

out. The dependence of the course of the reaction, of the final average chain length and of the chain length distribution upon the rate constants, in particular upon the rate of initiation and upon the initial concentration, is shown. Two limiting cases can be distinguished. If the ratio between the rate of cessation and that of initiation is large, and the ratio of the rate of propagation and that of cessation is also large, then the average molecu-

lar weight will be large at the end and remain approximately constant during the last stages. If these ratios are small, then the average molecular weight will increase continuously and reach a small final value. It is shown how the individual rates may be derived from a knowledge of these quantities. The theory of Schulz, and Norrish's and Brookman's results, appear as special cases.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

## On the Kinetics of Polymerization Reactions. II. Second and Combined First and Second Order Initiation Reactions. Mutual Stabilization of Growing Chains<sup>1</sup>

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In a previous publication<sup>3</sup> polymerization reactions have been considered in which growth and termination are brought about by the interaction of stable monomer molecules with the growing polymer. The initiation of active chains was represented by a first order reaction. For processes which occur with the aid of a true catalyst or in dilute solution, a first order initiation represents a possible mechanism. Second order activation, for instance, between monomers may be found in uncatalyzed chain polymerizations. In pure phase as well as in solution, first and second order processes may appear simultaneously, the first probably becoming more predominant as the concentration of monomer decreases. In this paper relations will be sought which allow a differentiation on the basis of experimental data between the two cases mentioned above.

As pointed out in (I), toward the end of the reaction it is probable that growth and termination will proceed by mutual interaction of the growing chains as well as by interaction with monomer. The complexity of the rate equations does not permit a rigorous treatment of such cases. An exact solution can be given, if the monomer-polymer interaction alone contributes to the growth and cessation. Approximate expressions will be developed which allow an estimation of the polymer-polymer interaction.

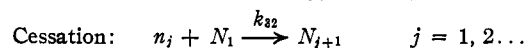
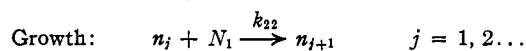
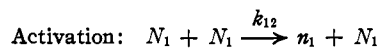
(1) Presented at the One-Hundred-Fourth meeting of the American Chemical Society held in Buffalo, New York, September 7th to 11th, 1942.

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(3) R. Ginell and R. Simha, *THIS JOURNAL*, **65**, 706 (1943), in the following designated by (I).

In regard to the general approach and the notation used, (I) may be consulted.

**Second Order Initiation of Nuclei.**—The calculations will be based on the following mechanism for the three elementary processes



The possibility that the initiation of a chain leads directly to the formation of a dimer would cause only minor changes in our final expressions. The same holds true for cessation without inclusion of monomer. Chain transfer can be treated by the same method, but has been omitted here.

The rate equations assume now the following form

$$\begin{aligned} \frac{dN_1}{dt} &= -k_{12}N_1^2 - k_{22}N_1 \sum_{j=1}^{\infty} n_j - k_{32}N_1 \sum_{j=1}^{\infty} n_j \\ \frac{dn_1}{dt} &= +k_{12}N_1^2 - k_{22}N_1n_1 - k_{32}N_1n_1 \quad (1) \\ \frac{dn_j}{dt} &= k_{22}N_1n_{j-1} - k_{22}N_1n_j - k_{32}N_1n_j; \quad j \geq 2 \\ \frac{dN_j}{dt} &= k_{32}N_1n_{j-1} \quad j \geq 2 \end{aligned}$$

with the additional equations

$$\begin{aligned} \frac{d}{dt} \sum_1^{\infty} n_j &= k_{12}N_1^2 - k_{22}N_1 \sum_1^{\infty} n_j \quad (2) \\ \frac{d}{dt} \sum_1^{\infty} N_j &= -k_{12}N_1^2 - k_{22}N_1 \sum_1^{\infty} n_j \end{aligned}$$

which follow directly from (1). As in (I) we

divide through by  $N_1$  and introduce the variable

$$\phi(t) = \int_0^t N_1 dt; \quad \phi_\infty = \int_0^\infty N_1 dt \quad (3)$$

In  $\phi$  our equations are linear. The boundary conditions are: for  $t = 0, \phi = 0, n_j = 0, \text{ for } j \geq 1; N_j = 0, j \geq 2, N_1 = N_1^{(0)}$ . For  $t = \infty, \phi = \phi_\infty, N_1 = 0$ . The solution of system (2) and (1) will evidently consist of exponential functions. The secular determinant of system (2) has the solution

$$\left. \begin{aligned} \lambda_{1,2} &= \frac{-(k_{32} + k_{12}) \pm \sqrt{(k_{32} + k_{12})^2 - 4k_{12}(k_{22} + 2k_{32})}}{2} \\ \lambda_1 \lambda_2 &= k_{12}(k_{22} + 2k_{32}); \quad \lambda_1, \lambda_2 < 0 \end{aligned} \right\} (4)$$

We first assume the square root to be a real quantity. This amounts to a consideration of cases in which  $k_{32} \gg k_{12}$ . The solution of (2) has then the form

$$\begin{aligned} \sum_1^\infty n_j &= h_1 a_{11} e^{\lambda_1 \phi} + h_2 a_{12} e^{\lambda_2 \phi} \\ N_1 &= h_1 a_{21} e^{\lambda_1 \phi} + h_2 a_{22} e^{\lambda_2 \phi} \end{aligned}$$

$$\left. \begin{aligned} n_j &= N_1^{(0)} k_{12} k_{22}^j - 1 e^{-(k_{22} + k_{32})\phi} \cdot \left\{ \frac{(k_{32} + \lambda_1)}{(\lambda_1 - \lambda_2)} \frac{1}{(k_{22} + k_{32} + \lambda_1)^j} \sum_{s=j-1}^\infty \frac{[(k_{22} + k_{32} + \lambda_1)\phi]^s}{s!} - \right. \\ &\quad \left. \frac{(k_{32} + \lambda_2)}{(\lambda_1 - \lambda_2)} \frac{1}{(k_{22} + k_{32} + \lambda_2)^j} \sum_{s=j-1}^\infty \frac{[(k_{22} + k_{32} + \lambda_2)\phi]^s}{s!} - \frac{k_{22}}{k_{22}(k_{22} + k_{32}) + k_{12}k_{32}} \frac{\phi^{j-1}}{(j-1)!} \right\}; \quad j \geq 1 \\ \text{and} \\ N_j &= k_{32} \int_0^\phi n_{j-1} d\phi; \quad j \geq 2 \end{aligned} \right\} (5a)$$

the  $h_i$  and  $a_{jk}$  are constants, to be determined from (2) and the boundary conditions. In this manner we obtain, if the relations between  $\lambda_1$  and  $\lambda_2$  are taken into account

$$\begin{aligned} N_1 &= \frac{N_1^{(0)}}{\lambda_1 - \lambda_2} [(k_{32} + \lambda_1)e^{\lambda_1 \phi} - (k_{32} + \lambda_2)e^{\lambda_2 \phi}] \\ \sum_{j=1}^\infty n_j &= \frac{N_1^{(0)} k_{12}}{\lambda_1 - \lambda_2} (e^{\lambda_1 \phi} - e^{\lambda_2 \phi}) \end{aligned}$$

and therefrom with the aid of (1)

$$\left. \begin{aligned} n_1 &= N_1^{(0)} k_{12} \left\{ \frac{k_{32} + \lambda_1}{(\lambda_1 - \lambda_2)(k_{22} + k_{32} + \lambda_1)} e^{\lambda_1 \phi} - \frac{(k_{32} + \lambda_2)}{(\lambda_1 - \lambda_2)(k_{22} + k_{32} + \lambda_2)} e^{\lambda_2 \phi} - \right. \\ &\quad \left. - \frac{k_{22}}{k_{22}(k_{22} + k_{32}) + k_{12}k_{32}} e^{-(k_{22} + k_{32})\phi} \right\} = P_1 e^{\lambda_1 \phi} + P_2 e^{\lambda_2 \phi} + P_3 e^{-(k_{22} + k_{32})\phi} \\ \sum_{j=1}^\infty N_j &= N_1^{(0)} \frac{k_{32}}{k_{22} + 2k_{32}} - \frac{N_1^{(0)} k_{12}}{\lambda_1 - \lambda_2} \left[ \frac{e^{\lambda_1 \phi}}{\lambda_1} (k_{22} + k_{32} + \lambda_1) - \frac{e^{\lambda_2 \phi}}{\lambda_2} (k_{22} + k_{32} + \lambda_2) \right] \end{aligned} \right\} (5)$$

We can now find the  $n_j$  for  $j \geq 2$ . They obey the equation

$$dn_j/d\phi = k_{22}n_{j-1} - (k_{22} + k_{32})n_j$$

together with the above expression for  $n_1$ .

