}{\chi(C_0 + E_0)} = 1 + \frac{k_p}{k_2}\frac{I_0}{(C_0 + E_0)} \tag{31}$$

Then, the polydispersity index decreases with increasing concentration of E. The effect is only pronounced if E_0 (the initial concentration of E) is at least comparable with C_0 (the initial concentration of C).

(ii) The opposite limiting case, $K\eta \gg 1$, is more important. Then, $\alpha \approx \epsilon/K\eta$, and the polydispersity index is

$$\bar{P}_w/\bar{P}_n = \frac{\chi\eta + 1}{\chi\eta + \epsilon/K\eta} \tag{32}$$

and if exchange is fast enough ($\chi \gg 1$) and $K\eta \gg C_0/E_0$, we obtain

$$\bar{P}_w/\bar{P}_n = 1 + \frac{1}{\chi\eta} = 1 + \frac{k_p}{k_2}\frac{I_0}{E_0} \tag{33}$$

In this case the polydispersity index also decreases with increasing concentration of E but does not depend on catalyst concentration. As a consequence, E_0 can even be considerably smaller than C_0 in order to have an effect.

Scheme 2b (Bi-/Unimolecular Isomerization). This case applies to GTP ("associative" mechanism) and to cationic polymerization via ion pairs (see Introduction). The fraction of active centers is given as

$$\alpha = \frac{\epsilon}{K + 1}$$

with $K = k_2/(k_1 I_0)$, and the exchange rate parameter results as[16]

$$\beta = \frac{\chi}{I_0} = \frac{k_2}{k_p I_0} \tag{34}$$

leading to the polydispersity index

$$\bar{P}_w/\bar{P}_n = \frac{\chi I_0 + 1}{\chi I_0 + \alpha} \tag{35}$$

For $\beta \gg \alpha$,

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{I_0}{\chi} = 1 + \frac{k_p I_0}{k_2} \tag{36}$$

Thus, the PDI linearly increases with increasing initiator concentration, similar to Scheme 1, but in contrast to Scheme 2a.

Scheme 2c (Uni-/Bimolecular Isomerization). This scheme is important for controlled radical polymerization, where E is a stable radical (e.g., nitroxide). For the fraction of active chains, α, we have

$$\alpha = \frac{\sqrt{(1 + K\eta)^2 + 4K} - (1 + K\eta)}{2K} \tag{37}$$

with $K = (k_2 I_0)/k_1$, and the exchange rate parameter results as

$$\beta = \chi(\alpha + \eta)$$

similar to Scheme 2a.

Two different cases can be imagined depending on how the polymerization is conducted. Either dormant species are used as initiators and the stable radicals are only formed from dissociation of the initiator at high temperatures ($E_0 = 0$), or the polymerization is initiated by classical initiators in the presence of stable radicals ($E_0 > 0$). In all cases, $\alpha \ll 1$.

(i) In the first case ($\eta = 0$)

$$\alpha = \frac{\sqrt{1 + 4K} - 1}{2K} \approx \frac{1}{\sqrt{K}}$$

for $K \gg 1$. Then,

$$\beta = \chi\alpha \approx \chi/\sqrt{K} \tag{38}$$

and for the polydispersity index we obtain

$$\bar{P}_w/\bar{P}_n = 1 + \frac{\sqrt{K}}{\chi} = 1 + \frac{k_p}{\sqrt{k_2 k_1}}\sqrt{I_0} \tag{39}$$

Hence, the PDI increases with the square root of the initiator concentration, in contrast to the former cases.

(ii) When a sufficiently high amount of stable radicals, E, is added and $K\eta^2 \gg 1$,

$$\alpha \approx \frac{1}{K\eta} \ll \eta$$

Then,

$$\beta \approx \chi\eta \tag{40}$$

and the polydispersity index is

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\chi\eta} = 1 + \frac{k_p I_0}{k_2 E_0} \tag{41}$$

Therefore, the polydispersity index increases linearly with increasing initiator concentration and decreases with initial concentration of stable radicals. However, it should be noted that for this case equilibrium initial conditions and neglect of termination reactions are not sufficient in order to describe the polymerization. In the initial state, many radicals will recombine before steady-state concentrations are reached.

