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Kinetic Analysis of “Living” Polymerization Systems Exhibiting Slow Equilibria. 3.[†] “Associative” Mechanism of Group Transfer Polymerization and Ion Pair Generation in Cationic Polymerization

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ABSTRACT: The averages of the molecular weight distribution are derived for a “living” polymerization process which proceeds via active and “dormant” species and where the active species are formed by addition of a catalyst to a “dormant” species. Such a mechanism is applicable to group transfer and “living” cationic polymerizations (assuming that ion pairs are formed exclusively in the latter case). Both equilibrium and nonequilibrium initial conditions are used for the calculation. The results are very similar to those obtained for degenerative transfer (i.e., direct exchange of activity between active and “dormant” species). The dominating parameter is $\beta = k_2/(k_pI_0)$, where k_2 and k_p are the rate constants of reversible deactivation and propagation, respectively, and I_0 is the initial initiator concentration (for degenerative transfer this parameter was given as $\beta = k_{ex}/k_p$, independent of initiator concentration). As an example, for $\beta > 1$ the polydispersity index decreases with monomer conversion (after a marked increase at low conversions), coinciding with a common observation in group transfer and cationic polymerizations. In a limiting case, at full conversion, $M_w/M_n \approx 1 + 1/\beta$. Differences between equilibrium and nonequilibrium initial conditions can only be seen for $\beta < 1$. The results are compared to experimental data of the GTP of methyl methacrylate using nucleophilic catalysts and to the cationic polymerization of isobutylene. Typically, exchange is moderately fast ($10 \leq \beta \leq 100$), thus the equilibrium initial conditions are sufficient for the calculations.

Introduction

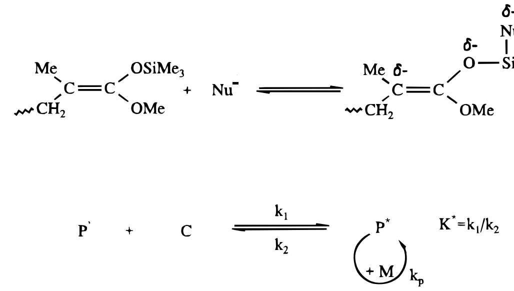
In parts 1 and 2 of this series[1,2] we analyzed the phenomenon of slow equilibria between species of different activities (two-state mechanism). This phenomenon is common to many “living” polymerization systems, e.g. anionic, cationic, radical, and group transfer polymerization. Important examples are isomerization, dissociation, association, and reversible deactivation, i.e. the reversible formation of “dormant” species. The last case is important for group transfer polymerization (GTP) and “living” cationic polymerization, because here a catalyst (“co-initiator”) is necessary in order to produce active chain ends. Since the number of active chains is much smaller than the total number of chains, it is essential to exchange activity between active and “dormant chains”.

Activity can be exchanged by various mechanisms which may lead to different kinetics or molecular weight distributions (MWD). In part 1 we first examined the MWD averages for direct activity exchange between active and “dormant” chain ends via degenerative transfer (Scheme 1).[1] It was show 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 (full conversion, $\beta > 1$, and $\bar{P}_n \gg 1$) $M_w/M_n \approx 1 + 1/\beta$. In part 2 we studied the MWD moments and function for constant monomer concentration, i.e. slow addition of monomer.[2] We showed that under conditions of slow monomer addition the resulting MWD is much narrower than for a batch process. The results were compared to experimental data of the GTP of methyl methacrylate using nucleophilic catalysts.

Scheme 1. Degenerative Transfer between Active and “Dormant” Chain Ends

$$P_i^* + P_j' \xrightleftharpoons{k_{ex}} P_i' + P_j^*$$

Scheme 2. “Associative” Mechanism of GTP and Corresponding Kinetic Scheme



However, some other mechanism is essential in order to *initially form active species*. Two possible mechanisms are described below. Through these mechanisms, activity can also be exchanged indirectly.[3] In the “associative” mechanism, proposed by Sogah and Webster[4−6] and modified by Mai and Müller[7,8] (Scheme 2), the addition of a nucleophilic catalyst, **C**, to dormant chain ends, **P′**, leads to an activated species, **P***, with a pentavalent silicon, whereas in the “dissociative” mechanism[9] the addition of catalyst leads to the formation of enolate anions (or ion pairs) and a silyl ester or trimethylsilyl fluoride. The latter mechanism will be studied in the next paper.

[†] Parts 1 and 2, cf. refs 1 and 2.

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Scheme 3. Covalent Species and Ion Pairs in Cationic Polymerization

$$\text{R-X} + \text{MtX}_n \rightleftharpoons \text{R}^+\text{MtX}^-_{n+1}$$

The mechanism in Scheme 2 is identical to that for living cationic polymerization with the assumption that only ion pairs are formed as active species (Scheme 3). Here, **P′** is a covalent species, **C** is a Lewis acid (frequently called co-initiator instead of catalyst), and **P*** is an ion pair. The polydispersity index resulting from such a mechanism was calculated by Puskas et al.[10] by using Figini's[11] steady-state approach, i.e. assuming that the system is in equilibrium initially.

In both GTP and "living" cationic polymerization it is assumed that the fraction of active chain ends, α, is very small: $\alpha \ll 1$. However, whereas in GTP and in cationic polymerization of vinyl ethers the ratio of catalyst over initiator is usually $\leq 10^{-2}$, in cationic polymerization of olefins this ratio can be much higher than unity.