In order to solve this system of equations, we start with the equation for  $n_2$ . Because of the

linearity of the above differential equation, the solution will consist of three terms. Each of these will satisfy the equation resulting from the introduction of the respective  $P_i$ -term for  $n_1$  in the above differential equation. It may be verified by insertion, that the  $P_3$ -term leads to the following term in  $n_j$

$$\frac{k_{22}^{j-1}}{(j-1)!} \phi^{j-1} P_3 e^{-(k_{22} + k_{32})\phi}$$

The contribution of the  $P_1$ -term on the other hand can be shown by induction to be

$$\frac{k_{22}^{j-1}}{(k_{22} + k_{32} + \lambda_1)^{j-1}} P_1 \left\{ e^{\lambda_1 \phi} - e^{-(k_{22} + k_{32})\phi} \sum_{s=0}^{j-2} \frac{[(k_{22} + k_{32} + \lambda_1)\phi]^s}{s!} \right\}$$

An analogous term results from the  $P_2$ -term. In this way we find the final expression for  $n_j$  by remembering the definition of the  $P_i$  and transforming the sums

(5a) gives the size distribution of the polymer. A comparison with the analogous formula (4a) of (I) shows that (5a) contains two terms of the same type as (4a), however with more complex

expressions in the rate constants. The third term is characteristic for the second order initiation process. With increasing  $\phi$  the distribution approaches more and more the one found in (I). For the second sum becomes smaller than the first, because  $\lambda_2 < \lambda_1$ , and this holds all the more

for the third term. The parameters of the distribution curve, however, remain different from those determining its shape in equation (4a) of (I). The distribution of the stable  $N_j$  is best found for the first phases of the reaction by numerical integration. Before discussing the conditions prevailing during the last phases we must consider the range of variation of the variable  $\phi$ . Its connection with the time  $t$  is established by means of the relation

$$t(\phi) = \int_0^\phi \frac{dx}{N_1(x)} = \frac{(\lambda_1 - \lambda_2)}{N_1^{(0)}} \int_0^\phi \frac{dx}{(k_{32} + \lambda_1)e^{\lambda_1 x} - (k_{32} + \lambda_2)e^{\lambda_2 x}} \quad (6)$$

from which  $\phi$  can be expressed in terms of  $t$  by inversion. As shown in the appendix, this integral can be evaluated by series expansion

$$N_1^{(0)}t(\phi) = \frac{1}{k_{32} + \lambda_1} \sum_{r=0}^{\infty} \left( \frac{k_{32} + \lambda_2}{k_{32} + \lambda_1} \right)^r \frac{1}{r + \lambda_1/(\lambda_1 - \lambda_2)} [1 - e^{-\lambda_1 \phi} e^{-r(\lambda_1 - \lambda_2)\phi}] \quad (6a)$$

It is not possible, in general, to solve this equation for  $\phi$  analytically. In an evaluation of experimental data, the value of  $\phi$  corresponding to a given value of  $t$  can be found from a plot of the weight of the polymerized material *versus* the time elapsed, in the manner described in (I).

It is easy however to invert (6a) for sufficiently large values of  $\phi$ . First it may be seen from (5) or (6) that  $\phi_\infty = \infty$ .<sup>4</sup> Evidently for our purpose we need consider the first term only in the sum because  $(\lambda_1 - \lambda_2) > 0$ . The one in the bracket can be neglected. Therefore

$$N_1^{(0)}(k_{32} + \lambda_1)t(\phi) \approx - \frac{(\lambda_1 - \lambda_2)}{\lambda_1} e^{-\lambda_1 \phi} \quad (6b)$$

as may be also found directly from (5) by omitting the second exponential in the integration.

The next step is the computation of the number and weight average chain length.<sup>5</sup> The definition of  $Z_n$ ,<sup>6</sup> leads, with the aid of equations (5) to

$$Z_n(\phi) = \frac{1}{\frac{k_{32}}{k_{22} + 2k_{32}} - \frac{k_{12}(k_{22} + k_{32})}{(\lambda_1 - \lambda_2)} \left( \frac{e^{\lambda_1 \phi}}{\lambda_1} - \frac{e^{\lambda_2 \phi}}{\lambda_2} \right)} \quad (7a)$$

(4) The alternative of making  $N_1 = 0$  by setting the two expressions in the bracket in (5) equal, is excluded. It can be seen that this would make  $\phi_\infty < 0$  because  $\lambda_2 < \lambda_1$ .

(5) E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.*, **39**, 153 (1935).

(6) See the appendix of (I).

$$Z_n(\phi; j \geq 2) = \frac{1 - \frac{N_1 + n_1}{N_1^{(0)}}}{\frac{k_{32}}{k_{22} + 2k_{32}} + \frac{k_{12}}{\lambda_1 - \lambda_2} \left[ \frac{(k_{32} + \lambda_1)e^{\lambda_1 \phi}}{\lambda_1} - \frac{(k_{32} + \lambda_2)e^{\lambda_2 \phi}}{\lambda_2} \right]} - \frac{n_1}{N_1^{(0)}} \quad (7b)$$

The equation for the weight average molecular weight requires a knowledge of the sum  $\sum_2^\infty j^2 (n_j + N_j)$ . The final expressions are rather complicated. It may suffice, therefore, to indicate in the appendix the method of derivation.

Before examining the relationships obtained, we will derive the analogous expressions for the case of complex roots  $\lambda_1$  and  $\lambda_2$  of the secular determinant. This situation will be encountered if we start to increase  $k_{12}$  at constant  $k_{22}$  and  $k_{32}$ . The solution will then be of a different type, but certain essential features will remain unchanged as shown in the following.

We write

$$\lambda_{1,2} = \lambda \pm i\mu$$

$$\lambda = \frac{-(k_{12} + k_{32})}{2}; \quad \mu = \sqrt{k_{12}(k_{22} + 2k_{32}) - \frac{(k_{12} + k_{32})^2}{4}} \quad (4')$$

Instead of (5) we obtain now

$$N_1 = N_1^{(0)} \left[ \cos \mu \phi - \frac{(\lambda + k_{12})}{\mu} \sin \mu \phi \right] e^{\lambda \phi}$$

$$= \frac{N_1^{(0)}}{\sin \mu \phi_\infty} \sin \mu (\phi_\infty - \phi) e^{\lambda \phi}; \quad \mu \phi_\infty = \tan^{-1} \frac{\mu}{\lambda + k_{12}}$$

$$\sum_{j=1}^{\infty} n_j = \frac{N_1^{(0)}}{\mu} k_{12} \sin \mu \phi e^{\lambda \phi}$$

$$n_1 = \frac{N_1^{(0)} k_{12}}{k_{22}(k_{22} + k_{32}) + k_{12} k_{32}} \left\{ e^{\lambda \phi} \left[ k_{22} \cos \mu \phi + \frac{k_{32}(k_{22} + k_{32}) + \lambda(k_{22} + 2k_{32})}{\mu} \sin \mu \phi \right] - k_{32} e^{-(k_{22} + k_{32})\phi} \right\} \quad (5')$$

$$\sum_{j=1}^{\infty} N_j = \frac{N_1^{(0)} k_{32}}{k_{22} + 2k_{32}} - \frac{N_1^{(0)} e^{\lambda \phi}}{k_{22} + 2k_{32}} \left[ \frac{k_{12}(k_{22} + 2k_{32}) + \lambda(k_{22} + k_{32})}{\mu} \sin \mu \phi - (k_{22} + k_{32}) \cos \mu \phi \right]$$