Scheme 3 (Degenerative Transfer). For this scheme, the fraction of active centers depends on the mechanism with which the centers are formed. Since both sides of Scheme 3 are chemically identical, $k_1 = k_2$. The exchange rate parameter is directly given as the ratio[19]

$$\beta = \chi = k_1/k_p \tag{42}$$

Hence, the PDI is given as

$$\bar{P}_w/\bar{P}_n = \frac{\chi + 1}{\chi + \alpha} \approx 1 + \frac{1}{\chi} = 1 + \frac{k_p}{k_1} \tag{43}$$

if exchange is not extremely slow, so that $\beta \gg \alpha$. Thus, the PDI is independent of reagent concentrations, in contrast to all other schemes. In fact, the data available for GTP and cationic polymerization do not show a significant dependence of PDI on initiator or catalyst concentrations, indicating that degenerative transfer might be the predominant mechanism of activity exchange, irrespective of the mechanism of active species formation.[9]

Scheme 4 (Aggregation). The fraction of active centers is given as

$$\alpha = \frac{\sqrt{1+4K}-1}{2K} \approx \frac{1}{\sqrt{K}} \quad \text{for} \quad \alpha \ll 1 \tag{44}$$

with $K = k_2 I_0/k_1$. The exchange rate parameter is given as[23]

$$\beta = \frac{\chi\alpha}{1-\alpha} \tag{45}$$

and consequently, the polydispersity index is

$$\bar{P}_w/\bar{P}_n = \frac{\chi\alpha + 1 - \alpha}{\chi\alpha + \alpha(1-\alpha)} \tag{46}$$

and for $\alpha \ll 1$

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\chi\alpha} = 1 + \frac{\sqrt{K}}{\chi} = 1 + \frac{k_p}{\sqrt{k_1 k_2}}\sqrt{I_0} \tag{47}$$

Thus, the polydispersity index increases with the square root of initiator concentration. In the anionic polymerization of (meth)acrylates in THF it was shown[22] that the aggregated species also have a certain activity. For *tert*-butyl acrylate, exchange is slow ($\beta < 1$) and nonequilibrium initial conditions have to be taken into account, especially when ester enolates are used as initiators. Low molecular weight ester enolates are more strongly aggregated than the corresponding polymers. Thus eq 47 cannot be used in such a case. A more detailed analysis of this case will be given in another paper.[23]

Effect of Nonequilibrium Initial Conditions

The results presented up to now were obtained assuming equilibrium initial conditions (eq 2). Generally, the equilibrium of eq 2 is not established at time $t = 0$. This happens if initiator and polymer chain ends have different chemical nature (and thus different position of equilibrium) and/or if all reagents including monomer are mixed instantaneously. Then, in the general case the initial conditions for eqs 1 are

$$P_l^*|_{t=0} = \varphi I_0 \delta_{l,0} \qquad P_l'|_{t=0} = (1-\varphi) I_0 \delta_{l,0}$$

where the initial fraction of more active centers, φ, can be higher or lower than the equilibrium value, α. During polymerization the actual fraction of more active centers will gradually change from the initial value, φ, to the equilibrium value, α.

It was shown for Schemes 2a[9] and 2b[16] for $k_p' = 0$ and $\varphi = 0$ that in the case of slow exchange, the nonequilibrium initial conditions result in an induction period in a first-order time–conversion plot, $\ln(1-x)$ vs t, indicating that the formation of active species is slow compared to monomer addition. However, for $\beta \gg 1$ the induction period disappears. At a given conversion, $\bar{P}_n$ and the polydispersity index of the polymer formed are higher than those obtained with equilibrium initial conditions. Again, the difference disappears at $\beta \gg 1$.

