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## A Multistate Mechanism for Homogeneous Ionic Polymerization. II. The Molecular Weight Distribution<sup>1</sup>

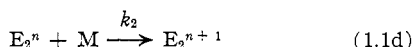
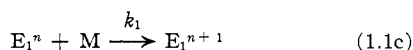
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To explain the "stereoblock" structures which occasionally result from homogeneous anionic polymerizations, we have examined, in paper I of this series, the diastereosequence distribution resulting from a mechanism in which a reactive polymer chain end has two possible states, 1 and 2, in dynamic equilibrium, both capable of adding monomer, but each with its own stereospecificity. Here we consider the molecular weight distribution resulting from such a mechanism when monofunctional initiators are used. We assume no side reactions such as irreversible termination or chain transfer and assume initiation to be instantaneous. As a result, under certain limiting conditions our molecular weight distribution reduces to the Poisson distribution obtained by Flory for the classical one-species polymerization. In general, however, the present mechanism yields a ratio,  $r$ , of the weight to number average degrees of polymerization which is larger than that obtained from the Poisson distribution. Whenever the rate constants for the reactions  $1 \rightleftharpoons 2$  are non-zero, our present distribution shares with the Poisson distribution the property that  $r$  approaches unity for long reaction times.

**1. Hypotheses.**—In an effort to explain the occurrence of "stereoblock" polymers in homogeneous<sup>2</sup> anionic polymerization of  $\alpha$ -olefins, we recently postulated<sup>3</sup> that it sometimes occurs in the course of such polymerizations that the reactive end of a growing polymer molecule exists in two possible states which are in dynamic equilibrium and that each state is capable of adding monomer with its own characteristic rate constant and stereospecificity. On calculating the diastereosequence distribution resulting from such a mechanism we found that this "two-state hypothesis" not only furnishes an alternative to the "Markoff-chain hypothesis"<sup>4,5</sup> which investigators<sup>6,7</sup> have used to interpret their n.m.r. data, but also yields the first explanation of "stereoblock" structures to be susceptible to experimental verification through definite predictions of the dependence of n.m.r. spectra on the conditions of polymerization. Here we shall consider the molecular weight distribution resulting from such a mechanism.

As in reference 3, we consider that at a certain time ( $t = 0$ ) monomer is added to a solution of monofunctional initiator. Polymerization then begins, with initiation being instantaneous, and proceeds without chain transfer, irreversible termination or depolymerization. We postulate that there are four reactions which can take place. To describe them we indicate the condition of a polymer molecule by the symbol  $E_x^n$ . The superscript  $n$ , representing the degree of polymerization, can take on all integral values, while  $x$ , signifying the state of the reactive end of the polymer, can take on two values:  $x = 1$  if the reactive end is in state 1 and  $x = 2$  for the alternative state 2. Our postulated reactions are



Here  $\lambda_b$  is a rate coefficient for that reaction which takes a growing chain from state 1 to state 2. In other words, the probability that a polymer molecule, known to be of

(1) The research reported here was supported in part by the Air Force Office of Scientific Research under Contract AF 49(638)541.

(2) T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell and J. D. Stroupe, *J. Am. Chem. Soc.*, **80**, 1768 (1958).

(3) B. D. Coleman and T. G. Fox, *J. Chem. Phys.*, **38**, 1065 (1963).

(4) B. D. Coleman, *J. Polymer Sci.*, **31**, 155 (1958).

(5) R. E. Hughes, Abstracts of Papers, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., April, 1958, p. 10R.

(6) U. Johnson, *Kolloid Z.*, **178**, 161 (1961).

(7) D. Braun, M. Herner, U. Johnsen and W. Kern, *Makromol. Chem.*, **51**, 15 (1962).

type  $E_1^n$  at time  $t$ , becomes of type  $E_2^n$  in the small time interval  $dt$  at  $t$  is given by  $\lambda_b dt + o(dt)$ . Similarly,  $\lambda_a dt + o(dt)$  gives the probability that  $E_2^n \rightarrow E_1^n$  occurs in  $dt$  at  $t$ , given  $E_2^n$  at time  $t$ . The numbers  $k_1$  and  $k_2$  are ordinary rate constants for the addition of monomer to polymer chains in states 1 and 2, respectively. For example, the probability that a polymer molecule known to be in the state  $E_1^n$  at time  $t$  makes the transition  $E_1^n \rightarrow E_1^{n+1}$  in  $dt$  at  $t$  is  $[M]k_1 dt + o(dt)$  where  $[M]$  denotes the monomer concentration. The numbers  $\lambda_a$ ,  $\lambda_b$ ,  $k_1$  and  $k_2$  will depend on the temperature and solvent used; we assume here that they are independent of the degree of polymerization  $n$ . We also make the usual "low conversion hypothesis" and assume that  $[M]$  does not change much in the course of a given polymerization.<sup>8</sup>