Explicit expressions for the  $n_j$  may be omitted. They can be found by collecting the real and imaginary terms in (5a). The end-point of the reaction corresponds to a finite value for  $\phi_\infty$ , found by setting the two terms in  $N_1$  equal to each other.<sup>7</sup> The general integral (6) leads again to complicated expressions. It is possible however to expand  $\sin \mu (\phi_\infty - \phi)$  and retain the first member only, if  $k_{12}$  and therefore  $\mu$  are small enough. (6) then reduces to an exponential integral. The first approximation valid for the last phases of the reaction, when  $\lambda(\phi_\infty - \phi) \ll 1$ , gives

(7) The alternative  $\phi_\infty = \infty$  must be rejected since it causes  $N_1$  to become a periodic function.

$$\left. \begin{aligned} \mu(\phi_\infty - \phi) &\approx \exp. \left[ -N_1^{(0)} \sqrt{k_{12}(k_{22} + k_{32})} e^{\lambda\phi_\infty} t \right] \\ N_1 &\approx N_1^{(0)} (\phi_\infty - \phi) \sqrt{k_{12}(k_{22} + k_{32})} e^{\lambda\phi} \end{aligned} \right\} \quad (6b')$$

if the definition of  $\sin \mu\phi_\infty$  is introduced. We furthermore obtain for the number average molecular weight

$$Z_n(\phi) = \frac{k_{22} + 2k_{32}}{k_{32} + (k_{22} + k_{32})(\cos \mu\phi - \frac{\lambda}{\mu} \sin \mu\phi) e^{\lambda\phi}} \quad (7a')$$

$$Z_n(\phi; j \geq 2) = \frac{\left[ 1 - \frac{(N_1 + n_1)}{N_1^{(0)}} \right] (k_{22} + 2k_{32})}{k_{32} + e^{\lambda\phi} \left\{ \frac{\sin \mu\phi}{\mu} [k_{12}(k_{22} + 2k_{32}) + k_{32}\lambda] - k_{32} \cos \mu\phi \right\} - \frac{n_1}{N_1^{(0)}} (k_{22} + 2k_{32})} \quad (7b')$$

A comparison of the pertinent results with those obtained in (I) for a first order creation of nuclei shows one simplification: an exact expression for the end-point of the reaction, as expressed in terms of  $\phi$ , can be given.  $\phi_\infty$  is infinite, if  $k_{12}$  is sufficiently small to make the roots  $\lambda_1$  and  $\lambda_2$  real. Otherwise it is given by equation (5'). Of course, also in (I) there was a rather sharp distinction between the case of approximately equal initiation and cessation velocity and that of small initiation rate, as shown in the respective equations (5a') and (5a'') of paper (I) and also in the corresponding expressions for the mean molecular weight of the end-product formed. Because of the above simplification exact expressions can also be given for the final molecular weight. Equations (7a) and (7b) yield

$$\lim_{t \rightarrow \infty} Z_n = \lim_{t \rightarrow \infty} Z (j \geq 2) = \frac{k_{22} + 2k_{32}}{k_{32}} \quad (7c)$$

This equation becomes identical with the corresponding one for a first order initiation (6c') in (I) in the limit of vanishing  $k_{11}$ . Here the result holds also for a finite value of  $k_{12}$ . From a practical standpoint however the situation is identical in both cases. If we set for instance  $k_{32} = 10^{-5}$ ,  $k_{22} = 10^{-2}$  (which is a reasonable assumption for the production of a fairly high molecular weight product), equation (4) requires a value of the order of magnitude of  $10^{-9}$  or less for  $k_{12}$ , if (7a), (7b) and (7c) hold. On the other hand, if we set in equation (6c') of paper (I)  $k_{11} = 10^{-9}$ , retain the above values for  $k_{22}$  and  $k_{32}$  and make  $N_1^{(0)} = 8.74$  (styrene polymerization in pure liquid phase), we arrive practically at the same result for the number average molecular weight. If, in the above example, the rate of initiation is increased by one power of 10, the roots  $\lambda_1$  and  $\lambda_2$  become complex quantities. (7a') and (7b') then yield

$$\lim_{t \rightarrow \infty} Z_n = \lim_{t \rightarrow \infty} Z_n (j \geq 2) = \frac{k_{22} + 2k_{32}}{k_{32} + \sqrt{k_{12}(k_{22} + k_{32})} e^{\lambda\phi_\infty}} \quad (7c')$$

This expression is found by introducing the definition of  $\phi_\infty$  into the trigonometric expressions of (7a'). As is to be expected in such cases, the final molecular weight depends upon the rate of initiation. The greater its value, the smaller

the average chain length of the end-product.

A comparison

with equation (6c') of (I) however shows that this dependence is less pronounced here. It is given approximately by  $\sqrt{k_{12}}$  because  $e^{\lambda\phi_\infty}$  varies only slightly with  $k_{12}$ . Furthermore, in the region  $k_{11} = k_{12} = 10^{-7}$  to  $10^{-8}$ ,  $k_{22} = 10^{-2}$ ,  $k_{32} = 10^{-5}$ , a second order initiation of nuclei will yield a smaller  $Z_n$  because the term added to  $k_{32}$  in (7c') will be slightly larger than the corresponding one in formula (6c') of paper (I). On the other hand, if  $k_{11}$  and  $k_{32}$  are of the same order of magnitude, equations (5a') and (6c) in (I) give for the number average chain length

$$Z_n \approx \sqrt{\frac{N_1^{(0)}(k_{22} + k_{32})}{2k_{11}}}$$

For the values of  $k_{22}$  and  $k_{32}$  previously chosen,  $Z_n$  will again be smaller in the second order case. In purely thermal polymerization reactions therefore, a second order initiation process should, under equal conditions of growth and cessation, lead to a shorter final number average molecular weight than a first order one if  $k_{12}$ , entering (4'), is not too small. Considering that in ordinary reactions second order constants are usually somewhat larger than first order ones, this should be true all the more. Also in a combined first and second order initiation reaction, the introduction of the latter mechanism will tend to decrease the chain length that would have resulted from a simple first order process. In order to submit these conclusions to a direct experimental test, it would be necessary to compare reactions possessing equal values of all the three rates and proceeding according to first and second order initiations, respectively, a situation infrequently met with. The dependence of the final chain length upon temperature must be determined to a large extent by the temperature variation of the initiation velocity, because it possesses the largest activation energy. If we

start therefore from a region in which  $Z_n$  is independent of  $k_1$  (be it a first or second order process), a temperature increase should first lead to a greater drop of  $Z_n$  (and  $Z_w$ ) if the initiation is of second order. Later on, however, this dependence must become less pronounced in reactions leading to long chains because of the square root in formula (7c') as compared with the linear term in (6c') of (I). However, if it is possible to raise the temperature so far that  $k_1 \approx k_3$  ( $Z_n$  of the order of magnitude of 100), this distinction between first and second order process tends to vanish.  $k_{32}$  in the denominator of (7c') becomes small compared with the square root term; (7c') and the above equation for  $Z_n$  shows then approximately the same dependence upon the three rates; the exponential changes only slowly with  $k_{12}$ .

A second and sharper distinction between first and second order initiation reaction can be found in the dependence of the final molecular weight upon the initial concentration. While at a given time  $t$ ,  $Z_n(\phi)$  depends upon  $N_1^{(0)}$  because of equation (6), this holds no longer for the final molecular weight, as given by (7c) and (7c') in contradistinction to the result shown in Fig. 7 of paper (I). Here all the quantities determining  $Z_n$  and  $Z_w$  contain the initial concentration as factor, because all the elementary steps in the chain reaction are of the same order.  $N_1^{(0)}$  therefore cancels out, if the ratio is formed. Previously, however,  $N_1^{(0)}$  appeared as an additive quantity (equation (4) in (I)). The considerations presented in (I) in regard to the dependence of the rate of change of  $Z_n$  in the course of the reaction, remain unchanged. If the rate of initiation is smaller than the other two, the average chain length will become the sooner constant, the smaller  $k_{12}$ .

