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Kinetic Analysis of "Living" Polymerization Processes Exhibiting Slow Equilibria. 1. Degenerative Transfer (Direct Activity Exchange between Active and "Dormant" Species). Application to Group Transfer Polymerization

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ABSTRACT: The MWD moments are derived for a "living" polymerization process which proceeds via active and "dormant" species and where the activity is directly exchanged between these chain ends. Such a mechanism is believed to be applicable to many "living" polymerizations (e.g. anionic, group transfer, cationic, radical). It is shown that for low ratios of rate constants of exchange to propagation, $\beta = k_{ex}/k_p < 1$, the polydispersity index, M_w/M_n, increases with monomer conversion whereas for $\beta > 1$ it decreases (after a marked increase at low conversions). The latter case coincides with a common observation in group transfer polymerization (GTP). For a given conversion, polydispersity has its maximum for $0.1 < \beta < 1$. In a limiting case, at full conversion, a very simple relation is valid: $M_w/M_n \approx 1 + 1/\beta$. The dependence of polydispersity on initiator and monomer concentrations is not very pronounced. The results are compared to experimental data of the GTP of methyl methacrylate using nucleophilic catalysts.

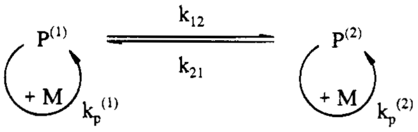
Introduction

Concept of Slow Equilibria. There is a large number of polymerization systems that are "living" in terms of the strict definition (i.e., the rates of both termination and transfer are negligible compared to the rate of propagation), but which lead to considerably broader molecular weight distributions (MWDs) than a Poisson distribution. In many of these systems slow initiation and experimental deficiencies (e.g., slow mixing of monomer and initiator) can be ruled out. As early as 1964, it was shown theoretically by Figini[1,2] that an equilibrium between species of different reactivities ("two-state mechanism"; cf. Scheme 1) can lead to a considerable broadening of the MWD if the rate of interconversion is slow or comparable to the rate of propagation. Independently, Coleman and Fox[3] calculated the polydispersity index for a two-state mechanism with the restriction of constant monomer concentration.

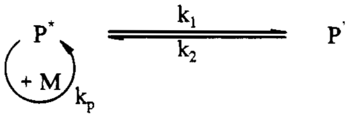
Böhm[4,5] extended the analysis to a multistate system. The results of Figini's and Böhm's calculations were first used by Schulz et al.[6−8] to calculate the rate constants of ion pair dissociation and of the interconversion of contact and solvent-separated ion pairs in the anionic polymerization of styrene in polar solvents. However, Figini's, Böhm's, and Coleman's derivations are based on steady-state conditions; i.e. they assumed that the position of the equilibrium at time $t = 0$ is equal to that during polymerization. This assumption will not be valid if the chemical nature of the initiator is different from that of the living polymer.

A special case of a two-state system is *reversible deactivation*, i.e., the *reversible* formation of *inactive or "dormant" species* ($k_p^{(2)} = 0$, cf. Scheme 2. **P*** and **P′** represent an active and a "dormant" polymer chain, respectively). Since all chains in this system are not active at a time, it has been named "quasi-living polymerization" by some authors[9−11] and distinguished from "ideal living" systems. However, since the system is "living" in terms of the rigorous definition given above, a more accurate terminology is "living polymerization with reversible deactivation", in extension of a definition given by Quirk et al.[12]

Scheme 1. Two-State Mechanism



Scheme 2. Reversible Deactivation



A broadening of the MWD due to slow exchange was proposed for several living processes, e.g., formation of inactive aggregates in anionic polymerization,[13] the existence of nonionic species in living carbocationic polymerization,[14,15] and the existence of nonactivated silyl ketene acetals in group transfer polymerization (GTP).[16,17] It is well conceivable that this concept can be applied to other "living" polymerizations, e.g., "living" radical polymerization.[18−21] Surveys and comparisons of various systems of this type have been published recently.[11,17,22,23] Derivations for the polydispersity index based on equilibrium (steady-state) initial conditions were given and applied to some of these systems by Gee et al.,[24] Szwarc and Hermans,[25] Krause et al.,[26] Puskas et al.,[15] and Kunkel et al.[13]

Since the fraction of active chain ends is much smaller than the total number of polymer chains, exchange of activity between the chain ends is necessary in order for all the chains to grow. Besides the indirect mechanism of activity exchange given in Scheme 2, i.e., by activation/deactivation, a direct exchange (*"degenerative*

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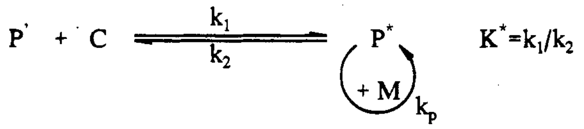
Scheme 3. Degenerative Transfer between Active and "Dormant" Chain Ends

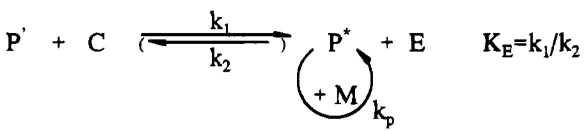
$$P_i^* + M \xrightarrow{k_p} P_{i+1}^* \qquad i \ge 0$$

$$P_i^* + P_j' \overset{k_{ex}}{\rightleftharpoons} P_i' + P_j^* \qquad i,j \ge 0$$

Scheme 4. Associative Mechanism of GTP



Scheme 5. Dissociative Mechanism of GTP



transfer") between living and dormant chain ends is also feasible (cf. Scheme 3, where the indices i and j denominate different chain lengths and $i = 0$ or $j = 0$ denominates initiator). Since degenerative transfer is a possible mechanism in group transfer polymerization[27,28] (see below) and other living processes exhibiting reversible deactivation, the MWD arising from such a process is of special interest.