It follows from the chemical hypotheses we have made that the probability  $\psi$  that a polymer molecule selected at random is in the state 1 at a given moment  $t$  is

$$\psi = \lambda_a / (\lambda_a + \lambda_b) \quad (1.2)$$

Let  $P_{n,x}(t)$ ,  $x = 1$  or 2, be the probability that a polymer molecule, selected at random, is in the state  $E_x^n$  at time  $t$ . Then  $Q_n(t)$ , defined by

$$Q_n(t) = P_{n,1}(t) + P_{n,2}(t) \quad (1.3)$$

is the probability that a randomly selected polymer molecule has its degree of polymerization equal to  $n$  at time  $t$ . By hypothesis, the degree of polymerization is unity at  $t = 0$ , hence

$$Q_1(0) = 1 \quad (1.4)$$

Since we assume that the reactions 1.1a and 1.1b are in equilibrium at  $t = 0$ , we have

$$P_{1,1}(0) = \psi, \quad P_{1,2}(0) = 1 - \psi \quad (1.5a)$$

Of course

$$P_{n,1}(0) = P_{n,2}(0) = 0, \text{ for } n > 1 \quad (1.5b)$$

For all  $t > 0$

$$\sum_{n=1}^{\infty} P_{n,1}(t) = \psi, \quad \sum_{n=1}^{\infty} P_{n,2}(t) = 1 - \psi \quad (1.6)$$

Furthermore, for  $n = 1$ ,  $t \geq 0$ , we have

$$dP_{1,1}(t)/dt = -([M]k_1 + \lambda_b)P_{1,1}(t) + \lambda_a P_{1,2}(t) \quad (1.7a)$$

$$dP_{1,2}(t)/dt = -([M]k_2 + \lambda_a)P_{1,2}(t) + \lambda_b P_{1,1}(t) \quad (1.7b)$$

and for  $n > 1$ ,  $t \geq 0$ , we have

$$\frac{dP_{n,1}(t)}{dt} = -([M]k_1 + \lambda_b)P_{n,1}(t) +$$

$$[M]k_1 P_{n-1,1}(t) + \lambda_a P_{n,2}(t) \quad (1.7c)$$

$$\frac{dP_{n,2}(t)}{dt} = -([M]k_2 + \lambda_a)P_{n,2}(t) +$$

$$[M]k_2 P_{n-1,2}(t) + \lambda_b P_{n,1}(t) \quad (1.7d)$$

(8) Since we are here interested in only degree of polymerization, and not in diastereosequences, we do not here differentiate between additions which result in isotactic and syndiotactic placements. Hence the six reactions of section 1 of ref. 3 here reduce to the four reactions 1.1.

Equations 1.2-1.7 furnish a complete mathematization of our chemical assumptions. On looking at 1.3 we see that the problem of characterizing the molecular weight distribution is that of investigating the behavior of the solution of the system of differential equations 1.7 subject to the initial conditions 1.5.

Our main interest here is in the moments

$$\bar{n}^m = \sum_{n=1}^{\infty} n^m Q_n(t) \quad (1.8)$$

of the distribution  $Q_n(t)$  of the degree of polymerization  $n$ . We are particularly interested in the number and weight average degrees of polymerization  $\bar{n}(t)$ ,  $\bar{n}_w(t)$ , respectively, and their ratio  $r(t)$ . These are defined by

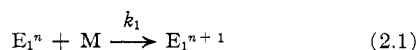
$$\bar{n} = \sum_{n=1}^{\infty} n Q_n(t) \quad (1.9a)$$

$$\bar{n}_w = \frac{\bar{n}^2}{\bar{n}} = \frac{\sum_{n=1}^{\infty} n^2 Q_n(t)}{\sum_{n=1}^{\infty} n Q_n(t)} \quad (1.9b)$$

$$r = \frac{\bar{n}_w}{\bar{n}} = \frac{\sum_{n=1}^{\infty} n^2 Q_n(t)}{\left[ \sum_{n=1}^{\infty} n Q_n(t) \right]^2} \quad (1.9c)$$

It should be emphasized that in writing our mechanism 1.1 and our equations 1.2-1.7 we make some very strong idealizations: We assume instantaneous initiation, no irreversible termination and no chain transfer or depolymerization. The molecular weight distribution is more sensitive than the previously considered diastereosequence distribution to departures from such idealizations.

