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Kinetic Analysis of “Living” Polymerization Processes Exhibiting Slow Equilibria. 6. Cationic Polymerization Involving Covalent Species, Ion Pairs, and Free Cations[†]

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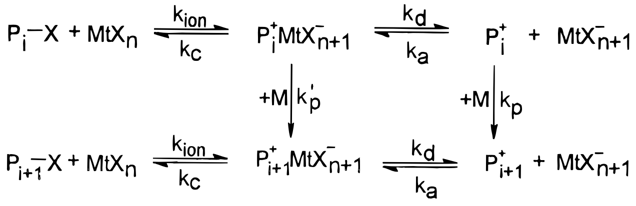
ABSTRACT: The kinetics of cationic polymerization is studied theoretically in accordance with a three-state mechanism which consists of two successive equilibria: the ionization/ion collapse equilibrium between covalent species and ion pairs, and the subsequent dissociation/association equilibrium between ion pairs and free ions. The number- and weight-average degrees of polymerization and the polydispersity index (PDI), $\bar{P}_w/\bar{P}_n$, are derived. The molecular weight distribution of the polymer generated from this mechanism is generally broader than that of polymers formed via a two-state mechanism, i.e. with only one equilibrium either between covalent species and ion pairs or between covalent species and free ions. Under this general mechanism, the exchange rate parameter, β, is more complicated than that of two-state mechanisms and is a combination of the corresponding exchange rate parameters for these two mechanisms. The molecular weight distribution becomes narrower if dissociation is reduced by adding common counterions to the reaction system. Excess common ions lead to a two-state polymerization with covalent species and ion pairs only. On the other hand, if dissociation is very strong, the PDI is predominantly given by the rate of the ionization/ion collapse equilibrium unless the dissociation/association equilibrium is very much slower than the former one.

Introduction

Recently, the living cationic polymerization of several monomers has stimulated great attention. Experimental data have been presented in favor of a mechanism in which dormant covalent species are in dynamic equilibria with both active ion pairs and active free cations:[1−4]

Scheme 1. Three-State Cationic Polymerization



where MtX_n is a Lewis acid such as BCl_3 or $TiCl_4$; $P_i{-}X$ and P_i^+ are the covalent and ionic species, respectively; $P_i^+MtX_{n+1}^-$ denotes ion pairs; MtX_{n+1}^- and M respectively represent counterion and monomer; k_{ion}, k_c, k_d, and k_a stand for the rate constants of ionization, ion collapse, dissociation, and association, respectively; and k_p and k'_p are the respective rate constants of propagation via free cations and ion pairs. Scheme 1 demonstrates that the ionization of covalent species by Lewis acids leads to ion pairs which can further dissociate to free ions, and both ion pairs and free cations are capable of chain propagation. Puskas et al.[4] and Müller et al.[5,6] have theoretically dealt with living carbocationic polymerizations with the respective equilibria between covalent species and ion pairs, and between covalent species and free ions. Puskas et al.[4] concluded that ion pairs are the chain carriers in the living polymerization of isobutylene. Alternatively, Nuyken[7] regarded unpaired ions as the active species in his tertiary chloride/BCl_3 system. Since the equilibrium constant of ionization ($K_i = k_{ion}/k_c < 10^{-5}$ L/mol) is regarded to be very low for isobutylene polymerization, the concentration of ionized species is also very low. In conjunction with rather high dissociation constants ($K_d = k_d/k_a \approx 10^{-6}$ mol/L based on electrostatic theory), this indicates that a considerable concentration of free ions must exist in equilibrium with ion pairs. Thus, generally both ion pairs and free ions should be involved in chain propagation. On the other hand, common counterions, which may be added to the system, will reduce dissociation. These common ions may also be generated from the reaction of adventitious protic impurities with proton traps and subsequent addition of the remaining anion with the Lewis acid.

It seems necessary to study the kinetics of the general mechanism shown in Scheme 1, which may facilitate comprehensive understanding of living cationic polymerization. By using the Monte Carlo numerical method, Matyjaszewski et al.[8] calculated MWD's for such a process, taking into account that $k_p \approx k'_p$. They showed that the MWD's are broader than those for a two-state mechanism. They even may be bimodal. However, Monte Carlo calculations are very time-consuming and do not lead to analytical expressions. Here, we present an analytical derivation of the number- and weight-average molecular weights and the polydispersity index for the three-state mechanism shown in Scheme 1. Special emphasis is put on the effect of common ions which reduce the fraction of free ions.

