Kinetic Analysis of “Living” Polymerization Systems Exhibiting Slow Equilibria. 4.[†] “Dissociative” Mechanism of Group Transfer Polymerization and Generation of Free Ions in Cationic Polymerization

Axel H. E. Müller,* Galina Litvinenko,[‡] and Deyue Yan[§]

Institut für Physikalische Chemie, Johannes Gutenberg-Universität Mainz, D-55099 Mainz, Germany

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ABSTRACT: The MWD moments are derived for a “living” polymerization process which proceeds via active and “dormant” species and where addition of a catalyst, **C**, to a “dormant” species, **P′**, leads to the formation of an active species, **P***, and another product, **E**. Such a mechanism is applicable to the “dissociative” mechanism of group transfer polymerization (GTP), where the active species is an enolate and **E** is a silyl ester, to “living” cationic polymerization, where **P*** is a free cation and **E** is the counterion, and to atom transfer radical polymerization (ATRP), where **P′** and **P*** are a covalent species and a free radical, respectively, and **C** and **E** are transition metal salts of lower and higher oxidation states, respectively. Both equilibrium and nonequilibrium initial conditions are used for the calculation. The results are very similar to those obtained for the “associative” mechanism of GTP (corresponding to the generation of ion pairs in cationic polymerization) and for degenerative transfer (i.e., direct exchange of activity between active and “dormant” species). In the absence of added **E**, the dominating parameter, β, is defined as $\beta = \alpha k_2/k_p$, where k_2 and k_p are the rate constants of reversible deactivation and propagation, respectively, and α is the fraction of active chain ends. The value of α in turn depends on the equilibrium constant K and the ratio of initial concentrations of catalyst and initiator, C_0/I_0. In contrast, for the “associative” mechanism of GTP (or ion pair generation in cationic polymerization) the parameter was defined as $\beta = k_2/(k_pI_0)$, depending on initiator concentration alone, whereas for degenerative transfer it was $\beta = k_{ex}/k_p$, irrespective of reagent concentrations. Again, 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 $\beta < 1$. Added **E** (e.g., “livingness enhancer” in GTP) always leads to narrower MWD’s. The results are discussed with respect to GTP using nucleophilic catalysts and to the cationic polymerization of various monomers. The accessible results indicate that the predominant mechanism for *activity exchange* in GTP and perhaps also in cationic polymerization is degenerative transfer whereas the mechanism for *generation of active species* from inactive ones has to be determined from analysis of the kinetic reaction orders.

Introduction

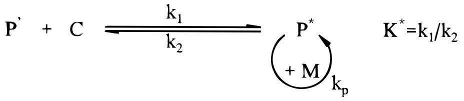
In parts 1−3 of this series the effect of slow activity exchange between active and “dormant” polymer chains on the kinetics of polymerization and molecular weight distribution (MWD) and its averages was analyzed for degenerative transfer (bimolecular exchange of activity) (Scheme 1)[1,2] and for the “associative” mechanism of group transfer polymerization (GTP, Scheme 2)[3] which is similar to the generation of ion pairs from covalent species in cationic polymerization, with negligible formation of free ions.

In Scheme 2, the active chain end, **P***, is an activated silyl ketene acetal with a nucleophilic catalyst, **C**, bound to the pentavalent silicon atom. For the case of cationic polymerization, it is an ion pair.

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

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

Scheme 2. Kinetic Scheme for the “Associative” Mechanism of GTP and for the Generation of Ion Pairs in Cationic Polymerization



In parts 1 and 3 it was shown that the polydispersity index, M_w/M_n, depends on a characteristic parameter, β, and monomer conversion. For degenerative transfer the characteristic parameter was given as $\beta = k_{ex}/k_p$, whereas for the “associative” mechanism of GTP (or generation of ion pairs in cationic polymerization) it is $\beta = k_2/(k_pI_0)$. For $\beta < 1$, M_w/M_n increases with conversion whereas for $\beta > 1$ it decreases (after a marked increase at low conversions). The latter case coincides with a common observation in GTP and cationic polymerization. For a given conversion, polydispersity has its maximum for $0.1 < \beta < 1$. In a limiting case (full conversion, $\beta > 1$, and $\bar{P}_n \gg 1$), $M_w/M_n \approx 1 + 1/\beta$. Recently, a “dissociative” mechanism (Scheme 3) has been put forward,[4] where the nucleophilic catalyst, **C**, abstracts the trimethylsilyl group from the dormant chain ends, **P′**, to form an enolate, **P***, as the activated species, and a silyl ester or fluorosilane, **E**. This mechanism is analyzed in this paper.

Depending on the nature of the nucleophilic catalyst, Nu$^-$, the formation of enolate can be reversible ($k_2 > 0$)

[†] Parts 1−3, cf. refs 1−3.

[‡] Permanent address: Karpov Institute of Physical Chemistry, 10 Vorontsovo pole, Moscow 103064, Russia.

[§] Permanent address: Department of Applied Chemistry, Shanghai Jiao Tong University, 1954 Hua Shan Rd, Shanghai 200030, P. R. China.