**2. Special Cases.—Case I:** When one of the two  $\lambda$ 's in 1.1 is zero, say  $\lambda_b$ , and the other,  $\lambda_a$ , is not zero, so that  $\psi = 1$ , then all of the polymer molecules are in state 1. In this case the four reactions 1.1 reduce to the one reaction



We have

$$P_{n,2}(t) = 0, \quad P_{n,1}(t) = Q_n(t) \quad n \geq 1$$

and the system of differential equations 1.7 reduces to the system

$$dQ_1(t)/dt = -[M]k_1Q_1(t) \quad (2.2a)$$

$$dQ_n(t)/dt = -[M]k_1Q_n(t) + [M]k_1Q_{n-1}(t) \quad (2.2b)$$

which is now subject to the initial condition

$$\text{for } n = 1, Q_1(0) = 1 \quad (2.3a)$$

$$\text{for } n > 1, Q_n(0) = 0 \quad (2.3b)$$

The solution of 2.2 subject to 2.3 is known even when  $[M]$  or  $k_1$ , or both, depend on  $t$ . For instance,  $[M]$  depends on  $t$ , *i.e.*,  $[M] = [M]^t$ , when an appreciable amount of monomer is consumed in the polymerization, and  $k_1$  depends on  $t$ , *i.e.*,  $k_1 = k_1^t$ , if the temperature changes in the course of the polymerization. Let us put

$$\theta(t) = \int_0^t [M]^{\tau} k_1^{\tau} d\tau \quad (2.4a)$$

The solution of 2.2 subject to 2.3 is

$$Q_n(t) = \frac{\theta^{n-1} e^{-\theta}}{(n-1)!} \quad (2.4b)$$

*i.e.*, a Poisson distribution in the "reduced time" parameter  $\theta(t)$ . This result is not surprising. For, when  $\lambda_b = 0$  our chemical hypotheses reduce to the familiar single-state polymerization with, of course, instantaneous initiation and no termination or depoly-

merization, which was shown by Flory<sup>9</sup> to yield a Poisson distribution for  $n$ . It follows from 2.4 and 1.9a that the number average degree of polymerization is given by

$$\bar{n} = 1 + \theta \quad (2.5a)$$

It also can be shown that

$$\bar{n}^2 = 1 + 3\theta + \theta^2 \quad (2.5b)$$

$$\bar{n}_w = \frac{1 + 3\theta + \theta^2}{1 + \theta} \quad (2.5c)$$

$$r = \frac{1 + 3\theta + \theta^2}{1 + 2\theta + \theta^2} \quad (2.5d)$$

Expressing  $r$  as a function of  $n$  we have

$$r = 1 + \frac{1}{\bar{n}} - \frac{1}{(\bar{n})^2} \quad (2.6)$$

Thus, for reasonably large  $\bar{n}$ ,  $r$  is very close to 1. For example, when  $\bar{n} \geq 50$ ,  $1 < r < 1.02$ .

**Case II:** Similar to case I is that case in which the  $\lambda$ 's and  $k$ 's are all strictly positive but  $k_1 = k_2$ . Clearly, we here again have the Poisson distribution and thus eq. 2.4-2.6.

**Case III:** Another special, or rather limiting, case is that in which all the  $k$ 's and  $\lambda$ 's are *strictly* positive but yet the reactions 1.1a and 1.1b are both so fast compared to 1.1c and 1.1d that, on the average, several transitions  $E_1^n \rightleftharpoons E_2^n$  occur between successive additions of monomer. For a fixed set of non-zero values of the  $\lambda$ 's and  $k$ 's this limit can be achieved by making  $[M]$  small. In this limit eq. 2.4-2.6 again describe the molecular weight distribution provided  $k_1^{\tau}$  in 2.4a is replaced by

$$\bar{k}_1^{\tau} = \psi k_1^{\tau} + (1 - \psi)k_2^{\tau} \quad (2.7)$$

where  $\psi$  is given by 1.2.