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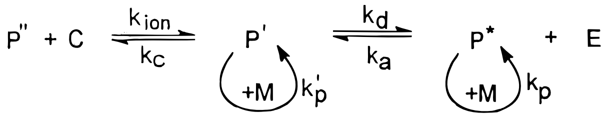
Kinetic Differential Equations

For the convenience of derivation, $P_i{-}X$, $P_i^+MtX_{n+1}^-$, and P_i^+, in Scheme 1 are replaced with P_i'', P_i' and P_i^* respectively; M, C, and E symbolize monomer, catalyst (coinitiator, Lewis acid), and counterion, respectively. Then we get the following kinetic scheme:

Scheme 2. Kinetic Scheme for Cationic Polymerization



Thus, the set of kinetic differential equations adapted to Scheme 2 can be written by

$$\frac{dP_0^*}{dt} = k_c P_0' - k_{ion} C P_0'' \tag{1}$$

$$\frac{dP_0'}{dt} = -k_p' M P_0' + k_{ion} C P_0'' + k_a E P_0^* - (k_c + k_d) P_0' \tag{2}$$

$$\frac{dP_0^*}{dt} = -k_p M P_0^* - k_a E P_0^* + k_d P_0' \tag{3}$$

$$\frac{dP_i^*}{dt} = k_p M (P_{i-1}^* - P_n^*) - k_a E P_i^* + k_d P_i' \tag{4}$$

$$\frac{dP_i'}{dt} = -k_p' M (P_{i-1}' - P_i') + k_a E P_i^* - k_d P_i' - k_c P_i' + k_{ion} C P_i'' \tag{5}$$

$$\frac{dP_i''}{dt} = k_c P_i' - k_{ion} C P_i'' \tag{6}$$

$$\frac{dM}{dt} = -(k_p P^* + k_p' P') M \tag{7}$$

where index $i = 0$ indicates the initiator, and $P^* = \sum_{i=1}^{\infty} P_i^*$ and $P' = \sum_{i=1}^{\infty} P_i'$ are the total concentrations of free cations and ion pairs, respectively. The experimental data presented in parts 3 and 4 of this series[5,6] indicate that a steady state is reached very early in the polymerization. Thus, equilibrium initial conditions can be used:

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

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

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

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

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

$$C|_{t=0} = C_0 - (\alpha + \sigma) I_0$$

where the Kronecker symbol

$$\delta_{i,0} = \begin{cases} 1, \text{ if } i = 0 \\ 0, \text{ if } i \neq 0 \end{cases}$$

The fraction of free ions, $\alpha = P^*/I_0$, and ion pairs, $\sigma = P'/I_0$, can be determined through the equilibrium conditions using the equilibrium constants, $K_i = k_{ion}/k_c$ and $K_d = k_d/k_a$:

$$K_i[C_0 - (\alpha + \sigma) I_0](1 - \alpha - \sigma) I_0 = \sigma I_0 \tag{8}$$

and

$$K_d \sigma I_0 = \alpha I_0 (\alpha I_0 + E_0) \tag{9}$$

Equation 9 is equivalent to

$$\sigma = \frac{\alpha}{K_d}(\alpha I_0 + E_0) \tag{10}$$

With the dimensionless constants

$$K_1 = K_i I_0; \quad K_2 = K_d/I_0; \quad \eta = E_0/I_0; \quad \epsilon = C_0/I_0$$

we obtain a quadruplicate equation in the general case:

$$\alpha^4 + \alpha_3 \alpha^3 + \alpha_2 \alpha^2 + \alpha_1 \alpha + \alpha_0 = 0 \tag{11}$$

The coefficients in eq 11 are given by

$$\alpha_3 = 2(K_2 + \eta); \quad \alpha_2 = (K_2 + \eta)^2 - K_2 - K_2\epsilon - \frac{K_2}{K_1} \tag{12a}$$

$$\alpha_1 = -K_2\left[(K_2 + \eta)(1 + \epsilon) + \frac{\eta}{K_1}\right]; \quad \alpha_0 = K_2{}^2\epsilon \tag{12b}$$

Typically, the fraction of ions and ion pairs is very low ($\alpha, \sigma \ll 1$). Then, eq 8 can be simplified as

$$K_i C_0 I_0 \approx \sigma I_0$$

namely

$$\sigma \approx K_i C_0 \tag{13}$$

By substituting eq 13 into eq 9, we obtain a quadratic equation for α with the solution

$$\alpha = \frac{\eta}{2}\left[\left(1 + \frac{4K_i K_d \epsilon}{\eta^2}\right)^{1/2} - 1\right] \tag{14}$$

