of the kinetics of the exchange reactions between alkyl iodides and iodide ions in alcoholic solution, using I^{128} as an indicator. A new method of obtaining I^{128} in concentrated form, and special measuring apparatus were required. Novel problems in rapid working were set by the short period (25 mins.) of I^{128}.

The following results were obtained: (1) The reactions are bimolecular. (2) The dependence of the bimolecular velocity constant on the concentrations of the reactants was determined for ethyl iodide at 30°. (3) The velocity constants and their temperature coefficients were determined for a series of alkyl iodides.

(4) The publication of this manuscript has been unavoidably delayed by the loss of mail in transit.—*The Editor.*

RECEIVED MARCH 7, 1942[4]

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

On the Kinetics of Polymerization Reactions. I. First Order Initiation Reaction[1]

BY ROBERT GINELL AND ROBERT SIMHA[2]

It is generally accepted today that there are essentially two types of polyreactions leading to the formation of polymers, namely, polycondensation processes, and polymerization reactions in a more restricted sense. The first is a step reaction consisting of a step-wise addition (accompanied by the removal of, *e. g.*, a water molecule) of monomer or polymer. Polymerization reactions on the other hand are processes involving several elementary reactions. Due to the efforts of several workers[3] it has been established that generally four elementary acts must be considered in a chain polymerization. First, an initiation reaction, leading to the activation of a stable monomer molecule of the polymerizable material. Second, a growth reaction of the activated nuclei, creating more or less large molecules. Third, a stabilization reaction of the growing particles. Finally the possibility must be admitted that a chain molecule is able to grow in two or more directions, thus leading to branched molecules. The particular mechanisms involved in these elementary steps, especially in the fourth one, have not as yet been completely clarified for actual polymerizable substances, like styrene or methyl methacrylate, under various experimental conditions as photo-polymerization, thermal activation or catalytic polymerization. However, it appears possible to derive on general grounds certain elementary relationships between the individual rates and the characteristic kinetic quantities like total rate of polymerization, change of average molecular weight and the molecular weight distribution during the course of the reaction. The rates can also be correlated with the properties of the final product.

The kinetic processes discussed above as well as the inverse one, the depolymerization of chain molecules, can be treated in principle by two methods, a deterministic and a statistical one.[4] In the first one, rate equations are formulated for the respective process, usually in the form of differential equations containing the time, *t*, as independent variable, and the concentrations of the various species appearing during the course of the reaction as dependent ones. On the other hand, in processes involving a large number of individual acts, as in radioactive disintegrations, chain and step reactions leading to the union of a relatively large number of reacting partners, a statistical approach to the problem can be chosen. The results so obtained for the relative occurrence of each species are usually expressed, in terms of one or more parameters, the significance of which follows from the nature of the respective problem. An additional consideration, similar to that employed in the first method, gives then the dependence of these parameters upon time.

The first type of approach for simple consecutive reactions was developed principally by Rak-

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

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[3] For references see R. E. Burk, A. J. Weith, H. E. Thompson and I. Williams, "Polymerization, and its Applications in the Fields of Rubber, Synthetic Resins and Petroleum," Reinhold Publishing Company, " New York, N. Y., 1937; and H. Mark and R. Raff, "High Polymeric Reactions," Interscience Publishers, Inc., New York, N. Y., 1941.

[4] A general discussion of some aspects of these methods and their application to radioactive and other processes has been recently given by I. Opatowski, *Proc. Nat. Acad. Sci.*, **28**, 83 (1942).

owski[5] and Wegscheider.[6] A solution of the rate equations describing a polycondensation process was first given by Smoluchowski[7] in another connection, namely, in his theory of rapid coagulation. This subject was later discussed again by Chalmers.[8] A statistical approach was first applied by Flory.[9] A statistical theory of step-wise depolymerization processes has been given by Montroll and Simha.[10] The results become identical with those derived directly from the rate equations by one of the authors.[11] It must be added, however, that the statistical method becomes increasingly difficult to apply if non-uniform conditions are obtaining. In the case of polycondensation reactions for instance, it has been assumed that all functional groups (*e. g.*, hydroxyls or amino groups and carboxyls) possess the same reactivity independently of the size and the internal configuration of the mother molecule to which they are attached. This seems actually to be the case.[12] Equal reactivity of all bonds in the hydrolysis of cellulose or in the thermal degradation of vinyl derivatives, on the other hand, does not appear to be as sound an assumption.[13] In this case the deterministic method is more general or can at least be handled more easily.

