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limit to d/dx. Conversion of the remaining part of the matrix equation to continuous variables and integration over x gives

$$\int_{-1}^{1}|x-y|^{-1/2}g(y)\,\mathrm{d}y = w(x) + K \qquad \text{(A18)}$$

where K is an integration constant. K has to be chosen so that $g(x)$ satisfies the continuous version of eq A11, i.e.

$$\int_{-1}^{1}g(x)\,\mathrm{d}x = 0 \qquad \text{(A19)}$$

A last transformation appreciably simplifies the integral equation. Let

$$g(x) = 1 + Kf(x) \qquad \text{(A20)}$$

Equation A18 becomes

$$\int_{-1}^{1}|x-y|^{-1/2}f(x)\,\mathrm{d}x = 1 \qquad \text{(A21)}$$

while (A19) gives

$$K = -2/\int_{-1}^{1}f(x)\,\mathrm{d}x \qquad \text{(A22)}$$

Equation A17 reduces to

$$D_1{}^{\mathrm{P}}/D_0 = 1 + [3K/8(2^{1/2})] \qquad \text{(A23)}$$

The solution of eq A21 has been obtained by two independent approaches. The method of Latta[17] is relatively elementary to work through. The integral transforms of the Gegenbauer polynomials presented by Auer and Gardner[18] are not so elementary to derive, but it is perhaps more straightforward to use their formulas. With either method one derives

$$f(x) = [\pi(2^{1/2})]^{-1}(1-x^2)^{-1/4} \qquad \text{(A24)}$$

With eq A22 to A24 it is a matter of manipulating Γ functions to derive the result given in eq 4.14.

We have verified the observation of Stockmayer that our result for the diffusion constant with preaveraged HI is identical with that based on the Kirkwood-Riseman equation; see Yamakawa,[9] p 272. The analytical formula of Zimm[2] contains a typographical error; the corresponding numerical result is in agreement with ours.

References and Notes

(1) Hynes, J. T. *Annu. Rev. Phys. Chem.* **1977**, *28*, 301–21.
(2) Zimm, B. H. *Macromolecules* **1980**, *13*, 592.
(3) Fixman, M. *Macromolecules*, preceding paper in this issue.
(4) We wish to acknowledge a stimulating workshop on the subject "Hydrodynamic Interactions in Stochastic Dynamics", organized by H. J. C. Berendsen. At the time of the workshop, Oct 1979, hydrodynamic interactions seem not to have been included in polymer simulations. However, dimers and trimers have been studied (Ermak, D. L.; McCammon, J. A. *J. Chem. Phys.* **1978**, *69*, 1352–60), and David Ceperley has studied decamers (private communication). These workers used matrix decomposition of the HI matrix, e.g., Cholesky factorization. Such methods are slow compared to the iterative technique, taking computation time $O(N^3)$, but are exact.
(5) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1527–37.
(6) Zwanzig, R. *Adv. Chem. Phys.* **1969**, *15*, 325–31.
(7) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1966**, *44*, 2107–15.
(8) Bixon, M.; Zwanzig, R. *J. Chem. Phys.* **1978**, *68*, 1890–5.
(9) Yamakawa, H. "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(10) Bellman, R. "Introduction to Matrix Algebra"; McGraw-Hill: New York, 1960; p 177, problem 5.
(11) Osaki, K. *Adv. Polym. Sci.* **1973**, *12*, 1–64.
(12) Horta, A.; Fixman, M. *J. Am. Chem. Soc.* **1968**, *90*, 3048–55. See also Dubois-Violette, E.; de Gennes, P. G. *Physica* **1967**, *3*, 181–98 for related results.
(13) Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3831–7.
(14) Fixman, M. *J. Chem. Phys.* **1978**, *69*, 1538–45.
(15) Lodge, A. S.; Wu, Y. *Rheol. Acta* **1971**, *10*, 539–53.
(16) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1965**, *42*, 3838–44.
(17) Cochran, J. A. "The Analysis of Linear Integral Equations"; McGraw-Hill: New York, 1972; p 301.
(18) Auer, P. L.; Gardner, C. S. *J. Chem. Phys.* **1955**, *23*, 1545–6.
(19) Rotne, J.; Prager, S. *J. Chem. Phys.* **1969**, *50*, 4831–7.
(20) Fixman, M. "Variational Theorem for the Generalized Diffusion Tensor", preprint submitted to *J. Chem. Phys.*
(21) Wilemski, G.; Tanaka, G. *Macromolecules* **1981**, *14*, 1531.
(22) Fixman, M. "Variational Bounds for Polymer Transport Coefficients", in preparation.
(23) Feynman, R. P. "Statistical Mechanics"; W. A. Benjamin: Reading, Mass., 1972, p 67.

Theoretical Study of Transfer Reactions in Ionic Polymerizations Involving Two Propagating Species

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ABSTRACT: The influence of a transfer agent on the molecular weight distribution of ionic polymerizations in which two active species intervene has been theoretically analyzed. A kinetic scheme that assumes instantaneous initiation as well as instantaneous reinitiation after transfer is used to obtain several mathematical expressions for the number- and weight-average molecular weights. In the same way, the effect of the rate constant of the different active species on the molecular weight averages is also discussed.