In the absence of added common ions ($\eta = 0$), this leads to

$$\alpha \approx (K_i K_d \epsilon)^{1/2} = (K_i K_d C_0/I_0)^{1/2} \tag{15}$$

and for excess common ions ($\eta \gg (K_i K_d \epsilon)^{1/2}$)

$$\alpha \approx K_i K_d \epsilon/\eta = K_i K_d C_0/E_0 \tag{16}$$

Number-Average Degree of Polymerization

In order to find number- and weight-average degrees of polymerization, we have to calculate various statistical moments in advance. The dependence of monomer conversion, x, on time is given by integration of eq 7:

$$x = \frac{M_0 - M}{M_0} = 1 - e^{-k_p I_0 t} \tag{17}$$

where

$$\bar{k}_{\rm p} = \alpha k_{\rm p} + \sigma k'_{\rm p} = k_{\rm p}(\alpha + \lambda\sigma) \tag{18}$$

is the apparent rate constant of propagation and $\lambda = k'_{\rm p}/k_{\rm p}$ is the reactivity ratio of ion pairs and free ions. Typically, this ratio is near unity.

The *n*th-order moment of the resulting polymer is defined by

$$\mu_n = \mu''_n + \mu'_n + \mu^*_n \tag{19}$$

and

$$\mu''_n = \sum_{i=1}^{\infty} i^n P''_i; \qquad \mu'_n = \sum_{i=1}^{\infty} i^n P'_i; \qquad \mu^*_n = \sum_{i=1}^{\infty} i^n P^*_i \tag{20}$$

Obviously

$$\mu_0 = I_0 \tag{21}$$

$$\mu_1 = M_0 - M = M_0 x \tag{22}$$

So, the number-average degree of polymerization is

$$\bar{P}_n = \frac{\mu_1}{\mu_0} = \frac{M_0 x}{I_0} = \gamma x \tag{23}$$

with $\gamma = M_0/I_0$.

However, the residual initiator, $P_0 = P''_0 + P'_0 + P^*_0$, is usually excluded by precipitation in the experimental determination of the MWD. Therefore we must subtract it from the zeroth-order moment of total polymer in order to compare the theoretical results with experimental data.

$$\mu_0 = I_0 - P_0 \tag{24}$$

The improved expression of number-average degree of polymerization becomes

$$\bar{P}_n = \frac{M_0 x}{I_0 - P_0} \tag{25}$$

As was shown in part 1 of this series,[9] it is difficult to find an analytical solution of P_0 from eqs 1−3, but it is easily obtained by numerical integration. However, the following simple consideration allows one to obtain an approximate analytical solution for P_0. Since the ion pairs, P', are sufficiently active, eq 1 can be simplified by neglecting the back-reaction:

$$\frac{{\rm d}P''_0}{{\rm d}t} \approx -k_{\rm ion} C P''_0 = -k_{\rm c}\sigma P''_0 \tag{26}$$

and eq 26 can be rewritten in terms of conversion:

$$(1 - x)\frac{{\rm d}P''_0}{{\rm d}x} \approx -\frac{k_{\rm c}\sigma}{\bar{k}_{\rm p} I_0} P''_0 = -\beta_1 P''_0 \tag{27}$$

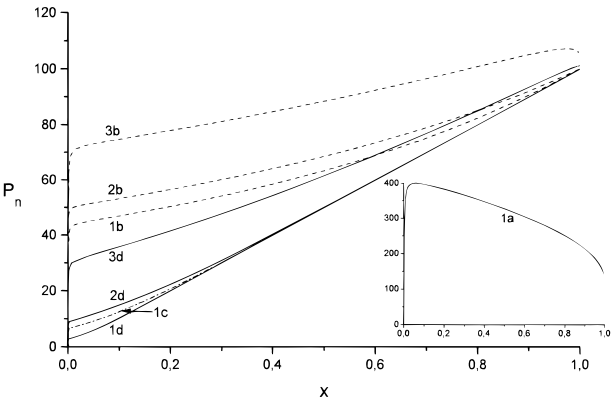


Figure 1. Dependence of the number-average degree of polymerization on monomer conversion for different degrees of ionization, σ, and of dissociation of ion pairs, $\alpha/(\alpha + \sigma)$, and different rates of the ionization equilibrium. Rate constants of polymerization are adjusted to a constant half-life of 16.6 s. M_0 = 1.0 mol/L, I_0 = 0.01 mol/L, C_0 = 0.1 mol/L, E_0 = 0 mol/L, $k_{\rm d} = 10^4$ s^{-1} , $k_{\rm a} = 10^9$ l mol^{-1} s^{-1} ($K_{\rm d} = 10^{-5}$ mol L^{-1}). (1) $K_{\rm i} = 10^{-3}$ L mol^{-1}, $\sigma = 10^{-4}$, $\alpha/(\alpha + \sigma)$ = 76%, $k_{\rm p} = k'_{\rm p} = 10^4$ L mol^{-1} s^{-1}; (2) $K_{\rm i} = 10^{-4}$, $\sigma = 10^{-5}$, $\alpha/(\alpha + \sigma)$ = 91%, $k_{\rm p} = k'_{\rm p}$ = 3.78 × 10^4; (3) $K_{\rm i} = 10^{-5}$ L mol^{-1}, $\sigma = 10^{-6}$, $\alpha/(\alpha + \sigma)$ = 97%, $k_{\rm p} = k'_{\rm p}$ = 12.8 × 10^4 L mol^{-1} s^{-1}. (a) $k_{\rm ion}$ = 0.1, (b) $k_{\rm ion}$ = 1, (c) $k_{\rm ion}$ = 10, (d) $k_{\rm ion}$ = 100 L mol^{-1} s^{-1}.