In this series of papers, we present both non-steady- and steady-state derivations of molecular weight averages and polydispersity index for the most common mechanisms exhibiting slow equilibria. These include various possible mechanisms of GTP, ionization, aggregation, and unimolecular isomerization in anionic or cationic polymerizations. In some cases, the full MWD function is given for constant monomer concentration. This condition is approximately given for low monomer conversion or slow monomer feed (dropwise or vapor phase addition, neglecting volume changes).

Mechanisms of Activity Exchange in Group Transfer Polymerization (GTP). In a preceding publication,[29] we compared various mechanisms of GTP that are presently being discussed and found kinetic criteria that allow partial discrimination between them. The "associative" mechanism originally proposed by Sogah and Webster[30-32] and modified by Mai and Müller[17,33] includes the formation of an active species with pentacoordinate silicon, **P***, from a silyl ketene acetal, **P′**, and a nucleophilic catalyst, **C** (e.g. difluoride or benzoate; Scheme 4). Since the initial concentration of the catalyst, C_0, is much smaller than that of the initiator, I_0 (typically 0.1–5%), it is essential that the catalyst is exchanged between the living chain ends in order that all initiator molecules form polymer chains.

Recently, the associative mechanism was questioned by Quirk et al.[27,28,34] It was proposed that enolate ions (or ion pairs) are formed from the silyl ketene acetal and catalyst in a reversible or irreversible reaction ("dissociative mechanism"; Scheme 5). In Scheme 5, **E** denotes a trimethylsilyl fluoride or a silyl ester, e.g. trimethylsilyl benzoate. The mechanism is reversible for $k_2 > 0$, and irreversible for $k_2 = 0$.

By calculating the reaction orders with respect to initiator and catalyst concentration for the different mechanisms and comparing them to the experimentally obtained ones, we were able to discriminate between various mechanisms. For catalysis by benzoate and HgI_2/trimethylsilyl iodide, the experimental data fit the reaction order only when calculated for the associative mechanism. For difluoride catalysis, a discrimination was not possible.[29]

In this series of papers we want to calculate the effect of slow equilibria (i.e., activation/deactivation or enolization/silylation) on the MWD of the polymers formed. Analysis of the MWD as a function of monomer conversion and initial concentrations of reagents can provide a clue for the distinction of the various mechanisms.

The question whether activity exchange between the active and "dormant" chain takes place through the indirect mechanisms of activity exchange given in Scheme 4, i.e., by dissociation/association of catalyst, and in Scheme 5, i.e. by silylation/enolization, or by direct exchange ("degenerative transfer", Scheme 3) cannot be solved by kinetic measurements.

Such a process, i.e., direct transfer of a trimethylsilyl group from a "dormant" silyl ketene acetal to an active enolate chain end, was proposed for the dissociative mechanism.[27,28] For the associative mechanism, this means direct transfer of catalyst between an activated and a nonactivated silyl ketene acetal. It should be noted that the rates for both directions are equal because the reactants and products have identical chemical natures. A slow exchange of activity ($k_{ex} \lesssim k_p$) again will affect the MWD, and the dependence of the MWD on conversion and initial concentrations of reagents may help to discriminate between direct and indirect activity exchange.

In the first part of this series, we will calculate the molecular weight averages and the polydispersity index for direct activity exchange (degenerative transfer), according to Scheme 3. The following publications will deal with the MWD function for constant monomer concentration and with the molecular weight averages for indirect activity exchange in the associative and dissociative mechanisms (Schemes 4 and 5) and combinations with direct activity exchange.

Degenerative Transfer in Anionic Polymerization. In 1965, Krause et al.[26] studied the anionic polymerization of methyl methacrylate (MMA) in nonpolar solvent and proposed a mechanism that included the following assumptions: (i) There is rapid initiation and formation of trimer followed by rapid deactivation of a part of the chain ends ("pseudotermination"). Thus, initially only a certain fraction of chain ends remains active. (ii) Active chains can react with dormant chain ends and exchange reactivity. The authors calculated the molecular weight averages and the polydispersity index for such a mechanism. Although no evidence was found for such a mechanism in later studies, it is evident that it is similar to degenerative transfer in GTP. An important difference is that in GTP living and dormant species with a degree of polymerization of unity (i.e. the initiator) and 2 participate significantly. It will be shown later that, for slow exchange, the fraction of residual initiator needs a special consideration in the calculation of the molecular weight averages. Furthermore, the total number of living species is very small compared to that of the dormant ones. These differences make a further theoretical treatment of Krause's derivation necessary.

Kinetic Differential Equations. Scheme 3 can be represented by the following kinetic differential equations, where M represents the concentration of monomer:

$$\frac{\mathrm{d}P_0^*}{\mathrm{d}t} = -k_\mathrm{p}MP_0^* - k_\mathrm{ex}\mathrm{P}_0^*P' + k_\mathrm{ex}P'_0P^* \qquad (1)$$

$$\frac{\mathrm{d}P'_0}{\mathrm{d}t} = k_\mathrm{ex}P_0^*P' - k_\mathrm{ex}P'_0P^* \qquad (2)$$

$$\frac{\mathrm{d}P_i^*}{\mathrm{d}t} = k_\mathrm{p}M(P_{i-1}^* - P_i^*) - k_\mathrm{ex}P_i^*P' + k_\mathrm{ex}P'_iP^* \qquad i \geq 1 \qquad (3)$$

$$\frac{\mathrm{d}P'_i}{\mathrm{d}t} = k_\mathrm{ex}P_i^*P' - k_\mathrm{ex}P'_iP^* \qquad i \geq 1 \qquad (4)$$

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -k_\mathrm{p}MP^* \qquad (5)$$

Here, P_i^* and P'_i are the concentrations of active and dormant chains of degree of polymerization i, respectively, P_0^* and P'_0 represent the corresponding concentrations of initiator, and $P^* = \sum_{i=0}^{\infty}P_i^*$ and $P' = \sum_{i=0}^{\infty}P'_i$ are the total concentrations of active and dormant species, respectively.