The aim of the present paper is to estimate the effect of slow activity exchange between active and "dormant" chain ends through dissociation/association of catalyst according to Scheme 2. Kinetics of polymerization, molecular weight averages, and the polydispersity index of the polymer formed are calculated by using both equilibrium and nonequilibrium initial conditions. Accordingly, the problem is treated in two ways:

(1) by assuming that the equilibrium of Schemes 2 or 3 has not been established at time $t = 0$ (nonequilibrium, or nonstationary state treatment). This happens if initiator, catalyst, and monomer are mixed instantaneously. In this case the concentration of active chain ends will increase from zero to an equilibrium value during polymerization;

(2) by assuming equilibrium concentrations at $t = 0$ (equilibrium or stationary state treatment). This case corresponds to an experiment where initiator and catalyst have enough time to establish equilibrium concentrations of dormant and active initiator. This treatment is less general and—except for the special treatment of unreacted initiator—similar to that of Figini[11] for a mechanism involving unimolecular isomerization of chain ends.

Kinetic Differential Equations

(A list of symbols and abbreviations is added as an Appendix.)

Scheme 2 can be represented by the following differential equations, describing the variation with time of the concentrations of monomer M, catalyst C, active P_i^* and dormant P_i^* macromolecules which added i monomer units

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -k_\mathrm{p} M P^* \tag{1}$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -k_1 C P' + k_2 P^* \tag{2}$$

$$\frac{\mathrm{d}P_i^*}{\mathrm{d}t} = k_\mathrm{p} M (P_{i-1}^* - P_i^*) + k_1 C P_i' - k_2 P_i^* \quad (i \geq 0) \tag{3}$$

$$\frac{\mathrm{d}P_\mathrm{i}'}{\mathrm{d}t} = -k_1 C P_i' + k_2 P_i^* \quad (i \geq 0) \tag{4}$$

Here, $P^* = \sum_0^\infty P_i^*$ and $P' = \sum_0^\infty P_i'$ are the concentrations of all active and dormant chains, respectively, including the initiator molecules, $P_0 = P_0^* + P_0'$.

For the nonequilibrium case, the initial conditions are as follows:

$$\begin{aligned} M|_{t=0} &= M_0 \\ C|_{t=0} &= C_0 \\ P_i'|_{t=0} &= I_0 \delta_{i,0} \\ P_i^*|_{t=0} &= 0 \end{aligned} \tag{5a}$$

where $\delta_{i,j}$ is the Kronecker symbol. During polymerization the fraction of active chain ends, P^*/I_0, will increase from zero to an equilibrium value, α, which is given below.

When equilibrium concentrations of the components are established at $t = 0$, then

$$\begin{aligned} M|_{t=0} &= M_0 \\ C|_{t=0} &= C_0 - \alpha I_0 \\ P_i'|_{t=0} &= (1 - \alpha) I_0 \delta_{i,0} \\ P_i^*|_{t=0} &= \alpha I_0 \delta_{i,0} \end{aligned} \tag{5b}$$

In this case, the fraction of active chains, α, will not change with conversion. The value of α can be obtained from the equilibrium conditions:[3]

$$\alpha = \{[1 + K^*(I_0 + C_0)] - \sqrt{[1 + K^*(I_0 + C_0)]^2 - 4K^{*2} I_0 C_0}\}/2K^* I_0 \tag{6}$$

where $K^* = k_1/k_2$ is the equilibrium constant of Scheme 2. For values of $\alpha \ll 1$, typical for GTP and cationic polymerization, it is approximated by[12]

$$\alpha \approx \frac{K^* I_0}{1 + K^* I_0} \frac{C_0}{I_0} = \frac{\epsilon}{K + 1} \tag{6a}$$

where $K = k_2/(k_1 I_0) = 1/(K^* I_0)$ and $\epsilon = C_0/I_0$.

Results

Concentration of Active Species and Monomer Conversion. Under steady-state conditions, i.e., when equilibrium relationships between the concentrations of components of the initiating system are established at $t = 0$, the fraction of active species, P^*, does not change with time, i.e. $P^* = \alpha I_0$, and monomer conversion, $x = (M_0 - M)/M_0$, increases with time as for a one-state living system,

$$x = 1 - \exp(-\tau)$$

where $\tau = \alpha k_\mathrm{p} I_0 t$ is a dimensionless time.

In the nonequilibrium case, it is important to know how the concentration of active centers increases with time. Let us denote the ratio of P^* at time t to its equilibrium value, αI_0, as

$$z = \frac{P^*}{\alpha I_0}$$

Then, from eqs 1–4 we obtain the following differential equations describing the variations of z and x with τ:

$$\frac{\mathrm{d}z}{\mathrm{d}\tau} = a(1 - z) \tag{7}$$

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = (1 - x)z \qquad (8)$$

where $a = \beta'(K + 1)/\alpha \equiv \beta'(K + 1)^2/\epsilon$ and $\beta' = k_1/k_p$.