where the exchange rate parameter for ionization,

$$\beta_1 = \frac{k_{\rm c}\sigma}{\bar{k}_{\rm p} I_0} = \beta_{10}\frac{\lambda\sigma}{\alpha + \lambda\sigma} \tag{28}$$

is introduced which describes the relative rate of exchange for the first part of Scheme 2. This parameter is related to the exchange rate parameter

$$\beta_{10} = \frac{k_{\rm c}}{k'_{\rm p} I_0} \tag{29}$$

obtained in part 3 of this series[5] for the ionization equilibrium alone. Equation 27 is easily integrated:

$$P_0 \approx P''_0 \approx (1 - \alpha - \sigma)I_0(1 - x)^{\beta_1} \approx I_0(1 - x)^{\beta_1} \tag{30}$$

By substitution eq 30 into eq 25, we get the simplified expression for the number-average degree of polymerization of the resultant polymer:

$$\bar{P}_n \approx \frac{\gamma x}{1 - (1 - x)^{\beta_1}} \tag{31}$$

The dependence of $\bar{P}_{\rm n}$ on conversion is analogous to those given in the earlier parts for equilibrium initial conditions, but even simpler since $\alpha, \sigma \ll 1$. Figure 1 shows the effect of different degrees and rates of ionization on $\bar{P}_{\rm n}$. Even at a fixed dissociation equilibrium constant, this leads to different degrees of dissociation of the ion pairs, given as the ratio of dissociated to all ionized species, $\alpha/(\sigma + \alpha)$. The values of $k_{\rm p} = k'_{\rm p}$ have been adjusted in a way that a constant half-life of polymerization ($t_{1/2}$ = 16.6 s) is obtained. We can see that a marked deviation of the expected linear dependence of $\bar{P}_{\rm n}$ on conversion is observed at $\beta_1 < 10$. For $\beta_1 > 1$ (case 1a), the deviations become very strong, since only few initiator molecules are converted to polymer molecules. This effect has been described in detail in part 1 of this series.[9] It is important that $\bar{P}_{\rm n}$ is defined by the exchange rate parameter of ionization only (first step in Scheme 1) and does not depend on the rates of the dissociation equilibrium.

Weight-Average Degree of Polymerization and Polydispersity Index

According to the definition, $\bar{P}_w = \mu_2/\mu_1$. The second moment of the MWD can be derived by the following procedures. We can find from eqs 4–6

$$\frac{d\mu_2}{dx} = \frac{d\mu_1}{dx} + 2M_0\left(\frac{k_p}{\bar{k}_p}\mu_1^* + \frac{k'_p}{\bar{k}_p}\mu'_1\right) \tag{32}$$

$$(1-x)\frac{d\mu_1^*}{dx} = M_0(1-x)\frac{\alpha k_p}{\bar{k}_p} + \beta_2\left[\mu'_1 - \frac{\sigma}{\alpha}\mu_1^*\right] \tag{33}$$

$$(1-x)\frac{d\mu'_1}{dx} = M_0\frac{\sigma k'_p}{\bar{k}_p}(1-x) + \beta_1\left[\mu''_1 - \frac{1-\alpha-\sigma}{\sigma}\mu_1^*\right] - \beta_2\left[\mu'_1 - \frac{\sigma}{\alpha}\mu_1^*\right] \tag{34}$$

with the exchange parameter for dissociation (second step of Scheme 2),

$$\beta_2 = \frac{k_d}{\bar{k}_p I_0} = \frac{k_a\alpha(\eta + \alpha)}{\sigma\bar{k}_p} = \beta_{20}\frac{\alpha}{\sigma(\alpha + \lambda\sigma)} \tag{35}$$