In this paper, the calculations will be based on the assumption of *fast formation of active species* by one of the mechanisms given above. Thus, in fact, for this derivation, a steady-state approach is used. Later, we will deal with the problem of slow formation of active species. Thus, the initial conditions of eqs 1–5 are

$$P_i^*|_{t=0} = \alpha I_0\delta_{i,0}$$

$$P'_i|_{t=0} = (1 - \alpha)I_0\delta_{i,0}$$

$$M|_{t=0} = M_0$$

where δ_{ij} is the Kronecker symbol, I_0 and M_0 are the initial concentrations of initiator and monomer, and α is the fraction of active chain ends:

$$\alpha = P^*/I_0 = \mathrm{const} \qquad (6)$$

P^* (and thus α) depends on the mechanism of formation of active species and was calculated in an earlier paper for various mechanisms discussed for GTP.[29] Typically, $\alpha \ll 1$.

Integration of eq 5 yields the monomer concentration for first-order kinetics:

$$M = M_0\mathrm{e}^{-k_\mathrm{p}P^*t} = M_0\mathrm{e}^{-\tau} \qquad (7)$$

where $\tau = k_\mathrm{p}P^*t = k_\mathrm{p}\alpha I_0t$. Monomer conversion, x, is then given by

$$x = \frac{M_0 - M}{M_0} = 1 - e^{-\tau} \qquad (8)$$

Results

Molecular Weight Averages and Polydispersity Index. In order to find the expressions of the number- and weight-average degrees of polymerization, $\bar{P}_\mathrm{n}$ and $\bar{P}_\mathrm{w}$, respectively, and the polydispersity index, $D = \bar{P}_\mathrm{w}/\bar{P}_\mathrm{n}$, we have to derive the zeroth, first, and second moments of the MWD. The nth moment of the MWD can always be expressed as the sum of the corresponding moments of active and "dormant" chains:

$$\mu_n = \mu_n^* + \mu'_n$$

which are defined as

$$\mu_n^* = \sum_{i=0}^{\infty} i^nP_i^* \quad \text{and} \quad \mu'_n = \sum_{i=0}^{\infty} i^nP'_i \qquad (9)$$

The zeroth moment is given by the concentration of active and dormant chains:

$$\mu_0 = \mu_0^* + \mu'_0 = \sum_{i=0}^{\infty}P_i^* + \sum_{i=0}^{\infty}P'_i = P^* + P' = I_0 \qquad (10)$$

whereas the first moment of the MWD is equal to the concentration of the polymerized monomers:

$$\mu_1 = \mu_1^* + \mu'_1 = M_0x = M_0(1 - \mathrm{e}^{-\tau}) \qquad (11)$$

Equations for the second moments of the MWD can be derived by multiplying each term of eqs 3 and 4 by i^2 and summarizing over i. Taking into account that $\mathrm{d}/\mathrm{d}t = \alpha k_\mathrm{p}I_0(1 - x)\,\mathrm{d}/\mathrm{d}x$, time can be replaced by conversion as the variable and the following differential equations are obtained for μ_2^* and μ'_2:

$$(1 - x)\frac{\mathrm{d}\mu_2^*}{\mathrm{d}x} = \frac{\gamma}{\alpha}(1 - x)(2\mu_1^* + \mu_0^*) - \beta\left(\mu_2^*\frac{1 - \alpha}{\alpha} - \mu'_2\right)$$

$$(1 - x)\frac{\mathrm{d}\mu'_2}{\mathrm{d}x} = \beta\left(\mu_2^*\frac{1 - \alpha}{\alpha} - \mu'_2\right)$$

where $\gamma = M_0/I_0$ and $\beta = k_\mathrm{ex}/k_\mathrm{p}$. Summation leads to the differential equation for the second moment of total polymer

$$\frac{\mathrm{d}\mu_2}{\mathrm{d}x} = \frac{\gamma}{\alpha}(2\mu_1^* + \mu_0^*) = \frac{\gamma}{\alpha}(2\mu_1^* + \alpha I_0) \qquad (12)$$

In order to calculate μ_2, the first moment of an active chain must be obtained beforehand. The dependence of the latter on conversion is described by the equation

$$(1 - x)\frac{\mathrm{d}\mu_1^*}{\mathrm{d}x} = \frac{\gamma}{\alpha}(1 - x)\mu_0^* - \beta\left(\mu_1^*\frac{1 - \alpha}{\alpha} - \mu'_1\right) \qquad (13)$$

Taking into account eq 11, we finally obtain

$$(1 - x)\frac{\mathrm{d}\mu_1^*}{\mathrm{d}x} = M_0[1 - (\beta - 1)x] - \frac{\beta}{\alpha}\mu_1^* \qquad (14)$$

The solution of eqs 12 and 14 at zero initial conditions for μ_1^* and μ_2 is

$$\mu_1^* = \alpha M_0\left\{1 + \frac{1 - \beta}{\beta - \alpha}(1 - x) - \frac{1 - \alpha}{\beta - \alpha}(1 - x)^{\beta/\alpha}\right\} \qquad (15)$$

$$\mu_2 = M_0\left\{x + x\gamma\left[2 + \frac{(2 - x)(1 - \beta)}{\beta - \alpha}\right] - \frac{2\alpha\gamma(1 - \alpha)}{\beta^2 - \alpha^2}[1 - (1 - x)^{1+\beta/\alpha}]\right\} \qquad (16)$$