In (I) it was pointed out that the total number of polymer molecules which equals the ratio

$$\frac{W_p}{M_0} \div Z_n \quad (j \geq 2)$$

at any given time  $t$ , gives a straight line with the slope  $k_{11}$  (apart from a small region in the neighborhood of the origin), if plotted *versus*  $\phi$ . Here however we obtain a curve the slope of which decreases steadily with increasing  $\phi$  (Fig. 5). This conclusion can be drawn from the denominator of equation (7b) as well as of (7b'). It allows a sharp distinction between first and second order activation of nuclei. The deter-

mination of the individual rates requires more effort here, especially in cases of high temperature polymerization. Such a situation is described by the equations with trigonometric terms. After  $\phi$  as function of  $t$  has been determined, it is best to make an estimate of  $k_{22}$  and  $k_{32}$  from a measurement of the final chain length (7c'), and then turn to the equation for  $W_p$

$$W_p \approx M_0(N_1^{(0)} - N_1)$$

as a function of  $\phi$ . In the case of real roots the procedure is somewhat simplified, because (7c) gives immediately the ratio  $k_{22}/k_{32}$  and equation (5) for  $N_1$  can be evaluated more easily.

As in (I) we can investigate whether an over-all order of the reaction can be defined by calculating

$$\frac{dN_1}{dt} = \frac{N_1 dN_1}{d\phi}$$

If equation (5) is applicable, we have

$$\frac{dN_1}{d\phi} \approx \lambda_1 \frac{N_1^{(0)}}{\lambda_1 - \lambda_2} (k_{32} + \lambda_1) e^{\lambda_1 \phi} \approx \lambda_1 N_1^{(0)}$$

This relation holds only if  $|\lambda_2|$  and  $\phi$  are so large that the second exponential in (5) can be neglected. The over-all reaction is therefore during its later stages represented by a second order process with a velocity constant

$$-\lambda_1 \approx \frac{k_{12}(k_{22} + 2k_{32})}{(k_{32} + k_{12})}$$

This expression in turn is valid only if its value is small compared with  $(k_{32} + k_{12})/4$ , as may be seen from the definition (4) of  $\lambda_1$ . If furthermore  $k_{22} \gg k_{32}$ , we find an over-all second order rate with a constant  $(k_{12}k_{22})(k_{32})^{-1}$ . In the previous publication we found under similar approximations the same expression for a first order over-all rate.

If, however, equations (5') and (6b') ought to be consulted, the above procedure does not yield a simple order for the rate of decrease of  $N_1$ .

It appears therefore that the over-all reaction is approximately of the first or second order in its later stages, as defined by the nature of the approximation, according to whether the rate of initiation of active nuclei follows a first or second order process. The over-all rate is in both cases given by the product of the velocities of initiation and growth, divided by that of the breaking of chains, if  $k_{22} \gg k_{32}$ . However, this conclusion can be reached only if the rate of initiation is negligibly small in comparison with that of cessation. Because of the conditions imposed

by equation (4), this latter restriction is much more stringent in the case treated at present. Naturally this result depends also upon the order of the second and third step of the chain process.

Figures 1 and 2 show for one particular example the progress of the polymerization as given by equations (5') and (7b'), respectively. The molecular weight used was that of styrene and the initial concentration was assumed to be 8.74 mole per liter. As in the previous paper an induction period occurs. It depends here in a more complicated manner upon all three rates.

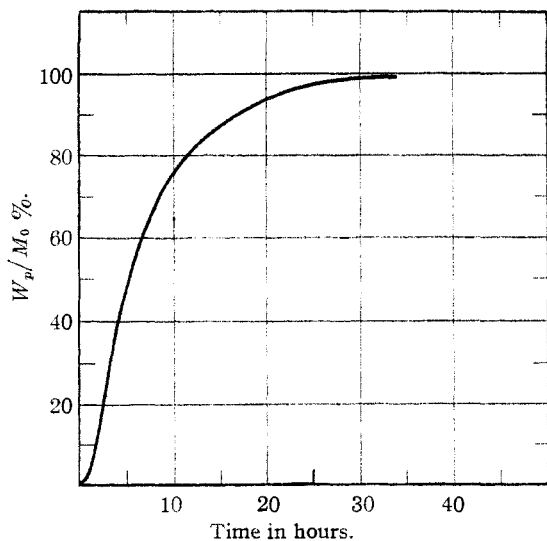


Fig. 1.—Percentage polymerization *versus* time:  $k_{12} = 10^{-8}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{32} = 10^{-5}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>.

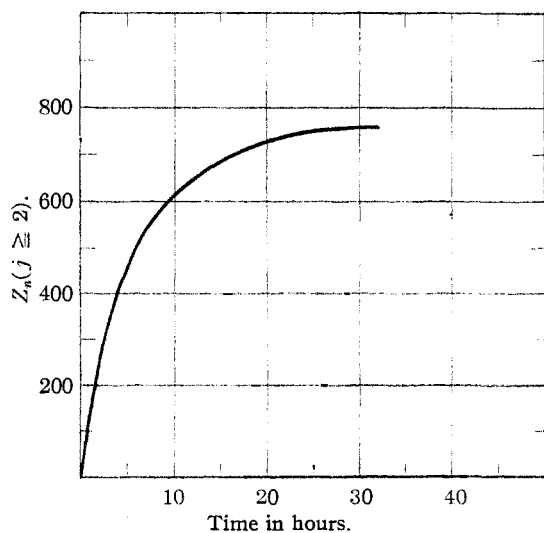


Fig. 2.—Change of number average chain length with time:  $k_{12} = 10^{-8}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{32} = 10^{-5}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>.

The reason, however, for its appearance in our theory is the same, namely, the nature of the boundary condition assumed at  $t = 0$  for the active nuclei.

Figure 3 shows the dependence of the final average chain length on  $k_{12}$  at constant  $k_{22}$  and  $k_{32}$ . These curves have the same general shape as those for the corresponding plot for  $k_{11}$  in (I) and hence the same general conclusions hold. However, it should be noticed that at any given value of  $k_1$  (the  $k_{22}$  and  $k_{32}$  being the same) the value of  $Z_n$  is lower in the case of second order initiation than in the case of first order initiation as previously discussed.

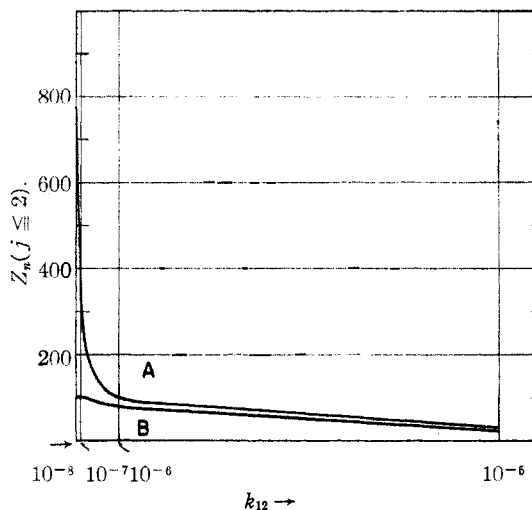


Fig. 3.—Final number average chain length *versus* rate of initiation: A,  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{32} = 10^{-5}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>; B,  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{32} = 10^{-4}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>.

Figure 4 gives the dependence of the final number average chain length on  $k_{32}$  at constant  $k_{12}$  and  $k_{22}$ . Here the curves are very similar to those in Fig. 6 in (I) and the same general conclusions may be drawn. It should be noted, however, that the scale in Fig. 6 in (I) is different from that in Fig. 4. This choice of scale was the result of the choice in values of  $k_{12}$ . They have been chosen smaller throughout than those in Fig. 6 of (I) since this brings about a case of more marked dependence of  $Z_n$  on  $k_{32}$ .

Finally the size distribution of the growing polymer as given by equation (5a) or a corresponding expression found therefrom for complex  $\lambda_1$  and  $\lambda_2$ , may be briefly discussed. As in paper (I) we propose merely to show that Schulz's<sup>8</sup> expression for the number of stable chains of

(8) G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935).

