Kinetic Analysis of “Living” Polymerization Processes Exhibiting Slow Equilibria. 5.[†] Effect of Monomer Transfer in Cationic Polymerization and Similar Living Processes[†]

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Received June 22, 1995; Revised Manuscript Received April 8, 1996[⊗]

ABSTRACT: This work deals with the kinetics of polymerization processes with chain transfer to monomer and reversible formation of dormant species. Such a mechanism is typical for cationic polymerization in the presence of Lewis acids as co-initiators. The expressions of number- and weight-average degrees of polymerization and polydispersity index are derived rigorously for a mechanism with free ions as the active species, but it is also applied to other mechanisms, e.g., ion pairs as active species. Plots of polydispersity index versus monomer conversion can be easily computed on a PC computer even though the expressions for the weight-average degree of polymerization and the concentration of residual initiator consist of confluent hypergeometric functions. Numerical calculations show that the polydispersity index of the resulting polymer approaches $M_w/M_n = 2$ with increasing rate constant of chain transfer. Addition of common ions led to narrower molecular weight distributions. For the polymerization of indene with the cumyl chloride/titanium tetrachloride initiating system in methylene chloride, the calculated results of number-average degree of polymerization are in agreement with the experimental data reported in the literature.

Introduction

According to current experimental evidence, all carbocationic polymerization systems are involved in reversible termination;[1] i.e., there is an equilibrium between dormant and active species. The equilibrium can be understood as the interconversion of reactive carbenium ions or ion pairs with covalent species or onium ions.[1] The moments of the molecular weight distribution (MWD) of polymers arising from such a process in the absence of irreversible side reactions have been calculated in our previous papers,[2,3] and it was shown that the same mechanisms are appliable to other living polymerizations, such as group transfer polymerization or living radical polymerization. Moreover, it was suggested that the exchange of activity between dormant and active species may predominantly occur via a bimolecular exchange reaction, i.e., degenerative transfer.[4,5] Due to the inherent instability of carbocations, chain transfer occurs inevitably in carbocationic polymerization systems and it is especially observed at higher degrees of polymerization. Sigwalt[6] considered that the reversible transfer is impossible whereas reversible termination is a strong possibility. Furthermore, Matyjaszewski and Sigwalt[7] reported that transfer reactions are either first or zero order in monomer concentration. Evidently, the former is chain transfer to monomer, and the latter is spontaneous transfer. We have studied the effect of spontaneous transfer on number- and weight-average molecular weights and polydispersity index of the resultant polymer in ionic polymerization.[8] Obviously, chain transfer to monomer is also important for cationic polymerization systems. It is interesting to investigate the kinetics of carbocationic polymerization with monomer transfer taking account of the equilibrium between covalent species and free ions. Finally, the approach developed is extended to other polymerization systems with various mechanisms of reversible deactivation, i.e., equilibria between covalent species and ion pairs, group transfer polymerization, and living radical polymerization.

Scheme 1. Kinetic Scheme for Cationic Polymerization with Monomer Transfer with Free Cations as Active Species

$$C + P_i' \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_i^* + E$$

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

$$P_i^* + M \xrightarrow{k_{tr}} P_1^* + P_i''$$

Theoretical Derivation

Let P_i^*, P_i', and P_i'' represent respectively the active, dormant, and inactive species with i monomeric units, M is a monomer, and C and E denote catalyst (co-initiator, Lewis acid) and counterion, respectively. The reaction scheme is given in Scheme 1. Here we assume that all active species are present in form of free cations, similar to a former derivation.[3] Other cases will be dealt with later.

[†] Part 4, ref 3.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1996.

S0024-9297(95)00887-4 CCC: $12.00

The set of differential equations adapted to Scheme 1 reads

$$\frac{dP_1^*}{dt} = k_{tr}M\sum_i P_i^* - k_pMP_1^* + k_1CP_1' - k_2EP_1^* - k_{tr}MP_1^* \quad (1)$$

$$\frac{dP_i^*}{dt} = -k_pMP_i^* + k_pMP_{i-1}^* + k_1CP_i' - k_2EP_i^* - k_{tr}MP_i^* \quad (i \geq 2) \quad (2)$$

$$\frac{dP_i'}{dt} = -k_1CP_i' + k_2EP_i^* \quad (3)$$

$$\frac{dP_i''}{dt} = k_{tr}MP_i^* \quad (4)$$

$$\frac{dM}{dt} = -(k_p + k_{tr})M\sum_i P_i^* \quad (5)$$

where P_1^* and P_1' indicate active and dormant initiators respectively; i.e., the initiator is regarded as the unimer for the convenience of theoretical treatment. If the equilibrium between active and dormant species maintains throughout the whole process of polymerization, the initial conditions are

$$P_i^*|_{t=0} = \alpha I_0\delta_{i,1}$$

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

$$P_i''|_{t=0} = 0$$

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

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

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

where I_0 and M_0 are the initial concentrations of initiator and monomer, respectively, $\delta_{i,1}$ is Kronecker symbol, i.e.,

$$\delta_{i,1} = \begin{cases} 1 & \text{when} \quad i = 1 \\ 0 & \text{when} \quad i \neq 1 \end{cases}$$