True polymerization reactions, however, represent a more difficult situation, as one may expect in such chain processes. Schulz[14] has calculated by means of probability considerations the final size distribution established, as a function of the ratio between the probability of cessation to that of propagation of a growing chain. However, no discussion of the change of the size distribution in the course of the reaction nor of the rate of attainment of the final conditions is presented. His results furthermore can be valid only for processes in which the rate of initiation is negligibly small as compared with the respective velocities of growth as well as cessation. Consequently, they are applicable only to reactions which yield products of high chain lengths of the order of magnitude of several hundreds or more and in which the average molecular weight remains relatively constant throughout the period of observation.

Another attack on this problem was undertaken by Dostal and Mark[15] by starting from the rate equations for each species present. However, their considerations take into account only two elementary steps of the chain reaction: an activation of the monomer and a growth of the nuclei generated in the first step. In further publications Dostal[16] attempted to remove this simplification. He assumed that the stabilization reaction was a first-order process, in particular, an isomerization, due, *e. g.*, in vinyl type compounds to an intramolecular migration of an H-atom, leading to saturation. However, his calculations apply merely to a period in the beginning of the reaction, during which the initial amount of monomer has not yet been appreciably depleted but remains approximately constant. In other words, the cessation reaction is considered as a small perturbation, either by referring to small values of the time or, as done in another paper, by assuming the third rate constant to be so small that the originally calculated distribution curve is only slightly deformed. While hitherto the rates were assumed to be independent of the size of the respective molecule, Dostal[16] pointed out the possibility that in the addition of monomer to a growing chain the steric factor may decrease with increasing chain length. It is hardly possible at present to compute this decrease in a quantitative fashion. A more or less arbitrarily assumed equation for this change of rate can be used to calculate the course of the reaction. Such a mechanism would evidently affect the reaction in the same way as the introduction of a definite chain breaking mechanism. However, the results do not lend themselves readily to a comparison with experimental data.

Chain breaking has been introduced in a more general fashion by Breitenbach.[17] He furthermore considered various possibilities for the order of each of the first three steps mentioned above, and investigated their influence on the over-all rate of polymerization and on the average chain length. In this work the rate equations are not formulated as above for all the growing chains of various lengths, but merely for their over-all con-

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(5) A. Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

(6) R. Wegscheider, *Monatsh.*, **36**, 471 (1915).

(7) M. v. Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).

(8) W. Chalmers. THIS JOURNAL, **56**, 912 (1934).

(9) P. J. Flory, *ibid.*, **58**, 1877 (1936). The formation of three-dimensional polymers has been treated in *ibid.*, **63**, 3083, 3091, 3096 (1941).

(10) E. W. Montroll and R. Simha, *J. Chem. Phys.*, **8**, 721 (1940).

(11) R. Simha, *J. Applied Phys.*, **12**, 569 (1941).

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

(13) See for cellulose, *e. g.*, K. Freudenberg and G. Blomquist, *Ber.*, **68**, 2070 (1935).

(14) G. V. Schulz, *Z. physik. Chem.*, **B30**, 379 (1935); **B44**, 227 (1939).

(15) H. Dostal and H. Mark, *ibid.*, **B29**, 299 (1935).

(16) H. Dostal, *Monatsh.*, **67**, 1, 637 (1935).