Here,

$$\beta_{20} = \frac{k_a(\alpha + \eta)}{k_p} \tag{36}$$

is the exchange parameter for the two-state mechanism where free ions are directly generated from covalent species as derived in part 4 of this series.[6] Taking into account that $\mu''_1 = M_0x - \mu'_1 - \mu_1^*$, from eqs 33 and 34 we get

$$\frac{\mu_1^*}{M_0} = \alpha + N(1-x) + y_1(1-x)^{r_1} + y_2(1-x)^{r_2} \tag{37}$$

$$\frac{\mu'_1}{M_0} = \sigma + \frac{1}{\beta_2}\left[N\left(\frac{\sigma}{\alpha}\beta_2 - 1\right) - \frac{\alpha}{\alpha + \lambda\sigma}\right](1-x) + y_1\left(\frac{\sigma}{\alpha} - \frac{r_1}{\beta_2}\right)(1-x)^{r_1} + y_2\left(\frac{\sigma}{\alpha} - \frac{r_2}{\beta_2}\right)(1-x)^{r_2} \tag{38}$$

where r_1 and r_2 are the solutions of the quadratic equation

$$r^2 - r\left(\beta_1\frac{1-\alpha}{\sigma} + \beta_2\frac{\alpha + \sigma}{\alpha}\right) + \frac{\beta_1\beta_2}{\alpha} = 0$$

$$r_{1,2} = \frac{1}{2}\left\{\beta_1\frac{1-\alpha}{\sigma} + \beta_2\frac{\alpha+\sigma}{\alpha} \pm \left[\left(\beta_1\frac{1-\alpha}{\sigma} + \beta_2\frac{\alpha+\sigma}{\alpha}\right)^2 - \frac{4\beta_1\beta_2}{\alpha}\right]^{1/2}\right\}$$

and

$$N = \frac{\frac{\alpha}{\alpha + \lambda\alpha}\left[\frac{1-\alpha}{\sigma}\beta_1 - 1\right] - \beta_2(\beta_1 - 1)}{(r_1 - 1)(r_2 - 1)} \tag{39}$$

$$y_1 = \frac{\frac{\alpha}{\alpha + \lambda\sigma} - (\alpha + N)r_2 + N}{r_1 - r_2}$$

$$y_2 = -\frac{\frac{\alpha}{\alpha + \lambda\sigma} - (\alpha + N)r_1 + N}{r_1 - r_2}$$

and thus, integration of eq 32 leads to

$$\mu_2 = \mu_1 + 2\frac{\gamma}{\alpha + \lambda\sigma}\int_0^x(\mu_1^* + \lambda\mu'_1)\,dx \tag{40}$$

By substitution of eqs 37 and 38 into eq 40, we finally obtain

$$\bar{P}_w = 1 + \gamma x + \gamma\left\{\frac{2-x}{\beta} + 2n_1\frac{1-(1-x)^{r_1+1}}{x(r_1+1)} + 2n_2\frac{1-(1-x)^{r_2+1}}{x(r_2+1)}\right\} \tag{41}$$

where

$$n_1 = y_1\left(\frac{1}{\alpha} - \frac{\lambda r_1}{\beta_2(\alpha + \lambda\sigma)}\right); \qquad n_2 = y_2\left(\frac{1}{\alpha} - \frac{\lambda r_2}{\beta_2(\alpha + \lambda\sigma)}\right)$$

and the generalized exchange rate parameter, β, for the mechanism of Scheme 2 is defined as

$$\frac{1}{\beta} = 1 - \frac{\lambda\alpha}{(\alpha + \lambda\sigma)^2} + \frac{1}{\alpha}\left(1 - \frac{\lambda\alpha}{\beta_2(\alpha + \lambda\sigma)}\right)N \tag{42}$$

Under typical polymerization conditions (α, $\sigma \ll 1$; β_1, $\beta_2 \gtrsim 1$), both r_1 and r_2 are very large, and the two last terms in eq 41 can be neglected even at low conversions. Thus, we obtain the simplified expression

$$\bar{P}_w = 1 + \gamma x + \gamma\frac{2-x}{\beta} \tag{43}$$

Correspondingly, the polydispersity index is

$$\frac{\bar{P}_w}{\bar{P}_n} = 1 + \frac{1}{\bar{P}_n} + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \approx 1 + \frac{1}{\beta}\left(\frac{2}{x} - 1\right) \tag{44}$$

for $\bar{P}_n \gg 1$. This dependence of PDI on conversion is identical to the equations obtained in parts 1, 3, and 4 of this series for degenerative transfer, ion pair generation, and free ion generation as exchange mechanisms. The important difference is the definition of β which is defined by the mechanism.[10] At full conversion, eq 44 again leads to

$$\frac{\bar{P}_w}{\bar{P}_n} \approx 1 + \frac{1}{\beta} \tag{45}$$

Since r_1, $r_2 \gg 1$, the combination $(r_1 - 1)(r_2 - 1) \approx r_1r_2 = \beta_1\beta_2/\alpha$ and parameter N in eq 39 is approximated by

$$N = \alpha\left(\frac{1}{\beta_1} + \frac{\alpha}{\sigma(\alpha + \lambda\sigma)}\frac{1}{\beta_2} - 1\right) \tag{39a}$$