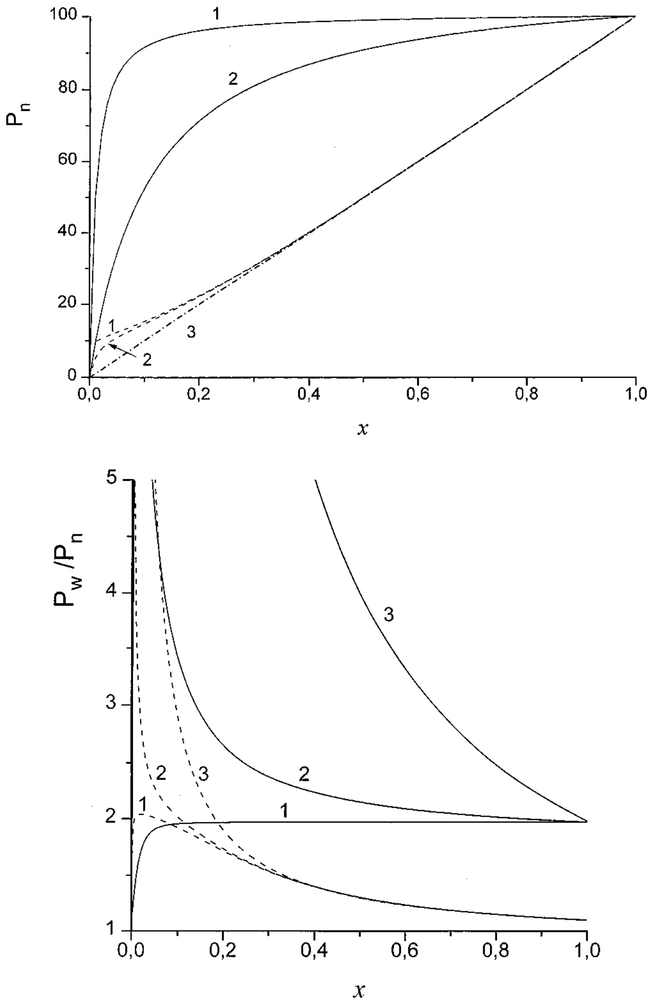


Figure 8. Dependence of number-average degree of polymerization, $\bar{P}_n$ (a) and polydispersity index (b) on conversion for nonequilibrium initial conditions and various initial ratios of active centers, φ. $\alpha = 0.01$, $\gamma = M_0/I_0 = 100$: (1) $\varphi = 0.01$, (2) $\varphi = 0.1$, (3) $\varphi = 1$ (equivalent to the case where residual initiator is included in the calculation of $\bar{P}_n$. (—) $\beta = 1$, (------) $\beta = 10$.

Since for GTP and cationic polymerization $\beta \geq 10$,[9,16,19] equilibrium is reached fast and no remarkable effect on the kinetics and MWD is expected.

For the case $\varphi > \alpha$, monomer will be initially consumed faster than in the equilibrium case. Thus, an apparent intercept or a kink in the first-order time–conversion plot should be found. If initiator can be considered as a polymer chain, $\bar{P}_n = \gamma x$, independently of initial conditions. Taking into account residual initiator leads to the following dependence of $\bar{P}_n$ on conversion

$$\bar{P}_n \approx \frac{\gamma x}{1 - (1-\varphi)(1-x)^{\beta} \exp(-\lambda\gamma^* x)} \tag{48}$$

(the derivation is similar to that for eq 17). This expression does not depend on the equilibrium fraction of active chains α. With increasing φ, the number-average degree of polymerization approaches the theoretical dependence $\bar{P}_n = \gamma x$ (see Figure 8a). The effect of initial conditions on the weight-average degree of polymerization is not so pronounced as for $\bar{P}_n$. As a result, the PDI will be higher than for equilibrium initial conditions (Figure 8b). Again, the difference between equilibrium and nonequilibrium cases will vanish for higher β.

