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Kinetic Analysis of "Living" Polymerization Processes Exhibiting Slow Equilibria. 2.[†] Molecular Weight Distribution for Degenerative Transfer (Direct Activity Exchange between Active and "Dormant" Species) at Constant Monomer Concentration

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ABSTRACT: The MWD function and 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 in a bimolecular reaction ("degenerative transfer"). Such a mechanism is believed to be applicable to many "living" polymerizations (e.g., anionic, group transfer, cationic, and radical). For constant monomer concentration (slow addition of monomer or low conversion), the polydispersity index, $\bar{P}_w/\bar{P}_n$, depends on the ratio of molar concentrations of monomer and initiator, $\gamma = M/I_0$, the degree of polymerization, $\bar{P}_n$, and the ratio of rate constants of exchange and propagation, $\beta = k_{ex}/k_p$. In a limiting case ($\beta > 1$ and $\bar{P}_n \gg 1$), $\bar{P}_w/\bar{P}_n \approx 1 + 2\gamma/(\beta\bar{P}_n)$. The molecular weight distributions are always narrower than those obtained for a batch process, where monomer concentration decreases during polymerization.

Introduction

In the first part of this series,[1] expressions for the average degrees of polymerization and the polydispersity index (PDI) were derived for a "living" polymerization process (i.e., absence of *irreversible* termination and transfer reactions) with bimolecular activity exchange between active and "dormant" species ("degenerative transfer"; cf. Scheme 1) and applied to group transfer polymerization (GTP). It was shown that the PDI mainly depends on the ratio of rate constants of exchange and propagation, $\beta = k_{ex}/k_p$, and conversion.

It was proposed earlier[2–5] that for processes involving any mechanism of reversible exchange between active and "dormant" species, for a given degree of polymerization the PDI should be inversely proportional to the monomer concentration M, because the rate of polymerization depends on M whereas the rate of exchange is independent of M. In fact, by decreasing the monomer concentration[3] or by adding monomer very slowly, e.g. by vapor condensation or by dropwise addition,[4,6] much narrower MWD's can be obtained in GTP. Such a process is realized in a semibatch reactor without outflow where the actual monomer concentration is very low and approximately constant. Similar results were obtained for incremental monomer addition in cationic polymerization.[5] In this paper, we present a quantitative treatment for a polymerization at constant, low monomer concentration, including the full MWD function. Due to the nature of the kinetic differential equations, it is not possible to give an analytical expression for the MWD for batch polymerizations, where monomer concentration decreases with time (cf. part 1). For comparison, we will use numerical integration to calculate the MWD for such a process.

Scheme 1. Degenerative Transfer between Active (P*) and "Dormant" (P′) Chain Ends

$$P_i^* + P'_j \overset{k_{ex}}{\rightleftharpoons} P'_i + P_j^*$$

The approach developed in this work is applicable to other "living" polymerization systems with various mechanisms of activity exchange between chain ends. A general theory will be reported later.

Kinetic Differential Equations

If we neglect volume changes arising from slow monomer addition, the stationary monomer concentration, M, can be obtained from the equation

$$\frac{dM}{dt} = \phi_M - k_p M P^* = 0 \qquad (1)$$

then,

$$M = \frac{\phi_M}{k_p \alpha I_0} \qquad (2)$$

Here ϕ_M is the monomer flow, i.e., the rate of monomer feed, e.g., in mol L^{-1} s^{-1}, I_0 and P^* represent the initial initiator concentration and the total concentration of active species, $P^* = \sum_{i=0}^{\infty} P_i^*$, P_i^* is the actual concentration of active i-mer, and $\alpha = P^*/I_0$ is the fraction of these active species. Assuming the rate constants of initiation and polymerization to be equal, the set of kinetic differential equations reads

$$\frac{dP_i^*}{dt} = k_p M(P_{i-1}^* - P_i^*) - k_{ex} P_i^* P' + k_{ex} P'_i P^* \quad (i \geq 0) \quad (3)$$

$$\frac{dP'_i}{dt} = k_{ex} P_i^* P' - k_{ex} P'_i P^* \qquad (i \geq 0) \qquad (4)$$

where P' is the total concentration of dormant species. The initial conditions for eqs 3 and 4 are

$$P_i^*|_{t=0} = \alpha I_0 \delta_{i,0} \qquad (5)$$

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

where $\delta_{i,j}$ is the Kronecker symbol.

[†] Part 1: see ref 1.