Then, the generalized exchange rate parameter can be expressed through β_1 and β_2 as

$$\frac{1}{\beta} = \frac{1}{\beta_1} + \left(\frac{\alpha}{\alpha + \lambda\sigma}\right)^2\frac{1}{\sigma\beta_2} = \frac{\alpha + \lambda\sigma}{\lambda\sigma}\frac{1}{\beta_{10}} + \frac{\alpha}{\alpha + \lambda\sigma}\frac{1}{\beta_{20}} = \left(1 + \frac{\alpha}{\lambda\sigma}\right)\frac{1}{\beta_{10}} + \left(1 + \frac{\lambda\sigma}{\alpha}\right)^{-1}\frac{1}{\beta_{20}} \tag{46}$$

Since the reactivities of ions and ion pairs are compa-

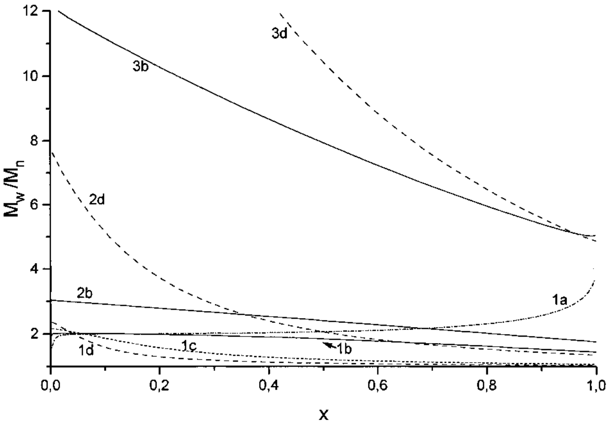


Figure 2. Dependence of the polydispersity index of polymerization on monomer conversion. Conditions, see Figure 1.

rable ($\lambda \approx 1$), β and thus the PDI depend on four parameters: the fractions of ion pairs and free ions, σ and α (eqs 13, 14), and the exchange rate parameters for these species, β_{10} and β_{20} (eqs 29 and 36). These parameters depend on the initial concentrations of initiator, catalyst, and counterions and on the rate constants of propagation, ion collapse, and association.

Thus, the dependence of the PDI on various polymerization conditions becomes complicated in this case, and some examples are given in Figure 2. For set 1 ($K_i = 10^{-3}$ L/mol, degree of dissociation of ion pairs = 76%) the dependence is similar to that shown in parts 1, 3, and 4 of this series. As an example, for $\beta > 1$ the polydispersity index again decreases with monomer conversion after a marked increase at low conversion, whereas for $\beta < 1$ it increases steadily. However, for sets 2 and 3 ($K_i \leq 10^{-4}$ L/mol, degree of dissociation of ion pairs >90%), we find dependences which are different from those shown for two-state systems with only one active species. Such a dependence can also occur in two-state systems with two differently active species.[10]

Special Cases

As follows from eq 46, in the general case β and thus the polydispersity index depend on the rates of both exchange processes. If, of course, one of steps is much faster than another, polydispersity will be defined by one parameter β_1 or β_2 only. Some limiting cases are considered below.

1. No Common Ion Salt Added ($E_0 = 0$). In this case the simplified expressions 13 and 15 can be used for σ and α, leading to the expression for the ratio of free ions to ion pairs,

$$\frac{\alpha}{\sigma} = \left(\frac{K_d}{K_i I_0}\right)^{1/2} \tag{47}$$

Introduction into eq 42 renders

$$\frac{1}{\beta} = \left[1 + \frac{1}{\lambda}\left(\frac{K_d}{K_i I_0}\right)^{1/2}\right]\frac{k'_p I_0}{k_c} + \left[1 + \lambda\left(\frac{K_i I_0}{K_d}\right)^{1/2}\right]^{-1} \frac{k_p}{k_a (K_d K_i C_0/I_0)^{1.2}} \tag{48}$$

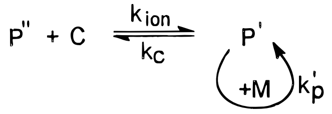
Thus, the PDI depends on the concentrations of initiator and catalyst in a complicated way. However, two limiting cases can be discussed.