(17) J. W. Breitenbach, *ibid.*, **71**, 275 (1938).

centration. By application of Bodenstein's[18] steady state method to this concentration of activated chains, the final results are obtained. They can be applied strictly only within a time period during which the rate of change of the concentration of active chains is infinitely small. More recently Herington and Robertson[19] have extended this treatment in order to obtain the size distribution of the polymer mixture. In the course of their work on the catalyzed polymerization of styrene, Norrish and Brookman[20] arrived at an equation for the average degree of polymerization as a function of time, catalyst concentration, and growth and cessation rate, which gives a result in qualitative agreement with experiment.[21] However, the distribution of sizes cannot be derived. Furthermore, it seems to us that the case treated is too specialized.

The important quantities in a theory which describes the entire course of a polymerization reaction in all its aspects, total turnover as well as chain length distribution, are naturally the rate constants of the elementary steps. These in turn depend upon a series of conditions besides the nature of the reactants, in particular, the medium in which the reaction is carried out and the amount and nature of catalyst present. It is hardly possible at present to formulate a polymerization theory which takes all these factors into account satisfactorily. In our present attempt the rates will be described by means of three or more phenomenological quantities which remain unchanged during the course of the reaction. Possibly this assumption will restrict the application of the results obtained to polymerizations in dilute phase or to the first stages of the reaction. For, otherwise, the increased viscosity of the mixture may appreciably decrease the original value of the rates of growth and cessation. Further changes may be caused by the heat developed in the exothermic growth reaction.

It has been found by several authors[22] that the concentration of substances like certain peroxides or quinones, which accelerate or slow down the polymerization of vinyl derivatives, decreases during this process. Consequently one may expect the rates not to be truly constant throughout the reaction.

In the following it will be assumed that the initiation reaction is of first order in the concentration of monomer. It will furthermore be postulated that the stable monomer is operative in growth as well as in cessation. Third, the cessation will be assumed to be a second-order reaction. The second of these three conditions should be fulfilled at least as long as the number of polymer molecules is exceeded by those of the monomer. We shall, in the course of another paper, revert to this point and consider by an approximation method the possibility of the mutual stabilization of the growing molecules. The third condition must be introduced in order to obtain a solution of the differential equations valid in the whole range of the variable t. As mentioned above, Dostal[16] has applied a perturbation method in the case of a first order cessation reaction. It is possible to improve his calculations somewhat. However, the necessary effort exceeds the importance and the range of validity of the results in respect to time. Their discussion has therefore been omitted here. It is furthermore not difficult to take into account the possibility of a growing chain becoming stabilized by transferring its reactivity, for instance, to a stable monomer. Dostal and Schulz's results will turn out as special cases of those derived below. Furthermore, the dependence of the average molecular weight upon the rate of initiation and its approximate constancy in respect to time under certain conditions, found experimentally, are a direct consequence of the results obtained in the following paragraphs.

After completion of the manuscript for this and the following publication, two interesting papers by Marei[23] came to our attention. The starting assumptions in this first paper are identical with those given in his first work. However, certain aspects of the polymerization problem have not been considered in Marei's treatment. On the other hand, this author has developed certain formulas for chain transfer. The range of validity of some approximations used seems more restricted than indicated in the paper. For the

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[18] M. Bodenstein, *Z. physik. Chem.*, **85**, 329 (1913); *Z. Elektrochem.*, **42**, 443 (1936). See in connection with polymerization reactions also G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **B36**, 184 (1937).

[19] E. F. G. Herington and A. Robertson, *Trans. Faraday Soc.*, **38**, 490 (1942).

[20] R. G. W. Norrish and E. F. Brookman, *Proc. Roy. Soc.*, **A171**, 147 (1939).

[21] See page 713.

[22] H. W. Starkweather and G. B. Taylor, THIS JOURNAL, **52**, 4708 (1930); S. Kamenskaja and S. Medwedew, *Acta Physicochim. U. R. S. S.*, **13**, 565 (1940); H. N. Alyea, J. J. Gartland, Jr., and H. R. Graham, Jr., *Ind. Eng. Chem.*, **34**, 458 (1942).