Introduction

Living polymers can be prepared only when both termination and transfer reactions are absent. When this is true and the initiation step is instantaneous, a single type of ionic species contributes to the growing chains, so that in most cases the resulting polymer has a narrow Poisson distribution of chain lengths.[1] In ionic polymerization, broadening of the distribution may occur because of different factors, such as slow initiation, spontaneous transfer, and transfer to monomer. The influence of most of these factors on the molecular weight distribution has been theoretically studied in the past.[2-15] Very recently, the

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influence of the transfer agent on the distribution of chain lengths in the case of both instantaneous and slow initiation has been reported.[16,17]

Ionic polymerizations in which two active species contribute to the growing chains have been widely investigated. Thus, in the polymerization of tetrahydrofuran with different ionic salts, Penczek and co-workers[18,19] have shown that the value of the propagation constants through the free macroion and the ionic pair are identical in nitromethane and in methylene chloride. Sangster and Worsfold,[20] however, have obtained different values for these quantities with triethyloxonium tetrafluoroborate as catalyst. In the polymerization of 3,3-dimethyloxetane, Goethals[21] has found that the difference between the two propagation constants approaches zero in methylene chloride. Other investigators arrive at different results in the polymerization of bicyclic amines,[22] the propagation constant in this case being larger for ionic pairs than for free ions. Finally, in the anionic polymerization of ethylene oxide with carbazide salts,[23] with potassium as counterion, the two propagation constants have similar values, but in the polymerization of propylene sulfide they are different.[23]

In the past years, a large amount of work has been done on different cationic polymerizations in which ionic and covalent active species act concurrently. Examples of reactions of this type are the polymerizations of styrene by perchloric acid[24] and acetyl perchlorate,[25] of *p*-methoxystyrene by superacids,[26] of cyclic ethers by acyl perchlorates[27-30] and by superacids and their derivatives,[31-33] and of cyclic imino ethers by alkyl halides.[34] All of these catalysts have counterions giving covalent character to the growing species. In addition, of course, there is an ester ⇄ ion equilibrium which will be displaced to the right or to the left depending on the polarity of the reaction medium.

In the case of ionic polymerizations through two active species, transfer reactions may also occur that affect the different growing species. Therefore, it may be important to study the influence of the transfer agent on the molecular weight distribution in order to achieve a better understanding of such ionic polymerization mechanisms. This work focuses on the theoretical analysis of the distribution of chain lengths in polymerizations where two active species intervene and, at the same time, transfer reactions take place with substances of the reaction medium.

Kinetic Scheme

Let us consider that the kinetic scheme involves the following stages:

initiation

$$\mathrm{I} + \mathrm{M} \xrightarrow{k_i} \mathrm{N}_1{}^* + \mathrm{N}_1{}^{**}$$

propagation

$$\mathrm{N}_i{}^* + \mathrm{M} \xrightarrow{k_p{}^*} \mathrm{N}_{i+1}{}^*$$

$$\mathrm{N}_i{}^{**} + \mathrm{M} \xrightarrow{k_p{}^{**}} \mathrm{N}_{i+1}{}^{**}$$

transfer

$$\mathrm{N}_i{}^* + \mathrm{T} \xrightarrow{k_t{}^*} \mathrm{N}_i + \mathrm{I}$$

$$\mathrm{N}_i{}^{**} + \mathrm{T} \xrightarrow{k_t{}^{**}} \mathrm{N}_i + \mathrm{I}$$

where I, M, $\mathrm{N}_i{}^*$, $\mathrm{N}_i{}^{**}$, T, and N_i represent, respectively, the initiator, the monomer, the two active species, the transfer agent, and the inactive species. In the same way, $k_p{}^*$, $k_p{}^{**}$, $k_t{}^*$, and $k_t{}^{**}$ denote the propagation and transfer constants for the two species. Let us now assume that $k_i \to \infty$, so that all of the initiator is converted into active growing species. In this case, the fraction of each of the two active centers will be determined by the equilibrium constant (for both ionic and covalent species) or by the dissociation constant of the ionic pair when ionic pairs and free ions are the two active species present.

According to the kinetic scheme indicated above and as a consequence of the spontaneous initiation, chain transfer will cause instantaneous regeneration of an active chain. Therefore, the following condition must be fulfilled:

$$\sum_{i=1} (N_i{}^* + N_i{}^{**}) = I_0 \tag{1}$$

where I_0 is the amount of initiator at the beginning of the reaction and $N_i{}^*$ and $N_i{}^{**}$ are the concentrations of $\mathrm{N}_i{}^*$ and $\mathrm{N}_i{}^{**}$. Moreover, since the time is counted from the very moment at which all of the initiator is depleted, the initial conditions will be

$$M_0 = M_{\mathrm{in}} - I_0 \qquad (N_1{}^* + N_1{}^{**})_0 = I_0$$

$$(N_i{}^* + N_i{}^{**}) = 0 \qquad i \geq 2$$

$$N_i = 0 \qquad i \geq 1$$

where M_{in} is the total amount of monomer present before initiator is added to the reaction medium.