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Results

Molecular Weight Averages and Polydispersity Index. By defining the dimensionless time, τ, similar to what was done in part 1

$$\tau = k_p \alpha I_0 t$$

and the MWD moments for the active, "dormant", and total chains, respectively,

$$\mu_n^* = \sum_{i=1}^{\infty} i^n P_i^* \qquad \mu_n' = \sum_{i=1}^{\infty} i^n P_i' \qquad \mu_n = \mu_n^* + \mu_n'$$

we obtain from eqs 3 and 4

$$\mu_0 = I_0 - P_0 \tag{6}$$

$$\frac{d\mu_1}{d\tau} = M \tag{7}$$

$$\frac{d\mu_1^*}{d\tau} = M(1 + \beta\tau) - \frac{\beta}{\alpha}\mu_1^* \tag{8}$$

$$\frac{d\mu_2}{d\tau} = M + \frac{2\gamma}{\alpha}\mu_1^* \tag{9}$$

where $\gamma = M/I_0 = \phi_M/(\alpha k_p I_0^2)$.

Equation 6 takes into account that the concentration of yet unreacted initiator, P_0 (cf. eq 23), has to be subtracted from the total number of chains because it will not be measured in the experimental determination of the molecular weight averages (for details, cf. part 1 of this series[1]). Integration of eqs 7–9 results in

$$\mu_1 = M\tau \tag{10}$$

$$\mu_1^* = M\alpha\tau + M\frac{(1-\alpha)}{\beta}(1 - e^{-\beta\tau/\alpha}) \tag{11}$$

$$\mu_2 = (1 + b + \gamma\tau)M\tau - M\frac{b\alpha}{\beta}(1 - e^{-\beta\tau/\alpha}) \tag{12}$$

where $b = 2\gamma(1-\alpha)/\beta$. Therefore, the number- and weight-average degrees of polymerization can be expressed by

$$\bar{P}_n = \frac{\mu_1}{\mu_0} = \frac{\gamma\tau}{1 - P_0/I_0} \tag{13}$$

$$\bar{P}_w = \frac{\mu_2}{\mu_1} = 1 + b + \gamma\tau - \gamma\frac{2\alpha(1-\alpha)}{\beta^2\tau}(1 - e^{-\beta\tau/\alpha}) \tag{14}$$

The dependencies of $\bar{P}_n$ and PDI on time calculated by using eqs 13, 14, and 23 (*vide infra*) are shown in Figures 1 and 2. As can be seen, if exchange is not extremely slow, say $\beta/\gamma > 0.1$, the effect of residual initiator is important only for very small τ, i.e., for oligomers. $\bar{P}_n$ quickly approaches the linear dependence on time,

$$\bar{P}_n \approx \gamma\tau = \frac{\phi_M}{I_0}t \tag{15}$$

This should be the case for values of $10 < \beta < 100$, typical for GTP (as estimated in part 1).

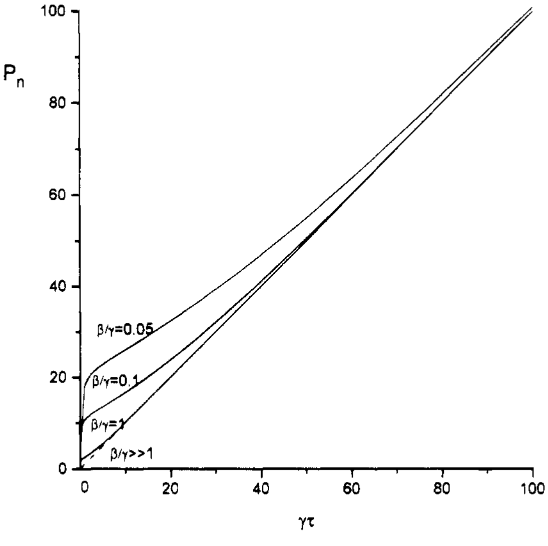

Figure 1. Dependence of number-average degree of polymerization on time for different rates of exchange, $\beta/\gamma = k_{ex}I_0/(k_pM)$; $\alpha = 0.01$.

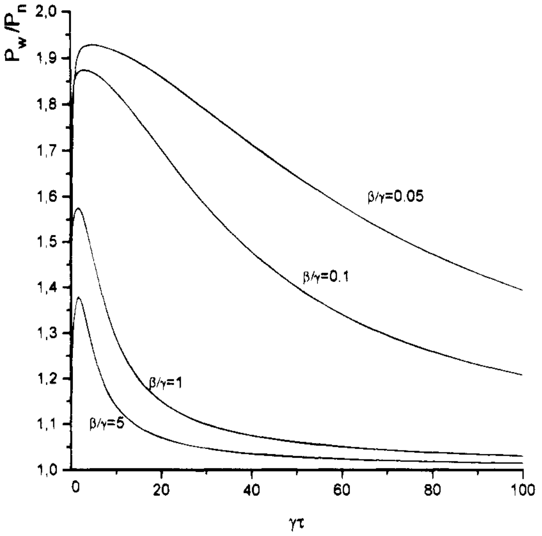

Figure 2. Dependence of polydispersity index on time for different rates of exchange.