Consequently,

$$\bar{P}_\mathrm{n} = \frac{\mu_1}{\mu_0} = \gamma x \qquad (17)$$

$$\bar{P}_\mathrm{w} = \frac{\mu_2}{\mu_1} = 1 + \gamma\left[2 + \frac{(2-x)(1-\beta)}{\beta-\alpha}\right] - \frac{2\alpha\gamma(1-\alpha)}{(\beta^2-\alpha^2)x}[1-(1-x)^{1+\beta/\alpha}] \quad (18)$$

$$D = \frac{\bar{P}_\mathrm{w}}{\bar{P}_\mathrm{n}} = \frac{1 + \gamma\left[2 + \frac{(2-x)(1-\beta)}{\beta-\alpha}\right] - \frac{2\alpha\gamma(1-\alpha)}{(\beta^2-\alpha^2)x}[1-(1-x)^{1+\beta/\alpha}]}{\gamma x} \quad (19)$$

It should be noted, that these equations are derived for polymer chains without initiator fragment. Thus, for $\bar{P}_\mathrm{n} \lesssim 20$, when comparing the calculated to experimental data, the experimental molecular weight averages have to be corrected for the molecular weight of the initiator incorporated.

Effect of Residual Initiator. Unreacted initiator is *not* a part of the polymer and in experimental determination of the MWD will not be measured. This means that the concentration of the residual initiator, $P_0 = P_0^* + P'_0$, has to be subtracted from the MWD moments and thus the summation for the molecular weight averages of the *polymer formed* has to start from $i = 1$. As can be seen from the definition of the moments (eq 9), this only affects the zeroth moment and thus the number-average degree of polymerization:

$$\bar{P}_\mathrm{n} = \frac{\sum_{i=1}^{\infty} i(P_i^* + P'_i)}{\sum_{i=1}^{\infty}(P_i^* + P'_i)} = \frac{\mu_1}{\mu_0 - P_0} \quad (20)$$

For $k_\mathrm{ex}/k_\mathrm{p} > 10$, the concentration of residual initiator decreases very fast with monomer concentration and can be neglected at higher conversions. In the limiting case of very fast exchange, i.e. $\beta = k_\mathrm{ex}/k_\mathrm{p} \gg 1$, a Poisson distribution will be reached which is easily shown from eqs 27 and 28 (*vide infra*) by setting $\beta \gg 1$ and $P_0 = 0$.

For $k_\mathrm{ex}/k_\mathrm{p} < 10$, the calculations show that P_0 cannot be neglected at all. This is easily understood if one imagines the limiting case $k_\mathrm{ex}/k_\mathrm{p} = 0$ corresponding to zero exchange rate. In this case, only a small part of the initiator (i.e., αI_0) will add monomer to form polymer chains that will grow to a very large degree of polymerization. In the experimental determination of the MWD, the residual initiator will be separated from the polymer and not measured. Thus,

$$\bar{P}_{\mathrm{n}(k_\mathrm{ex}=0)} = \frac{\text{number of monomers consumed}}{\text{number of polymer chains}} = \frac{M_0 x}{\alpha I_0} = \frac{\gamma}{\alpha}x = \gamma^* x \quad (21)$$

Here, γ^* is the value of $\bar{P}_\mathrm{n}$ obtained at full conversion. In contrast, the value of $\bar{P}_\mathrm{n}$ expected for fast exchange is

$$\bar{P}_{\mathrm{n}(k_\mathrm{ex}\gg k_\mathrm{p})} = \frac{M_0 x}{I_0} = \gamma x$$

because here *all* initiator molecules form polymer chains. Since $\alpha \ll 1$,

$$\bar{P}_{\mathrm{n}(k_\mathrm{ex}=0)} \gg \bar{P}_{\mathrm{n}(k_\mathrm{ex}\gg k_\mathrm{p})}$$

In order to correct for this error, it is absolutely necessary to calculate the concentration of residual initiator, P_0.

In some cases, initiators are used for GTP that contain two or more monomer units.[17] If the polymer is recovered by evaporation of solvent rather than precipitation, residual initiator will be measured by GPC in that case and the following correction is not necessary.

Concentration of Residual Initiator. The concentration of residual initiator should be obtained by solving the differential eqs 1 and 2. These can be rewritten in terms of conversion to yield the following equations

$$(1-x)\frac{\mathrm{d}P_0^*}{\mathrm{d}x} = -\gamma^*(1-x)P_0^* + \beta\left(P'_0 - \frac{1-\alpha}{\alpha}P_0^*\right) \quad (22)$$

$$(1-x)\frac{\mathrm{d}P'_0}{\mathrm{d}x} = -\beta\left(P'_0 - \frac{1-\alpha}{\alpha}P_0^*\right) \quad (23)$$

It is possible to solve eqs 22 and 23 exactly (see Appendix). However, the analysis of this exact solution is a very complicated problem. The simplest way to solve eqs 22 and 23 is *numerical integration*. This was easily performed by using library routines, e.g., the Runge–Kutta method,[35] and the results given below are calculated in this way. A Turbo-Pascal library routine was used with standard error handling and 10^4 steps in the interval $0 \le x \le 1$. An increase to 10^6 steps did not change the results.