α is the fraction of active chain ends. Because chain transfer does not influence the concentration of active species, α can be expressed by[10]

$$\alpha = \frac{w - \sqrt{w^2 - 4K_E(K_E - 1)I_0C_0}}{2I_0(K_E - 1)} \quad (6)$$

where

$$w = K_E(C_0 + I_0) + E_0 \quad \text{and} \quad K_E = k_1/k_2$$

From the experimental data given in the earlier parts of this series, it appears reasonable to assume that the polymerizations typically proceed under stationary state conditions; i.e., the equilibrium in Scheme 1 is established very early in the polymerization. Thus, the fraction of active chain ends, α, and the concentration of catalyst and counterion keep constant, i.e.,

$$C = C_0 - \alpha I_0 \quad E = E_0 + \alpha I_0$$

Integration of eq 5 leads to

$$M = M_0e^{-\lambda t} \quad (7)$$

where

$$\lambda = (k_p + k_{tr})\alpha I_0$$

Monomer conversion x is given by

$$x = 1 - e^{-\lambda t} \quad (8)$$

In order to find the expressions of the number- and weight-average degrees of polymerization, and the polydispersity, we have to derive various moments of the resulting polymer. The nth order moment of the total polymer generated is defined by the summation of corresponding moments of active, dormant, and inactive species:

$$\mu_n = \mu_n^* + \mu_n' + \mu_n'' \quad (9)$$

where

$$\mu_n^* = \sum_i i^nP_i^*$$

$$\mu_n' = \sum_i i^nP_i'$$

$$\mu_n'' = \sum_i i^nP_i''$$

Intergrating eq 4, we have

$$\sum_i P_i'' = \theta M_0x \quad (10)$$

where

$$\theta = k_{tr}/(k_{tr} + k_p)$$

Hence, the zeroth moment of total products is given by:

$$\mu_0 = I_0 + \theta M_0x \quad (11)$$

Furthermore, we can derive from eqs 1–5

$$d\mu_1/dt = \lambda M \quad (12)$$

$$d\mu_2/dt = \lambda M + 2k_pM\mu_1^* \quad (13)$$

Equation 12 results in

$$\mu_1 = I_0 + M_0x \quad (14)$$

From eqs 1 and 2, we have

$$d\mu_1^*/dt = \lambda M - k_{tr}M\mu_1^* + k_1C\mu_1' - k_2E\mu_1^* \quad (15)$$

Differentiation of both sides of eq 15 leads to

$$\frac{d^2\mu_1^*}{dt^2} = \frac{d(\lambda M)}{dt} - (k_{tr}M + k_2E)\frac{d\mu_1^*}{dt} - k_{tr}\mu_1^*\frac{dM}{dt} + k_1C\frac{d\mu_1'}{dt} \quad (16)$$

From eq 4, one gains

$$\frac{d\mu_1'}{dt} = \frac{d\mu_1}{dt} - \frac{d\mu_1''}{dt} - \frac{d\mu_1^*}{dt} = \lambda M - k_{tr}M\mu_1^* - \frac{d\mu_1^*}{dt} \quad (17)$$

Combining eqs 16 and 17, and using $\xi = e^{-\lambda t}$ as the new variable, one has

$$\xi\frac{d^2\mu_1^*}{d\xi^2} + (\varphi - \rho\xi)\frac{d\mu_1^*}{d\xi} + \sigma\mu_1^* = H_0 \quad (18)$$

where

$$\varphi = 1 - (k_1C + k_2E)/\lambda$$

$$\rho = k_{tr}M_0/\lambda$$

$$\sigma = k_{tr}M_0(k_1C - \lambda)/\lambda^2$$

and

$$H_0 = M_0(k_1C - \lambda)/\lambda$$

One of the initial conditions of eq 18 is

$$\mu_1^*|_{\xi=1} = \alpha I_0$$

and the other one can be found from

$$\left.\frac{d\mu_1^*}{dt}\right|_{t=0} = k_p\alpha I_0M_0$$

hence

$$\left.\frac{d\mu_1^*}{d\xi}\right|_{\xi=1} = -(1 - \theta)M_0$$

The general solution of eq 18 reads

$$\mu_1^* = C_1F\left(-\frac{\sigma}{\rho},\varphi,\rho\xi\right) + C_2\xi^{1-\varphi}F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\xi\right) + \frac{H_0}{\sigma} \quad (19)$$

where, $F(a,b,c)$ is the Kummer function, which is defined by

$$F(a,b,c) = 1 + \sum_{k=1}^{\infty}\prod_{j=1}^{k}\left(\frac{j-1+a}{j-1+b}\right)\frac{(c)^k}{k!}$$