After a sharp increase at very short times, the polydispersity index begins to decrease. At full conversion of initiator to polymer chains, the weight-average degree of polymerization and the polydispersity index can be simplified into

$$\bar{P}_w \approx 1 + b + \gamma\tau \tag{16}$$

$$\frac{\bar{P}_w}{\bar{P}_n} \approx 1 + \frac{b+1}{\bar{P}_n} \tag{17}$$

For $\bar{P}_n \gg 1$ ($1/\bar{P}_n$ vanishes) and $\alpha \ll 1$, eq 17 leads to

$$\frac{\bar{P}_w}{\bar{P}_n} \approx 1 + \frac{2\gamma}{\beta\bar{P}_n} = 1 + \frac{2}{\alpha k_{ex} I_0 t} \tag{17a}$$

It is interesting to note that eq 17 describes the polydispersity index obtained for a Poisson distribution with an additional nonuniformity arising from the finite rate of exchange, $b/\bar{P}_n$, which decreases with time.

Molecular Weight Distribution. In order to calculate chain length distribution of active and dormant species, let us introduce the generating functions

$$G^*(s,\tau) = \sum_{i=0}^{\infty} s^i P_i^*(\tau), \qquad G'(s,\tau) = \sum_{i=0}^{\infty} s^i P_i'(\tau);$$
$$G(s,\tau) = G^*(s,\tau) + G'(s,\tau) \tag{18}$$

for active, dormant, and total chains, respectively. According to definition, P_i^* is related to G^* as

$$P_i^* = \frac{1}{i!}\left.\frac{\mathrm{d}^i G^*}{\mathrm{d}s^i}\right|_{s=0}$$

A similar relationship connects P_i' and G'. If the generating functions are known, it is also easy to calculate the MWD moments:

$$\mu_0 = G_{s=0}; \qquad \mu_1 = \left.\frac{\mathrm{d}G}{\mathrm{d}s}\right|_{s=0}; \qquad \mu_2 = \mu_1 + \left.\frac{\mathrm{d}^2G}{\mathrm{d}s^2}\right|_{s=0}$$

From eqs 3 and 4 we get

$$\frac{\mathrm{d}G^*}{\mathrm{d}\tau} = \frac{\gamma}{\alpha}(s-1)G^* + \beta\left(G' - \frac{1-\alpha}{\alpha}G^*\right) \tag{19}$$

$$\frac{\mathrm{d}G'}{\mathrm{d}\tau} = -\beta\left(G' - \frac{1-\alpha}{\alpha}G^*\right) \tag{20}$$

The solution of eqs 19 and 20 for initial conditions (5) gives for the generating function of all chains

$$G = I_0\left\{\frac{\lambda_2 - \gamma(1-s)}{\lambda_2 - \lambda_1}\mathrm{e}^{-\lambda_1\tau} - \frac{\lambda_1 - \gamma(1-s)}{\lambda_2 - \lambda_1}\mathrm{e}^{-\lambda_2\tau}\right\} \tag{21}$$

where λ_1 and λ_2 are the solutions of the quadratic equation

$$\alpha\lambda^2 - (\beta + \gamma(1-s))\lambda + \beta\gamma(1-s) = 0$$

$$\lambda_{1,2} = \frac{1}{2\alpha}\{\beta + \gamma(1-s) \pm [(\beta + \gamma(1-s))^2 - 4\alpha\beta\gamma(1-s)]^{1/2}\}$$