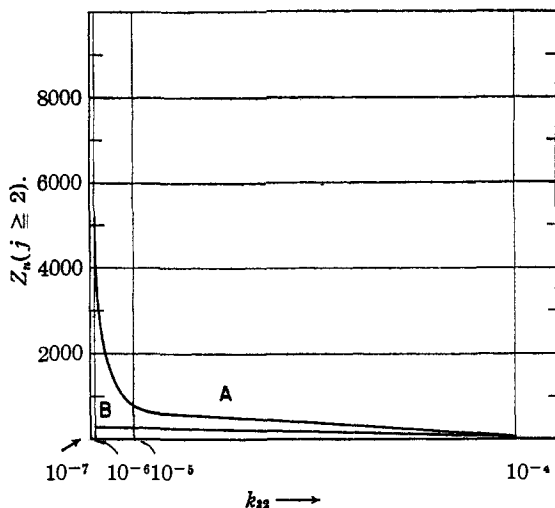


Fig. 4.—Final number average chain length versus rate of termination: A,  $k_{12} = 10^{-8}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>; B,  $k_{12} = 10^{-7}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>.

polymerization degree “ $j$ ” is the limiting value for  $k_{12} \rightarrow 0$ . Only in this case do Schulz’s elementary statistical considerations and our theory lead to the same result. We can for this purpose restrict ourselves to the case treated in (5a). It has already been pointed out after the derivation of this equation that it assumes the same functional type as (4a) in (I), if the value of  $\phi$  is chosen large enough to permit an omission of the second and third term in the brace of (5a). As shown previously by Dostal<sup>9</sup> we can approximate the sum by a step function equal to  $\exp. \{ (k_{22} + k_{32} + \lambda_1)\phi \}$ , if  $j$  is smaller than the exponent and equal to zero if the reverse inequality holds. In between, there will be a transition region, the contribution of which can however be neglected, if  $\phi$  approaches  $\phi_\infty = \infty$ . Accordingly (5a) reduces to

$$\lim_{\phi \rightarrow \infty} n_{j-1} = N_1^{(0)} \frac{k_{12}}{k_{22}} \frac{(k_{32} + \lambda_1)}{(\lambda_1 - \lambda_2)} \left( \frac{k_{22}}{k_{22} + k_{32} + \lambda_1} \right)^{j-1} e^{\lambda_1 \phi}$$

This expression can now be integrated from zero to infinity because of the nature of the step function, and gives in this fashion the limiting value for  $N_j$  according to (5a). Then we neglect the terms of higher than the first order in  $k_{12}$  in equation (4) for  $\lambda_1$  and  $\lambda_2$ . In the result so derived for  $N_j$  we set throughout  $k_{12} = 0$  and obtain finally, if  $k_{22} \gg k_{32}$

$$\lim_{k_{12} \rightarrow 0} N_j \approx N_1^{(0)} (1 - \alpha)^2 \alpha^{j-1}$$

$$\alpha = k_{22} / (k_{22} + k_{32})$$

(9) H. Dostal, *Monatsh.*, **67**, 1 (1935).

This is Schulz’s<sup>8</sup> equation. As on previous occasions, the range of validity of the approximation is smaller than in the first order case. If for instance  $k_{22} = 10^{-2}$ ,  $k_{32} = 10^{-5}$ , then for  $k_{12} \leq 10^{-10}$ , the formula becomes satisfactory.

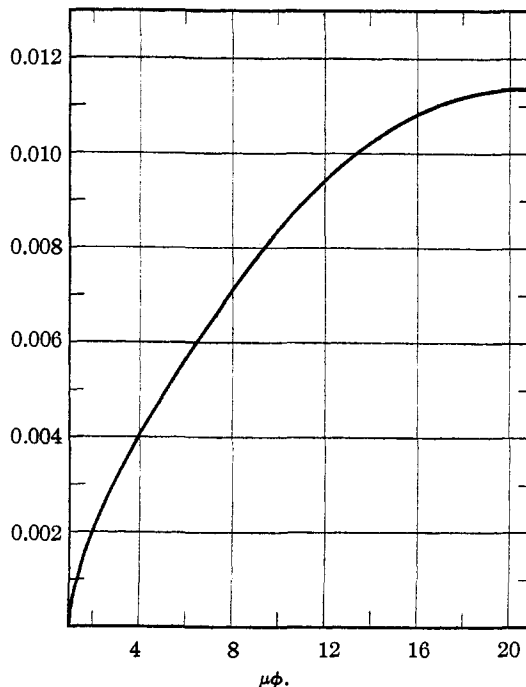


Fig. 5.—Total number of polymer molecules vs. synthetic time:  $k_{12} = 10^{-8}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{22} = 10^{-2}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>;  $k_{32} = 10^{-5}$  mole<sup>-1</sup> liter sec.<sup>-1</sup>.

With decreasing values of the rate of initiation, furthermore, the final average chain length and the final distribution of polymer sizes is reached sooner in the course of the reaction. Schulz’s result, however, as already pointed out by himself, is obtained only under special conditions. It may be seen by integration of the above limiting form for  $n_{j-1}$ , that for larger values of  $k_{12}$ , the expression for  $N_j$  as function of the degree of polymerization “ $j$ ” will be

$$\lim_{t \rightarrow \infty} N_j \approx N_1^{(0)} f(k_{12}, k_{22}, k_{32}) \left( \frac{k_{22}}{k_{22} + k_{32} + \lambda_1} \right)^{j-1}$$

where the function  $f$  depends upon all three velocity constants. For the mechanism discussed in the preceding publication, we obtain for larger values of  $k_{11}$  a formula of a similar type

$$\lim_{t \rightarrow \infty} N_j \approx \frac{k_{11}}{k_{22}} k_{32} \phi_\infty \left( \frac{k_{22}}{k_{22} + k_{32}} \right)^{j-1}$$

as can be seen from (4a) in (I). The approximations involved in the derivation have been pointed out in the discussion of Schulz’s distribution in (I).

**Combined First and Second Order Initiation of Nuclei.**—As mentioned in the introduction, the possibility of a simultaneous or successive appearance of second and first order initiation of nuclei should be admitted. The further alternative of activation by means of  $n_j$  chains (chain transfer) has already been pointed out. Successive appearance of second and first order starting reactions should reflect itself in the rate of increase of the average chain length, as discussed before,<sup>10</sup> and will of course influence the behavior of the over-all reaction. We shall deal here only with the simplest possible case by assuming a simultaneous first and second order creation of active monomer. Instead of (1) and (2) we obtain then by division through  $N_1$

$$\left. \begin{aligned} \frac{dN_1}{d\phi} &= -(k_{22} + k_{32}) \sum_1^{\infty} n_j - k_{12}N_1 - k_{11} \\ \frac{dn_1}{d\phi} &= -(k_{22} + k_{32})n_1 + k_{12}N_1 + k_{11} \\ \frac{d}{d\phi} \sum_1^{\infty} n_j &= -k_{32} \sum_1^{\infty} n_j + k_{12}N_1 + k_{11} \\ \frac{d}{d\phi} \sum_1^{\infty} N_j &= -k_{22} \sum_1^{\infty} n_j - k_{12}N_1 - k_{11} \end{aligned} \right\} (1a)$$

with the solution

$$\left. \begin{aligned} N_1 &= \frac{(N_1^{(0)} + \frac{k_{11}}{k_{12}})}{\lambda_1 - \lambda_2} [(k_{32} + \lambda_1)e^{\lambda_1\phi} - (k_{32} + \lambda_2)e^{\lambda_2\phi}] - \frac{k_{11}}{k_{12}} \\ \sum_1^{\infty} n_j &= \frac{(N_1^{(0)} + \frac{k_{11}}{k_{12}})k_{12}}{\lambda_1 - \lambda_2} (e^{\lambda_1\phi} - e^{\lambda_2\phi}) \end{aligned} \right\} (5b)$$

Because for  $\phi = 0$ ,  $n_1 = 0$ ;  $\sum_1^{\infty} N_j = N_1^{(0)}$ , it follows from (1a) and (5b) that  $n_1$  will turn out as in (5) except for the replacement of the factor  $N_1^{(0)}$  by  $(N_1^{(0)} + \frac{k_{11}}{k_{12}})$ . The same will be true for the rest of the  $n_j$ ,  $j \geq 2$ .  $\sum_1^{\infty} N_j$  will also contain this factor and furthermore an additive constant  $-k_{11}/k_{12}$ .  $\lambda_1$  and  $\lambda_2$  retain their original meaning. As is to be expected, the end-point of the reaction,  $N_1(\phi_{\infty}) = 0$ , corresponds now to a finite value of  $\phi$ . The ratio of  $k_{11}$  to  $k_{12}$  would probably be of the order of magnitude of one or less. As an estimation of all quantities in (5b) shows,  $\phi_{\infty}$  will have a very large value. It can

(10) See page 718.