The following kinetic equations describe the depletion rate of the active species:

$$\mathrm{d}(N_1{}^* + N_1{}^{**})/\mathrm{d}t = -[(k_p{}^*M + k_t{}^*T)N_1{}^* + (k_p{}^{**}M + k_t{}^{**}T)N_1{}^{**}] + (k_t{}^*\sum N_i{}^* + k_t{}^{**}\sum N_i{}^{**})T \tag{2}$$

$$\mathrm{d}N_i{}^*/\mathrm{d}t = -(k_p{}^*M + k_t{}^*T)N_i{}^* + k_p{}^*MN_{i-1}{}^* \qquad i \geq 2 \tag{3a}$$

$$\mathrm{d}N_i{}^{**}/\mathrm{d}t = -(k_p{}^{**}M + k_t{}^{**}T)N_i{}^{**} + k_p{}^{**}MN_{i-1}{}^{**} \qquad i \geq 2 \tag{3b}$$

Here M and T are the concentrations of M and T.

In the same way, inactive species will be formed according to the following equation:

$$\mathrm{d}N_i/\mathrm{d}t = (k_t{}^*N_i{}^* + k_t{}^{**}N_i{}^{**})T \qquad i \geq 1 \tag{4}$$

The depletion rates of monomer and transfer agent are expressed by

$$-\mathrm{d}M/\mathrm{d}t = (k_p{}^*\sum N_i{}^* + k_p{}^{**}\sum N_i{}^{**})M + (k_t{}^*\sum N_i{}^* + k_t{}^{**}\sum N_i{}^{**})T \tag{5}$$

$$-\mathrm{d}T/\mathrm{d}t = (k_t{}^*\sum N_i{}^* + k_t{}^{**}\sum N_i{}^{**})T \tag{6}$$

The number and weight chain length distributions can be obtained from the above equations. However, for the sake of simplicity, the analysis will be limited to the determination of the polydispersity index i_w/i_n, where chain length averages i_w and i_n are defined as

$$i_n = \frac{\sum_i i(N_i{}^* + N_i{}^{**} + N_i)}{\sum_i (N_i{}^* + N_i{}^{**} + N_i)} \tag{7a}$$

$$i_w = \frac{\sum_i i^2(N_i{}^* + N_i{}^{**} + N_i)}{\sum_i i(N_i{}^* + N_i{}^{**} + N_i)} \tag{7b}$$

The differential rate equations (2)–(6) refer to the general case in which the two active species are not interdependent, on the understanding that the lack of interdependence between them is only relative because the concentrations of the two active species are usually related by an equilibrium constant when covalent and ionic species coexist or through a dissociation constant when ionic pairs and free ions are the active centers present. In our case it will be assumed that the concentration of the two active species remains constant during the course of the reaction; that is

$$\Sigma N_i^{**} = K\Sigma N_i^{*} \qquad (8)$$

It should be stressed that K denotes the equilibrium constant or the dissociation constant, depending, as was indicated above, on the nature of the active species.

In order to correlate the averages i_n and i_w with the kinetic parameters, we define three generating functions:

$$G^* = \Sigma N_i^* y^i \qquad G^{**} = \Sigma N_i^{**} y^i \qquad G = \Sigma N_i y^i \qquad (9)$$

By using the differential equations indicated in (3) and (4) one obtains

$$\mathrm{d}G/\mathrm{d}t = k_t^* TG^* + k_t^{**} TG^{**} \qquad (10)$$

$$\mathrm{d}G^*/\mathrm{d}t = -\{(1-y)k_p^* M + k_t^* T\}G^* + k_t^* T\Sigma N_i^* y \qquad (11)$$

$$\mathrm{d}G^{**}/\mathrm{d}t = -\{(1-y)k_p^{**} M + k_t^{**} T\}G^{**} + k_t^{**} T\Sigma N_i^{**} y \qquad (12)$$

Finally, by applying the operator $y(\partial/\partial y)$ successively to the three equations and putting $y = 1$, one obtains the following differential equations:

$$\Sigma i(N_i^* + N_i^{**} + N_i) = I_0 + \int_0^t \{[k_p^*\Sigma N_i^* + k_p^{**}\Sigma N_i^{**}]M + [k_t^*\Sigma N_i^* + k_t^{**}\Sigma N_i^{**}]T\}\,\mathrm{d}t \qquad (13)$$

$$\Sigma i^2(N_i^* + N_i^{**} + N_i) = \Sigma i(N_i^* + N_i^{**} + N_i) + \int_0^t \{2k_p^*[\Sigma iN_i^*] + 2k_p^{**}[\Sigma iN_i^{**}]\}M\,\mathrm{d}t \qquad (14)$$

$$\mathrm{d}(\Sigma iN_i^*) + k_t^* T(\Sigma iN_i^*)\,\mathrm{d}t = (k_p^* M + k_t^* T)(I_0/\gamma)\,\mathrm{d}t \qquad (15)$$

$$\mathrm{d}(\Sigma iN_i^{**}) + k_t^{**} T(\Sigma iN_i^{**})\,\mathrm{d}t = (k_p^{**} M + k_t^{**} T)(I_0/\gamma)K\,\mathrm{d}t \qquad (16)$$

$$\Sigma N_i = \int_0^t [k_t^*(\Sigma N_i^*) + k_t^{**}(\Sigma N_i^{**})]T\,\mathrm{d}t \qquad (17)$$