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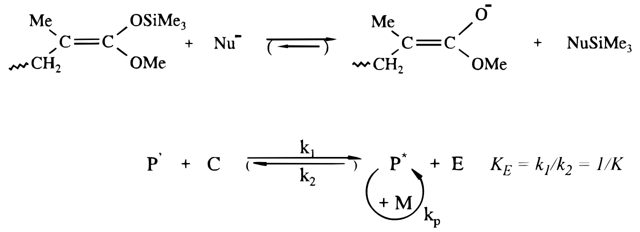
Scheme 3. "Dissociative" Mechanism of GTP and Corresponding Kinetic Scheme



Scheme 4. Covalent Species and Free Ions in Cationic Polymerization

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

Scheme 5. Covalent Species and Free Radicals in Atom Transfer Radical Polymerization

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

or irreversible ($k_2 = 0$). The *irreversible* dissociative mechanism can explain the *formation* of active initiator, but not the *exchange of activity* between chain ends which is needed because the concentration of catalyst is much smaller than that of the initiator. In such a case, degenerative transfer (cf. parts 1 and 2) is the only feasible mechanism of activity exchange and the mechanism in Scheme 3 is only important for the initial stage of polymerization or for small k_1/k_p.

The mechanism in Scheme 3 is identical to that for the (exclusive) formation of free ions from "dormant" covalent species in living cationic polymerization (Scheme 4). Here, **P′** is a covalent species, **C** is a Lewis acid (frequently called co-initiator instead of catalyst), **P*** is a cation, and **E** is the counterion. Of course, this is the limiting case of full dissociation. Another limiting case (no dissociation) was treated in part 3. By using numeric techniques, Matyjaszewski et al.[5] showed that such a three-state mechanism can lead to additional broadening and bimodal MWD's even if the reactivities of ion pairs and cations are similar due to the large interionic distance in the ion pair. The MWD and its moments for such a three-state mechanism were derived by Böhm[6,7] using equilibrium initial conditions. A treatment with nonequilibrium initial conditions will be published later.[8]

Another mechanism which follows the kinetic scheme 3 is atom transfer radical polymerization (ATRP) discovered recently by Wang and Matyjaszewski.[9] Here, **P′** and **P*** are a covalent (halogenated) species and a free radical, respectively, and **C** and **E** are transition metal salts of lower and higher oxidation states, respectively, e.g. CuCl and CuCl_2 (Scheme 5). Under certain conditions the effect of bimolecular termination is negligible and Scheme 3 can be applied. A full treatment of the MWD obtained in ATRP will be published later.[10]

For all mechanisms it is assumed that the fraction of active chain ends, α, is very small: $\alpha \ll 1$ (cf. Part 3).

The aim of the present paper is to estimate the effect of slow activity exchange between active and "dormant" chain ends according to the indirect mechanism of Scheme 3. Kinetics of polymerization, molecular weight averages, and the polydispersity index of the polymer formed are calculated and compared to the "associative" mechanism (Scheme 2) and degenerative transfer (Scheme 1).

Similar to part 3, the problem is treated in two ways:

(1) by assuming that the equilibrium of Scheme 3 has not been established at time $t = 0$ (nonequilibrium or nonstationary state treatment);

(2) by assuming equilibrium concentrations at $t = 0$ (equilibrium or stationary state treatment).

In the general derivation, it will be assumed that some species **E** was added deliberately. In GTP this corresponds to a silyl ester, used as a "livingness enhancer",[11,12] and for ATRP it is the transition metal salt of higher oxidation state, whereas in cationic polymerization it could be regarded as a common ion salt. However, common ion salts will suppress dissociation, leading to the formation of ion pairs rather than to the formation of covalent species. Thus, the analogy cannot be applied to cationic polymerization. In this case, a three-state mechanism has to be used.

Finally, the results will be simplified to the typical case where no species E is added.

Differential Kinetic Equations

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

The evolution of the concentrations of monomer M, catalyst C, and active P_i^* and dormant P_i' macromolecules which added i monomer units is described by the following set of differential equations adopted for the kinetic scheme:

$$\frac{\mathrm{d}M}{\mathrm{d}t} = -k_p M P^*$$

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

$$\frac{\mathrm{d}E}{\mathrm{d}t} = k_1 P' C - k_2 P^* E \tag{1}$$

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

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

Here, $P^* = \sum_0^\infty P_i^*$ and $P' = \sum_0^\infty P_i'$ are the total concentrations of active and dormant chains.

For the nonequilibrium case the initial concentrations of all reagents are

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

$$C|_{t=0} = C_0$$

$$E|_{t=0} = E_0$$

$$P_i'|_{t=0} = I_0 \delta_{i,0} \tag{2}$$

$$P_i^*|_{t=0} = 0$$

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

If equilibrium is already established at $t = 0$ (steady-state assumption), the initial concentrations are

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

$$C|_{t=0} = C_0 - \alpha I_0$$

$$E|_{t=0} = E_0 + \alpha I_0$$

$$P_i'|_{t=0} = (1 - \alpha) I_0 \delta_{i,0} \tag{3}$$

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

Here, $\alpha = P^*/I_0$ represents the equilibrium fraction of active species. For $\alpha \ll 1$

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

where $K = K_E^{-1} = k_2/k_1$, $\epsilon = C_0/I_0$, and $\eta = E_0/I_0$ are the initial ratios of catalyst and ester concentrations, respectively, to initiator concentration.[13] If no ester is added prior to polymerization ($\eta = 0$),

$$\alpha = \frac{\sqrt{1 + 4\epsilon K} - 1}{2K} \tag{4a}$$

if the equilibrium is shifted to the right hand side, i.e. $4\epsilon K \ll 1$, $\alpha \approx \epsilon$. In the opposite case, i.e., $4\epsilon\kappa \gg 1$ (which should be typical of cationic polymerization), $\alpha \approx \sqrt{\epsilon/K} \ll \epsilon$.