In the nonequilibrium case $z(0) = 0$, and the solutions of eqs 7 and 8 are

$$z = 1 - e^{-a\tau}$$

$$-\ln(1 - x) = \tau - \frac{1 - e^{-a\tau}}{a} \qquad (9)$$

The dependence of conversion on time for different values of a is shown in Figure 1 in a first-order plot. For values of $a \leq 10$ an induction period can be observed, indicating that the formation of active species is slow compared to monomer addition. However, for $a \geq 10^2$ the time−conversion plot is identical to that obtained for equilibrium conditions ($z \equiv 1$), indicating fast formation of active species. Thus, it can be concluded that for $a \geq 10^2$ the nonequilibrium system transforms into the equilibrium one.

Division of eqs 7 and 8 and integration give a relation between z and conversion:

$$a \ln(1 - x) = z + \ln(1 - z) \qquad (10)$$

The increase of z with conversion calculated from this relationship is demonstrated in Figure 2 for different values of a. For $a \leq 1$, the equilibrium value $z = 1$ is not reached before the polymerization is finished. For $a > 10$ the equilibrium concentration of active centers is achieved at low conversions, and for $a > 10^2$ we can apply $z = 1$ from the very beginning of polymerization.

Since $\alpha \leq 10^{-2}$, it follows from the definition of a that small values of a assume both $\beta' \ll 1$ and K not very high ($K \leq 1$). This means that a marked deviation from a straight line in the first-order time−conversion plot will only be found if the rates of both catalyst association and dissociation are very slow with respect to propagation.

Average Degrees of Polymerization. In order to obtain average degrees of polymerization, we derive the moments of the MWD

$$\mu_n \equiv \sum_{i=0}^{\infty} i^n (P_i^* + P_i') \qquad (11)$$

The number and weight-average degrees of polymerization are then given as

$$\bar{P}_n = \mu_1/\mu_0 \quad \text{and} \quad \bar{P}_w = \mu_2/\mu_1 \qquad (12)$$

It becomes clear from Figure 2 and it was pointed out in part 1 of this series that for slow exchange high amounts of unreacted initiator, $P_0 = P_0^* + P_0'$, are present in the system even at monomer conversions higher than 99%. Since the residual initiator normally is not included in the experimental determination of the MWD, it has to be excluded from the calculations by starting the summation from $i = 1$. Only in some special cases (e.g. dimeric or oligomeric initiator) will it be measured, and it has to be taken into account by starting the summation from $i = 0$.

It is obvious from eq 11 that inclusion or exclusion of the residual initiator, P_0, only comes into effect for $n = 0$ and, thus, for the calculation of $\bar{P}_n$.

Number-Average Degree of Polymerization. As follows from the definition of the MWD moments, the first moment μ_1 represents the amount of monomer converted into polymer, $\mu_1 = M_0 x$. Thus, the problem of $\bar{P}_n$ calculation is reduced to the calculation of the dependence of the zeroth MWD moment on conversion.

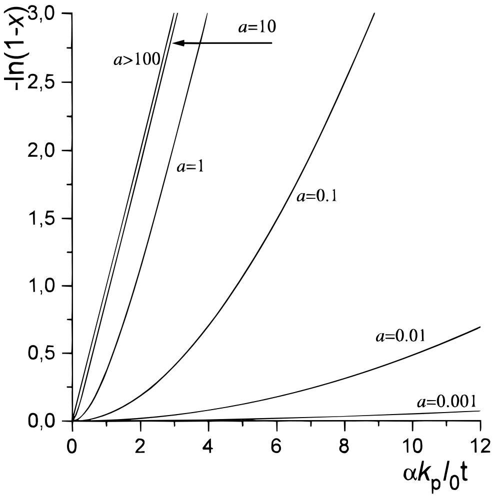

Figure 1. First-order time−conversion plots calculated with different parameters $a = \beta'(K + 1)/\alpha$.

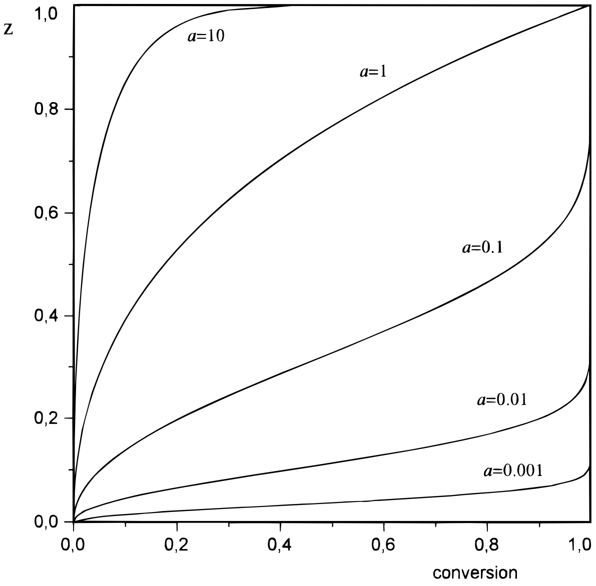

Figure 2. Dependence of $z = P^*/(\alpha I_0)$ on monomer conversion as a function of parameter a. At $z = 1$ equilibrium is reached.

If residual initiator is included in the polymer, the zeroth moment simply becomes

$$\mu_0 \equiv \sum_{0}^{\infty} (P_i^* + P_i') = I_0 \qquad (13a)$$

and, consequently, we obtain the usual dependence for living polymerization

$$\bar{P}_n = \frac{M_0}{I_0} x \equiv \gamma x$$

where $\gamma = M_0/I_0$.