**Case IV:** A special case of our mechanism which is strikingly different in its behavior from those discussed above is that in which  $k_1 > 0$ ,  $k_2 > 0$ ,  $k_1 \neq k_2$ ,  $0 < \psi < 1$  but  $\lambda_a = \lambda_b = 0$  (exactly). In this case the reactions 1.1a and 1.1b do not occur at all and polymerization behaves as though we had a mixture of two non-interacting species, each with its own Poisson distribution

$$Q_n(t) = \psi P_{n,1}(t) + (1 - \psi)P_{n,2}(t) \quad (2.8a)$$

where

$$P_{n,x} = \frac{\theta_x^{n-1} e^{-\theta_x}}{(n-1)!}, \quad \theta_x = [M] \int_0^t k_x^{\tau} d\tau, \quad x = 1, 2 \quad (2.8b)$$

Here we again make the low conversion hypothesis and assume  $[M]$  to be stationary in time; this saves us from the task of taking into account the competition for monomer between the species 1 and 2. We can, however, continue here to allow  $k_1$  and  $k_2$  to depend on time. It follows from 2.8 that

$$\bar{n}^m(t) = \psi \bar{n}_1^m(t) + (1 - \psi) \bar{n}_2^m(t) \quad (2.9a)$$

where

$$\bar{n}_x^m = \sum_{n=1}^{\infty} n^m P_{n,x}, \quad x = 1, 2 \quad (2.9b)$$

is the  $m$ th moment of the Poisson distribution for species  $x$ . Equations 2.8, 2.9 and 1.9 yield

$$\bar{n} = \psi \bar{n}_1 + (1 - \psi) \bar{n}_2 \quad (2.10a)$$

$$\bar{n}_w = \frac{\psi \bar{n}_1^2 + (1 - \psi) \bar{n}_2^2}{\psi \bar{n}_1 + (1 - \psi) \bar{n}_2} \quad (2.10b)$$

$$r = \frac{\psi \bar{n}_1^2 + (1 - \psi) \bar{n}_2^2}{(\psi \bar{n}_1 + (1 - \psi) \bar{n}_2)^2} \quad (2.10c)$$

(9) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1561 (1940).

where, by 2.8 and 2.9b

$$\bar{n}_x = 1 + \theta_x, \quad x = 1, 2 \quad (2.11a)$$

$$\bar{n}^2_x = 1 + 3\theta_x + \theta_x^2, \quad x = 1, 2 \quad (2.11b)$$

It follows from 2.11a, 2.10a and 2.8 that

$$\bar{n} = 1 + [M] \int_0^t \bar{k}^r d\tau \quad (2.12)$$

where  $\bar{k}^r$  is again defined by 2.7. When  $k_1$  and  $k_2$  are independent of  $t$ , 2.10c can be written in the form

$$r = 1 + \frac{1}{\bar{n}} - \frac{1}{(\bar{n})^2} + \frac{(k_1 - k_2)^2 \psi (1 - \psi) (\bar{n} - 1)^2}{(\psi k_1 + (1 - \psi) k_2)^2 \bar{n}^2} \quad (2.13)$$

On examining (2.13) for large  $\bar{n}$  (*i.e.*, large  $t$ ) we find that

$$r = 1 + \frac{\psi(1 - \psi)(k_1 - k_2)^2}{(\psi k_1 + (1 - \psi) k_2)^2} + 0(1/\bar{n}) \quad (2.14)$$

Hence, our present case is similar to cases I-III in that  $\lim_{\bar{n} \rightarrow \infty} r$  is independent of  $[M]$  but differs in the

important respect that  $r$  can now be appreciably greater than 1 for large  $\bar{n}$ . We remark that eq. 2.14 holds only if  $\lambda_a$  and  $\lambda_b$  are *exactly* zero; for the analysis of the next section will show that if  $\lambda_a$  and  $\lambda_b$  do not both vanish, then, no matter how small the  $\lambda$ 's be, the limit  $t \rightarrow \infty$  must yield  $r \rightarrow 1$ .

**3. The General Case.**—We now return to consideration of the general equations 1.2-1.7, assuming that  $\lambda_a$ ,  $\lambda_b$ ,  $k_1$ ,  $k_2$  and  $[M]$  are all constant in time.