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 in time, as for a one-state living system,

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

where $\tau = \alpha k_p I_0 t$ is a dimensionless time.

If, however, at $t = 0$ the system is not in equilibrium, the fraction of active chains will increase from 0 to its equilibrium value αI_0. If we denote, as was done in part 3, the ratio of the actual concentration of active centers to its equilibrium value as $z = P^*/\alpha I_0$, from the set of eqs 1 we obtain the following differential equations describing the variations of z and x with τ:

$$\frac{dz}{d\tau} = a(1 - z)(1 + \delta z) \tag{5}$$

$$\frac{dx}{d\tau} = (1 - x)z \tag{6}$$

with $z(0) = 0$ and $x(0) = 0$. The solution of eqs 5 and 6 are

$$z = \frac{1 - e^{-a(\delta+1)\tau}}{1 + \delta e^{-a(\delta+1)\tau}}$$

$$-\ln(1 - x) = \tau - \frac{1}{a\delta} \ln \frac{1 + \delta}{1 + \delta e^{-a(\delta+1)\tau}} \tag{7}$$

As can be seen, the behavior of x and z are governed by two-dimensionless parameters

$$a = \beta'(K\alpha + K\eta + 1)/\alpha = \beta'\epsilon/\alpha^2$$

with $\beta' = k_1/k_p$ and

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

Depending on particular values of β', ϵ, η, and K, a can achieve arbitrary magnitudes. For a given β', a increases from β'/ϵ for small K (i.e., $K(\epsilon + \eta) \ll 1$) to $\beta'K$ for $K(\epsilon + \eta) \gg 1$. On the contrary, δ is always between 0 for $K(\epsilon + \eta) \ll 1$ and unity for $K(\epsilon + \eta) \gg 1$. If $\delta \ll 1$, eqs 7 obtain the same form as for the "associative" mechanism of GTP (cf. part 3):

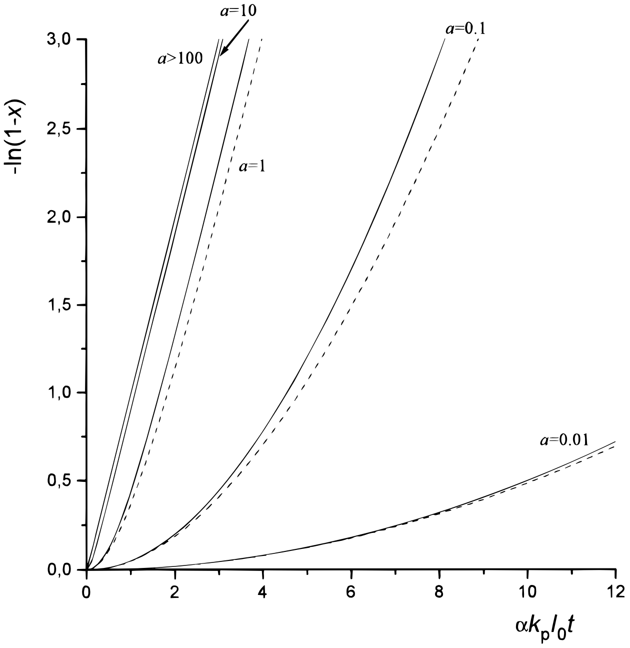


Figure 1. First-order time–conversion plots calculated with different parameters a and δ: solid lines, $\delta = 1$; dotted lines, $\delta = 0$.

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

$$-\ln(1 - x) = \tau - \frac{1 + e^{-a\tau}}{a} \tag{7a}$$

however, a is a different function of the rate constants and reagent concentrations. When δ is close to unity, expressions 7 transform into

$$z = \tanh a\tau$$

$$-\ln(1 - x) = \frac{1}{a} \ln(\cosh a\tau) \tag{7b}$$

The dependence of conversion on τ for different values of a and δ is shown in Figure 1 in a first-order plot. As can be seen, for small δ equilibrium is achieved at a lower conversion than for $\delta \approx 1$, but this effect is significant only for small $a \le 1$ and disappears already at $a > 10$. In turn, for $a \le 10$ an induction period is observed, indicating that the formation of active species is slow compared to monomer addition. However, for $a \ge 10^2$ the nonequilibrium system converts into the equilibrium one. This conclusion is quite similar to the "associative mechanism" of GTP (cf. part 3).

From eqs 7 it is easy to derive the relationship between z and conversion:

$$a(\delta + 1) \ln(1 - x) = \ln(1 - z) + \frac{1}{\delta} \ln(1 + \delta z) \tag{8}$$

The analysis of eqs 8 shows that the evolution of z with conversion is similar to that for the associative mechanism (see Figure 2). Again, at $a \le 1$, the equilibrium value $z = 1$ is not reached before the polymerization is finished, and for $a > 10^2$ one can apply $z = 1$ from the very beginning of polymerization. At equal conversions