When the residual initiator is excluded, the zeroth MWD moment, μ_0, is equal to the total number of polymer chains in the system, i.e.,

$$\mu_0 \equiv \sum_{1}^{\infty} (P_i^* + P_i') = I_0 - P_0 \qquad (13b)$$

Thus, in this case the concentration of residual initiator has to be calculated by solving eqs 3 and 4 for $i = 0$. For this purpose, it is convenient to rewrite eqs 3 and 4 in terms of conversion

$$z(1-x)\frac{\mathrm{d}P_0^*}{\mathrm{d}x} = -\gamma^*(1-x)P_0^* + \beta'[(K+1-z)P'_0 - P_0^*K/\alpha]$$

$$z(1-x)\frac{\mathrm{d}P'_0}{\mathrm{d}x} = -\beta'[(K+1-z)P'_0 - P_0^*K/\alpha]$$

Here $\gamma^* = \gamma/\alpha$ is the degree of polymerization expected for living polymer formed via centers P^* only, i.e., without any activity exchange with dormant species.

For initial nonequilibrium conditions the same procedure as that made in part 1 leads to the following dependence of P_0 and $\bar{P}_\mathrm{n}$ on conversion with high accuracy for $\gamma^*x \gg 1$

$$P_0 \approx (1-x)^{\beta'K}e^{-\alpha z}\left\{1 + \frac{\beta'(K+1-z)}{\gamma^*(1-x)}\right\} + \frac{\beta'(K+1)}{\gamma^*}\exp\left(-\gamma^*\int_0^x \frac{\mathrm{d}u}{z(u)}\right)$$

For $\beta'K > 1$ this simplifies into

$$P_0 \approx I_0(1-x)^{\beta'K}e^{-\alpha z} \equiv I_0(1-x)^{\beta}\mathrm{e}^{-\alpha z}$$

leading to

$$\bar{P}_\mathrm{n} \approx \frac{\gamma x}{1-(1-x)^{\beta}\mathrm{e}^{-\alpha z}} \tag{14}$$

with $\beta \equiv \beta'K = k_2/(k_pI_0)$.

For equilibrium initial conditions this procedure results in

$$P_0 \approx (1-\alpha)(1-x)^{\beta}\left\{1 + \frac{\beta}{\gamma^*(1-x)}\right\} + \left\{\alpha - \frac{\beta}{\gamma^*(1-x)}\right\}\mathrm{e}^{-\gamma^*x}$$

$$P_0 \approx P'_0 \approx (1-\alpha)I_0(1-x)^{\beta}$$

$$\bar{P}_\mathrm{n} \approx \frac{\gamma x}{1-(1-\alpha)(1-x)^{\beta}} \tag{15}$$

By comparing eqs 14 and 15, one can conclude that nonequilibrium initial conditions result in a smaller concentration of polymer chains formed at a given conversion and, consequently, in a higher $\bar{P}_\mathrm{n}$. However, this difference is significant only for very slow exchange and disappears for $\beta \geqq 1$ (or $a \gg 1$).

The expression for $\bar{P}_\mathrm{n}$ in eq 15 is identical to the one obtained in part 1 for degenerative transfer, except that the parameter β was defined as $\beta = k_\mathrm{ex}/k_\mathrm{p}$ for degenerative transfer. Thus, again, a marked deviation of the expected linear dependence of P_n on conversion is observed at $\beta < 10$ (Figure 3). For $\beta = 1$ the number-average degree of polymerization first sharply increases at low conversion up to $\bar{P}_\mathrm{n} = \gamma$ and after that remains practically constant. For $\beta < 1$, $\bar{P}_\mathrm{n}$ passes a maximum.

For full conversion, both eqs 14 and 15 give the value expected for living polymers, $\bar{P}_\mathrm{n} = \gamma = M_0I_0$. However, it becomes clear from Figure 3 that for slow exchange ($\beta < 1$) this is only true for *very* high conversions. Even at 99% conversion, $\bar{P}_\mathrm{n}$ is much higher than the expected value.

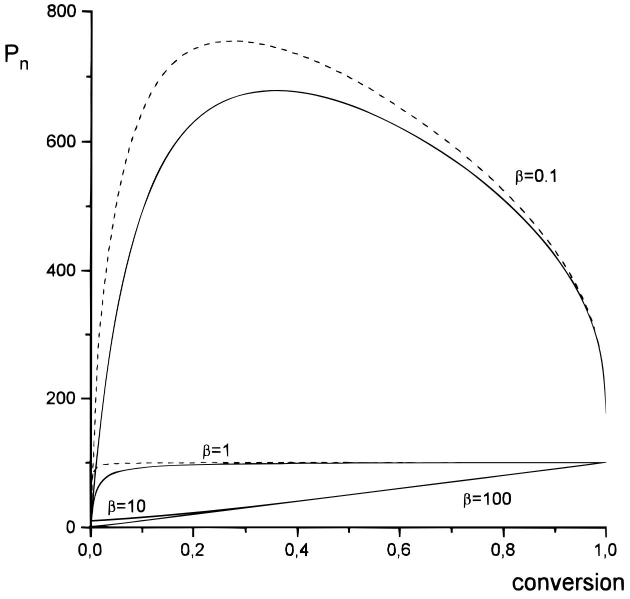

Figure 3. Dependence of the number-average degree of polymerization on monomer conversion for $\beta' = k_1/k_\mathrm{p} = 0.1$ (- - -) and $\beta' = 10$ (—). Calculations were made for $\gamma = M_0/I_0 = 100$ and $\epsilon = C_0/I_0 = 10^{-2}$. No difference is observed between equilibrium and nonequilibrium conditions in this range of parameters.