Let us consider the function  $Q(s, t)$  defined by

$$Q(s, t) = \sum_{n=1}^{\infty} s^n Q_n(t), \quad \infty > s > 0 \quad (3.1)$$

This function obeys formulas of the type

$$\left. \frac{dQ(s, t)}{ds} \right|_{s=1} = \sum_{n=1}^{\infty} n Q_n(t) = \bar{n}(t) \quad (3.2a)$$

$$\left. \frac{d^2 Q(s, t)}{ds^2} \right|_{s=1} = \sum_{n=1}^{\infty} n(n-1) Q_n(t) = \bar{n}^2(t) - \bar{n}(t) \quad (3.2b)$$

etc. Hence the determination of  $Q(s, t)$  near  $s = 1$  solves the problem of finding the moments  $\bar{n}^m$  of  $Q_n(t)$ .

It is interesting to note that the generating function  $Q(s, t)$  also yields the functions  $Q_n(t)$  through the formula

$$Q_n(t) = \frac{1}{n!} \left. \frac{\partial^n Q(s, t)}{\partial s^n} \right|_{s=0} \quad (3.3)$$

but we do not use this relationship here.

Let us put

$$R_1(s, t) = \sum_{n=1}^{\infty} s^n P_{n,1}(t), \quad R_2(s, t) = \sum_{n=1}^{\infty} s^n P_{n,2}(t) \quad (3.4)$$

Equations 1.3, 3.1, and 3.4 yield

$$Q(s, t) = R_1(s, t) + R_2(s, t) \quad (3.5)$$

Let us define the following Laplace transforms

$$\hat{P}_{n,i}(p) = \int_0^{\infty} e^{-pt} P_{n,i}(t) dt, \quad i = 1, 2 \quad (3.6a)$$

$$\hat{R}_i(s, p) = \int_0^{\infty} e^{-pt} R_i(s, t) dt = \sum_{n=1}^{\infty} s^n \hat{P}_{n,i}(p), \quad i = 1, 2 \quad (3.6b)$$

$$\hat{Q}(s, p) = \int_0^{\infty} e^{-pt} Q(s, t) dt = \hat{R}_1(s, p) + \hat{R}_2(s, p) \quad (3.6c)$$

The Laplace transform  $\hat{P}'_{n,i}(p)$  of  $dP_{n,i}(t)/dt$  obeys the familiar formula

$$\hat{P}'_{n,i}(p) = p \hat{P}_{n,i}(p) - \hat{P}_{n,i}(0), \quad i = 1, 2$$

On taking the Laplace transform of both sides of eq. 1.7 and using 1.5, we find that for  $n = 1$

$$p \hat{P}_{1,1}(p) - \psi = -([M]k_1 + \lambda_b) \hat{P}_{1,1}(p) + \lambda_a \hat{P}_{1,2}(p) \quad (3.7a)$$

$$p \hat{P}_{1,2}(p) - (1 - \psi) = -([M]k_2 + \lambda_a) \hat{P}_{1,2}(p) + \lambda_b \hat{P}_{1,1}(p) \quad (3.7b)$$

and for  $n > 1$

$$p \hat{P}_{n,1}(p) = -([M]k_1 + \lambda_b) \hat{P}_{n,1}(p) + k_1 [M] \hat{P}_{n-1,1}(p) + \lambda_a \hat{P}_{n,2}(p) \quad (3.7c)$$

$$p \hat{P}_{n,2}(p) = -([M]k_2 + \lambda_a) \hat{P}_{n,2}(p) + k_2 [M] \hat{P}_{n-1,2}(p) + \lambda_b \hat{P}_{n,1}(p) \quad (3.7d)$$

We now multiply 3.7a by  $s$  and 3.7c by  $s^n$  and sum these equations over  $n$  to obtain

$$\sum_{n=1}^{\infty} s^n p \hat{P}_{n,1}(p) - s\psi = -([M]k_1 + \lambda_b) \sum_{n=1}^{\infty} s^n \hat{P}_{n,1}(p) + k_1 [M] \sum_{n=2}^{\infty} s^n \hat{P}_{n-1,1}(p) + \lambda_a \sum_{n=1}^{\infty} s^n \hat{P}_{n,2}(p) \quad (3.8)$$