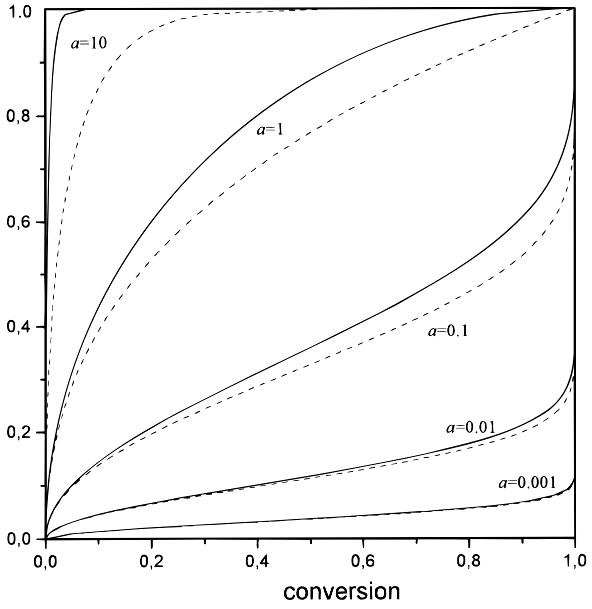


Figure 2. Dependence of $z = P^*/\alpha I_0$ on monomer conversion as a function of parameters a and δ: solid lines, $\delta = 1$; dotted lines, $\delta = 0$.

z is higher for higher δ; however, this difference becomes unimportant for large a. For small δ, eq 8 obtains the same form as for the associative mechanism (eq 10 of part 3)

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

however, a of part 3 has the same meaning and magnitude ($a \approx \beta'/\epsilon$) only for $K \ll 1$.

It follows from the definition of a that $a > \beta'/\epsilon$, because always $\alpha < \epsilon$. Since ϵ is normally very small (of the order of 10^{-2}), this means that a marked difference between the behavior of the equilibrium and nonequilibrium systems can be observed only if β' is very small and K is not very high, $(\epsilon + \eta)K \leq 1$.

Two limiting cases are worthy of special analysis. If no ester was added deliberately ($\eta = 0$), α is defined by eq 4a. If the equilibrium is shifted to the right hand side, i.e. $4\epsilon K \ll 1$, $\alpha \approx \epsilon$, $\alpha \approx \beta'/\epsilon$, and $\delta \approx \epsilon K \ll 1$. In this case, as was already mentioned, the forms of dependencies of z on conversion and conversion on time are the same as for the associative mechanisms of exchange. In the opposite case, for $4\epsilon K \gg 1$, $\alpha \approx \sqrt{\epsilon/K} \ll \epsilon$, $\delta \cong 1$ and $a = \beta K$.

In order to calculate average degrees of polymerization, we use the moments of MWD for active $\mu_n^* = \sum_0^\infty i^n P_i^*$ and dormant $\mu_n' = \sum_0^\infty i^n P_i'$ chains and $\mu_n \equiv \sum_0^\infty i^n (P_i^* + P_i')$ for total polymer. The procedure of calculation is the same as in Part 3.

Number-Average Degree of Polymerization. If residual initiator can be regarded as a part of the polymer, the usual expression for living polymerization is valid for the number-average degree of polymerization

$$\bar{P}_\mathrm{n} \equiv \frac{\mu_1}{\mu_0} = \frac{M_0}{I_0} x \equiv \gamma x$$

where $\gamma = M_0/I_0$.

If, however, the residual initiator is excluded, the zeroth MWD moment, μ_0, should be defined as the total number of polymer chains in the system, i.e., $\mu_0 \equiv \sum_1^\infty (P_i^* + P_i') = I_0 - P_0$. Thus, in this case the concentration of residual initiator P_0 has to be calculated by solving equations for P_0' and P_0^* of set 1. Rewritten in terms of conversion, these equations are

$$z(1 - x) \frac{\mathrm{d}P_0^*}{\mathrm{d}x} = -\gamma^*(1 - x)P_0^* + \beta'\left[\left(\frac{\epsilon}{\alpha} - z\right)P_0' - K\left(\frac{\eta}{\alpha} + z\right)P_0^*\right]$$

$$z(1 - x) \frac{\mathrm{d}P_0'}{\mathrm{d}x} = -\beta'\left[\left(\frac{\epsilon}{\alpha} - z\right)P_0' - K\left(\frac{\eta}{\alpha} + z\right)P_0^*\right]$$

Here $\gamma^* = \gamma/\alpha$ is again the degree of polymerization expected for living polymer formed via centers P^* in the total absence of exchange.

The same procedure as followed in part 3 leads to the following dependence of P_0 and $\bar{P}_\mathrm{n}$ on conversion for $\gamma^* x \gg 1$

$$P_0 = I_0(1 - x)^{\beta' K(\alpha+\eta)}(1 + \delta z)^{-\epsilon/(K\alpha)} \equiv I_0(1 - x)^{\beta}(1 + \delta z)^{-\epsilon/(K\alpha)} \quad (9a)$$

$$\bar{P}_\mathrm{n} = \frac{\gamma x}{1 - (1 - x)^{\beta}(1 + \delta z)^{-\epsilon/(K\alpha)}}$$

for initial nonequilibrium conditions, and

$$P_0 \approx P_0' \approx I_0(1 - \alpha)(1 - x)^{\beta} \quad (9b)$$

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

for equilibrium initial conditions, where the characteristic parameter is now given as $\beta \equiv \beta' K(\alpha + \eta) = (k_2/k_\mathrm{p})(\alpha + \eta)$.

Comparing $\bar{P}_\mathrm{n}$ obtained according to eqs 9a and 9b (Figure 3), one can see that nonequilibrium initial conditions result in a smaller concentration of polymer chains formed at a given conversion and, consequently, in a higher $\bar{P}_\mathrm{n}$. The difference, however, disappears when exchange is not very slow, that is, for $\beta' \gg \epsilon$ or small K or for $(\beta')^2 K \gg \epsilon$ for large K.