Furthermore, the following simple considerations allow obtaining an *approximate solution* (i.e., the upper limit) for P_0. As can be seen from eq 22, when exchange is slow compared to propagation, $\beta/\gamma \ll 1$, the active species P_0^*, formed from the dormant 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 P'_0 is approximately equal to the total concentration of residual initiator. Thus, eq 23 can be simplified by neglecting the back-reaction:

$$(1-x)\frac{\mathrm{d}P'_0}{\mathrm{d}x} = -\beta P'_0 \quad (24)$$

This equation is easily integrated:

$$P_0 \approx P'_0 = (1-\alpha)I_0(1-x)^\beta \quad (25)$$

Figure 1 shows that the error of the approximate solution (eq 25) is not very high as compared to numerical integration.

Equation 25 shows that the concentration of the residual initiator at full conversion ($x = 1$) vanishes. However, initiator consumption is very slow for $\beta = k_\mathrm{ex}/k_\mathrm{p} < 1$; i.e. it is only reached in a very late stage of the polymerization that is hard to reach in a real polymerization. As an example, for $\alpha \ll 1$ and $\beta = k_\mathrm{ex}/k_\mathrm{p} = 0.1$, $P_0/I_0 = 0.63$ for $x = 99\%$ and $P_0/I_0 = 0.40$ for $x = 99.99\%$.

Number-Average Degree of Polymerization and Polydispersity Index Excluding Residual Initiator. By extracting the concentration of residual initiator, the following expression for the number-average degree of polymerization is obtained

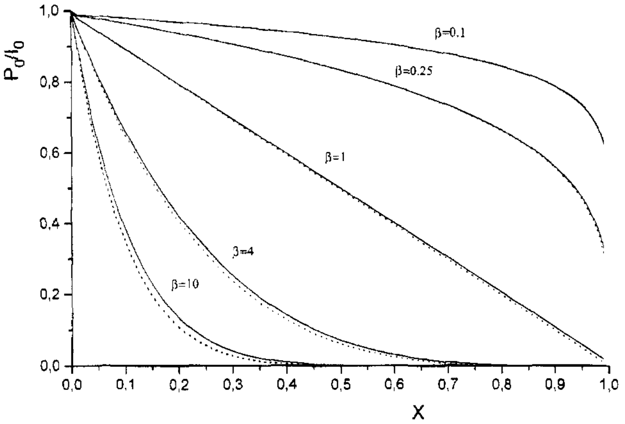


Figure 1. Residual initiator concentration, P_0, vs monomer conversion, x. Comparison of simplified derivation (—; eq 25) vs numerical integration (···) for various values of $\beta = k_{ex}/k_p$. $\alpha = 0.01$, $\gamma = M_0/I_0 = 100$.

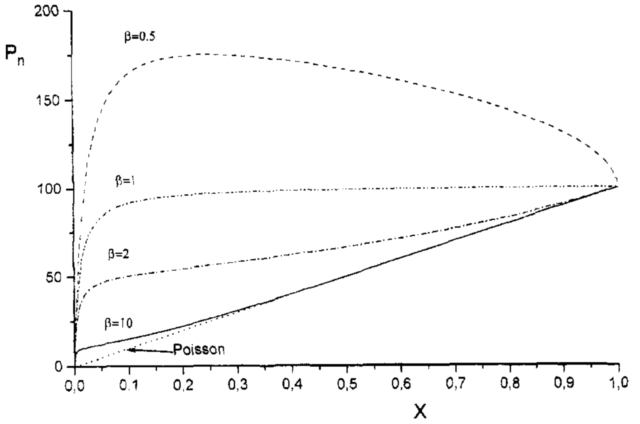


Figure 2. Effect of residual initiator concentration on the number-average degree of polymerization, plotted vs monomer conversion, for various values of $\beta = k_{ex}/k_p$. $\alpha = 0.01$, $\gamma = M_0/I_0 = 100$. The dotted straight line ($\beta \gg 1$) also represents the values obtained when residual initiator is included in the calculation.

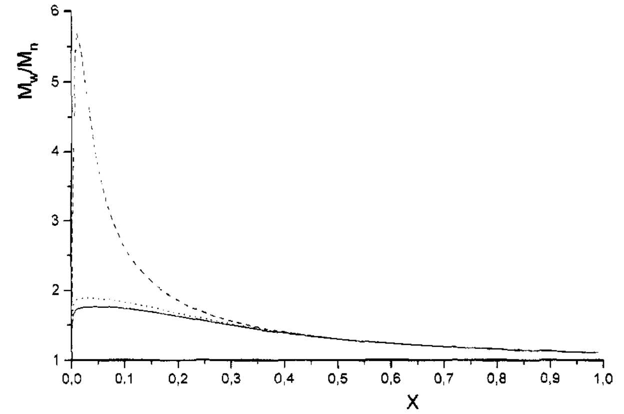


Figure 3. Effect of residual initiator concentration on polydispersity index: (— — —) without extraction of initiator concentration; (···) and (—) residual initiator concentration extracted by using the simplified method and numerical integration, respectively. $\beta = 10$, $\alpha = 0.01$, $\gamma = 100$.

$$\bar{P}_n \approx \frac{\gamma x}{1 - (1 - \alpha)(1 - x)^{\beta}} \qquad (26)$$

Figures 2 and 3 show that the values of $\bar{P}_n$ and $\bar{P}_w/\bar{P}_n$ obtained by including and excluding residual initiator concentration considerably differ for $\beta < 100$.