We note that

$$\sum_{n=2}^{\infty} s^n \hat{P}_{n-1,1}(p) = s \sum_{n=1}^{\infty} s^n \hat{P}_{n,1}(p) \quad (3.9)$$

Equations 3.6, 3.8 and 3.9 yield

$$(p + (1 - s)[M]k_1 + \lambda_b) \hat{R}_1(s, p) - \lambda_a \hat{R}_2(s, p) = s\psi \quad (3.10a)$$

Applying the same process to eq. 3.7b and 3.7d we get

$$(p + (1 - s)[M]k_2 + \lambda_a) \hat{R}_2(s, p) - \lambda_b \hat{R}_1(s, p) = s(1 - \psi) \quad (3.10b)$$

Equations 3.10, being two independent algebraic equations in two unknowns  $\hat{R}_1$  and  $\hat{R}_2$ , can be solved. On doing this and adding the results in accordance with 3.6c, we find

$$\hat{Q}(s, p) = \frac{s(p + \lambda_a + \lambda_b) + (\psi[M]k_2 + (1 - \psi)[M]k_1)(s - s^2)}{(p + [M]k_1(1 - s) + \lambda_b)(p + [M]k_2(1 - s) + \lambda_a) - \lambda_a \lambda_b} \quad (3.11)$$

We now apply to 3.11 standard techniques for the inversion of Laplace transforms. The denominator of the fraction on the right in 3.11 is quadratic in  $p$  and can therefore be written in the form

$$(p + [M]k_1(1 - s) + \lambda_b)(p + [M]k_2(1 - s) + \lambda_a) - \lambda_a \lambda_b = (p - \nu_1(s))(p - \nu_2(s)) \quad (3.12)$$

where the roots  $\nu_1(s)$  and  $\nu_2(s)$  are functions of  $s$ . An elementary calculation yields

$$2\nu_i(s) = \pm \frac{\omega}{\sqrt{(1 - s)^2 [M]^2 (k_1 - k_2)^2 + a^2 - 2[M](\lambda_a - \lambda_b)(k_1 - k_2)(1 - s) - (1 - s)[M](k_1 + k_2) - a}} \quad (3.13a)$$

where  $i = 1, 2$  and

$$a = \lambda_a + \lambda_b \quad (3.13b)$$

Let us put

$$\omega = (1 - \psi)k_1 + \psi k_2 \quad (3.13c)$$

Using 3.12 and 3.13, 3.11 may be rewritten in the form

$$\hat{Q}(s, p) = \frac{s p}{(p - \nu_1(s))(p - \nu_2(s))} + \frac{s(a + [M]\omega(1 - s))}{(p - \nu_1(s))(p - \nu_2(s))} \quad (3.14)$$

Laplace transforms with the simple dependence on  $p$  shown in 3.14 are easily inverted, and a slight rearrangement of the result of such an inversion yields the following expression for  $Q(s, t)$

$$Q(s, t) = \frac{s}{\nu_1(s) - \nu_2(s)} [(\nu_1(s) + a + \omega[M](1 - s))e^{\nu_1(s)t} - (\nu_2(s) + a + \omega[M](1 - s))e^{\nu_2(s)t}] \quad (3.15)$$

Using eq. 3.2, 3.15 and 3.13 we can now calculate  $\bar{n}$  and  $\bar{n}^2$  by differentiation. On doing this straightforward, but lengthy, calculation we find

$$\bar{n} = 1 + [M] \bar{k} t \quad (3.16)$$

where

$$\bar{k} = \psi k_1 + (1 - \psi) k_2 \quad (3.17)$$

and

$$\bar{n}^2 = 1 - [M]^2 b(1 - e^{-at})/a^2 + (3[M]\bar{k} + [M]^2 b/a)t + [M]^2 \bar{k}^2 t^2 \quad (3.18)$$

where

$$b = 2(k_1 - k_2)^2 \psi(1 - \psi) \quad (3.19)$$

It follows from 3.18, 3.16 and 1.9b that

$$\bar{n}_w = 1 + \frac{\left(1 + \frac{[M]b}{\bar{k}a}\right)([M]\bar{k}t) - \frac{[M]^2 b}{a^2}(1 - e^{-at})}{1 + [M]\bar{k}t} + \bar{k}[M]t \quad (3.20)$$

We have written eq. 3.16, 3.18 and 3.20 in such a way that the dependence of the averages on  $[M]$  is exhibited explicitly.