The dependence of $\bar{P}_\mathrm{n}$ on conversion for equilibrium conditions is again identical to those given in parts 1 and 3, with the new combination of parameters, $\beta \equiv \beta' K(\alpha + \eta)$ or $\beta \equiv \beta' K\alpha$ for $E_0 = 0$. For the associative mechanism of GTP, this combination is $\beta = \beta' K = k_2/(k_\mathrm{p} I_0)$, and for degenerative transfer it is just $\beta = k_\mathrm{ex}/k_\mathrm{p}$. Since α depends on K according to eqs 4 and 4a, the dependence of $\bar{P}_\mathrm{n}$ on β' and K is somewhat more complicated in this case, and some examples are given in Figure 3.

If β' is small, the deviation between equilibrium and nonequilibrium conditions is significant and disappears only for very large K. On the contrary, if $\beta' > 10^2$, the dependence of $\bar{P}_\mathrm{n}$ on conversion is close to the expected linear behavior already for relatively small K (e.g., for $\beta' = 100$, K should be higher than 10). In Figure 3 the deviation can only be seen for $\beta' = 0.1$. Generally, it can be concluded that the equilibrium (steady-state) treatment is sufficient if $\beta \equiv \beta' K(\alpha + \eta) > 1$. This condition is fulfilled for both GTP and cationic polymerization (see parts 1 and 3).

Weight-Average Degree of Polymerization. According to definition, $\bar{P}_\mathrm{w} = \mu_2/\mu_1$. The first MWD moment is simply $M_0 x$, and μ_2 can be expressed as

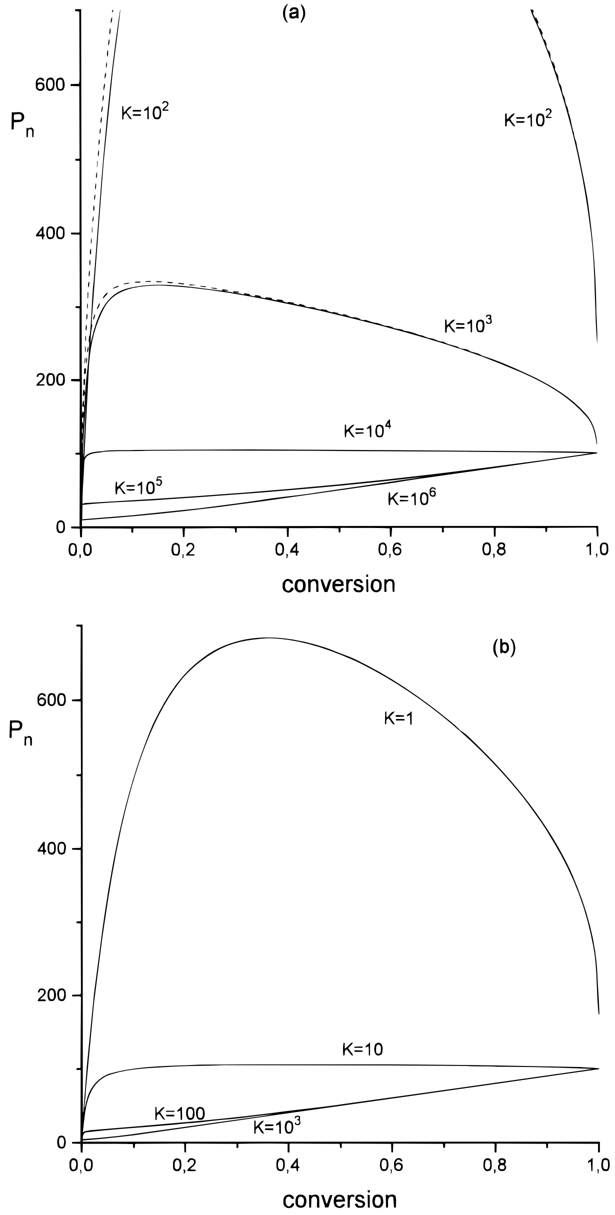


Figure 3. Dependence of the number-average degree of polymerization on monomer conversion for $\epsilon = C_0/I_0 = 0.01$, $\gamma = M_0/I_0 = 100$, $\beta' = k_1/k_p = 0.1$ (a) and $\beta' = 10$ (b): (—) equilibrium; (- - -) nonequilibrium initial conditions. A difference between equilibrium and nonequilibrium conditions is only seen for $\beta' < 1$ (and $\beta = \beta' K\alpha < 1$).

$$\mu_2 = \mu_1 + 2\gamma^* \int_0^x \frac{\mu_1^*(u)}{z(u)}\, \mathrm{d}u \qquad (10)$$

and the first moment of the active chains, μ_1^*, is in its turn, calculated from the equation

$$z(1-x)\frac{\mathrm{d}\mu_1^*}{\mathrm{d}x} = \gamma^*(1-x)(\mu_0^* + P_0^*) + \beta\left[\left(\frac{\epsilon}{\alpha} - z\right)(M_0 x - \mu_1^*) - K\left(\frac{\eta}{\alpha} + z\right)\mu_1^*\right] \qquad (11)$$

Similar to part 3, μ_1^* can be expressed by the integral

$$\mu_1^* = M_0 x - M_0 \beta' K \int_0^x \frac{u(\eta/\alpha + z(u))}{z(u)(1-u)} \exp[-g(x) + g(u)]\, \mathrm{d}u \qquad (12)$$

where

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

and

$$\nu = \beta'\left[K\frac{\alpha + \eta}{\alpha} + \frac{\epsilon}{\alpha} - 1\right] \approx \beta' K(1 + \eta/\alpha) = \beta/\alpha$$

For nonequilibrium conditions, integrals 10 and 12 were calculated numerically, by using the dependence of z on conversion (eq 8).