Let us now consider three different situations which can arise depending on whether both M and T remain constant or not. The case in which both M and T change with time will be the first considered.

As indicated above, the concentration of each of the two species remains constant, the sum of them being equal to the initial catalyst concentration:

$$\Sigma N_i^{**} = K\Sigma N_i^* \qquad \Sigma N_i^* = I_0/(1+K) \qquad (18)$$

Upon substitution of these equations into (6) one gets

$$-\frac{\mathrm{d}T}{\mathrm{d}t} = \left(k_t^*\frac{I_0}{1+K} + k_t^{**}\frac{I_0}{1+K}K\right)T \qquad (19)$$

$$T = T_0 \exp\left(-\frac{\alpha}{\gamma}I_0 t\right) \qquad (20)$$

where $\alpha = k_t^* + k_t^{**}K$ and $\gamma = 1 + K$. In the same way, the dependence of M on time, obtained from eq 5, 18, and 20, is given by

$$-\frac{\mathrm{d}M}{\mathrm{d}t} = \left(k_p^*\frac{I_0}{1+K} + k_p^{**}\frac{I_0}{1+K}K\right)M + \left(k_t^*\frac{I_0}{1+K} + k_t^{**}\frac{I_0}{1+K}\right)T \qquad (21)$$

and

$$M = \left(M_0 + \frac{T_0}{r}\right)\exp\left(-\frac{\beta}{\gamma}I_0 t\right) - \frac{T_0}{r}\exp\left(-\frac{\alpha}{\gamma}I_0 t\right) \qquad (22)$$

where $\beta = k_p^* + k_p^{**}K$ and $r = \beta/\alpha - 1$.

The time at which the monomer concentration becomes zero is

$$\tau = \frac{\gamma}{(\beta - \alpha)I_0}\ln\left(1 + \frac{M_0}{T_0}r\right) \qquad (23)$$

where only the case $r > 0$ has been considered, that is, $k_p^* > k_t^*$ and $k_p^{**} > k_t^{**}$. There are two limiting values: if $r \rightarrow 0$

$$\tau = \frac{\gamma M_0}{\alpha I_0 T_0} \qquad (24)$$

if $r \rightarrow \infty$

$$\tau = \frac{\gamma}{\beta I_0}\ln\frac{\beta M_0}{\alpha T_0} \qquad (25)$$

The calculation of the averages i_n and i_w was carried out as set out above, with the results

$$\Sigma(N_i^* + N_i^{**} + N_i) = I_0 + T_0 - T \qquad (26)$$

$$\Sigma i(N_i^* + N_i^{**} + N_i) = M_{in} - M \qquad (27)$$

Therefore

$$i_n = \frac{M_{in} - M}{I_0 + T_0 - T} \qquad (28)$$

Once the monomer has been depleted, the number-average chain length is expressed by

$$(i_n)_\tau = M_{in}\Bigg/\left\{I_0 + T_0\left[1 - \left(1 + \frac{M_0 r}{T_0}\right)^{-1/r}\right]\right\} \qquad (29)$$

Two limiting situations can occur:

if $r \rightarrow \infty$

$$(i_n)_\tau = M_{in}/I_0 \qquad (30)$$

if $r \rightarrow 0$

$$(i_n)_\tau = M_{in}/\{I_0 + T_0[1 - \exp(-M_0/T_0)]\} \qquad (31)$$

The former case is similar to that which would be obtained if transfer agent were not present in the reaction medium and the latter reduces to $(i_n)_\tau = M_{in}/(I_0 + T_0)$ if $M_0 \gg T_0$, a normal situation in most ionic polymerizations. Moreover, the equations are similar to those previously reported for a single active species,[16] the only difference being that then the value of r is $(k_p - k_t)/k_t$.