The derivation of eq 19 is given in Appendix 1. Then, we can determine C_1 and C_2:

$$C_1 = \left[\left(\alpha I_0 - \frac{H_0}{\sigma}\right)(1 - \varphi)F\left(1-\varphi-\frac{\sigma}{\rho},1-\varphi,\rho\right) + (1 - \theta)M_0F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\right)\right]\Big/\left[(1 - \varphi)F\left(1-\varphi-\frac{\sigma}{\rho},1-\varphi,\rho\right)F\left(-\frac{\sigma}{\rho},\varphi,\rho\right) + \frac{\sigma}{\varphi}F\left(1-\frac{\sigma}{\rho},1+\varphi,\rho\right)F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\right)\right]$$

$$C_2 = \left[(\sigma\alpha I_0 - H_0)F\left(1-\frac{\sigma}{\rho},1+\varphi,\rho\right) - \varphi(1 - \theta)M_0F\left(-\frac{\sigma}{\rho},\varphi,\rho\right)\right]\Big/\left[\varphi(1 - \varphi)F\left(1-\varphi-\frac{\sigma}{\rho},1-\varphi,\rho\right) \times F\left(-\frac{\sigma}{\rho},\varphi,\rho\right) + \sigma F\left(1-\frac{\sigma}{\rho},1+\varphi,\rho\right)F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\right)\right]$$

Substituting eq 19 into eq 13 and integrating the resulting differential equation, one obtains

$$\mu_2 = I_0 + M_0x + \frac{2M_0k_p}{\lambda}\left\{C_1\frac{\varphi - 1}{\sigma + \rho}\left[F\left(-1-\frac{\sigma}{\rho},\varphi-1,\rho-\rho x\right) - F\left(-1-\frac{\sigma}{\rho},\varphi-1,\rho\right)\right] - \frac{C_2}{2 - \varphi}\left[(1 - x)^{2-\varphi}F\left(1-\varphi-\frac{\sigma}{\rho},3-\varphi,\rho-\rho x\right) - F\left(1-\varphi-\frac{\sigma}{\rho},3-\varphi,\rho\right)\right] + \frac{H_0}{\sigma}x\right\} \quad (20)$$

The expressions of number- and weight-average degrees of polymerization are

$$\overline{P_n'} = \frac{\mu_1}{\mu_0} = \frac{I_0 + M_0x}{I_0 + \theta M_0x} \quad (21)$$

$$\overline{P_w'} = \mu_2/\mu_1 \quad (22)$$

and the polydispersity index is expressed by

$$D' = \overline{P_w'}/\overline{P_n'} \quad (23)$$

Equations 11, 14, and 20 are the rigorous expressions of respective moments of resulting polymer; therefore, eqs 21 and 22 are the precise formulas of number- and weight-average degrees of polymerization, respectively.

Effect of Residual Initiator

Up to now, the initiator was regarded as the unimer; however, the residual initiator is usually excluded by precipitation in real experiments. Therefore its concentration ($P_1 = P_1^* + P_1' + P_1''$) must be ruled out from various moments when we carry out the calculation of average degrees of polymerization, even though eqs 21 and 22 were derived without any approximation. It was shown earlier that the effect of residual initiator can lead to enormous deviations in the MWD averages and the polydispersity index.[4] The concentration of residual initiator can be found from eqs 1, 3, and 4:

$$\frac{dP_1}{d\xi} = \frac{k_pM_0}{\lambda}P_1^* - \theta M_0 \quad (24)$$

where only $i = 1$ in eqs 3 and 4 is taken into account. From eqs 1, 3, and 4, we can get the following second-order differential equation which is analogous to eq 18:

$$\xi\frac{d^2P_1^*}{d\xi^2} + (\varphi - \rho'\xi)\frac{dP_1^*}{d\xi} + \sigma'P_1^* = H_0' \quad (25)$$

with the initial conditions

$$P_1{}^*|_{\xi=1} = \alpha I_0$$

$$\left.\frac{\mathrm{d}P_1{}^*}{\mathrm{d}\xi}\right|_{\xi=1} = (1-\theta)M_0$$

where

$$\rho' = M_0/\alpha I_0$$

$$\sigma' = M_0(k_1C - \lambda)/\alpha I_0\lambda$$

and

$$H_0{}' = \theta M_0(k_1C - \lambda)/\lambda$$

Similarly, we can find the solution of eq 25 and, combining with eq 24, finally obtain