(i) Little Dissociation/Excess Common Ion Salt. If the dissociation equilibrium is shifted to the left-hand side, either because $K_d/K_i \ll I_0$ or because of addition of excess common ion salt, the fraction of free ions becomes very small compared to the fraction of ion pairs ($\alpha \ll \sigma$), and for comparable reactivities of P' and P^* ($\alpha \ll \lambda\sigma$) we find from eq 46

$$\frac{1}{\beta} \approx \frac{1}{\beta_{10}} + \frac{\alpha}{\lambda\sigma}\frac{1}{\beta_{20}} \approx \frac{1}{\beta_{10}} = \frac{k'_p I_0}{k_c} \tag{49}$$

Even if the second step of exchange is quite slow compared to the first one ($\beta_{10} \gtrsim \beta_{20}$), the second term in eq 49 can be neglected. Thus, polydispersity depends only on the exchange rate of the first step, $\beta \approx \beta_{10}$ and thus, polydispersity index linearly increases with initiator concentration. This result is identical to that obtained in part 3 for ion pair generation (Scheme 3); i.e. the PDI will increase with initial initiator concentration.

Scheme 3. Ion Pair Generation in Cationic Polymerization



(ii) Complete Dissociation. Recent experimental data of Mayr et al.[11] indicate that the rate constant of propagation in the polymerization of isobutylene may be much higher than was assumed earlier. In order to explain the observed apparent rate constants of propagation, we must assume that the ionized species would have a much lower concentration; i.e. the ionization equilibrium (first equilibrium in Scheme 2) is extremely shifted to the left-hand side. Due to their low concentration, the ion pairs will be nearly completely dissociated if no common ions are present. In that case, $\sigma \ll \alpha$ and we obtain from eq 46

$$\frac{1}{\beta} \approx \frac{\alpha}{\lambda\sigma}\frac{1}{\beta_{10}} + \frac{1}{\beta_{20}} \tag{50}$$

Even if $\beta_{10} \gtrsim \beta_{20}$, i.e. the ionization equilibrium is much faster than the dissociation equilibrium, the main contribution to the polydispersity index is from the first step, and in the absence of common ions, we obtain

$$\frac{1}{\beta} \approx \frac{\alpha}{\lambda\sigma}\frac{1}{\beta_{10}} = \frac{k'_p}{k_c}\left(\frac{K_d}{K_i}\right)^{1/2} {C_0}^{1/2} \tag{51}$$

Hence, the polydispersity index will not depend on initiator concentration, but decreases with the square root of catalyst concentration.

If first step of exchange is very much faster than the second ($\beta_{10} \gg \beta_{20}$), we obtain

$$\frac{1}{\beta} \approx \frac{1}{\beta_{20}} = \frac{k_p}{k_a(\alpha + \eta)} \tag{52}$$

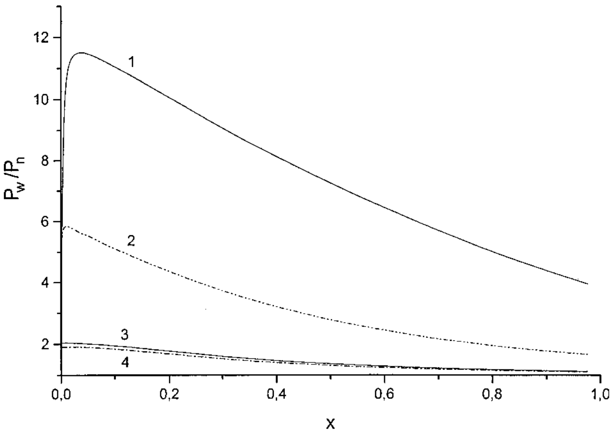
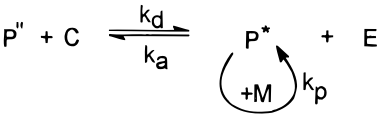


Figure 3. Effect of common ion salt on the equilibrium between free ions and ion pairs, $k_{\mathrm{ion}} = 1$ L mol^{-1} s^{-1}, $k_c = 10^3$ s^{-1}($K_i = 10^{-3}$ L mol^{-1}), $k_d = 100$ s^{-1} , $k_a = 10^7$ L mol^{-1} s^{-1} ($K_d = 10^{-5}$ mol L^{-1}), $k_p = k_p' = 10^4$ L mol^{-1} s^{-1}. (1) $E_0 = 0$; (2) $E_0 = 10^{-5}$; (3) $E_0 = 10^{-4}$ mol/L; (4) excess common ion salt (no free cations). Other conditions, see Figure 1.

This case is identical to a two-state polymerization where only free ions are generated (Scheme 4). This case was considered in detail in part 4 of this series.

Scheme 4. Generation of Free Ions in Cationic Polymerization



In the absence of added common ion salt, eq 52, this leads to

$$\frac{1}{\beta} \approx \frac{k_p^*}{k_a (K_i K_d)^{1/2}} \left(\frac{I_0}{C_0}\right)^{1/2} \tag{53}$$

where the PDI should decrease with the square root of the ratio of catalyst to initiator concentration. However, such a case is not very probable and we have to conclude that the ionization equilibrium is the step determining the MWD.