Weight-Average Degree of Polymerization. In order to calculate the second moment of the MWD let us introduce the moments of the active and dormant chains, $\mu_n^* = \sum_0^\infty i^nP_i^*$ and $\mu'_n = \sum_0^\infty i^nP'_i$, respectively. Hence, the nth MWD moment of the total polymer is the sum of corresponding moments μ_n^* and μ'_n. Multiplying every term of eqs 3 and 4 by i^n and summarizing, one obtains equations for μ_n^* and μ'_n

$$\frac{\mathrm{d}\mu_n^*}{\mathrm{d}t} = k_\mathrm{p}M\sum_{k=0}^{n-1}\binom{n}{k}\mu_k^* + k_1C\mu'_n - k_2\mu_n^* \tag{16}$$

$$\frac{\mathrm{d}\mu'_n}{\mathrm{d}t} = -k_1C\mu'_n + k_2\mu_n^* \tag{17}$$

and, hence,

$$\frac{\mathrm{d}\mu_n}{\mathrm{d}t} = k_\mathrm{p}M\sum_{k=0}^{n-1}\binom{n}{k}\mu_k^* \tag{18}$$

where $\binom{n}{k} = n!/[k!(n-k)!]$. As follows from eq 18, the nth MWD moment of the total polymer, μ_n, depends on the moments of active chains of orders less than n. Really, we need only μ_2 to calculate $\bar{P}_\mathrm{w}$ and, hence, only the first-order moment of active chains. Moreover, because $\mu_1^* + \mu'_1 = M_0x$, we really need to solve only one of eqs 16 or 17. Rewritten in terms of conversion, these equations for $n = 1$ obtain the form

$$z(1-x)\frac{\mathrm{d}\mu_1^*}{\mathrm{d}x} = \gamma^*(1-x)(\mu_0^* + P_0^*) + \beta'[(K+1-z)\mu'_1 - \mu_1^*K/\alpha] \tag{16a}$$

$$z(1-x)\frac{\mathrm{d}\mu'_1}{\mathrm{d}x} = -\beta'[(K+1-z)\mu'_1 - \mu_1^*K/\alpha] \tag{17a}$$

From eq 18 one gets for the dependence of μ_2 on conversion

$$z\frac{d\mu_2}{dx} = \gamma^*(2\mu_1^* + \mu_0^* + P_0^*)$$

It follows from eq 18 for $n = 1$ that

$$\gamma^*(\mu_0^* + P_0^*) = z\frac{d\mu_1}{dx}$$

and so, μ_2 can be represented in the following form

$$\mu_2 = \mu_1 + 2\gamma^*\int_0^x \frac{\mu_1^*(u)}{z(u)}\,du \qquad (19)$$

Taking into account that $\mu_0^* + P_0^* = \alpha I_0 z$ is the concentration of all active species, μ_1^* can be expressed from eq 17a through the integral

$$\mu_1^* = M_0 x - M_0\frac{\beta}{\alpha}\int_0^x \frac{u}{z(1-u)}\exp[-g(x) + g(u)]\,du \qquad (20)$$

where

$$g(x) = \beta'\int_0^x \frac{K + 1 + K/\alpha - z(u)}{(1-u)z(u)}\,du = \frac{K}{K+1}z - \nu\ln(1-x)$$

and

$$\nu = \beta' K\frac{\alpha + 1}{\alpha} \approx \frac{\beta' K}{\alpha} = \frac{\beta}{\alpha} = a\frac{K}{K+1}$$

For $K > 1$ the values of ν and a are comparable.

For nonequilibrium conditions, the integrals 19 and 20 were calculated numerically, by using the dependence of z on conversion (eq 11).

For equilibrium initial conditions $z \equiv 1$ and expression 20 is easily integrated

$$\mu_1^* = M_0 x - \frac{M_0}{\alpha + 1}\left[x - \frac{(1-x) - (1-x)^{\nu}}{\nu - 1}\right]$$

Substituting this expression into eq 19, we finally obtain

$$\bar{P}_w = 1 + \gamma x + \frac{\gamma^*}{(\nu - 1)}\left\{2 - x - 2\frac{1 - (1-x)^{\nu+1}}{x(\nu + 1)}\right\} \qquad (21)$$

By comparing the polydispersity index calculated for the equilibrium and nonequilibrium cases (Figures 4a,b), one can see that at small values of parameter a, $\bar{P}_w/\bar{P}_n$ is higher for the nonequilibrium case. However, for $a > 10^2$ any difference disappears. As was stated above, $\beta = k_2/(k_p I_0)$ has a meaning similar to the parameter $\beta = k_{ex}/k_p$ in degenerative transfer. It is shown below (see also part 1) that values of $10 \le \beta \le 100$ typically represent experimental data in GTP and cationic polymerization.