$$P_1 = I_0 + \theta M_0 x - \frac{M_0 k_{\mathrm{p}}}{\lambda}\Big\{C_1{}'\frac{\varphi-1}{\sigma'+\rho'}\Big[F\Big(-1-\frac{\sigma'}{\rho'},\varphi-1,\rho'-\rho'x\Big) - F\Big(-1-\frac{\sigma'}{\rho'},\varphi-1,\rho'\Big)\Big] - \frac{C_2{}'}{2-\varphi}\Big[(1-x)^{2-\varphi}F\Big(1-\varphi-\frac{\sigma'}{\rho'},3-\varphi,\rho'-\rho'x\Big) - F\Big(1-\varphi-\frac{\sigma'}{\rho'},3-\varphi,\rho'\Big)\Big] + \frac{H_0{}'}{\sigma'}x\Big\} \quad (26)$$

where $C_1{}'$ and $C_2{}'$ are determined by

$$C_1{}' = \Big[\Big(\alpha I_0 - \frac{H_0{}'}{\sigma'}\Big)(1-\varphi)F\Big(1-\varphi-\frac{\sigma'}{\rho'},1-\varphi,\rho'\Big) + (1-\theta)M_0F\Big(1-\varphi-\frac{\sigma'}{\rho},2-\varphi,\rho'\Big)\Big]\Big/\Big[(1-\varphi)F\Big(1-\varphi-\frac{\sigma'}{\rho'},1-\varphi,\rho'\Big)F\Big(-\frac{\sigma'}{\rho'},\varphi,\rho'\Big) + \frac{\sigma'}{\varphi}F\Big(1-\frac{\sigma'}{\rho'},1+\varphi,\rho'\Big)F\Big(1-\varphi-\frac{\sigma'}{\rho'},2-\varphi,\rho'\Big)\Big]$$

$$C_2{}' = \Big[(\sigma'\alpha I_0 - H_0)F\Big(1-\frac{\sigma'}{\rho'},1+\varphi,\rho'\Big) - \varphi(1-\theta)M_0F\Big(-\frac{\sigma'}{\rho'},\varphi,\rho'\Big)\Big]\Big/\Big[\varphi(1-\varphi)F\Big(1-\varphi-\frac{\sigma'}{\rho'},1-\varphi,\rho'\Big)F\Big(-\frac{\sigma'}{\rho'},\varphi,\rho'\Big) + \sigma'F\Big(1-\frac{\sigma'}{\rho'},1+\varphi,\rho'\Big)F\Big(1-\varphi-\frac{\sigma'}{\rho'},2-\varphi,\rho'\Big)\Big]$$

Finally, the modified number- and weight-average degrees of polymerization are given by

$$\overline{P_n} = \frac{\mu_1 - P_1}{\mu_0 - P_1} \quad (27)$$

$$\overline{P_{\mathrm{w}}} = \frac{\mu_2 - P_1}{\mu_1 - P_1} \quad (28)$$

The modified expression of polydispersity index is

$$D = \overline{P_{\mathrm{w}}}/\overline{P_n} \quad (29)$$

which is more appropriate to experimental data than eq 23.

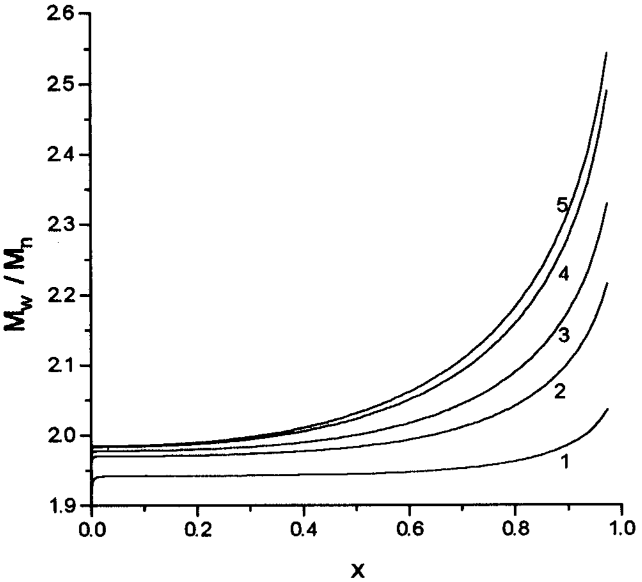


Figure 1. Dependence of polydispersity index on rate constant of chain transfer to monomer: $I_0 = 0.01$ mol L^{-1}, $M_0 = 1$ mol L^{-1}, $C_0 = 0.1$ mol L^{-1}, $E_0 = 0$; $k_{\mathrm{p}} = 2 \times 10^4$, $k_1 = 0.01$, $k_2 = 10^9$. (1) $k_{\mathrm{tr}} = 300$, (2) $k_{\mathrm{tr}} = 100$, (3) $k_{\mathrm{tr}} = 50$, (4) $k_{\mathrm{tr}} = 10$, and (5) $k_{\mathrm{tr}} = 1$ (all in L mol^{-1} s^{-1}).