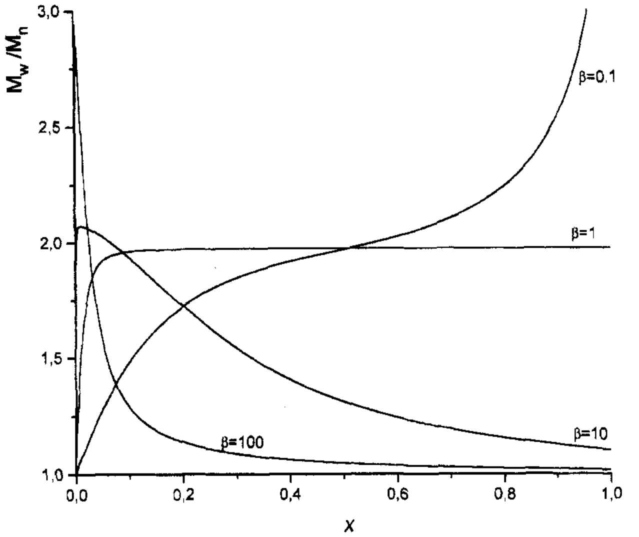


Figure 4. Calculation of polydispersity index vs monomer conversion for various values of $\beta = k_{ex}/k_p$. $\alpha = 0.01$, $\gamma = 100$.

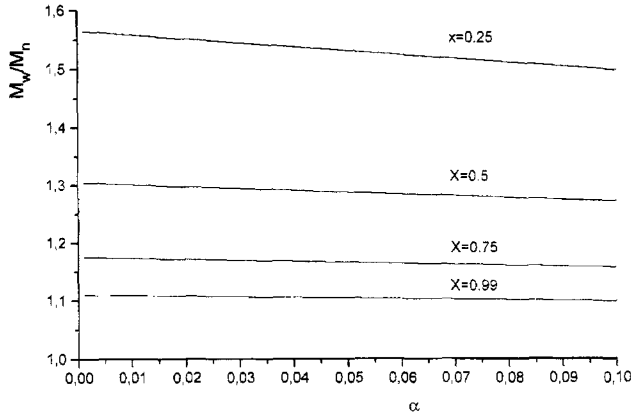


Figure 5. Calculation of polydispersity index as a function of $\alpha = P^*/I_0$ for different monomer conversions. $\beta = 10$, $\gamma = 100$.

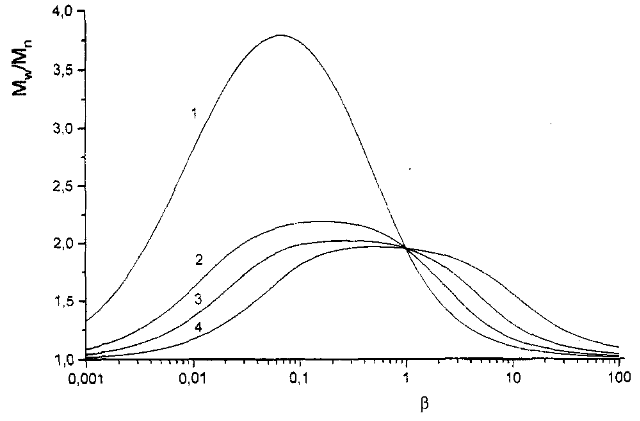


Figure 6. Polydispersity index as a function of $\beta = k_{ex}/k_p$ for different monomer conversions: (1) $x = 0.99$; (2) $x = 0.75$; (3) $x = 0.5$; (4) $x = 0.25$. $\alpha = 0.01$, $\gamma = 100$.

Discussion

Figures 4–6 and 7a show the dependence of the polydispersity index on monomer conversion, x, on $\alpha = P^*/I_0$, on $\beta = k_{ex}/k_p$, and on $\gamma = M_0/I_0$.

The character of the dependence of polydispersity index on conversion is as follows.

(1) $\beta < 1$ (moderately slow exchange): $\bar{P}_w/\bar{P}_n$ continuously increases to the final value defined by eq 31 at x

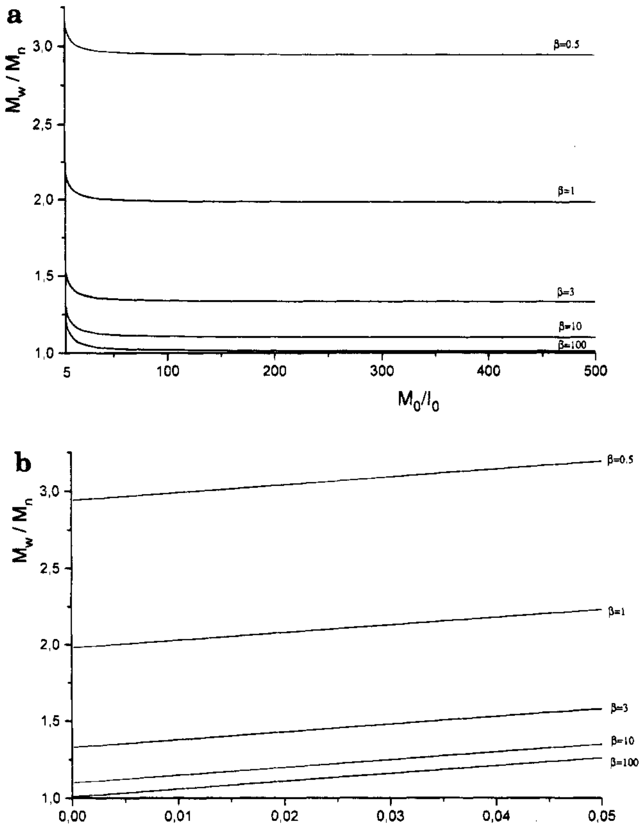


Figure 7. Polydispersity index at full conversion as a function of (a) $\gamma = M_0/I_0$ and (b) I_0 for different values of β. $\alpha = 0.01$, $M_0 = 0.2$ mol/L.

$= 1$. The rather strong increase for $x > 0.8$ shown in Figure 4 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. Between $x = 0.8$ and $x = 1$ the remaining initiator molecules become consecutively activated, leading to the formation of many oligomer molecules, thus broadening the MWD.