be calculated in good approximation by omitting the second exponential in  $N_1$ . For the number average chain length we find now

$$\left. \begin{aligned} Z_n(\phi) &= \frac{N_1^{(0)}}{(N_1^{(0)} + \frac{k_{11}}{k_{12}}) \left[ \frac{k_{32}}{k_{22} + 2k_{32}} - \frac{k_{12}}{\lambda_1 - \lambda_2} (k_{22} + k_{32}) \left( \frac{e^{\lambda_1\phi}}{\lambda_1} - \frac{e^{\lambda_2\phi}}{\lambda_2} \right) \right] - \frac{k_{11}}{k_{12}}} \\ \lim_{\phi \rightarrow \infty} Z_n &\approx \frac{k_{22} + 2k_{32}}{k_{32} + \frac{k_{11}(k_{22} + k_{32})}{N_1^{(0)}(k_{32} + \lambda_1)}} \end{aligned} \right\} (8)$$

This latter equation holds if the second exponential can be neglected throughout. Because of the smallness of  $k_{12}$  and the usually large value of  $\phi_{\infty}$  this is permissible. This equation may be compared with equation (6c') in (I) describing a first order initiation, if  $k_{11} \ll k_{32}$ . This condition must also be fulfilled here if  $\phi_{\infty}$  is to be determinable in the above manner. For  $k_{11}$  and  $k_{12}$  should be of the same order of magnitude, and  $k_{12}$  must be small enough, to make  $\lambda_1$  and  $\lambda_2$  real. For  $k_{12} = 0$ , (6c') in (I) and (8) become identical. For finite  $k_{12}$ , equation (8) gives a smaller  $Z_n$  than (6c'). The introduction of a second order initiation process causes a shift of the average polymer size to smaller values than those obtained by a simple first order initiation. The effect, furthermore, is determined by the initial concentration. At large concentrations, the reaction will follow essentially the pattern given by a second order initiation and the molecular weight will, at the end, be independent of the rate of initiation. In dilute solution, however,  $Z_n$  depends upon  $k_{11}$  and  $k_{12}$ . This influence of the initial concentration on  $Z_n$  works in the same direction as that found in equation (6c') of (I).

An experimental distinction of the various possibilities for the initiation reaction should be possible on such a basis. No essential change occurs, if  $k_{12}$  becomes so large that  $\lambda_1$  and  $\lambda_2$  are complex quantities. The equation for  $N_1$  may immediately be found from equation (5') and (5b). Furthermore

$$\lim_{\phi \rightarrow \infty} Z_n = \frac{k_{22} + 2k_{32}}{k_{32} + (k_{22} + k_{32}) \left[ 1 + \frac{k_{11}}{k_{12}} \cdot \frac{1}{N_1^{(0)}} \right] \frac{k_{12}}{\mu} \sin \mu \phi_{\infty} \cdot e^{\lambda \phi_{\infty}}}$$

with

$$\cos \mu \phi_{\infty} - \frac{(\lambda + k_{12})}{\mu} \sin \mu \phi_{\infty} = \frac{k_{11}}{k_{12} \left( N_1^{(0)} + \frac{k_{11}}{k_{12}} \right)} e^{-\lambda \phi_{\infty}}$$

If the ratio  $k_{11}/k_{12}$  is sufficiently small for a given  $N_1^{(0)}$ , we can replace  $\phi_{\infty}$  on the right-hand



side by its original value (5') and then solve for  $\phi_\infty$  on the left-hand side. The value so obtained for  $\mu\phi_\infty$  will evidently be smaller than the previous one. Under our assumptions then,  $Z_n$  will assume values in between those in (7c') and (6c') of (I).

The last stages of the reaction follow a combined first-second order law. Omission of the second exponential in (5b) yields

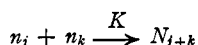
$$\frac{dN_1}{d\phi} \approx \lambda_1 N_1 + \lambda_1 \frac{k_{11}}{k_{12}}$$

That is, a second order constant  $-\lambda_1$  and a first order one  $-\lambda_1 k_{11}/k_{12}$ . In the limit of  $k_{12} \ll k_{32}$ , both reduce to the respective values found before separately.

Granting the assumptions of our theory, the appearance of a combined second and first order initiation of nuclei can, therefore, be experimentally detected by means of a study of the influence of the initial concentration of monomer on the average chain length of the final polymer formed and by following the course of the polymerization, especially during its later stages.

**Mutual Stabilization of Growing Chains.**—As discussed in the beginning, the interaction of polymer molecules in growth and breaking of active chains may become predominant or at least appreciable as soon as the concentration of monomer by number ceases to be very large compared with that of polymer. In an interesting paper, Dostal<sup>11</sup> has shown on the basis of his equations,<sup>12</sup> that this interaction is negligible except for the end of the process. He furthermore compared the order of magnitude of the corresponding rate constant with that of monomer growth and arrived at the conclusion that the activation energy is less while the steric factor decreases. The rate should therefore be decreased approximately by a factor  $j^{-1/2}$  arising from the collision number. On the other hand, in polyesterifications,<sup>13</sup> one single rate, independent of size, describes the reaction satisfactorily.

It still remains to be seen how the above effect enters into the final distribution and how its extent depends upon the rate of initiation and cessation (due to monomer). If we assume a



process to take place, then its relative importance will depend upon the ratio  $k_1/k_3$  which in turn

measures the number of growing polymer molecules. Melville and Gee<sup>14</sup> have derived, apparently by statistical considerations, an equation for the size distribution obtained by means of photo-activation of nuclei. It is not clear from the short discussion given, what further assumptions have been made. We shall later on compare their expression with ours.

It is easy to see how this additional possibility of formation of stable  $j$ -mers will affect the rate equations (1). The rate of decrease of monomer remains, of course, unchanged, while that for the activated chains,  $dn_j/dt$ , will decrease as expressed in an additional term

$$- K n_j \sum_{i=1}^{\infty} n_i; \quad j = 1, 2, \dots$$

It gives the interaction of a growing  $j$ -mer with all unstable chains. Consequently the rate of change of stable  $j$ -mer will increase and contain an additional term

$$\frac{K}{2} \sum_{i=1}^{j-1} n_i n_{j-i}; \quad j \geq 2$$

In the case of a first order initiation, for instance, we find in this manner

$$\frac{d}{dt} \sum_1^{\infty} n_j = k_{11} N_1 - k_{32} N_1 \sum_1^{\infty} n_j - K \left( \sum_1^{\infty} n_j \right)^2 \quad (2a)$$

and correspondingly for a second order initiation.

This equation together with that for  $N_1$  should now be considered. The introduction of  $\phi$  does not facilitate the task here and an exact solution is not available. An attempt at a solution by treating the last term as a small perturbation soon becomes cumbersome and furthermore does not lead to a result for the later stages of the reaction. One could consider for our purpose starting the other way by introducing our previous result into the first two terms of (2a) and then solve the differential equation for  $\sum_1^{\infty} n_j$ . The result can be represented in such an involved fashion only, that a simplified approach must be chosen, although our procedure is somewhat artificial.

We first estimate the relative importance of the first two and the third term in (2a). Let, for instance,  $k_{11} = 10^{-5}$ ,  $k_{32} = 10^{-4}$ , such that  $k_{11}/k_{32}$  is not very small. At a time when about 1% of monomer is left,  $\phi \approx 1.6 \times 10^4$ , as is found from our equations in (I). This gives for the two

(11) H. Dostal, *Monatsh.*, **67**, 637 (1935).

(12) Compare also the introduction of (I).

(13) P. J. Flory, *THIS JOURNAL*, **61**, 3334 (1939).

(14) Given in a paper by R. A. Blease and R. F. Tuckett, *Trans. Faraday Soc.*, **37**, 571 (1941).

terms, respectively:  $1.6 \times 10^{-7}$  and  $K \cdot 6.4 \times 10^{-3}$ . With  $K = 10^{-4}$ , the two terms become about equal, when approximately 96% of monomer has disappeared. On the other hand, if in this example we choose  $N_1 = 8.5$ ,  $\phi = 10^3$ , we find instead  $7.5 \times 10^{-6}$  and  $K \times 10^{-4}$ . The  $K$ -influence seems, therefore, to be important only when  $N_1$  has reached very small values, if  $K$  and  $k_{32}$  are of the same order of magnitude. We neglect now the transition region where both terms

are of equal importance and assume that below a critical instant  $\tau$  in the course of the reaction, the  $K$ -effect is negligible; for  $t \leq \tau$  the reaction is entirely governed by our previous equations, while for  $t > \tau$  the rate constant  $K$  alone determines its course. In this manner we neglect the influence of the polymer-polymer interaction on  $N_1$  and the changes of  $n_j$  and  $N_j$  resulting therefrom.  $\tau$  will correspond to a time when a few per cent. of the original monomer only is unreacted.