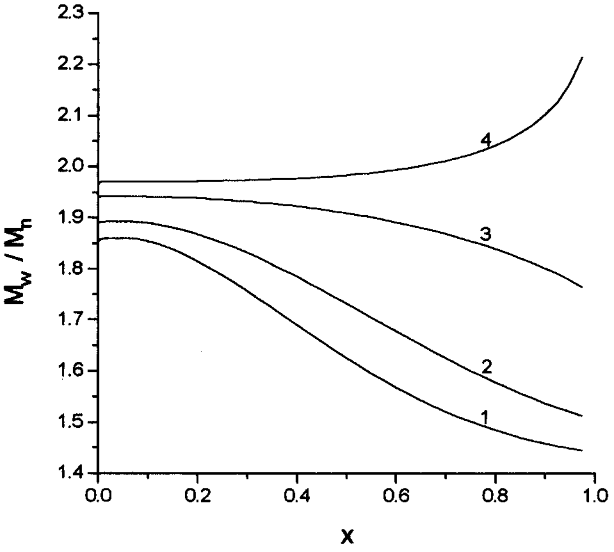


Figure 2. Relationship between polydispersity index and monomer conversion with various rate constants of activation, k_1 (and equilibrium constants, K_{E}): (1) $k_1 = 1$, (2) $k_1 = 0.5$, (3) $k_1 = 0.1$, and (4) $k_1 = 0.01$ (all in L mol^{-1} s^{-1}); for other reaction conditions, see Figure 1.

Extension to Other Systems

There are a number of polymerization systems with reversible deactivation mechanisms, which may also involve monomer transfer. The differential equations 11, 14, 20, and 26 are appropriate to all of these reaction systems; therefore, the expressions of average degrees of polymerization, polydispersity index, concentration of residual initiator, i.e., eqs 21−23 and 27−29, remain valid for various polymerization systems with monomer transfer if the coefficients in these equations are replaced by the corresponding ones listed in Table 1 and Table 2. A more detailed comparison of the various mechanisms of activity exchange will be given in a later publication.[11] The symbols in Table 1 and Table 2 have the same meanings as previously.

Table 1. List of Reversible Deactivation Mechanisms and Coefficients in the Expressions of Various Moments[a]

No.	Mechanism of activity exchange	α	φ
1	$C + P_i' \underset{k_2}{\overset{k_1}{\rightleftharpoons}} + P_i^* + E$ cat. pol (free ion generation); atom transfer radical polymerization; dissociative mech of GTP	$\dfrac{w - \sqrt{w^2 - 4K_E(K_E - 1)I_0C_0}}{2I_0(K_E - 1)}$ $W = K_E(I_0 + C_0) + E_0$	$1 - \dfrac{k_1(C_0 - \alpha I_0) + k_2(E_0 + \alpha I_0)}{(k_p + k_{tr})\alpha I_0}$
2	$P_i' \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_i^* + E$ TEMPO-mediated radical polymerization	$\dfrac{-(E_0 + K_E) + \sqrt{(E_0 + K_E)^2 + 4K_EI_0}}{2I_0}$	$1 - \dfrac{k_1 + k_2(E_0 + \alpha I_0)}{(k_p + k_{tr})\alpha I_0}$
3	$C + P_i' \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_i^*$ cat. pol (ion pair generation); associative mech of GTP	$\dfrac{w - \sqrt{w^2 - 4K_E^{\,2}I_0C_0}}{2I_0K_E}$ $w = K_E(I_0 + C_0) + 1$	$1 - \dfrac{k_1(C_0 - \alpha I_0) + k_2}{(k_p + k_{tr})\alpha I_0}$
4	$P_i' \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P_i^*$ isomerization	$\dfrac{K_E}{1 + K_E}$	$1 - \dfrac{k_1 + k_2}{(k_p + k_{tr})\alpha I_0}$
5	$P_i^* + P_j' \underset{k_{ex}}{\overset{k_{ex}}{\rightleftharpoons}} P_j' + P_i^*$ degenerative transfer	depending on mechanism of activation	$1 - \dfrac{k_{ex}}{(k_p + k_{tr})}$

No.	σ	ρ	H_0
1	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})^2\alpha^2 I_0^{\,2}}$	$\dfrac{k_{tr}M_0}{(k_p + k_{tr})\alpha I_0}$	$\dfrac{M_0k_1(C_0 - \alpha I_0)}{(k_p + k_{tr})\alpha I_0} - M_0$
2	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})^2\alpha^2 I_0^{\,2}}$	$\dfrac{k_{tr}M_0}{(k_p + k_{tr})\alpha I_0}$	$\dfrac{M_0k_1}{(k_p + k_{tr})\alpha I_0} - M_0$
3	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})^2\alpha^2 I_0^{\,2}}$	$\dfrac{k_{tr}M_0}{(k_p + k_{tr})\alpha I_0}$	$\dfrac{M_0k_1(C_0 - \alpha I_0)}{(k_p + k_{tr})\alpha I_0} - M_0$
4	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})^2\alpha^2 I_0^{\,2}}$	$\dfrac{k_{tr}M_0}{(k_p + k_{tr})\alpha I_0}$	$\dfrac{M_0k_1}{(k_p + k_{tr})\alpha I_0} - M_0$
5	$\dfrac{-M_0k_{tr}(k_p + k_{tr} - k_{ex})\alpha I_0}{(k_p + k_{tr})^2\alpha^2 I_0^{\,2}}$	$\dfrac{k_{tr}M_0}{(k_p + k_{tr})\alpha I_0}$	$\dfrac{M_0k_{ex}}{(k_p + k_{tr})} - 1$