Table 3. Polydispersity Index at Constant Monomer Concentration (Semibatch Polymerization) for Different Mechanisms of Activity Exchange Where P′ is Dormant (α ≪ 1) [$\epsilon = C_0/I_0$; $\eta = E_0/I_0$; $\chi = k_2/k_p$]

Scheme No	Mechanism of exchange	$\bar{P}_w/\bar{P}_n$ for a given $\bar{P}_n$	
1	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	$1+\frac{2M}{\bar{P}_n}\cdot\frac{k_p}{k_2}$	
2a	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	equilibrium left $E_0=0; \chi>>1$: $1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{\sqrt{k_1k_2}}\cdot\frac{M}{\sqrt{C_0I_0}}$ $E_0 \gtrsim C_0, \chi>>1$: $1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{k_2}\cdot\frac{M}{E_0}$	equilibrium right, $\varepsilon << 1$ $E_0=0; \chi>>1$: $1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{k_2}\cdot\frac{M}{C_0}$ $E_0 \gtrsim C_0, \chi>>1$: $1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{k_2}\cdot\frac{M}{(C_0+E_0)}$
2b	$P_l' + C \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^*$	$1+\frac{2M}{\bar{P}_n}\cdot\frac{k_p}{k_2}$	
2c	$P_l' \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + E$	$E_0>0$: $1+\frac{2}{k_2I_0(\alpha+\eta)\alpha t}$	$E_0>0$: $1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{k_2}\cdot\frac{M}{E_0}$
3	$P_l' + P_m^* \underset{k_1}{\overset{k_1}{\rightleftarrows}} P_m' + P_l^*$	$1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{k_2}\cdot\frac{M}{I_0}$	
4	$(P_l' \bullet P_m') \underset{k_2}{\overset{k_1}{\rightleftarrows}} P_l^* + P_m^*$	$1+\frac{2}{\bar{P}_n}\cdot\frac{k_p}{\sqrt{k_1k_2}}\cdot\frac{M}{\sqrt{I_0}}$	

Slow Monomer Addition (Semibatch Polymerization)

It has been reported that by decreasing the monomer concentration[24] or by adding monomer very slowly, e.g. by condensation or dropwise,[12,25] much narrower MWD can be obtained in GTP. Such a process is realized in a semibatch reactor without outflow where the actual monomer concentration will be very low and approximately constant. Similar results were obtained for incremental monomer addition in cationic polymerization when the number of incremental monomer additions is large.[15] A quantitative treatment for such a polymerization was given by Müller et al.[20] for the degenerative transfer mechanism (Scheme 3). Nevertheless, all results obtained in this work can be extended to any other scheme of exchange by using the generalized exchange rate parameter, β.

Thus, for the number-average degree of polymerization and polydispersity index the following values were obtained:

$$\bar{P}_n \approx \gamma\tau = \frac{\phi_M}{I_0}t \tag{49}$$

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{2\gamma(1-\alpha)}{\beta\bar{P}_n} \approx 1 + \frac{2M}{\beta I_0\bar{P}_n} = 1 + \frac{2}{\beta\tau} \tag{50}$$

where $\tau = k_p\alpha I_0 t$ is a dimensionless time, $M = \phi_M/(k_p\alpha I_0)$ is the constant monomer concentration in the system, ϕ_M is the monomer flow, and $\gamma = M/I_0$. The polydispersity indices for the various mechanisms are given in Table 3.

As follows from eq 50, in the case of slow monomer addition it is possible to obtain polymer with low PDI even if exchange is fairly slow provided the monomer concentration, M, is sufficiently small.

For such a case the MWD function can be derived, and the effect of exchange rate on the weight distribution is shown in Figure 9 in comparison with a conventional batch polymerization where monomer is added instantaneously.