As for the weight-average chain length, the integral involved in eq 14 can only be solved exactly, if r happens to be an integer m, by defining a new variable $x \exp[-(\alpha/\gamma)I_0 t] = T/T_0$. Under these circumstances

$$i_w = 1 + A/(M_{in} - M) \qquad (32)$$

where

$$A = \int_0^t [2k_p^*(\sum iN_i^*) + 2k_p^{**}(\sum iN_i^{**})]M\,\mathrm{d}t = \frac{2}{m}(\rho_1 + K\rho_2)T_0[1 - (T/T_0)] - \frac{2}{m+1}(\rho_1 + K\rho_2)\left(M_0 + \frac{T_0}{m}\right)[1 - (T/T_0)^{m+1}] + 2\exp(-T_0\sigma_1/I_0)\left[\frac{\phi_1}{I_0}\left(M_0 + \frac{T_0}{m}\right)\{\varphi_2 \exp(T_0\sigma_1/I_0) - \varphi_3 \exp(T\sigma_1/I_0)\} + \Lambda_1\frac{1}{m}\{\exp(T_0\sigma_1/I_0) - \exp(T\sigma_1/I_0)\}\right] + 2K\exp(-T_0\sigma_2/I_0)\left[\frac{\phi_2}{I_0}\left(M_0 + \frac{T_0}{m}\right) \times \{\varphi_2' \exp(T_0\sigma_2/I_0) - \varphi_3' \exp(T\sigma_2/I_0)\} + \Lambda_2\frac{1}{m}\{\exp(T_0\sigma_2/I_0) - \exp(T\sigma_2/I_0)\}\right] - \epsilon_1\left[\frac{\varphi_4}{m}(T_0/I_0) - \frac{\varphi_5}{I_0}\left(M_0 + \frac{T_0}{m}\right)\right] - \epsilon_2\left[\frac{\varphi_4'}{m}(T_0/I_0) - \frac{\varphi_5'}{I_0}\left(M_0 + \frac{T_0}{m}\right)\right] \quad (33)$$

In this equation the following definitions have been used:

$$\rho_1 = -\frac{1}{\alpha}\,\frac{k_p^*}{k_t^*}\left(k_t^* - \frac{k_p^*}{m}\right)$$

$$\sigma_1 = (\gamma/\alpha)k_t^*$$

$$\nu_1 = -\frac{k_p^*}{k_t^*}\left[1 - \frac{1}{k_t^*}\left(k_t^* - \frac{k_p^*}{m}\right)\right]$$

$$\epsilon_1 = 2\frac{k_p^{*2}}{\alpha^2}\gamma\left(M_0 + \frac{T_0}{m}\right)$$

$$\phi_1 = \left(\frac{k_p^*}{\alpha} + \rho_1\right)I_0 - \gamma\frac{k_p^{*2}}{\alpha^2}\left(M_0 + \frac{T_0}{m}\right)\varphi_1$$

$$\Lambda_1 = \frac{\nu_1}{\gamma}I_0 + \frac{k_p^{*2}}{k_t^*}\,\frac{1}{\alpha}\left(M_0 + \frac{T_0}{m}\right)\varphi_1$$

$$\varphi_1 = \sum_{j=0}^{m}\frac{m!}{(m-j)!}\left(\frac{I_0}{T_0\sigma_1}\right)^{j+1}$$

$$\varphi_2 = \sum_{j=0}^{m}(-1)^j\frac{m!}{(m-j)!}\left(\frac{I_0}{T_0\sigma_1}\right)^{j+1}$$

$$\varphi_3 = \sum_{j=0}^{m}(-1)^j\frac{m!}{(m-j)!}\left(\frac{I_0}{T_0\sigma_1}\right)^{j+1}\left(\frac{T}{T_0}\right)^{m-j}$$

$$\varphi_4 = \sum_{j=0}^{m}\frac{m!}{(m-j)!}\left(\frac{I_0}{T_0\sigma_1}\right)^{j+1}\frac{1}{(m-j+1)}\left[1 - \left(\frac{T}{T_0}\right)^{m-j+1}\right]$$

$$\varphi_5 = \sum_{j=0}^{m}\frac{m!}{(m-j)!}\left(\frac{I_0}{T_0\sigma_1}\right)^{j+1}\frac{1}{2m-j+1}\left[1 - \left(\frac{T}{T_0}\right)^{2m-j+1}\right]$$

The quantities ρ_2, σ_2, ν_2, ϕ_2, Λ_2, ϵ_2, φ_1', φ_2', φ_3', φ_4', and φ_5' are similar to the above-indicated quantities but obviously with the kinetic parameters corresponding to the second active species.

In the case of a single active species all the terms corresponding to the second species vanish, so the value of i_w given by eq 32 and 33 reduces to that reported elsewhere.[16]

Let us now analyze the particular case in which M is changing while T is constant. The instantaneous monomer concentration is easily obtained from the linear differential equation (21) which when integrated with T constant gives

$$M = \left(M_0 + \frac{\alpha}{\beta}T_0\right)\exp\left(-\frac{\beta}{\gamma}I_0t\right) - \frac{\alpha}{\beta}T_0 \quad (34)$$

As a consequence, the time necessary for the total consumption of the monomer is

$$(t)_{M=0} = \tau = \frac{\gamma}{\beta I_0}\ln\left(1 + \frac{\beta M_0}{\alpha T_0}\right) \quad (35)$$

As in the general case

$$\begin{gathered}\sum i(N_i^* + N_i^{**} + N_i) = M_{\mathrm{in}} - M \\ \sum(N_i^* + N_i^{**}) = I_0 \\ \sum N_i = \frac{\alpha}{\gamma}T_0I_0t\end{gathered} \quad (36)$$

Hence, the number-average chain length is expressed by the following equation:

$$i_n = (1 + bY)\Big/\left[1 - ab\ln\left(1 - \frac{Y}{1+a}\right)\right] \quad (37)$$

where $a = \alpha T_0/\beta M_0$, $b = M_0/I_0$, and $Y = (M_0 - M)/M_0$.