[a] Equilibrium constant $K_E = k_1/k_2$ (k_1, k_2 are rate constants of activation and deactivation, respectively).

Table 2. List of Coefficients in the Expression of Residual Initiator Concentration for Various Reversible Termination Mechanisms

no.	ρ′	σ′	H_0'
1	$\dfrac{M_0}{\alpha I_0}$	$\dfrac{-M_0[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})\alpha^2 I_0^{\,2}}$	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})^2\alpha I_0}$
2	$\dfrac{M_0}{\alpha I_0}$	$\dfrac{-M_0[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})\alpha^2 I_0^{\,2}}$	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})^2\alpha I_0}$
3	$\dfrac{M_0}{\alpha I_0}$	$\dfrac{-M_0[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})\alpha^2 I_0^{\,2}}$	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1(C_0 - \alpha I_0)]}{(k_p + k_{tr})^2\alpha I_0}$
4	$\dfrac{M_0}{\alpha I_0}$	$\dfrac{-M_0[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})\alpha^2 I_0^{\,2}}$	$\dfrac{-M_0k_{tr}[(k_p + k_{tr})\alpha I_0 - k_1]}{(k_p + k_{tr})^2\alpha I_0}$
5	$\dfrac{M_0}{\alpha I_0}$	$\dfrac{-M_0(k_p + k_{tr} - k_{ex})\alpha I_0}{(k_p + k_{tr})\alpha^2 I_0^{\,2}}$	$\dfrac{-M_0k_{tr}(k_p + k_{tr} - k_{ex})}{(k_p + k_{tr})^2}$

Numerical Results and Discussion

As a typical example, the average molecular weights and the polydispersity index of the polymer generated from cationic polymerization with monomer transfer and an equilibrium between covalent species and free ions are calculated in terms of the expressions given in preceding sections. From Figure 1 it can be concluded that the polydispersity index of the resulting polymer approaches $D = 2$ with increasing monomer transfer rate constant, k_{tr}; i.e., the resultant polymer approximately corresponds to a Schulz–Flory distribution when the ratio of k_{tr} to k_p is larger. The same conclusion was reported for ionic polymerization without dormant species.[9] The ratio of k_1 to k_2 (i.e., the equilibrium constant

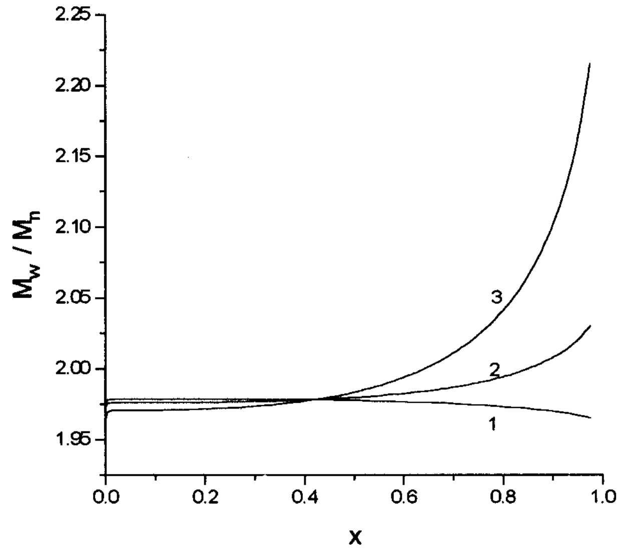


Figure 3. Plot of polydispersity index versus monomer conversion with various ratios of M_0/I_0: (1) $I_0 = 0.002$, (2) $I_0 = 0.004$, and (3) $I_0 = 0.01$ (all in mol L^{-1}); for other reaction conditions, see Figure 1.