For equilibrium initial conditions ($z \equiv 1$) expression 12 can be easily integrated

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

Substituting this expression into eq 10, we finally obtain

$$\bar{P}_w = 1 + \gamma x + \frac{\gamma^*}{(\nu - 1)}\left\{2 - x - 2\frac{1 - (1-x)^{\nu+1}}{x(\nu + 1)}\right\} \qquad (13)$$

The dependence of the polydispersity index on conversion for different values of K and β' is shown in Figure 4.

For typically high values of ν (i.e. $\beta' K \gg 1$) eq 13 already at low conversions obtains the form

$$\bar{P}_w \approx 1 + \gamma x + \frac{\gamma^*}{\nu}(2 - x) = 1 + \gamma x + \frac{\gamma}{\beta}(2 - x)$$

similar to the "associative" mechanism. In this important particular case the number-average degree of polymerization very quickly approaches the dependence expected for living chains,

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

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

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\bar{P}_n} + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \approx 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \qquad (14)$$

for $\bar{P}_n \gg 1$. At full conversion expression 13 converts into

$$\bar{P}_w = 1 + \gamma\frac{\beta'(\epsilon - \alpha) + \alpha}{\beta'(\epsilon - \alpha) + \alpha^2} \equiv 1 + \gamma\frac{\beta' K(\eta + \alpha) + 1}{\beta' K(\eta + \alpha) + \alpha} \equiv 1 + \gamma\frac{\beta + 1}{\beta + \alpha} \qquad (15)$$

which for $\beta' K \gg 1$ (or $\beta \gg \alpha$) again leads to the simple expression

$$\bar{P}_w = 1 + \gamma(1 + 1/\beta)$$

and correspondingly, the polydispersity index is

$$\bar{P}_w/\bar{P}_n \approx 1 + \frac{1}{\bar{P}_n} + \frac{1}{\beta} \approx 1 + \frac{1}{\beta} \qquad (\text{for } \bar{P}_n \gg 1) \qquad (16)$$

Special Cases. As was already mentioned, the dependence of MWD averages on parameters is more complex than for the "associative" mechanism of exchange. In the latter case the main parameter which governs the width of the MWD is given as $\beta = \beta' K$,

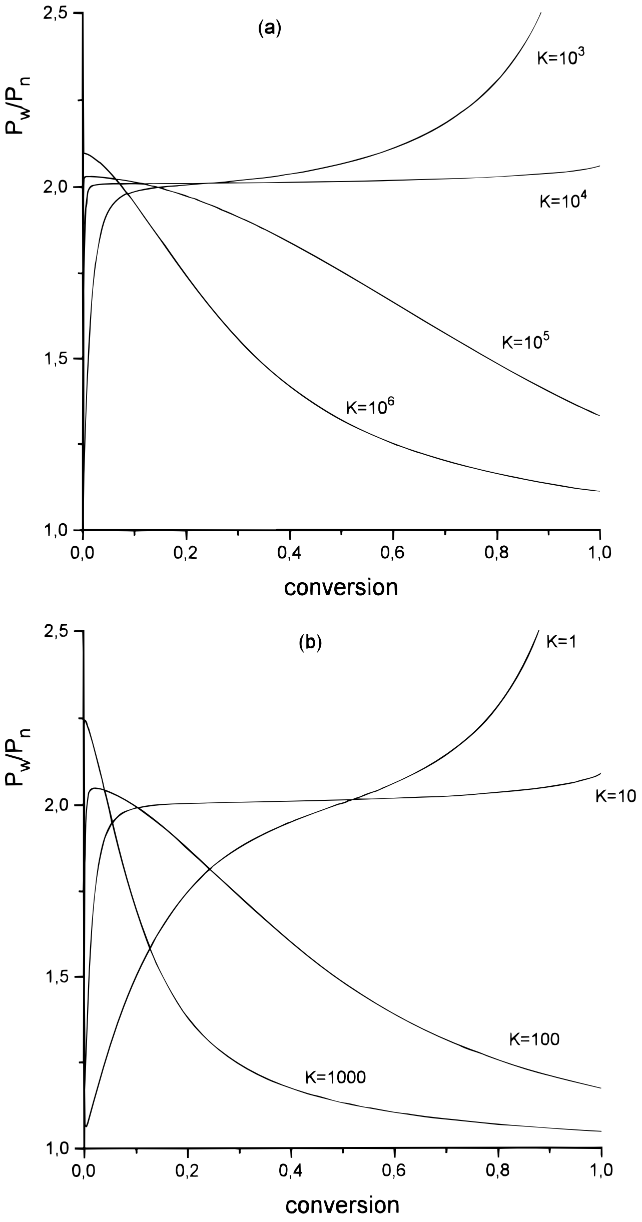


Figure 4. Dependence of polydispersity index on monomer conversion for $\epsilon = C_0/I_0 = 0.01$, $\gamma = M_0/I_0 = 100$, $\beta' = k_1/k_p = 0.1$ (a) and $\beta' = 10$ (b). No difference between equilibrium and nonequilibrium conditions is found within this range of parameters.

whereas now it is $\beta = \beta' K(\alpha + \eta)$. Since α depends on K (and η), the effects of β' and K should be analyzed separately.