In the same way, the weight-average chain length is given by

$$i_w = 1 + A/(1 + bY)I_0 \quad (38)$$

where

$$A = \int_0^t 2[k_p^*(\sum iN_i^*) + k_p^{**}(\sum iN_i^{**})]M\,\mathrm{d}t = \frac{I_0}{\gamma}(a_1b - d_1)^{-1}\left\{\frac{b^2(1+a)}{d_1}Y\left(2 - \frac{Y}{1+a}\right) - \frac{2b}{d_1}Y[ba - (1 - f_1)(a_1b - d_1)] + 2[b(1+a) - f_1(a_1b - d_1)]f_1 \times \left[1 - \left(1 - \frac{Y}{1+a}\right)^{a_1b/d_1}\right] - \frac{2[b(1+a) - f_1(a_1b - d_1)]}{a_1b + d_1}(1 + a)b\left[1 - \left(1 - \frac{Y}{1+a}\right)^{1+(a_1b/d_1)}\right] + 2(1 - f_1)\frac{ab}{d_1}(a_1b - d_1)\ln\left(1 - \frac{Y}{1+a}\right)\right\} + \frac{I_0}{\gamma}K(a_2b - d_2)^{-1}\left\{\frac{b^2(1+a)}{d_2}Y\left(2 - \frac{Y}{1+a}\right) - \frac{2b}{d_2}Y[ba - (1 - f_2)(a_2b - d_2)] + 2[b(1+a) - f_2(a_2b - d_2)]f_2 \times \left[1 - \left(1 - \frac{Y}{1+a}\right)^{a_2b/d_2}\right] - \frac{2[b(1+a) - f_2(a_2b - d_2)]}{a_2b + d_2}(1 + a)b\left[1 - \left(1 - \frac{Y}{1+a}\right)^{1+(a_2b/d_2)}\right] + 2(1 - f_2)\frac{ab}{d_2}(a_2b - d_2)\ln\left(1 - \frac{Y}{1+a}\right)\right\} \quad (39)$$

where $a_1 = k_t^*T_0/k_p^*M_0$, $d_1 = \beta/\gamma k_p^*$, and $f_1 = \alpha k_p^*/\beta k_t^*$. The quantities a_2, d_2, and f_2 are similar, respectively, to a_1, d_1, and f_1, but with the kinetic parameters corresponding to the second active species; α, β, and γ were defined for the general case.

Table I
Fraction of Transfer Agent Remaining after Total Depletion of Monomer for Different Values of m and M_0/T_0

M_0/T_0	m					
	1	5	20	50	200	1000
1	0.5000	0.6988	0.8588	0.9244	0.9738	0.9931
10	0.0909	0.4555	0.7671	0.8831	0.9627	0.9908
50	0.0200	0.3312	0.7079	0.8552	0.9550	0.9892
100	0.0099	0.2884	0.6838	0.8434	0.9517	0.9886
500	0.0020	0.2091	0.6310	0.8167	0.9441	0.9870
1000	0.0009	0.1821	0.6095	0.8054	0.9408	0.9863

The limiting values of i_n and i_w at the moment in which all of the monomer has been consumed are easily obtained from the above equation by putting $Y = 1$. As in the general case, the chain length averages can be reduced to those reported for a single active center by substituting $a_1 = a_2 = a$, $d_1 = d_2 = 1$, and $f_1 = f_2 = 1$ into eq 38 and 39.

Finally, a third situation may occur that will be briefly analyzed. We refer to the case in which both M and T remain constant during the polymerization reaction. For this particular situation eq 3 can be solved directly to obtain analytical formulas for N_i, N_i^*, and N_i^{**} as a function of time and index i. Accordingly, the number-average chain length is given by

$$i_n = \frac{1 + St}{1 + (\alpha/\gamma)T_0 t}$$

where $S = (1/\gamma)(\beta M_0 + \alpha T_0)$ and the weight-average chain length is expressed by the following equation:

$$i_w = 1 + A/(1 + St)I_0$$

where

$$A = \frac{2I_0}{\gamma}\{S_1 R_1 t + R_1^2[\exp(-k_t^* T_0 t) - 1]\} + \frac{2I_0}{\gamma}K\{S_2 R_2 t + R_2^2[\exp(-k_t^{**} T_0 t) - 1]\}$$

$R_1 = k_p^* M_0/k_t^* T_0$, and $R_2 = k_p^{**} M_0/k_t^{**} T_0$ Once again, the values of i_n and i_w reduce to those reported for a single active species when all of the terms corresponding to the second active species are cancelled out, that is, when $\gamma = 1$ and $K = 0$ are substituted into the above equations.