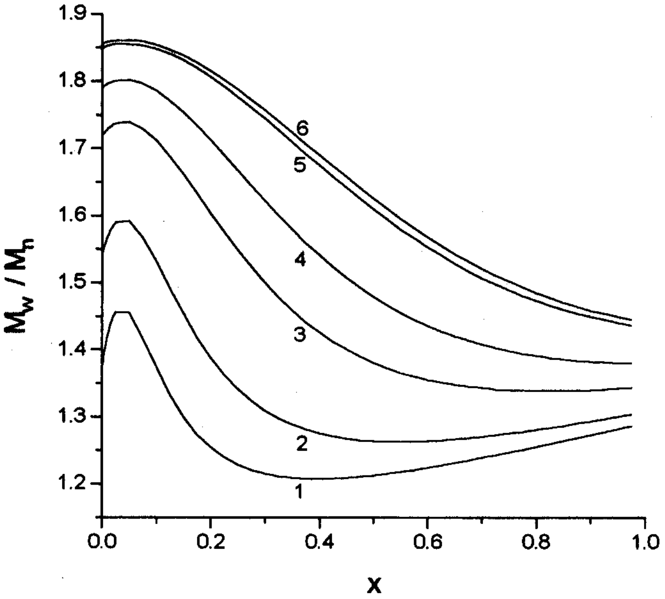


Figure 4. Effect of common ion concentration, E_0, on polydispersity index: (1) $E_0 = 10^{-5}$, (2) $E_0 = 5 \times 10^{-6}$, (3) $E_0 = 2 \times 10^{-6}$, (4) $E_0 = 1 \times 10^{-6}$, (5) $E_0 = 10^{-7}$, and (6) $E_0 = 0$ (all in mol L^{-1}); $k_1 = 50$ L mol^{-1} s^{-1}; for other reaction conditions, see Figure 1.

K_E) can also influence the polydispersity. A higher value of K_E will lead to a lower polydispersity index (Figure 2). The dependence of polydispersity index on various reaction conditions is given in Figures 3 and 4. It is found that the polydispersity index increases with the decreasing M_0/I_0. Figure 4 indicates that the polydispersity index of the resulting polymer is lowered if the foreign counterions are put into the reaction system and decreases with the increasing of salt concentration. For the polymerization of indene with the cumyl chloride/titanium tetrachloride initiating system at 5 °C in methylene chloride,[1] the comparison of calculated number-average degree of polymerization with experimental data reported by Matyjaszewski and Sigwalt[1] is illustrated in Figure 5. Line 2 in Figure 5 was drawn when the monomer conversion equals 0.9,

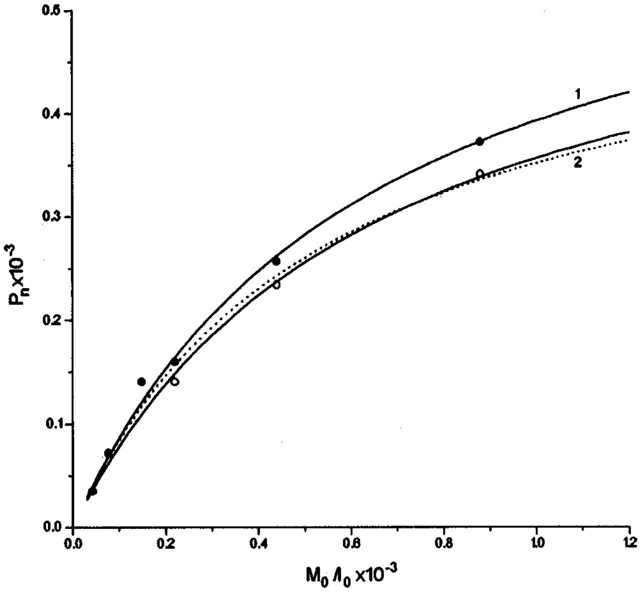


Figure 5. Dependence of P_n on the initial molar ratio of monomer to initiator in the polymerization of indene with the cumyl chloride/titanium tetrachloride initiating system at 5 °C in methylene chloride:[7] (●) experiments without DMSO; (○) experiments in the presence of DMSO; (1) theoretical curve, $k_{tr}/k_p = 1.5 \times 10^{-4}$, complete conversion; (2) theoretical curve, $k_{tr}/k_p = 1.75 \times 10^{-3}$, monomer conversion 90%; dotted line, theoretical curve, $k_{tr}/k_p = 1.75 \times 10^{-3}$, complete conversion.

which fits for the experimental data better than that for full monomer conversion (dotted line).

Acknowledgment. This work was sponsored by the National Natural Sciences Foundation of China.

Appendix 1

For the convenience of derivation, eq 18 is written by

$$\xi \frac{d^2y}{d\xi^2} + (\varphi - \rho\xi)\frac{dy}{d\xi} + \sigma y = H_0 \tag{A1}$$

The corresponding homogeneous differential equation of eq A1 reads

$$\xi \frac{d^2y}{d\xi^2} + (\varphi - \rho\xi)\frac{dy}{d\xi} + \sigma y = 0 \tag{A2}$$

We can find the following solution of eq A2 by a normal procedure of series solution:

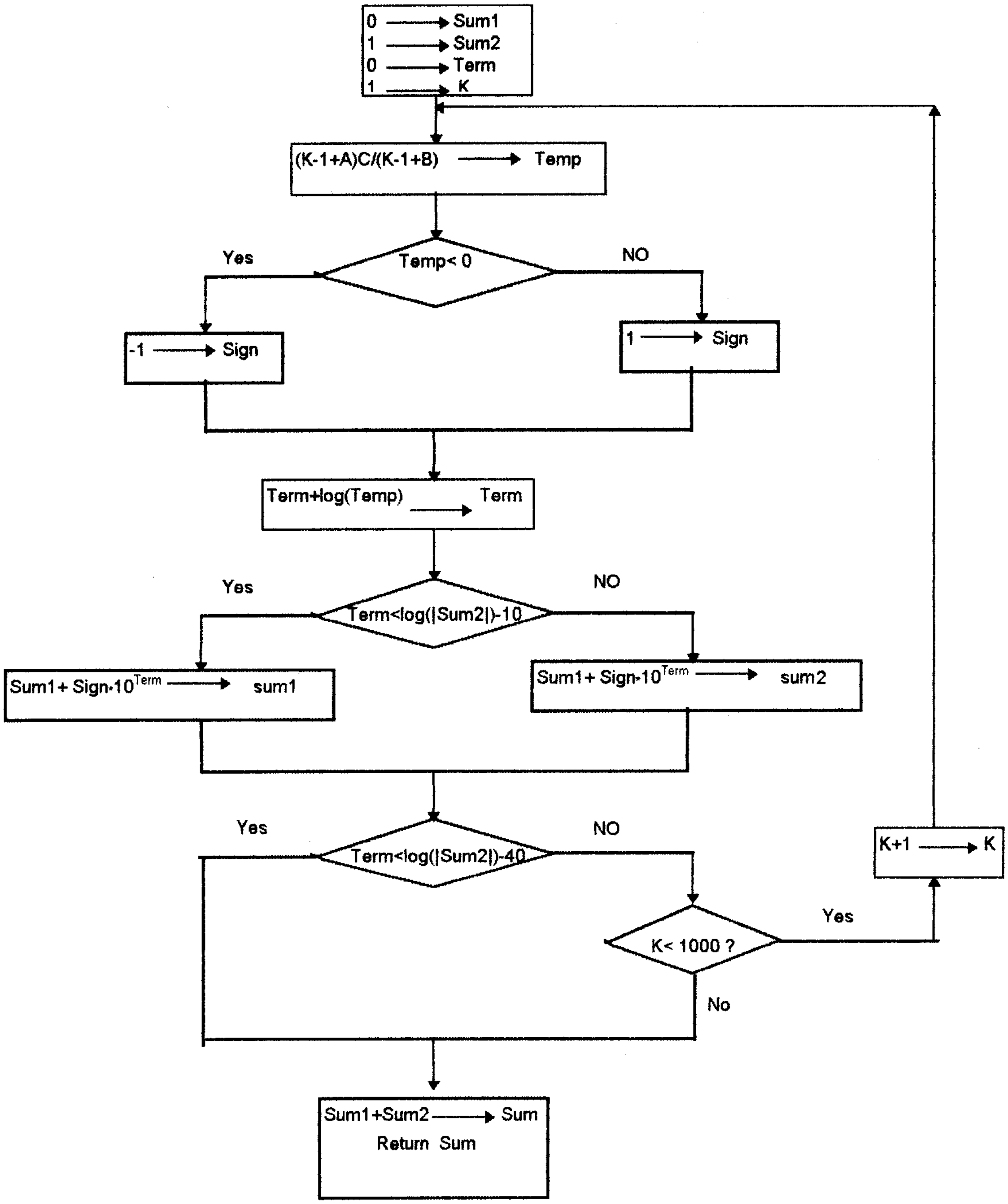
$$y(\xi) = AF\left(-\frac{\sigma}{\rho},\varphi,\rho\xi\right) + B\xi^{1-\varphi}F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\xi\right) \tag{A3}$$

Furthermore, one can suppose that the special solution of eq A1 is as follows:

$$y^*(\xi) = F\left(-\frac{\sigma}{\rho},\varphi,\rho\xi\right) + \xi^{1-\varphi}F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\xi\right) + Q \tag{A4}$$

where Q is a constant to be determined. By substitution

Chart 1



of eq A4 into eq A1, one has

$$Q = H_0/\sigma$$

Hence, the general solution of eq A1 can be given by

$$y = y(\xi) + y^*(\xi) = C_1 F\left(-\frac{\sigma}{\rho},\varphi,\rho\xi\right) + C_2\xi^{1-\varphi}F\left(1-\varphi-\frac{\sigma}{\rho},2-\varphi,\rho\xi\right) + \frac{H_0}{\sigma} \tag{A5}$$

Appendix 2

The main difficulty in this program is calculation of the Kummer function. The values of the terms in the function are very large and there exists the large-term "eating" the small-term problem due to the precision limit of the computer. The flow chart for the Kummer function, Kummer(*A*, *B*, *C*), is shown in Chart 1.

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