[23] F. Marei, *Acta Physicochim. U. R. S. S.*, **9**, 741 (1938); **9**, 759 (1938).

sake of clarity, the fundamental rate equations are presented explicitly in the following.

TABLE OF SYMBOLS EMPLOYED

k_{11}	First order rate constant of initiation reaction (sec.$^{-1}$)
k_{12}	Second order rate constant of initiation reaction (mole^{-1} liter sec.$^{-1}$)
k_{22}	Rate constant of the growth reaction (mole^{-1} liter sec.$^{-1}$)
k_{32}	Rate constant of the cessation reaction (mole^{-1} liter sec.$^{-1}$)
K	Rate constant of the cessation reaction (mole^{-1} liter sec.$^{-1}$) between growing chains
$N_1^{(0)}$	Initial concentration (mole liter^{-1}) of monomer
$n_j(t)$	Concentration of unstable chains consisting of "j" monomer units at time "t"
$N_j(t)$	Concentration of stable chains consisting of "j" monomer units at time "t"
M_0	Molecular weight of monomer
W_p	Concentration by weight of polymerized material
Z_n	Number average chain length
$Z_n(j \geqq 2)$	Number average chain length excluding monomer
Z_w	Weight average chain length
$Z_w(j \geqq 2)$	Weight average chain length, excluding monomer

Mathematical Development

The calculations will be based on the following mechanism for the three elementary processes.

$$\text{Activation: } N_1 \xrightarrow{k_{11}} n_1$$

$$\text{Growth: } n_j + N_1 \xrightarrow{k_{22}} n_{j+1}, j = 1, 2 \ldots$$

$$\text{Cessation: } n_j + N_1 \xrightarrow{k_{32}} N_{j+1}, j = 1, 2 \ldots$$

The possibility that a growing j-mer is stabilized by a monomer without its being included in the chain does not appear probable. It would introduce only minor changes in our final formulas. The following equations express the change of the relative frequency of each species with time

$$\left.\begin{aligned}
\frac{dN_1}{dt} &= -k_{11}N_1 - k_{22}N_1\sum_{j=1}^{\infty} n_j - k_{32}N_1\sum_{j=1}^{\infty} n_j \\
\frac{dn_1}{dt} &= +k_{11}N_1 - k_{22}N_1n_1 - k_{32}N_1n_1 \\
\frac{dn_j}{dt} &= k_{22}N_1n_{j-1} - k_{22}N_1n_j - k_{32}N_1n_j; \quad j \geqq 2 \\
\frac{dN_j}{dt} &= k_{32}N_1n_{j-1} \qquad j \geqq 2
\end{aligned}\right\} \quad (1)$$

This system satisfies the law of the conservation of mass because

$$\frac{d}{dt}\sum_1^{\infty} j(n_j + N_j) = 0$$

It is useful to write explicitly two additional equations, namely

$$\left.\begin{aligned}
\frac{d}{dt}\sum_1^{\infty} n_j &= k_{11}N_1 - k_{32}N_1\sum_1^{\infty} n_j \\
\frac{d}{dt}\sum_1^{\infty} N_j &= -k_{11}N_1 - k_{22}N_1\sum_1^{\infty} n_j
\end{aligned}\right\} \quad (2)$$

which follow immediately from (1). We furthermore introduce as new independent variable

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

This amounts to considering $k_{ij}N_1$ as rate constants rather than the true rates,[24] and results in a linearization of our system.

We combine now (2) with the first two equations in (1) and divide through by N_1. As boundary conditions we have for the beginning of the reaction $t = 0$; $\phi = 0$, according to the definition (3); $n_j = 0$, $j \geqq 1$; $N_j = 0, j \geqq 2$, $N_1 = N_1^{(0)}$. For the end $t = \infty$, $\phi = \phi_\infty$, $N_1 = 0$. The first equation in (2) yields

$$\frac{d}{d\phi}\sum_1^{\infty} n_j + k_{32}\sum_1^{\infty} n_j - k_{11} = 0$$

This linear differential equation of the first order has the standard solution

$$\sum_1^{\infty} n_j = e^{-k_{32}\phi}\left[C + k_{11}\int e^{k_{32}\phi}\, d\phi\right] = Ce^{-k_{32}\phi} + \frac{k_{11}}{k_{32}}$$

where C is an integration constant equal to $-k_{11}/k_{32}$ in view of our boundary conditions.