Since, typically, $\beta \ge 10$ and $\alpha \le 10^{-2}$, the value of ν is much higher than unity. In this case already at low conversions one can neglect the last term in the brackets of eq 21 in comparison with all other terms. Then, eq 21 obtains the form

$$\bar{P}_w \approx 1 + \gamma x + \frac{\gamma^*}{\nu}(2 - x) = 1 + \gamma\left[x + \frac{2 - x}{\beta' K}\right] \equiv 1 + \gamma\left[x + \frac{2 - x}{\beta}\right] \qquad (21a)$$

In this particular case the number-average degree of polymerization very quickly approaches the dependence expected for living chains,

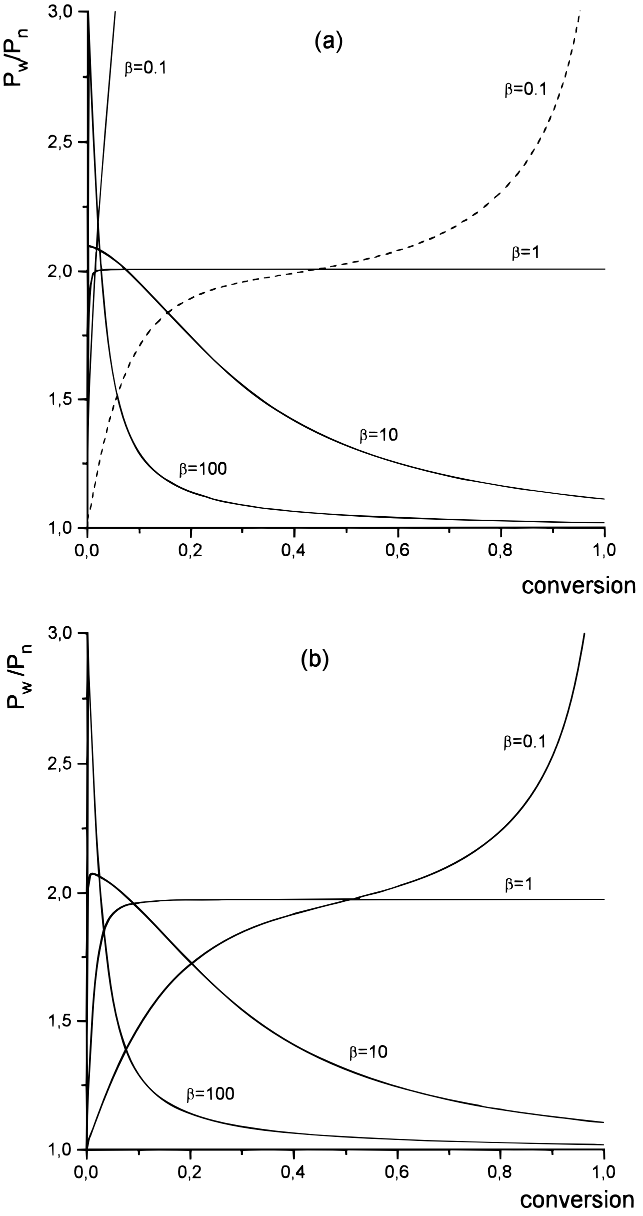

Figure 4. Dependence of polydispersity index on monomer conversion for equilibrium (- - -) and nonequilibrium (—) conditions. If no dotted line is shown, both conditions lead to the same polydispersity index. $\gamma = M_0/I_0 = 100$, $\epsilon = C_0/I_0 = 10^{-2}$. (a) $\beta' = 0.1$; (b) $\beta' = 10$. A difference between equilibrium and nonequilibrium conditions is only seen if both $\beta' = k_1/k_p < 1$ and $K = k_2/(k_1 I_0) < 1$ (i.e., $\beta = \beta' K < 1$).

$$\bar{P}_n = \gamma x$$

and, consequently, one obtains the following dependence of polydispersity index on conversion

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\bar{P}_n} + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \approx 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \qquad (22)$$

for $\bar{P}_n = \gamma x \gg 1$. As can be seen, in this case the polydispersity index depends on the product $\beta = \beta' K$, but not on each parameter separately. However, this is not the case if ν is small.

At full conversion eq 21 transforms into

$$\bar{P}_w = 1 + \gamma\frac{\beta' K + 1}{\beta'(K + \alpha) + \alpha} \approx 1 + \gamma\frac{\beta + 1}{\beta + \alpha} \qquad (23)$$

If exchange is not extremely slow, i.e. $\beta \gg \alpha$, this leads

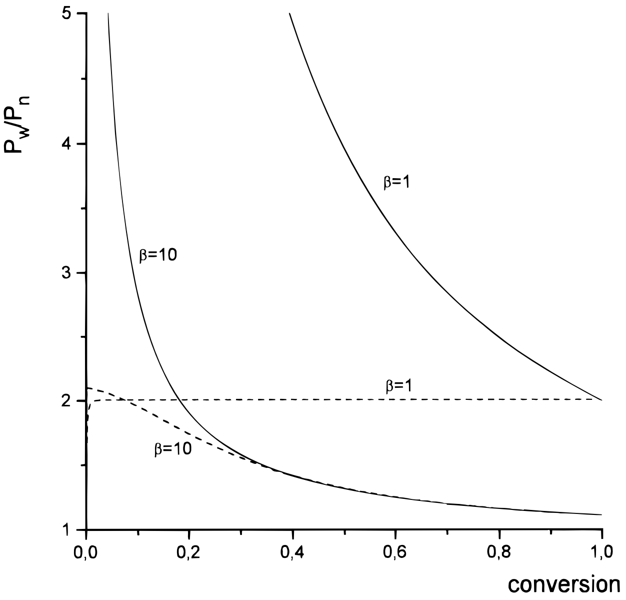

Figure 5. Effect of residual initiator on the polydispersity index. Initiator included (—) and excluded (- - -), respectively, from the total number of chains. $\gamma = M_0/I_0 = 100$, $\epsilon = C_0/I_0 = 10^{-2}$, $\beta' = 0.1$.