Accordingly we restrict ourselves to a treatment of the simplified equation (2a), obtained by retaining the last term on the right-hand side only. The solution will be valid for times  $t > \tau$ , while as boundary conditions for  $t = \tau$ , we have

$$\sum_1^{\infty} n_i = \sum_1^{\infty} n_i(\tau)$$

where the second quantity has the value calculated from equation (2) in this or in the previous paper, according to the assumptions made in regard to the initiation process. In this way we have

$$\sum_1^{\infty} n_j(t > \tau) = \frac{\sum_1^{\infty} n_j(\tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)} \quad (9)$$

Neglecting in the same manner all terms except the  $K$ -term in the equation for the individual  $n_j$ , we find

$$n_j(t \geq \tau) = \frac{n_j(\tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)} = \frac{K n_j(\tau) \sum_1^{\infty} n_j(\tau)(t - \tau)}{n_j(\tau) + K \sum_1^{\infty} n_j(\tau)(t - \tau)} \quad (9a)$$

(9a) shows how the number of growing polymer

molecules originally present, is depleted by the polymer-polymer chain breaking process.

As indicated above, the rate of increase of stable chains depends in our approximation upon the sum  $\sum_{l=1}^{j-1} n_l n_{j-l}$ . Solving the differential equation for  $N_j$  with the aid of (9a), we find for  $j \geq 2$

$$N_j(t \geq \tau) = \frac{K}{2} \sum_{l=1}^{j-1} n_{j-l}(\tau) n_l(\tau) \cdot \frac{(t - \tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)} + N_j(\tau) \quad (10)$$

and therefrom

$$\sum_1^{\infty} N_j(t \geq \tau) = \frac{K}{2} \sum_{j=2}^{\infty} \sum_{l=1}^{j-1} n_{j-l}(\tau) n_l(\tau) \cdot \frac{(t - \tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)} + \sum_1^{\infty} N_j(\tau) \quad (10a)$$

As can be seen from (9a), no unstable material is left at the end of the reaction,  $t = \infty$ . In our previous cases, a small amount remained unstabilized. Its magnitude depended upon the ratio of the rate of initiation to the other rates. When it was small, no  $n_j$  was left, in case the initiation was second order, (equation 5a). If it was first order, the amount unreacted was very small. The reason for this lies in the fact that the monomer was consumed in all three elementary acts of the chain process and therefore the amount present was not sufficient for the stabilization of all growing chains. This will be true all the more in a first order initiation, with a more rapid consumption of monomer than in a second order one. Because in reactions producing real high polymers,  $n_1$  will be negligible in any case at large times  $t$ , the over-all course of the reaction, as expressed in a plot of  $W_p$  versus  $t$ , will not be changed by the new assumptions made. In other cases this change may be found from (9a) by calculating the quantity  $N_1^{(0)} - N_1 - n_1$  and comparing with our previous expressions.

The changes in the average chain length and in the distribution curve will of course be more appreciable. From (9) and (9a) we obtain

$$\sum_1^{\infty} (n_j + N_j)_{t \geq \tau} = \sum_1^{\infty} (n_j + N_j)_{\tau} - \frac{K}{2} \frac{\left[ \sum_1^{\infty} n_j(\tau) \right]^2 (t - \tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)}$$

if we consider that

$$\sum_{j=2}^{\infty} \sum_{l=1}^{j-1} n_{j-l} n_l = \left[ \sum_1^{\infty} n_j \right]^2$$

Therefore

$$(Z_n)_{\bar{n}}^{-1} = (Z_n)_\tau^{-1} - \frac{K}{2N_1^{(0)}} \frac{\left[ \sum_1^{\infty} n_j(\tau) \right]^2 (t - \tau)}{1 + K \sum_1^{\infty} n_j(\tau)(t - \tau)} \quad (11)$$

The chain length obtained without the  $K$ -effect at the (large) time  $\tau$  will not differ appreciably from the final one, especially in that type of reaction in which the average molecular weight remains approximately constant after an initial sharp increase. We can, therefore, consider the second term on the right-hand side of (11) as a correction for the final chain length obtained without mutual termination of chains. As is to be expected, this correction is, in the limit  $t \rightarrow \infty$ , proportional to the total number of unstable chains present at the time the polymer interaction became operative. In order to obtain a numerical estimation, let us consider the case of first order initiation. The value of  $\phi$  corresponding to  $\tau$  will not deviate considerably from  $\phi_\infty$ . We can therefore use (except for the higher end of the distribution curve) the approximation for  $n_j$  described in (I) and also in this paper for the derivation of Schulz's equation. Equations (4a) and (4) of (I) then yield in combination with (10)

$$\lim_{t \rightarrow \infty} N_j \approx N_j(\tau) + \frac{1}{2} \frac{k_{11}k_{32}}{k_{22}^2} \left( \frac{k_{22}}{k_{22} + k_{32}} \right)^j \frac{(j-1)}{(1 - e^{-k_{22}\phi_\infty})} \quad (12)$$

(12) expresses the fact that deviations from the previously calculated size distribution will be small if  $k_{11}$  is small in comparison with the other rates, or if the growth occurs too rapidly. In such a situation an insufficient number of unstable chains, contributing to the above effect, is formed. For  $N_j(\tau)$  we can write the final distribution previously obtained, in the form discussed in this paper on page 721. We find then

$$\lim_{t \rightarrow \infty} N_j \approx \frac{k_{11}k_{32}}{k_{22}} \left( \frac{k_{22}}{k_{22} + k_{32}} \right)^j \left[ \phi_\infty + \frac{(j-1)}{2k_{22}(1 - e^{-k_{22}\phi_\infty})} \right] \quad (12a)$$

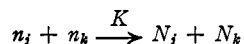
If we set in (12a)  $k_{22} \approx 10^{-2}$ ,  $\phi_\infty$  of the order of magnitude of a few hundred thousands, corresponding to an average value of  $j$  of 600-800, we find a correction of the order of magnitude of 10-20%. For a second order initiation, the limiting form of  $n_j$  for large times, previously derived, leads to similar conclusions for our correction. We can expect the polymer inter-

action to be less important, at least for small  $k_{12}$ , than in the other case, because the amount of monomer decreases less rapidly with time.

The correction for the reciprocal number average chain length of the final polymer is simply

$$\frac{1}{2N_1^{(0)}} \sum_1^{\infty} n_j(\tau)$$

If in the first order case we set for instance  $k_{11} = 10^{-3}$ ,  $k_{22} = 10^{-2}$ ,  $k_{32} = 10^{-5}$ , we find a final number average chain length of 899. The above correction with  $N_1^{(0)} = 8.74$ , then leads to a value of about 950, if at the critical time  $\tau$  the uncorrected value of  $Z_n$  had already reached its full magnitude of 899. An examination of Fig. 4 of (I) shows that the error so committed is not very serious in view of the approximate nature of these considerations. Furthermore, if we do not introduce this assumption, then also a larger value for  $\sum_1^{\infty} n_j$  than the final one should consequently be chosen, and the result approaches again the one found in the simple fashion. We may therefore conclude that under our assumptions, the correction in the case of high molecular weight products leads to an increase of the number (and also weight) average molecular weight of about 10% over that found, if the stable monomer only is operative in the termination of the growing chains. An alternative mechanism, the disproportionation of growing chains<sup>14</sup>



could be treated in a similar manner and would not lead to essentially different conclusions.

Equations (12) and (12a) are not identical with Melville and Gee's<sup>14</sup> size distribution for the case of mutual stabilization. No derivation has been published. It seems, however, that their premises are not identical with ours, but involve the sole action of growing polymers in the termination reaction throughout its course. In the same publication,<sup>14</sup> reference is made to another equation of Melville and Gee for the size distribution. In this case their mechanisms for growth and cessation are identical with ours and the initiation is considered to be a photochemical reaction. Their result coincides with the one derived here and in the previous paper for the final distribution, if  $k_1 \ll k_2$ . Because under such conditions the result is independent of  $k_1$  it holds, of course, for any type of initiation reaction.