It follows from 3.20, 3.16 and 1.9c that

$$r = 1 + (1 + [M]b/\bar{k}a)(\bar{n})^{-1} - (1 + [M]b/\bar{k}a + [M]^2 a^{-2} b(1 - e^{-at}))(\bar{n})^{-2} \quad (3.21)$$

From which we see that whenever  $a$  is non-zero

$$\lim_{n \rightarrow \infty} r = 1 \quad (3.22)$$

*i.e.*, in the limit of high number average molecular weight the molecular weight distribution must become perfectly sharp. This does not mean, however, that  $r$  is close to 1 for all degrees of polymerization. If  $[M]b$  be  $\gg \bar{k}a$ , then 3.21 can yield  $r \gg 1$  even for large  $\bar{n}$ , although  $r - 1$  approaches zero with order  $O(1/\bar{n})$ .

We note that eq. 3.21 becomes identical with 2.6 in the following limits

case I:  $\lambda_a \rightarrow 0$ , while  $\lambda_b, k_1, k_2, [M]$ , and  $t$  remain fixed at arbitrary positive values

case II:  $k_1 \rightarrow k_2$ , while  $\lambda_a, \lambda_b, k_2, [M]$ , and  $t$  remain fixed at arbitrary positive values

case III:  $[M] \rightarrow 0$ , while  $\lambda_a, \lambda_b, k_1, k_2$ , and  $t$  remained fixed at arbitrary positive values

in agreement with the discussion of section 2.

If in 3.21 we take the limit  $a \rightarrow 0$ , keeping  $\psi$  fixed at a positive value less than one, and keeping  $k_1, k_2$  and  $t$  fixed at arbitrary positive values (it is important here that  $t$  be held finite), we then obtain 2.13.

A special case of the present theory is that in which  $\lambda_a, \lambda_b$  and  $k_1$  are strictly positive but  $k_2 = 0$ . This gives

a model for reversible termination: a dynamic equilibrium between two states 1 and 2, one of which, 1, can add monomer, but the other, 2, cannot. In this case  $\bar{k}$  and  $b$  simplify to

$$\bar{k} = \psi k_1 = \frac{\lambda_a k_1}{\lambda_a + \lambda_b} \quad (3.23)$$

$$b = 2k_1^2 \psi(1 - \psi) = \frac{2k_1^2 \lambda_a \lambda_b}{(\lambda_a + \lambda_b)^2} \quad (3.24)$$

but the essential character of our results 3.16, 3.20 and 3.21 is unchanged: In particular, 3.22 still holds.

For the experimenter, the outstanding characteristics of the present mechanism are (1) for a fixed set of rate constants such that  $\lambda_a > 0, \lambda_b > 0$ , and fixed extent of reaction (*i.e.*, fixed  $\bar{n}$ ),  $r$  depends on  $[M]$  and approaches  $1 + (\bar{n})^{-1} - (\bar{n})^{-2}$  as  $[M] \rightarrow 0$ ; (2) for fixed rate constants with  $\lambda_a > 0, \lambda_b > 0$ , and fixed  $[M]$ ,  $r \rightarrow 1$  as  $t \rightarrow \infty$ .

Unfortunately, no systematic experimental studies designed to verify conclusions 1 and 2 have yet been reported.

Data<sup>10</sup> on the n.m.r. spectra and on the molecular weights of the products of homogeneous anionic polymerization of methyl methacrylate in toluene, and also in mixtures of toluene with ether or tetrahydrofuran, show values greater than one for  $r$  and for the persistence ratio  $\rho$  defined in section 3 of ref. 3. Data<sup>11,12</sup> on the products of homogeneous anionic polymerization of  $\alpha$ -methylstyrene indicate that values of  $r$  and of  $\rho$  close to 1 are readily obtained for this monomer. Values of  $r < 1.05$  are reported in anionic polymerizations of styrene.<sup>13</sup> If our mechanism applies to these systems it appears that, at the monomer concentrations employed, in methyl methacrylate reactions 1a and 1b are slower than 1c and 1d, whereas the reverse seems to be true for  $\alpha$ -methyl styrene and possibly also for styrene for which  $\rho$ -values are not yet available.

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(13) F. Wenger, *Makromol. Chem.*, **56**, 200 (1960).