(a) No E Added ($\eta = 0$). In this important and most common case $\beta = \beta' K\alpha = \alpha k_2/k_p$ and a combination of eqs 15 and 16 (for $\bar P_n \gg 1$) simplifies into

$$\bar P_w/\bar P_n = \frac{\beta' K\alpha + 1}{\beta' K\alpha + \alpha} \tag{15a}$$

(i) If the equilibrium in Scheme 3 is shifted to the right hand side (i.e., $4\epsilon K \ll 1$, to be expected for GTP with strongly nucleophilic catalysts like bifluoride), eq 4a simplifies to $\alpha \approx \epsilon$ and

$$\bar P_w/\bar P_n = \frac{\beta' K\epsilon + 1}{\beta' K\epsilon + \epsilon}$$

This value depends on the magnitude of the product $\beta' K$. If $\beta' K \gg 1$ in spite of $4\epsilon K \ll 1$ (this implies high β' and not very small K)

$$\bar P_w/\bar P_n \approx 1 + \frac{1}{\beta' K\epsilon} = 1 + \frac{1}{\beta' K}\frac{I_0}{C_0} = 1 + \frac{k_p}{k_2}\frac{I_0}{C_0} \tag{17}$$

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., $4\epsilon K \gg 1$, to be expected for GTP with weakly nucleophilic catalysts, like benzoates, or for cationic and atom transfer radical polymerization),

$$\alpha \approx \sqrt{\epsilon/K} \ll \epsilon$$

and

$$\bar P_w/\bar P_n \approx \frac{\beta' K + (K/\epsilon)^{1/2}}{\beta' K + 1}$$

If exchange is not extremely slow so that $\beta' K \gg 1$, the polydispersity is

$$\bar P_w/\bar P_n = 1 + \frac{1}{\beta'\sqrt{\epsilon K}} = 1 + \frac{k_p}{k_2}\sqrt{\frac{k}{\epsilon}} = 1 + \frac{k_p}{k_2}\sqrt{\frac{KI_0}{C_0}} = 1 + \frac{k_p}{\sqrt{k_1 k_2}}\sqrt{\frac{I_0}{C_0}} \tag{18}$$

In this limiting case the polydispersity index increases with the square root of the ratio of initial concentrations of initiator and catalyst. In contrast to the former cases, it depends on both rate constants of activation and deactivation.

(b) Product E Added ($\eta > 0$). As becomes clear from Scheme 3, addition of product **E** (e.g. a 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 4 can be approximated as $\alpha \approx \epsilon$, and

$$\bar P_w/\bar P_n = \frac{\beta' K(\eta + \epsilon) + 1}{\beta' K(\eta + \epsilon) + \epsilon} \tag{19}$$

If now β' is sufficiently high (fast exchange) so that $\beta' K \gg 1$, despite small $K\eta \ll 1$, eq 19 simplifies to

$$\bar P_w/\bar P_n = 1 + \frac{1}{\beta' K(\eta + \epsilon)} = 1 + \frac{I_0}{\beta' K(C_0 + E_0)} = 1 + \frac{k_p}{k_2}\frac{I_0}{(C_0 + E_0)}$$

Then, the polydispersity index decreases with increasing concentration of **E**. The effect is only pronounced if E_0 is at least comparable to C_0.

(ii) In the opposite limiting case, $K\eta \gg 1$, $\alpha \approx \epsilon/K\eta$, and the polydispersity index is

$$\bar P_w/\bar P_n = \frac{\beta' K\eta + 1}{\beta' K\eta + \epsilon/K\eta}$$

and if β' is not extremely small, so that $\beta' K \gg 1$, we obtain

$$\bar{P}_w/\bar{P}_n = 1 + \frac{1}{\beta' K\eta} = 1 + \frac{I_0}{\beta' K E_0} = 1 + \frac{k_p}{k_2}\frac{I_0}{E_0}$$

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

Comparison to Experimental Data

The dependence of the polydispersity index on conversion is identical for the three exchange mechanisms studied so far and thus cannot serve as a mechanistic criterion. However, the dependence on initial concentrations of initiator and catalyst may serve to discriminate between them. For the "dissociative" mechanisms the polydispersity index depends on both initiator and catalyst concentrations; for the "associative" mechanism it only depends on initiator concentration alone, and for degenerative transfer it is roughly independent of both.

In an earlier paper[13] the kinetic reaction orders with respect to initiator and catalyst concentrations were calculated for the "associative" and "dissociative" mechanisms of GTP and compared to experimental data obtained with strongly nucleophilic catalysts, e.g. bifluorides, corresponding to case i and less nucleophilic catalysts, like benzoates, corresponding to case ii. From the comparison it was concluded that experimental reaction orders with benzoates do not conform with the "dissociative" mechanism whereas no discrimination was possible for bifluorides. However, the enolate formation (Scheme 3) with bifluoride as the nucleophile will lead to a fluorosilane. Since fluorosilanes are very stable, the reverse reaction is quite improbable. Thus, if the "dissociative" mechanism is really applicable to bifluoride catalysis, it will be irreversible ($k_2 = 0$). As a consequence, exchange of activity can only proceed through degenerative transfer, as analyzed in parts 1 and 2 of this series.