In an interesting paper, Blease and Tuckett<sup>14</sup> correlate the distribution curve of polyvinyl acetate samples, as found by fractionation, to the mechanism of the cessation reaction. On the basis of Melville and Gee's results they conclude that mutual termination only is present. A kinetic investigation, with the aid of the theory presented here, should throw further light on this and similar points.

In a recent paper which appeared after this work had been submitted for publication, Herrington and Robertson<sup>15</sup> consider termination reactions involving two active chains only, on the basis of the steady state method, which is essentially applicable if the rate of initiation is very small. Their results are of the same functional type as the second term in (12a), which gives rise to a maximum in the  $N_j$ - $j$  curve.

The  $K$ -effect does not change our previous conclusions in respect to the dependence of the final chain length upon the initial concentration. In how far it affects the approximate constancy of the average molecular weight previously found, is difficult to decide on the basis of our equations. A sudden introduction of the possibility of mutual interaction of growing chains, as assumed here, will of course cause  $Z_n$  to increase suddenly. One may expect that a gradual onset will not cause considerable changes. They will, however, be more noticeable in the weight average than in the number average molecular weight which is less influenced by the addition of a relatively small number of longer chains.

**Further Aspects.**—Limitations of the theory presented in these papers have already been pointed out in the introduction to publication (I). In an extension of these investigations, three problems arise. First, the chain polymerization need not necessarily be described by three constant parameters; the further possibility of time dependent rates should be considered. They would express the changes in the mechanisms of the elementary steps due to structural and concentration variations during the course of the reaction. In the light of our present experimental knowledge of this subject, it seems that any quantitative treatment of the rate equations in this fashion must, of necessity, remain purely formal in character. Our treatment

(15) E. F. G. Herrington and A. Robertson, *Trans. Faraday Soc.*, **38**, 490 (1942).

of the mutual termination of growing polymer chains is a step in this direction.

Second, the question of the branching and cross linking of growing chain molecules, which was briefly mentioned in the beginning of (I), should be further considered although, again, experimental material is scant. The methods developed here would lead to rather complicated expressions if one attempted to calculate the time dependence of the chain length distribution of the numerous species of molecules possible. A statistical approach promises more success. As has been shown previously, probability considerations can be applied to obtain the final size distribution if it is determined solely by the interaction of growth and cessation; in other words the rate of initiation must be small. This is the important case which can lead to the formation of high molecular weight material. Results in this direction have been obtained by Schulz<sup>16</sup> and recently by Flory.<sup>17</sup> The latter author gives a statistical theory of the formation of three-dimensional polymers in polycondensation processes. His results, however, should apply also to chain polymerizations under the above-mentioned restrictions.

Last, a similar situation is encountered when one considers copolymerization. Again a treatment of the rate equations is possible only by means of approximation methods with a restricted range of applicability.<sup>18</sup> Part of this problem, namely, the intramolecular arrangement of the two polymerizing species in a chain, has already been considered in a statistical fashion.<sup>19</sup> In a paper to appear,<sup>20</sup> the kinetics and size distribution of copolymers are investigated for the limiting case mentioned above.

## Appendix

**2. The Relation between  $\phi$  and  $t$  for Real Roots  $\lambda_1$  and  $\lambda_2$ .**—From (6) and (5) we have

$$\frac{N_1^{(0)}}{(\lambda_1 - \lambda_2)} (k_{32} + \lambda_1)t(\phi) = \int_0^\phi \frac{dx e^{-\lambda_1 x}}{1 - \frac{(k_{32} + \lambda_2)}{(k_{32} + \lambda_1)} e^{-(\lambda_1 - \lambda_2)x\phi}}$$

Setting

$$\frac{k_{32} + \lambda_2}{k_{32} + \lambda_1} = q$$

(16) G. V. Schulz, *Z. physik. Chem.*, **B44**, 227 (1939).  
 (17) P. J. Flory, *THIS JOURNAL*, **63**, 3083, 3091, 3096 (1941). See also N. H. Stockmayer, *J. Chem. Phys.*, **11**, 45 (1943).  
 (18) See F. T. Wall, *THIS JOURNAL*, **63**, 1846 (1941).  
 (19) F. T. Wall, *ibid.*, **62**, 803 (1940); **63**, 821 (1941); R. Simha, *ibid.*, **63**, 1479 (1941).  
 (20) H. Branson and R. Simha, *J. Chem. Phys.*, in press.

We find for the indefinite integral by expansion of the denominator

$$\sum_{r=0}^{\infty} \int dx e^{-\lambda_1 x} q^r e^{-r(\lambda_1-\lambda_2)x} = \sum_{r=0}^{\infty} q^r \int e^{-(\lambda_1+r(\lambda_1-\lambda_2))x} dx = -\frac{e^{-\lambda_1 x}}{\lambda_1 - \lambda_2} \sum_{r=0}^{\infty} q^r \frac{e^{-r(\lambda_1-\lambda_2)x}}{r + \frac{\lambda_1}{\lambda_1 - \lambda_2}}$$

Determination of the integration constant to give  $\phi = 0$ , for  $t = 0$ , then leads to the result given in the text. It holds in the whole range of  $\phi$  because  $q < 1$ , and  $(\lambda_1-\lambda_2) > 0$ . The series expansion is therefore convergent throughout.

**2. Formulation of Relations for the Determination of the Weight Average Molecular Weight.**—The rate equations (1) yield

$$\frac{d}{d\phi} \sum_{j=2}^{\infty} j n_j = -(k_{22} + k_{32}) \sum_{j=2}^{\infty} j n_j + k_{22} \sum_{j=2}^{\infty} j n_{j-1}$$

Now

$$\sum_{j=2}^{\infty} j n_{j-1} = \sum_{j=2}^{\infty} (j-1) n_{j-1} + \sum_{j=2}^{\infty} n_{j-1} = \sum_{j=1}^{\infty} j n_j + \sum_{j=1}^{\infty} n_j$$

and therefore

$$\frac{d}{d\phi} \sum_{j=2}^{\infty} j n_j + k_{32} \sum_{j=2}^{\infty} j n_j = k_{22} \left( n_1 + \sum_{j=1}^{\infty} n_j \right) \quad (A)$$

We find from (1) furthermore

$$\frac{d}{d\phi} \sum_{j=2}^{\infty} j^2 n_j = -(k_{22} + k_{32}) \sum_{j=2}^{\infty} j^2 n_j + k_{22} \sum_{j=2}^{\infty} j^2 n_{j-1}$$

Writing

$$j^2 = (j-1)^2 + 2j - 1$$

in the last term of the right-hand side, we arrive at the equation

$$\frac{d}{d\phi} \sum_{j=2}^{\infty} j^2 n_j + k_{32} \sum_{j=2}^{\infty} j^2 n_j = k_{22} \left( 3n_1 + \sum_{j=2}^{\infty} j n_j + \sum_{j=1}^{\infty} n_j \right) \quad (B)$$

Knowing  $\sum_{j=2}^{\infty} j n_j$  from (A), we can solve (B).

Finally we have from (1)

$$\frac{d}{d\phi} \sum_{j=2}^{\infty} j^2 N_j = k_{32} \sum_{j=2}^{\infty} j^2 n_{j-1} = k_{32} \left( \sum_{j=2}^{\infty} j^2 n_j + 3n_1 + \sum_{j=2}^{\infty} j n_j + \sum_{j=1}^{\infty} n_j \right) \quad (C)$$

using the same transformation as in the derivation of (B) to arrive at the last expression. In this manner the weight average chain length, as defined in the appendix of (I), can be calculated with the aid of our equations (5) for  $n_1$  and  $\sum_{j=1}^{\infty} n_j$ .

### Summary

The considerations of the previous paper are extended to second order initiation of monomer. Again two limiting cases are found. A comparison of this case with the previous one, shows that second order initiation gives rise to a product with a smaller final average molecular weight. Only if the rate of initiation is vanishingly small, do the results become identical. No dependence of the final mean chain length on the initial concentration is found. The effect of the mutual termination of growing chains on the final average molecular weight and the size distribution is considered in an approximate manner. Possible extensions of this theory are pointed out.

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