2. Effect of Added Common Ions ($E_0 > 0$). The analytical expression for this case is given by eq 46 where σ and α are given by eqs 13 and 14. Since the concentration of common ions enters in a nonlinear way, it is difficult to derive a simple analytical expression for the effect of added common ions, and some examples are given in Figures 3 and 4. Figure 3 indicates that if a certain amount common counterions is added into the reaction system, the equilibria will shift to the ion-pair side therefore the PDI decreases. Figure 4 shows the dependence of the polydispersity index at 97.5% conversion on the concentration of added common ions under various polymerization conditions.

Conclusions

It has been shown in part 3 of this series[5] that the observed dependence of the PDI on conversion is well described by eq 44 with $\beta \geq 10$. However, it was shown in part 4[6] that the sparse experimental data available do not seem to indicate a dependence of the PDI on catalyst or initiator concentration. This leads to the tentative conclusion that the MWD is predominantly determined by degenerative transfer processes, i.e. a direct bimolecular exchange between active and dormant species. It is at least possible that more than one mechanism of exchange operates in this system. Thus, more experimental material is necessary before a final mechanism of exchange can be established.

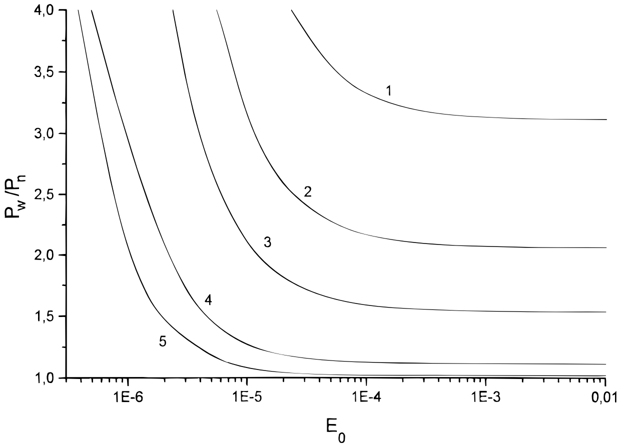


Figure 4. Dependence of the polydispersity index of polymerization on the concentration of added common ions at a monomer conversion of 97.5% for $k_p = k_p' = 10^5$ L mol^{-1} s^{-1}. (1) $k_c = 500$; (2) $k_c = 1000$; (3) $k_c = 2000$; (4) $k_c = 10^4$; (5) $k_c = 10^5$ s^{-1}; other conditions, see Figure 1.

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Appendix: List of Symbols and Abbreviations

α	fraction of free ions
β	general exchange rate parameter governing the polydispersity index
β_{10}	exchange rate parameter for the two-state mechanism in Scheme 3
β_1	weighted exchange rate parameter for the two-state mechanism in Scheme 3
β_{20}	exchange rate parameter for the two-state mechanism in Scheme 4
β_2	weighted exchange rate parameter for the two-state mechanism in Scheme 4
η	E_0/I_0
ϵ	C_0/I_0
γ	M_0/I_0
λ	k_p'/k_p
μ_n	nth MWD moment of total polymer
μ_n^*, μ_n', μ_n''	nth moment of the MWD of free ions, ion pairs, and covalent species
σ	fraction of ion pairs
a_0, a_1, a_2, a_3	coefficients used in the quadruple equation of α; see eq 11
C	catalyst (coinitiator) concentration (C_0: initial concentration)
E	counterion concentration (E_0: initial concentration of common ions)
I_0	initial initiator concentration
k_{ion}	rate constant of ionization
k_c	rate constant of ion collapse
k_d	rate constant of dissociation
k_a	rate constant of association
k_p^*	rate constant of polymerization of free ions
k_p'	rate constant of polymerization of ion pairs
$\bar{k}_p$	$=\alpha k_p + \sigma k_p'$, apparent propagation rate constant
K_i	$=k_{\mathrm{ion}}/k_c$, equilibrium constant of ionization

K_d	$=k_d/k_a$, equilibrium constant of dissociation
K_1	$=K_iI_0$, dimensionless ionization equilibrium constant
K_2	$=K_d/I_0$, dimensionless dissociation equilibrium constant
M	monomer concentration (M_0: initial concentration)
n_1, n_2	coefficients used in the analytical expression of $\bar{P}_w$
N, r_1, r_2, y_1, y_2	coefficients used in the analytical expressions of μ_n^* and μ_n'
PDI	polydispersity index
P_0''	concentration of inactive (covalent) initiator
P_0'	concentration of initiator in ion pairs
P_0^*	concentration of initiator in free ions
P_i^*	concentration of covalent species with degree of polymerization i
P_i'	concentration of ion pairs with degree of polymerization i
P_i^*	concentration of free ions with 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	monomer conversion

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