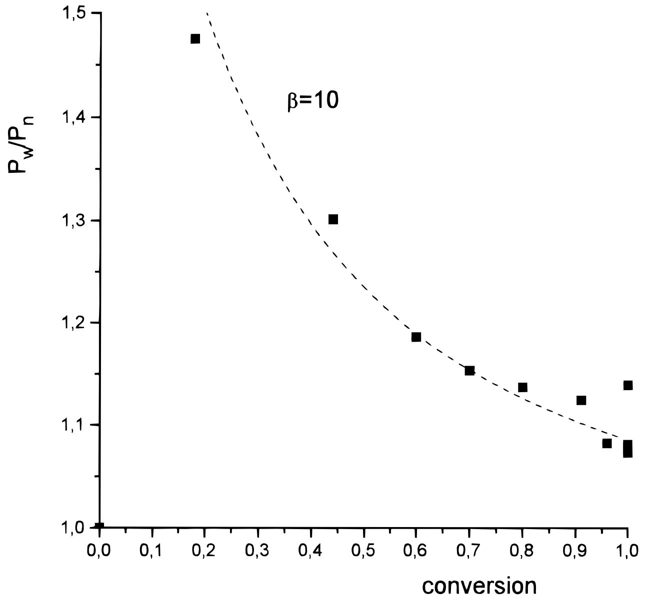

Figure 6. Dependence of polydispersity index on monomer conversion for the GTP of methyl methacrylate in THF at 23 °C using a dimeric initiator and tris(dimethylamino)sulfonium bifluoride as a catalyst.[14] $M_0 = 0.225$ mol/L, $I_0 = 8 \times 10^{-4}$ mol/L, $C_0 = 3.7 \times 10^{-5}$ mol/L.

to

$$\bar{P}_{\rm w} = 1 + \gamma(1 + 1/\beta)$$

and, consequently, the polydispersity index at $x = 1$ is

$$\bar{P}_{\rm w}/\bar{P}_{\rm n} = 1 + \frac{1}{\bar{P}_{\rm n}} + \frac{1}{\beta} \approx 1 + \frac{1}{\beta} = 1 + \frac{k_{\rm p}}{k_2} I_0 \qquad (24)$$

for $\bar{P}_{\rm n} \gg 1$. Thus, in this mechanism the polydispersity index depends on initial initiator concentration but is independent of catalyst concentration.

On the contrary, for extremely slow exchange ($\beta \lesssim \alpha$) the polydispersity index at full conversion will be very high ($\bar{P}_{\rm w}/\bar{P}_{\rm n} = \alpha^{-1}$). However, it has to be taken into account, again, that in this case the dependence of $\bar{P}_{\rm n}$ on x is very pronounced at high conversions and, in fact, even for $x = 0.99$ the polydispersity index will be near unity.

The effect of residual initiator on the polydispersity index can be seen from Figure 5. Although there is no difference between equilibrium and nonequilibrium conditions, even for $\beta = 1$ the effect is significant up to very high conversions.

Discussion

The dependencies of $\bar{P}_{\rm n}$ and $\bar{P}_{\rm w}/\bar{P}_{\rm n}$ on conversion (eqs 15, 22, and 24) are quite similar to those obtained in part 1 of this series for degenerative transfer.[1] This follows from the fact that in spite of different mechanisms of exchange, the rate of exchange is in both cases first order with respect to each species involved. A more detailed comparison of polymerization mechanisms involving slow equilibria will be given in a subsequent publication.[13]

Thus, for initial equilibrium conditions, all the conclusions made for degenerative transfer (cf. part 1) can be successfully transferred to the problem under consideration if one redefines $\beta = k_{\rm ex}/k_{\rm p}$ by $\beta \equiv k_2/(k_{\rm p}I_0)$. For example, the effect of the exchange rate on the polydispersity of the polymer formed is the most pronounced for β varying within the range from 10^{-1} to 10^1.

The character of the dependence of polydispersity index on conversion (for the case when the concentration of residual initiator is extracted from the zeroth MWD moment) is the same as for degenerative transfer: For $\beta < 1$ (moderately slow exchange), $\bar{P}_{\rm w}/\bar{P}_{\rm n}$ continuously increases to the final value defined by eq 22 at $x = 1$. For $\beta = 1$ the polydispersity index rapidly increases to a limiting value of $\bar{P}_{\rm w}/\bar{P}_{\rm n} \approx 2$, and for $\beta > 1$ (moderately fast exchange) after a fast marked increase at very small conversions, $\bar{P}_{\rm w}/\bar{P}_{\rm n}$ continuously decreases to the final value defined by eq 24. The latter case is observed in GTP and "living" cationic polymerization.