The concentration of residual initiator is simply G at $s = 0$. For the total concentration of chains of length $i > 0$, the ith derivative of eq 21 with respect to s leads to

$$P_i/I_0 = \left(\frac{\gamma}{\alpha}\right)^i \sum_{j=0}^{i}\sum_{k=0}^{i-j}\binom{i+k}{k}\binom{i}{j+k}\frac{(-1)^k\tau^j}{j!(\lambda_1-\lambda_2)^{i+k+1}} \times \{Y(\lambda_1) + (-1)^{i+k+1}Y(\lambda_2)\} \tag{22}$$

where an auxiliary function $Y(\lambda)$ is introduced,

$$Y(\lambda) = \left[\frac{i+1}{j+k+1}\alpha(\beta-\lambda) + 2\beta(1-\alpha) + \frac{j+k}{i}\frac{\beta^2(1-\alpha)^2}{\alpha(\beta-\lambda)}\right]\mathrm{e}^{-\lambda\tau}(\beta-\lambda)^{j+k}$$

and corresponding λ's are taken at $s = 0$. For the important limiting case $\alpha \ll 1$, λ_1 and λ_2 are

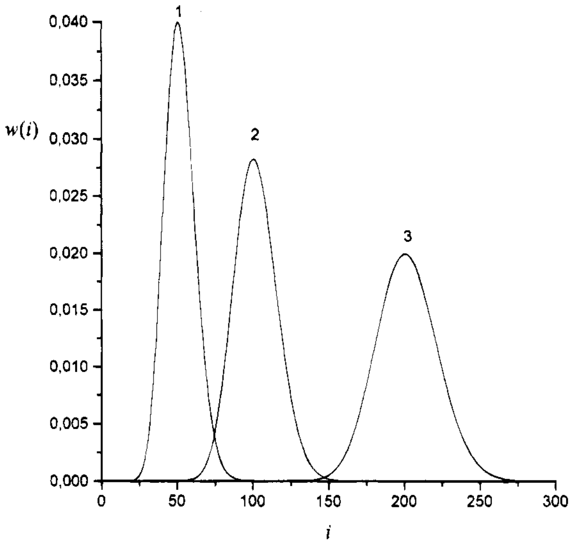

Figure 3. Evolution of MWD with time for $\beta/\gamma = k_{\mathrm{ex}}I_0/(k_{\mathrm{p}}M) = 1$: (1) $\bar{P}_{\mathrm{n}} = 50$, $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} = 1.06$; (2) $\bar{P}_{\mathrm{n}} = 100$, $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} = 1.03$; (3) $\bar{P}_{\mathrm{n}} = 200$, $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} = 1.015$. For a Poisson distribution, the polydispersity indices would be $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} = 1.02$, 1.01, and 1.005, respectively.

$$\lambda_1 \approx \frac{\beta\gamma(1-s)}{\beta + \gamma(1-s)}; \qquad \lambda_2 \approx \frac{\gamma(1-s) + \beta}{\alpha}$$

Then, eq 21 can be represented as follows:

$$\frac{G}{I_0} = \left[1 - \alpha\left(\frac{\lambda_1}{\beta}\right)^2\right]\mathrm{e}^{-\lambda_1\tau} + \alpha\left(\frac{\lambda_1}{\beta}\right)^2\mathrm{e}^{-\lambda_2\tau} \tag{21a}$$

This expression has two characteristic times of decay, $1/\lambda_1$ and $1/\lambda_2$. Because $\alpha \ll 1$, $\lambda_2 \gg \lambda_1$ whatever the relationship between β and γ, the contribution from the second term can be neglected for $\beta\tau/\alpha \gg 1$. Consequently, we obtain approximately

$$\frac{G}{I_0} \approx \mathrm{e}^{-\lambda_1\tau} \tag{23}$$

which leads to the concentration of residual initiator

$$P_0/I_0 \approx \exp\left[-\frac{\gamma\beta}{\gamma+\beta}\tau\right] \tag{24}$$

By taking the ith derivative of the right-hand side of eq 23, one obtains finally for the chain length distribution

$$P_i \approx \exp\left[-\left(\frac{\beta\tau}{\beta+\gamma}\right)\right]\frac{\beta^2\tau/\gamma}{(1+\beta/\gamma)^{i+1}}\sum_{k=0}^{i-1}\binom{i-1}{k} \times \left(\frac{\beta^2\tau}{\beta+\gamma}\right)^k\frac{1}{(k+1)!} \tag{25}$$