Results and Discussion

In the course of this work we have often referred to the analogy of the present results with those reported in an earlier paper[16] on transfer reactions where a single active species intervenes in the growing chain. As in that work, the discussion of the results is focused on the comparison between the general case, both M and T changing with time, and the particular one in which M is variable but T is constant.

Let us first analyze the influence of the transfer agent for different situations. It is obvious that if $k_p^* \gg k_t^*$ and $k_p^{**} \gg k_t^{**}$, eq 28 or 29 and 33 or 39, respectively, will produce similar values for the chain length averages i_n and i_w. The reason is that the change of transfer agent concentration with time is negligible at total conversion. In the general case, when M and T both change with time, the fraction of transfer agent remaining after all of the monomer has been consumed shows the same dependence on m and M_0/T_0 as in the case of a single active species; that is, $T/T_0 = (1 + mM_0/T_0)^{-1/m}$. The only difference is that m depends on five representative constants in the former case and only on two in the latter. In Table I different values of T/T_0 are given for different values of M_0/T_0. An important point that should be stressed is that the results shown in this table are similar to those reported in ref 16 for a single active species. It would appear, then, as though for a single active species the values of the propagation constant and the transfer constant were equivalent to the sum of the two propagation constants and to $k_t^* + k_t^{**}K$, respectively, in the case of two propagating species. If M_0/T_0 increases, the fraction of transfer agent at total monomer conversion will decrease because more time is needed for the complete consumption of monomer. The influence of m is also stressed in Table I. It can be observed that the situation in which $m \rightarrow \infty$ represents practically a polymerization without transfer reactions and the number-average polymerization degree at total conversion is given by M_{in}/I_0.

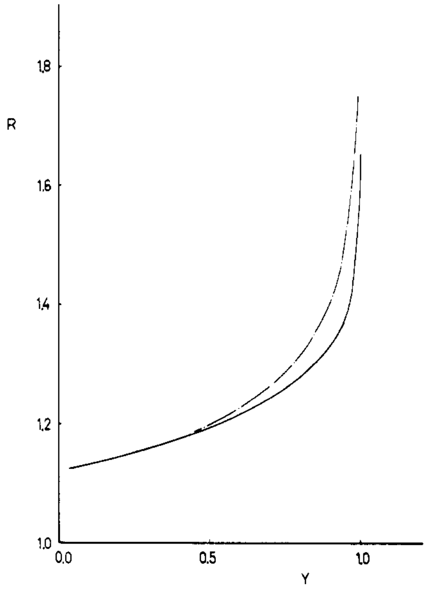

Figure 1. Polydispersity index (R) vs. conversion (Y) for different values of the constants. $k_p^*/k_t^* = k_p^{**}/k_t^{**} = 4$, $k_p^*/k_p^{**} = 2$, and $K = 1$. (—) M and T variable; (-·-) M variable and T constant.

An interesting case which may arise is that both active species have the same concentration and at the same time the respective propagation constants are similar. When this occurs, it is probable that the two transfer constants have also the same value so that the molecular weight averages will be identical with those that would be obtained if a single active species had been present in the reaction medium. Such may be the case for the polymerization of 3,3-dimethylthietane with triethyloxonium tetrafluoroborate,[21] where the propagation constants for free ion and the ionic pair have identical values. The normal situation, however, will be that the propagation and the transfer constants for the two species are quite different and, therefore, use must be made of the equation derived for the general case.

In order to compare the molecular averages of ionic polymerizations in which both M and T change with time with those corresponding to polymerizations in which M is variable and T is constant, the values of i_n and i_w were computed in the two cases. Obviously, the large number of combinations which arise for the five constants participating in the polymerization process precludes the possibility of obtaining general conclusions about the influence of each of the constants on the polydispersity index.

In Figure 1 the polydispersity index is plotted as a function of conversion for determined values of the propagation and transfer constants, assuming an equilibrium constant K equal to unity. It can be observed that the

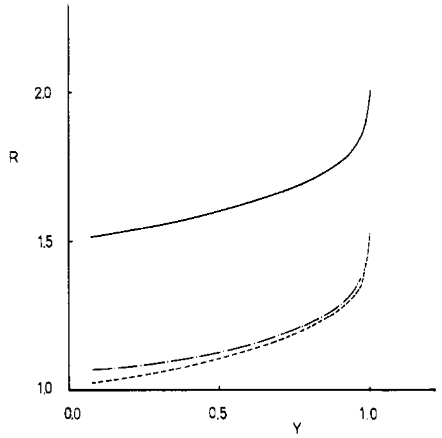

Figure 2. Influence of the equilibrium constant on the polydispersity index for the general case M and T variable, $k_p^*/k_p^{**} = 6$, $k_p^*/k_t^* = k_p^{**}/k_t^{**} = 3$, and (---) $K = 10^{-3}$, (—) $K = 1$, and (-·-) $K = 10^3$.

polydispersity index depends on whether T is constant or variable, its value being larger in the former case. In the example considered, appreciable deviations are not observed until conversions above 50% are reached. Moreover, it may be noted that the deviations will become more noticeable as the transfer agent concentration increases, so use of the simplified equation (M variable and T constant) is valid only for polymerizations in which T_0 is very small.