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

(3) $\beta > 1$ (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 31 at $x = 1$. This coincides with a common observation in GTP (see below).

Figure 5 shows that the dependence of the polydispersity index on the fraction of active chain ends is not very pronounced and can be neglected, especially at higher conversions.

The polydispersity index has its maximum in the region $0.1 < \beta < 10$, depending on conversion (cf. Figure 6). For very fast exchange ($\beta \gg 1$), a Poisson distribution will be reached. The same is expected for extremely slow exchange (or in the limiting case of no exchange at all, $\beta = 0$). However, in the latter case the number-average degree of polymerization will be much higher (cf. eq 21).

As can be seen from Figure 7a, the ratio of initial monomer to initiator concentrations, γ, only has a pronounced effect for $\gamma x \lesssim 25$. Figure 7b shows that there is a slight effect on the initial initiator concentration, but this is not very pronounced for realistic concentrations ($I_0 < 10^{-2}$ mol/L).

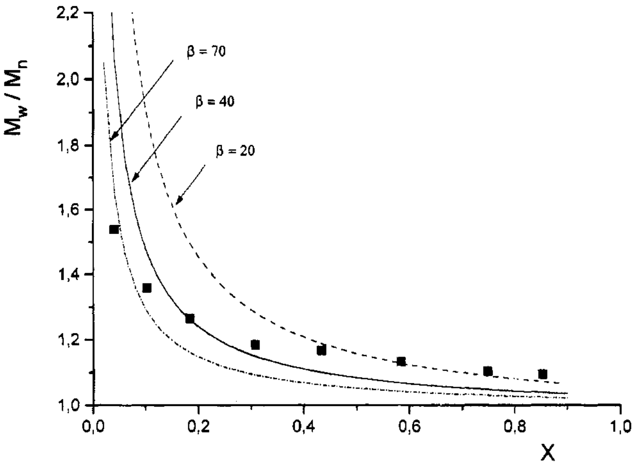


Figure 8. Plot of polydispersity index vs monomer conversion for GTP of MMA with dimeric initiator and tris(dimethylamino)sulfonium benzoate as a catalyst at 22.1 °C.[17] $I_0 = 1.0 \times 10^{-3}$ mol/L, $M_0 = 0.19$ mol/L, $C_0 = 1.9 \times 10^{-5}$ mol/L. Curves are calculated with $\alpha = 0.001$, $\beta = 20$, 40, and 70, respectively, and $\gamma = 190$.

For most polymerizations, i.e., for $\gamma x \gtrsim 25$, we obtain the following simplification for eq 18:

$$\bar{P}_w \approx \gamma\left[2 + \frac{(2-x)(1-\beta)}{(\beta-\alpha)} - \frac{2\alpha(1-\alpha)}{\beta^2-\alpha^2}\,\frac{1-(1-x)^{1+\beta/\alpha}}{x}\right] \tag{28}$$

It is easily seen that $D = \bar{P}_w/\bar{P}_n$ becomes independent of γ. For full conversion ($x = 1$) these equations become even simpler

$$\bar{P}_n \approx \gamma \tag{29}$$

$$\bar{P}_w \approx \gamma\frac{\beta+1}{\beta+\alpha} \tag{30}$$

leading to a very simple relation for the polydispersity index

$$D = \frac{\bar{P}_w}{\bar{P}_n} \approx \frac{\beta+1}{\beta+\alpha} \tag{31}$$

which finally leads to an even simpler equation for $\beta \gg \alpha$:

$$D = \frac{\bar{P}_w}{\bar{P}_n} \approx 1 + \frac{1}{\beta} = 1 + \frac{k_p}{k_{ex}} \tag{32}$$

Comparison to Experimental Data. In the GTP of methacrylates initiated by the "unimeric" initiator 1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene (MTS) in THF, slow initiation is observed.[17,33] Thus, data for fast initiation are only available for initiation of methyl methacrylate (MMA) with a dimeric initiator (i.e., the addition product of MTS and MMA) and tris(dimethylamino)sulfonium benzoate as the catalyst.[17,36] Kinetic reaction orders indicate that for this catalyst the activation proceeds via the formation of a pentacoordinate silicon species (cf. Scheme 2) and the equilibrium is shifted to the left hand side (i.e. $\alpha \ll 1$).[17,29] Figure 8 shows a fit of polydispersity index vs conversion. Since in these experiments the residual initiator (i.e. dimer) is measured by GPC, its concentration does not have to

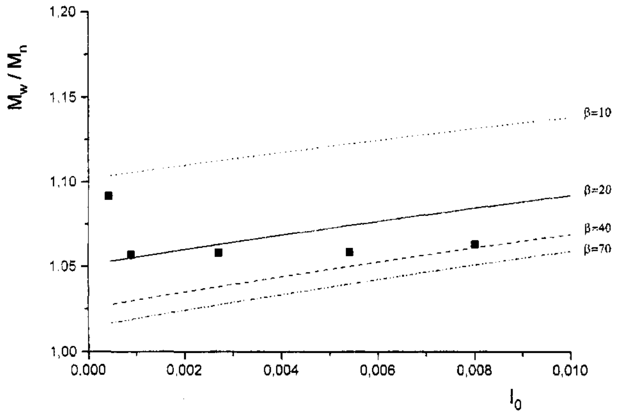


Figure 9. Plot of polydispersity index at full conversion vs initial initiator concentration for GTP of MMA with dimeric initiator and tris(dimethylamino)sulfonium benzoate as a catalyst at 22 °C.[36] $M_0 = 0.20$ mol/L, $C_0 = 6.5 \times 10^{-5}$ mol/L. Curves are calculated with $\alpha = 0.001$ and $\beta = 10$, 20, 40, and 70, respectively.

be subtracted. Thus, eq 19 was used to calculate the molecular weight averages.