At long times, when $\beta^2\tau/(\beta+\gamma) \gg 1$ (that is, all the initiator has been consumed), eq 25 can be approximated by a continuous function, leading to the weight distribution:

$$w(i) \equiv \frac{iP_i}{M\tau} = \left(\frac{\beta}{4\pi\gamma^2\tau}\right)^{1/2} z^{1/2}\exp(-\beta\tau(1-z)^2) \tag{26}$$

where $z = (i/\gamma\tau)^{1/2}$. Figure 3 shows the evolution of the

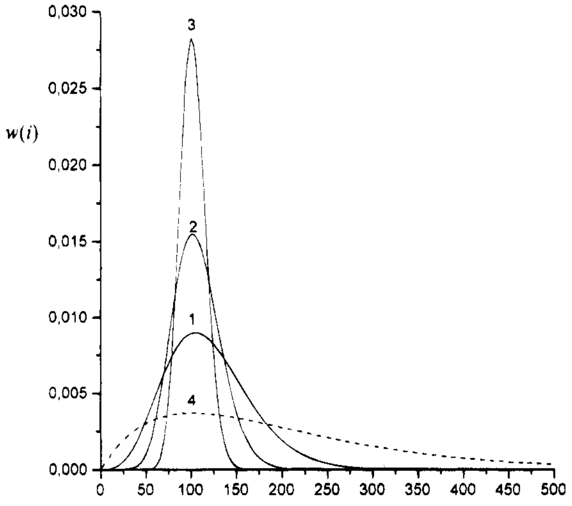

Figure 4. Effect of exchange rate on the MWD. $\beta = 1$, $\bar{P}_n = \gamma\tau = 100$. Since the MWD depends on β/γ, the same effects are observed for the variation of β at constant γ. (1) $\gamma = M/I_0 = 10$, $\bar{P}_w/\bar{P}_n = 1.21$; (2) $\gamma = 3.33$, $\bar{P}_w/\bar{P}_n = 1.08$; (3)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

MWD with time. The results were obtained by using both the exact solution (22) and the approximate expression (26); the comparison shows that for $\alpha < 0.1$, both expressions give practically identical values. The effect of monomer concentration and exchange rate on the MWD can be seen from Figure 4.

All the equations above were derived neglecting volume changes. This is valid if the volume fraction of the polymer formed in the system is much less than unity, the upper limit being ca. 0.1. Because typically the molar concentration of pure monomer is ~ 10 mol L^{-1}, this means that the total (not stationary) concentration of all monomer consumed $\phi_M t = M\tau = \bar{P}_n I_0$ should be less than 1 mol L^{-1}, and hence, the results obtained are valid for $\bar{P}_n < 1/I_0$ (I_0 in mol L^{-1}). However, in the equations derived above, all concentrations only enter as ratios for a given $\bar{P}_n$, so it can be assumed that the error due to volume increase is not important even at higher $\bar{P}_n$.

Comparison of MWD's for both Constant and Variable Monomer Concentration. When comparing the polydispersity index for slow monomer addition (eq 17) with that obtained for a normal batch polymerization process, i.e., at decreasing monomer concentration[1] (cf. part 1 of this series), a strong difference becomes obvious. For the batch process, in the limiting (but common) case $\alpha \ll 1$, $\bar{P}_n \gg 1$, and $\beta \gg \alpha$

$$\frac{\bar{P}_w}{\bar{P}_n} \approx 1 + \frac{1}{\bar{P}_n} + \frac{1}{\beta} \approx 1 + \frac{1}{\beta} \qquad (27)$$

was obtained at full monomer conversion. This value is independent of α and $\bar{P}_n$. As an example, for $\beta = 1$, eq 27 leads to $\bar{P}_w/\bar{P}_n = 2$. For constant monomer concentration, the polydispersity index decreases with time (or with $\bar{P}_n$ obtained). For a given $\bar{P}_n$, it increases with decreasing monomer concentration and increasing β or I_0. As an example, for $\beta = 1$, $\gamma = M/I_0 = 1$, and $\bar{P}_n = 100$, we obtain $\bar{P}_w/\bar{P}_n = 1.03$. If we increase the monomer concentration by a factor of 10 ($\gamma = 10$), we still obtain a much narrower distribution, $\bar{P}_w/\bar{P}_n = 1.21$. For group transfer and cationic polymerizations, β is typically in the range of 10–50.[1,7] Thus, the narrowing of MWD through slow or incremental monomer addition is less pronounced but still visible.[3–6]

Since the MWD function for a batch process with degenerative transfer cannot be obtained by analytical solution of the corresponding differential equations, a numerical solution was performed, and an example of the results is compared to the corresponding distributions for constant monomer concentration in Figure 4. The program package PREDICI was used, which employs new numerical strategies for time discretization (adaptive Rothe method[8,9]) and representation of chain length distributions (discrete Galerkin h–p method[10]).

The broader distributions for batch polymerizations are not unexpected since it was shown earlier that the width of the MWD depends on the ratio of the rates of exchange and of polymerization, and thus on the actual monomer concentration.[3–5] As a consequence, 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 lifetime of the active centers.

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