The second equation in (2) has the solution

$$\sum_1^{\infty} N_j = -\int\left(k_{11} + k_{22}\sum_1^{\infty} n_j\right)d\phi$$

In a similar manner N_1 and n_1 can be found from (1), since $\sum_1^{\infty} n_j$ is known. The final result is

$$\left.\begin{aligned}
N_1 &= N_1^{(0)} + \frac{k_{11}(k_{22} + k_{32})}{k_{32}^2} - k_{11}\left[1 + \frac{(k_{22} + k_{32})}{k_{32}}\right]\phi - \\
&\qquad \frac{k_{11}(k_{22} + k_{32})}{k_{32}^2}\, e^{-k_{32}\phi} = A - B\phi - Ce^{-k_{32}\phi} \\
n_1 &= \frac{k_{11}}{k_{22} + k_{32}}\left[1 - e^{-(k_{22} + k_{32})\phi}\right] \\
\sum_1^{\infty} N_j &= N_1^{(0)} + \frac{k_{11}k_{22}}{k_{32}^2} - \frac{k_{11}(k_{22} + k_{32})}{k_{32}}\,\phi - \frac{k_{11}k_{22}}{k_{32}}\, e^{-k_{32}\phi} \\
\sum_1^{\infty} n_j &= \frac{k_{11}}{k_{32}}\,(1 - e^{-k_{32}\phi})
\end{aligned}\right\} \quad (4)$$

There remains to be found an expression for n_j, $j \geqq 2$. The solution obeys the equation

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

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[24] For the mathematical theory of chain processes with time dependent parameters see for instance O. Lundberg, "On Random Processes and their Application to Sickness and Accident Statistics." Uppsala, 1940.

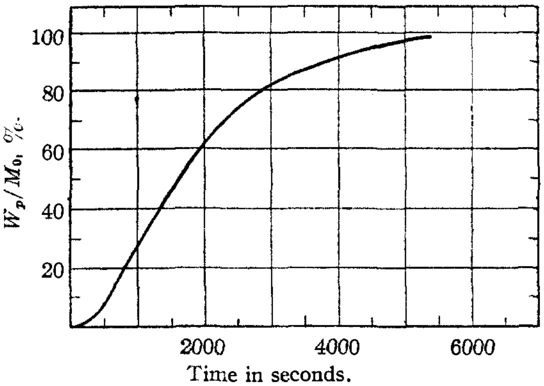

Fig. 1.—Percentage polymerization *vs.* time: $k_{11} = 10^{-5}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-4}$ mole^{-1} liter sec.$^{-1}$

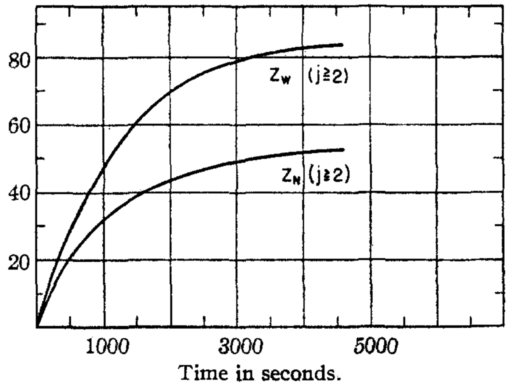

Fig. 2.—Change of weight and number average chain length with time: $k_{11} = 10^{-5}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-4}$ mole^{-1} liter sec.$^{-1}$

together with the above expression for n_1. It may be seen by insertion that the final result is

$$\left.\begin{aligned} n_j &= \frac{k_{11}}{k_{22}}\left(\frac{k_{22}}{k_{22}+k_{32}}\right)^j e^{-(k_{22}+k_{32})\phi}\sum_{s=j}^{\infty}\frac{[(k_{22}+k_{32})\phi]^s}{s!}, j \geqq 1 \\ &\text{and} \\ N_j &= k_{32}\int_0^{\phi} n_{j-1}\,\mathrm{d}\phi;\ j \geqq 2 \end{aligned}\right\} \quad (4a)$$