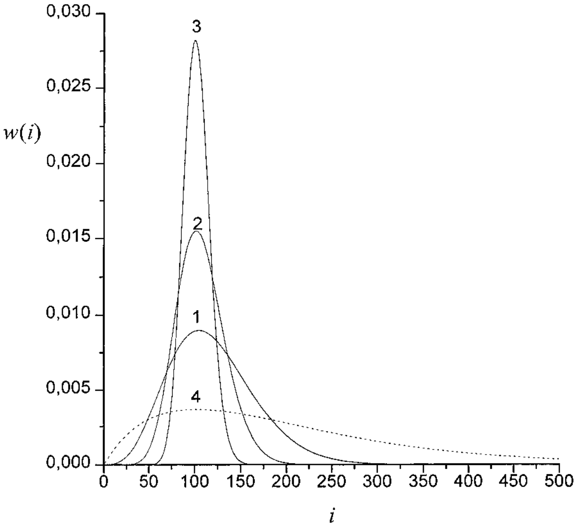


Figure 9. Effect of exchange rate on the MWD for constant monomer concentration. $\beta = 1$, $\bar{P}_n = \gamma\tau = 100$. Since the MWD depends on β/γ, the same effects are observed for the variation of β at constant γ: (1) $\gamma = M/I_0 = 10$, $\bar{P}_w/\bar{P}_n = 1.21$; (2) $\gamma = 3.33$, $\bar{P}_w/\bar{P}_n = 1.08$; (3) $\gamma = 1.0$, $\bar{P}_w/\bar{P}_n = 1.03$; (4) batch polymerization at full conversion (numeric calculation), $\alpha = 0.01$, $M_0/I_0 = 100$, $\bar{P}_w/\bar{P}_n = 2$.

When comparing the polydispersity index for slow monomer addition (eq 50) with that obtained for a normal batch polymerization process, i.e., at decreasing monomer concentration, a strong difference becomes obvious. Whereas for the batch process, $\bar{P}_w/\bar{P}_n$ is roughly independent of $\bar{P}_n$ and M_0 (for $\bar{P}_n \gg 1$), for constant monomer concentration the PDI decreases with time (and thus with $\bar{P}_n$ obtained). For a given $\bar{P}_n$, the PDI is independent of M_0 for a batch process, whereas for slow monomer addition it increases with increasing monomer concentration. The dependence on I_0 is also different (cf. Tables 2 and 3). Thus, a conclusion can be made that in the case of slow equilibria it is advisable to work at the lowest possible rate of monomer addition. However, this rate is limited by the stability of the active centers toward termination and transfer processes.

Conclusions

For all mechanisms of exchange the averages of the molecular weight distribution, the DPI, and their dependences on monomer conversion are governed by three universal parameters:

(i) the reactivity ratio of the two species, $\lambda = k'_p/k^*_p$. (Generally, the broadest distributions are obtained when one species is dormant ($\lambda = 0$) and the polydispersity index decreases with increasing λ, finally approaching the value for a Poisson distribution for $\lambda = 1$.)

(ii) the fraction of the more active species, $\alpha = P^*/I_0$, which is determined by the initial concentrations of reagents. (Typically, the PDI passes a maximum, the position of which depends on λ. When one kind of the species is dormant ($\lambda = 0$), the PDI decreases with increasing α.)

(iii) a generalized exchange rate parameter, β, which quantifies the rate of exchange relative to that of propagation. (It is always proportional to the ratio of the rate constant of formation of less active species to the propagation rate constant of the more active species, $\chi = k_2/k^*_p$. The dependence of β on the initial concentrations of reagents is defined by the mechanism of exchange and can be used as a mechanistic criterion to distinguish between various possible mechanisms. In fact, it has been applied to GTP and cationic polymerization, and the tentative conclusion was that degenerative transfer may be the predominant mechanism of exchange in these polymerizations.[9])

For the typical case $\beta > 1$, the PDI decreases with monomer conversion, which is a common observation in many living polymerizations where $10 \le \beta \le 100$ was determined. At full conversion, the simple relation

$$\bar{P}_w/\bar{P}_n \approx 1 + \Theta/\beta$$

is valid, where Θ depends on α and λ. Generally, $\Theta < 1$ and for $\lambda = 0$ (i.e., P′ is dormant) $\Theta = 1 - \alpha$.

Moreover, the PDI depends on the way monomer is added. Generally it is lower for slow monomer addition (semibatch mode) than for a batch polymerization where monomer and initiator are added simultaneously. Whereas the PDI is roughly independent of $\bar{P}_n$ for a batch process, it decreases with $\bar{P}_n$:

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{2M}{\beta I_0 \bar{P}_n} \qquad (\text{for} \quad \lambda = 0)$$

Thus, this work opens a comprehensive pathway for controlling the MWD in living polymerizations, most of which proceed via more than one kind of center. Comparisons to experimental data have been already given in previous publications which dealt with special mechanisms of exchange.[9,16,19,22] Sometimes it is difficult to compare calculated and experimental data, due to imperfections like slow initiation, termination, or transfer or due to the superposition of various mechanisms in a three-state mechanism.