The polydispersity indices calculated only roughly fit the experimental data with $\beta \approx 40$, i.e. $k_{\mathrm{ex}} \gg k_{\mathrm{p}}$. In this range of β, the effect of residual initiator concentration is no longer important and can be neglected. The rather poor fit could be due to some additional termination. Termination would lead to an increase of polydispersity index with conversion and thus partly compensate for the decrease due to moderately slow exchange.

In Figure 9, the dependence of polydispersity index on initial initiator concentration is fitted. In contrast to the theoretical predictions, the experimental polydispersity indices are roughly independent of I_0. This might indicate that other or more refined mechanisms have to be found which better describe the MWD in GTP. However, it has to be taken into account that the experimental polydispersity indices are rather low and the accuracy is in the range of ±0.02.

Conclusions

The MWD for a mechanism including degenerative transfer strongly depends on the ratio of rate constants, $\beta = k_{\mathrm{ex}}/k_{\mathrm{p}}$. Depending on conversion, the maximum values of the polydispersity index are obtained for $0.1 < \beta < 10$. The polydispersity index increases with monomer conversion, x, for $\beta < 1$ and it decreases for $\beta > 1$. The dependence on the fraction of active chain ends, α, and on initial monomer, initiator, or catalyst concentrations is less pronounced or absent. For $\beta \lesssim 10$, it is of utmost importance to take the effect of unreacted initiator into account.

In the following publications, the MWD function and moments for constant monomer concentration (e.g., very slow addition of monomer) will be given. In addition, the polydispersity index for the "associative" and "dissociative" GTP mechanisms will be calculated and compared to each other and to experimental data. The latter mechanisms are formally identical to the generation of ion pairs or free cations in cationic polymerization.

Appendix: Calculation of the Concentration of Residual Initiator

In order to obtain the exact solution of eqs 22 and 23, P_0^* should be expressed through P_0' from eq 23 and then substituted into eq 22. Thus we have a second-order differential equation which contains only P_0'

$$(1-x)\frac{d^2P_0'}{dx^2} + \left[\frac{\gamma}{\alpha}(1-x) - 1 + \frac{\beta}{\alpha}\right]\frac{dP_0'}{dx} + \frac{\gamma\beta}{\alpha}P_0' = 0 \tag{A1}$$

If we introduce a new variable $\xi = (\gamma/\alpha)(1 - x)$, eq A1 yields the usual form of the confluent hypergeometric equation

$$\xi\frac{d^2P_0'}{d\xi^2} + \left[1 - \frac{\beta}{\alpha} - \xi\right]\frac{dP_0'}{d\xi} + \beta P_0' = 0 \tag{A2}$$

Its general solution is

$$P_0' = C_1F(-\beta, 1 - \beta/\alpha, \xi) + C_2\xi^{\beta/\alpha}F(\beta(1-\alpha)/\alpha, 1 + \beta/\alpha, \xi) \tag{A3}$$

where $F(a, b, \xi)$ is the Kummer function,

$$F(a, b, \xi) = 1 + \sum_{k=1}^{\infty}\frac{a(a+1)...(a+k-1)}{b(b+1)...(b+k-1)}\frac{\xi^k}{k!}$$

and coefficients C_1 and C_2 should be obtained from the initial conditions ($\xi = \xi_0 \equiv \gamma/\alpha$):

$$P_0'|_{\xi=\xi_0} = (1-\alpha)I_0 \qquad \left.\frac{dP_0'}{d\xi}\right|_{\xi=\xi_0} = 0$$

However, this exact solution is represented as a very complex expression which is very difficult to analyze. Fortunately, the problem can be greatly simplified because of a large parameter γ/α. Comparing different terms of eqs A1 and A2 by their order of magnitude, one can see that for $\gamma x/\alpha \gg 1$ (i.e., even for very small conversions) the second-order derivative can be successfully neglected. Thus, instead of eq A1 we have

$$\left[1 - x + \frac{\beta}{\gamma}\right]\frac{dP_0'}{dx} \approx \beta P_0' \tag{A4}$$

In deriving eq A4 we also neglected a small value $\alpha/\gamma \ll 1$. Equation A4 can be easily integrated

$$P_0' = (1-\alpha)I_0\left(\frac{1 - x + \beta/\gamma}{1 + \beta/\gamma}\right)^{\beta}$$

By inserting this into eq 23 we find that $P_0^*/P_0' \approx \alpha\beta/[\gamma(1 - x + \beta/\gamma)] < \alpha \ll 1$ and thus can be neglected.

Consequently, the number-average degree of polymerization is

$$\bar{P}_{\mathrm{n}} \approx 1 + \frac{\gamma x}{1 - (1-\alpha)\left(\frac{1 - x + \beta/\gamma}{1 + \beta/\gamma}\right)^{\beta}} \tag{A5}$$

If the exchange is not very fast, i.e. $\beta/\gamma \ll 1$, eq A5 can be simplified to eq 26.

As follows from eq 26, for $\beta > 10$ the number-average degree of polymerization approaches the usual dependence expected for living polymers, $\bar{P}_{\mathrm{n}} \approx \gamma x$, from very low conversions.

When exchange is extremely fast, i.e. $\beta/\gamma \gg 1$, eq A5 transforms into

$$P_0' \approx (1-\alpha)I_0\exp\left(-\frac{\gamma}{\alpha}x\right)$$

P_0' vanishes at extremely low conversions and hence has not been taken into further consideration. Thus, in this case $\bar{P}_n = \gamma x$. As a consequence, eq 26 can be applied to the calculation of the number-average degree of polymerization over the whole range of exchange rates.

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