Comparison to Experimental Data in GTP and Cationic Polymerization

As was stated above, the dependence of polydispersity index on conversion has exactly the same shape as for the degenerative transfer mechanism, except for the fact that the parameter β has a different definition. Thus, from the GTP experiments with benzoate catalyst analyzed in part 1 it was concluded that $\beta \approx 40$. The polydispersity indices found for bifluoride catalysis are similar, leading to $\beta \approx 10$ (cf. Figure 6). It may be dangerous to draw conclusions from numeric values of the ratio $k_2/k_{\rm p}$ because the rate constants are of different reaction orders and dimensions: formation of dormant species is a first-order reaction, whereas monomer addition is a second-order reaction.

There still exists one important difference between the mechanisms of degenerative transfer and the "associative" GTP mechanism. Whereas the parameter β for direct activity exchange is only given as a ratio of rate constants, and thus the polydispersity index only depends on β and conversion, in the mechanism under consideration here, β and, thus, the polydispersity index depend on the concentration of initiator. This dependence can be used as a mechanistic criterion.

Unfortunately, it is not easy to obtain kinetic and MWD data which are not hampered by the effect of slow initiation. Only few experiments were performed with a dimeric initiator which leads to fast initiation. In these cases, and also for the unimeric initiator MTS,[14] the polydispersity index was roughly dependent on initiator concentration, indicating that degenerative

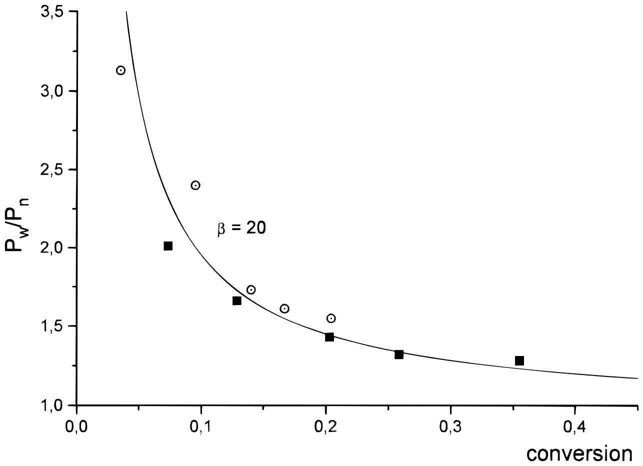

Figure 7. Dependence of polydispersity index on monomer conversion for cationic polymerization of isobutylene in methyl chloride at −40 °C using 2,4,4-trimethylpentyl chloride as an initiator and BCl_3 as a catalyst in the presence of 2×10^{-3} di-*tert*-butylphenol.[15] $I_0 = 1.16 \times 10^{-2}$ mol/L, $C_0 = 0.24$ mol/L. ■ $M_0 = 1.44$ mol/L; ⊙ $M_0 = 1.91$ mol/L.

transfer is more probable than the indirect exchange of Scheme 2. However, in this case the values of the polydispersity index obtained at full conversion are very small ($\bar{P}_w/\bar{P}_n \leq 1.05$; see part 1) and the corresponding experimental errors may be too large to allow for final conclusions.

Figure 7 shows that "living" cationic polymerization displays a very similar dependence of polydispersity index on conversion, indicating that slow equilibria are also inherent to cationic polymerization. However, which exchange mechanism is applicable can only be concluded from the dependence of polydispersity index on the initial concentrations of reagents. This will be discussed in the next part of this series where we will inspect the MWD moments for the "dissociative" mechanism of GTP and for the generation of free ions in cationic polymerization.[16]

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Appendix: List of Symbols and Abbreviations

α	P^*/I_0, fraction of active chain ends (in equilibrium)
β	general parameter governing the polydispersity index. Here, $\beta \equiv \beta' K = k_2/(k_p I_0)$
β'	k_1/k_p
$\delta_{i,j}$	Kronecker symbol
ϵ	C_0/I_0
γ	M_0/I_0
γ^*	γ/α, degree of polymerization expected for living polymer formed via centers P^* only
μ_n	nth moment of the MWD
μ_n^*, μ_n'	nth moment of the MWD of active and "dormant" chains, respectively
ν	$\beta' K(\alpha + 1)/\alpha \approx \beta' K/\alpha = \beta/\alpha = \alpha K/(K + 1)$
τ	$\alpha k_p I_0 t$, dimensionless time
a	$\beta'(K + 1)/\alpha \equiv \beta'(K + 1)^2/\epsilon$, auxiliary parameter for nonequilibrium initial conditions
C	catalyst (co-initiator) concentration
I	initiator concentration
K^*	k_1/k_2, equilibrium constant of Scheme 2
K	$k_2/(k_1 I_0) = 1/(K^* I_0)$
k_1	rate constant of activation
k_2	rate constant of deactivation
k_{ex}	rate constant of exchange for degenerative transfer
k_p	rate constant of polymerization
M	monomer concentration
MTS	1-methoxy-1-(trimethylsiloxy)-2-methyl-1-propene
M_w/M_n	polydispersity index
P_0'	concentration of "dormant" initiator
P_0^*	concentration of active initiator
P_1'	concentration of "dormant" polymer chain ends of degree of polymerization i
P_i^*	concentration of active polymer chain ends of degree of polymerization i
$\bar{P}_n$	number-average degree of polymerization
$\bar{P}_w$	weight-average degree of polymerization
$\bar{P}_w/\bar{P}_n$	polydispersity index
t	time
x	$(M_0 - M)/M_0$, monomer conversion
z	$P^*/(\alpha I_0)$, ratio of P^* at time t to its equilibrium value, αI_0, for nonequilibrium initial conditions

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