Examples of polymerizations which involve more than two species are anionic polymerization via contact ion pairs, solvent-separated ions pairs, and free anions, and cationic polymerization involving covalent species, ion pairs, and free cations. The MWD averages and function for a multistate mechanism were derived by Böhm[26,27] and the results were applied by Schulz et al.[28] in order to determine the rate constants of exchange in the anionic polymerization of styrene in polar solvents. The MWD averages for the three-state mechanism of cationic polymerization were derived by Yan et al.[29] An important result of both derivations is that the PDI can be expressed as the superposition of the PDI's calculated for the two two-state mechanisms involved:

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{A_1}{\beta_1} + \frac{A_2}{\beta_2}$$

Since most real polymerizations are not living according to the strict definition, the extension to imperfect polymerizations is a necessary step. Litvinenko et al.[30] calculated the PDI for transfer to solvent and spontaneous transfer in the presence of direct (bimolecular) activity exchange (degenerative transfer, Scheme 3). This work is being extended to all mechanisms of exchange and covers transfer to monomer,[31] spontaneous transfer,[32] and unimolecular termination.[33]

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Appendix: List of Symbols and Abbreviations

α	P^*/I_0, equilibrium fraction of more active chain ends
β	general exchange rate parameter
λ	k'_p/k^*_p, reactivity ratio
$\delta_{l,m}$	Kronecker symbol: $\delta_{i,j} = 1$ for $l = m$; $\delta_{i,j} = 0$ otherwise
ϵ	C_0/I_0
η	E_0/I_0
γ	M_0/I_0, expected degree of polymerization at full conversion; $\gamma = M/I_0$ for semibatch experiments
γ^*	$\dfrac{\gamma}{\alpha + \lambda(1 - \alpha)}$
χ	k_2/k^*_p
φ	$P^*(t{=}0)/I_0$, initial fraction of more active chain ends
ϕ_M	monomer flow in semibatch experiments
μ_n	*n*th moment of the MWD
μ^*_n, μ'_n	*n*th moment of the MWD of more and less active chains, respectively
ν	β/α
τ	$\alpha k_p I_0 t$, dimensionless time
Θ	$\dfrac{\alpha^2(1 - \alpha)(1 - \lambda)^2}{[\alpha + \lambda(1 - \alpha)]^2} < 1$
A, *B*	general concentrations used in eq 1, defined in Table 1
ATRP	atom transfer radical polymerization
C	catalyst (co-initiator) concentration
E	concentration of (added or formed) byproduct, i.e. silyl ester in GTP, counterion in cationic polymerization, salt of higher oxydation state in ATRP, stable radical in radical polymerization

GTP	group transfer polymerization
I	initiator concentration
K	dimensionless equilibrium constant, see Table 1
k_1	rate constant of activation (formation of more active species)
k_2	rate constant of deactivation (formation of less active species)
k_p	rate constant of polymerization, used instead of k_p^* when $k_p' = 0$
k_p'	rate constant of polymerization of less active species
k_p^*	rate constant of polymerization of more active species
$\bar{k}_p$	$\alpha k_p^* + (1 - \alpha)k_p'$, apparent rate constant of polymerization
M	monomer concentration
P_0	concentration of residual initiator
P_0'	concentration of less active initiator
P_0^*	concentration of more active initiator
P_l'	concentration of less active polymer chain ends of degree of polymerization l
P_l^*	concentration of more active polymer chain ends of degree of polymerization l
$\bar{P}_n$	number-average degree of polymerization
$\bar{P}_w$	weight-average degree of polymerization
$\bar{P}_w/\bar{P}_n$	polydispersity index
PDI	polydispersity index
t	time
x	$(M_0 - M)/M_0$, monomer conversion

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