As was pointed out in Part 3, comparison of experimental with calculated polydispersity indices is hampered by the effect of slow initiation observed with normal GTP initiators, like MTS. Only a few experiments were performed with a dimeric initiator which leads to fast initiation. Since the values of the polydispersity index are very small ($\bar{P}_w/\bar{P}_n \le 1.05$; see part 1), the corresponding experimental errors may be too large to allow for final conclusions. In the cases reported in parts 1 and 3, the polydispersity index did not depend on initiator concentration. The same is true for experiments with slow initiation.[14−17] This indicates that degenerative transfer is a more probable mechanism for activity exchange than the indirect mechanisms of Schemes 2 and 3.

Since degenerative transfer seems to be the predominant mechanism of activity exchange, we tentatively have to conclude that MWD's of the polymers formed cannot discriminate whether the active chain ends in GTP are activated silyl ketene acetals ("associative" mechanism) or enolates ("dissociative" mechanism). This can only be done by analyzing the kinetic reaction orders, as was pointed out above.

In "living" cationic polymerization, too, there are only few data published on the dependence of the polydispersity index on initiator and catalyst concentrations.[18−21] However, from the experimental data at full conversion given in Table 1 one can tentatively conclude that there is no significant dependence. As a consequence, it appears that in cationic polymerization, too, degenerative transfer is the predominant mechanism of activity exchange. This process is similar to the inifer process which is a bimolecular activity exchange between active chain ends and "dormant" residual initiator. It was proposed to occur in the polymerization of isobutylene initiated by cumyl chloride and related compounds.[21,22]

Table 1. Dependence of Polydispersity Index (at $x > 0.9$) on Initiator and Catalyst Concentrations in the "Living" Cationic Polymerization of Various Monomers

monomer, M_0/mol L^{-1}	solvent, T/°C	$10^3 I_0$/ mol L^{-1}	$10^3 C_0$/ mol L^{-1}	M_w/M_n	ref
α-methylstyrene,[a] 0.5	CH_2Cl_2, −78	10	20	1.14	18
		5	20	1.14	
		2.5	20	1.12	
styrene,[b] 0.35	MeCl:MeChx (40:60), −80	2[d]	16	1.8	19
		1[e]	36.4	1.8	
isobutylene,[b] 1.67	nBuCl, −80	1.97[d]	36.4	1.2	20
		1.97[d]	18.2	1.2	
isobutylene,[c] 0.6	MeCl, −75	0.46	100	2.02	21
		0.92	100	1.82	
		1.84	100	1.81	
		2.76	100	1.82	
		3.68	100	1.76	
		4.61	100	1.77	
		8.92	100	2.28	
		18.2	100	1.73	

[a] Initiator: 1-(2-chloroethoxy)chloroethane. Catalyst: $SnBr_4$. [b] Initiator: 2,4,4-trimethylpentyl chloride. Catalyst: $TiCl_4$. [c] Initiator: 1,4-bis(1-chloro-1-methylethyl)benzene. Catalyst: BCl_3 (slow initiation). [d] In the presence of 4 × 10^{-3} mol/L di-*tert*-butylpyridine (DTBP). [e] In the presence of 2 × 10^{-3} mol/L DTBP.

Scheme 6. Degenerative Transfer between Covalent Species and Free Ions in Cation Polymerization

$$P_i\text{-}X + P_j^+ \rightleftharpoons P_i^+ + X\text{-}P_j$$

Two arguments can be put forward against the assumption of degenerative transfer or inifering to occur to a larger extent in cationic polymerization. (i) From a chemical point of view, a bimolecular activity exchange can be much easier visualized to occur between covalent species and free cations (cf. Scheme 6) than between covalent species and ion pairs. Thus, the rate of such a process should depend on the fraction of free ions which increases with the decreasing concentration of ion pairs; in turn it would depend on initiator and catalyst concentration which is not observed. (ii) Model studies of Mayr and Schade[23] (addition of isobutylene to ditolylmethyl chloride catalyzed by trityl tetrafluoro- and tetrachloroborate) indicate that the reaction of isobutylene-ended cations with residual initiator (inifer process) is much slower than that with the BCl_4^- cation (reverse reaction of Scheme 3). However, in these investigations the initiator concentration was quite high ($I_0 = 0.05$ mol/L), and thus the fraction of free cations very low. As a consequence, more detailed investigations are needed to elucidate the true mechanism of activity exchange in "living" cationic polymerization.

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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 polydispersity index; here, $\beta \equiv \beta' K(\alpha + \eta) = (\alpha + \eta)k_2/k_p$
β'	k_1/k_p
δ	$\frac{K\alpha}{K\alpha + K\eta + 1}$; auxiliary parameter for nonequilibrium initial conditions
$\delta_{i,j}$	Kronecker symbol
ϵ	C_0/I_0
η	E_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	$\beta'\left[\frac{K\alpha + \eta}{\alpha} + \frac{\epsilon}{\alpha} - 1\right] \approx \beta/\alpha$
τ	$\alpha k_p I_0 t$, dimensionless time
a	$\beta'(K\alpha + K\eta + 1)/\alpha = \beta'\epsilon/\alpha^2$, auxiliary parameter for nonequilibrium initial conditions
C	catalyst (co-initator) concentration
E	concentration of (added or formed) byproduct, i.e. silyl ester in GTP, counterion in cationic polymerization, or salt of higher oxidation state in ATRP
I	initiator concentration
K_E	k_1/k_2, equilibrium constant of Scheme 3
K	$k_2/k_1 = 1/K_E$
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_i'	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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