As for the equilibrium constant, it is obvious that it has a noticeable effect on the molecular weight distribution. Figure 2 shows, as an example, the polydispersity index as a function of the equilibrium constant for the general case (M and T both variables), assuming $k_p^*/k_p^{**} = 6$ and $k_p^*/k_t^* = k_p^{**}/k_t^{**} = 3$. The data indicate, however, that the dependence of i_w/i_n on K does not follow a well-defined rule.

It is clear from the discussion that the polydispersity index of ionic polymerizations, carried out in the presence of a transfer agent, is strongly dependent on the number of active species which intervene in the reaction, even for small transfer agent concentrations. Situations may arise in which a new species created by transfer is less reactive than the initial one, so that a new reinitiation rate constant should be introduced in the kinetic scheme. It has been shown, however, that only in the case in which the ratio k_p/k_i is very high do the results differ significantly from those obtained in the present work.[17]

References and Notes

(1) Szwarc, M. "Carbanion Living Polymers and Electron Transfer Processes"; Wiley: New York, 1968.
(2) Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.
(3) Szwarc, M.; Litt, M. *J. Chem. Phys.* **1958**, *62*, 568.
(4) Brown, W. B.; Szwarc, M. *Trans. Faraday Soc.* **1958**, *54*, 416.
(5) Orofino, T. A.; Wenger, F. *J. Chem. Phys.* **1961**, *35*, 532.
(6) Figini, R. V. *Makromol. Chem.* **1961**, *44-46*, 497.
(7) Litt, M. *J. Polym. Sci.* **1962**, *58*, 429.
(8) Coleman, B. D.; Gornick, F.; Weiss, G. *J. Chem. Phys.* **1963**, *39*, 3233.
(9) Coleman, B. D.; Fox, T. G. *J. Chem. Phys.* **1963**, *38*, 1065.
(10) Nanda, V. S.; Jain, R. K. *J. Polym. Sci., Part A* **1964**, *2*, 4583.
(11) Szwarc, M.; Hermans, J. J. *J. Polym. Sci., Part B* **1964**, *2*, 815.
(12) Figini, R. V. *Makromol. Chem.* **1964**, *71*, 193.
(13) Miyake, A.; Stockmayer, W. H. *Makromol. Chem.* **1965**, *88*, 90.
(14) Nanda, V. S.; Jain, S. C. *Eur. Polym. J.* **1970**, *6*, 1605.
(15) Jain, S. C.; Nanda, V. S. *Eur. Polym. J.* **1977**, *13*, 137.
(16) Largo-Cabrerizo, J.; Guzmán, J. *Macromolecules* **1979**, *12*, 526.
(17) Largo-Cabrerizo, J.; Millán, I. G.; Guzmán, J. *Macromolecules*, submitted for publication.
(18) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 69.
(19) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.
(20) Sangster, J. M.; Worsfold, D. J. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1415.
(21) Goethals, E. J.; Drijvers, W.; van Ooteghen, D.; Buyle, A. M. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1975.
(22) Razvodovskii, E. F.; Berlin, A.; Nekrasov, A. V.; Ponomarenko, A. T.; Pushchaeva, L. M.; Puchkova, N. G.; Enikolopyan, N. S. *Vysokomol. Soedin.* **1973**, *15*, 2233.
(23) Sigwalt, P. *J. Polym. Sci., Polym. Symp.* **1975**, *No. 50*, 95.
(24) Gandini, A.; Plesch, P. H. *J. Chem. Soc.* **1965**, 4826.
(25) Higashimura, T.; Kishiro, O. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 967.
(26) Sawamoto, M.; Higashimura, T. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *20* (1), 727.
(27) Furukawa, J.; Tada, K. "Kinetics and Mechanisms of Polymerization"; Frisch, K. C., Reegen, S. L., Eds.; Marcel Dekker: New York, 1969; Vol. 2.
(28) Alamo, R.; Guzmán, J.; Fatou, J. G. *Makromol. Chem.* **1981**, *182*, 725.
(29) Dreyfuss, P.; Adaway, J.; Kennedy, J. P. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1977**, *30*, 183.
(30) Matyjaszewski, K.; Penczek, S.; Franta, E. *Polymer* **1980**, *20*, 1184.
(31) Pruckmayr, G.; Wu, T. K. *Macromolecules* **1973**, *6*, 33.
(32) Smith, S.; Hubin, J. *J. Macromol. Sci., Chem.* **1973**, *7*, 1399.
(33) Kobayashi, S.; Morikawa, K.; Saegusa, T. *Macromolecules* **1975**, *8*, 386.
(34) Saegusa, T.; Kobayashi, S. *MTP Int. Rev. Sci.: Phys. Chem. Ser.* **1975**, *8*, 153–90.