Equation (4a) gives the size distribution of the polymer. By putting $N_j = 0$ and $k_{32} = 0$ in (4) and (4a) we come back to Dostal's equations. The connection between the variable ϕ and the time t is established by means of the relation

$$t(\phi) = \int_0^{\phi}\frac{\mathrm{d}x}{N_1(x)} = \int_0^{\phi}\frac{\mathrm{d}x}{A - Bx - Ce^{-k_{32}x}} \quad (5)$$

from which ϕ can be expressed in terms of t by inversion. The above integral cannot be evaluated exactly in analytical form. Series expansion of the integrand leads to results which cannot easily be inverted. Numerical integration has been used in all examples presented in the text. In an evaluation of experimental polymerization–time curves the area bounded by the curve representing the total weight of polymerized material, the ordinate axis, the horizontal asymptote indicating complete polymerization and a vertical drawn through the desired point on the time axis (upper part of Figs. 1 and 3) gives the corresponding value of the quantity $M_0\phi$ as can be seen from equation (3). For we have

$$\int_0^t \frac{W_p}{M_0}\,\mathrm{d}t = \int_0^t \sum_2^{\infty} j(N_j + n_j)\mathrm{d}t =$$
$$\int_0^t (N_1^{(0)} - N_1 - n_1)\mathrm{d}t \approx \int_0^t (N_1^{(0)} - N_1)\mathrm{d}t$$

The relatively small number of activated monomer molecules n_1 can be neglected here. In this manner it is then possible to express all important results necessary for an evaluation of the rate constants k_{ij} from experimental data, as function of ϕ instead of t.

We require for our purposes the quantity ϕ_∞ characterizing the end-point of the polymerization reaction reached, according to our basic mechanism, when $N_1 = 0$. Accordingly ϕ_∞ fulfils the condition

$$A - B\phi_\infty - Ce^{-k_{32}\phi_\infty} = 0 \quad (5a)$$

Again no exact solution of this transcendental equation is available. We consider therefore two limiting cases. Let us assume first that $k_{32}\phi_\infty$ is sufficiently small to permit expansion of the exponential up to the quadratic term. The growth reaction will furthermore proceed much more rapidly than the initiation, $k_{22} > k_{11}$. Remembering the definition of A, B and C we find in this fashion from (5a)

$$\phi_\infty \approx \sqrt{\frac{2N_1^{(0)}}{k_{11}(k_{22}+k_{32})}} \quad (5a')$$

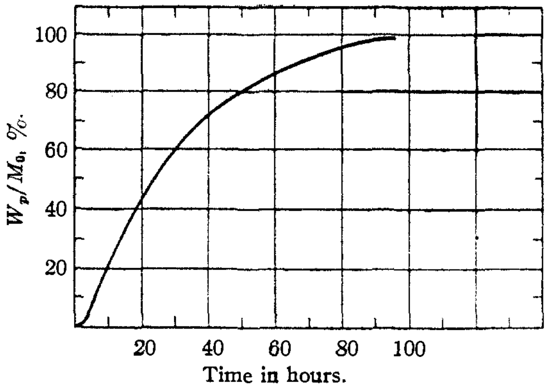

Fig. 3.—Percentage polymerization *vs.* time: $k_{11} = 10^{-8}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-5}$ mole^{-1} liter sec.$^{-1}$.

According to its derivation, (5a′) is valid if $k_{32}\phi_\infty \ll 1$, or

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

Putting for instance $N_1^{(0)} \approx 10$, $k_{22} = 10^{-2}$, we obtain a k_{11} and k_{32} of the same order of magnitude. Evidently, if this is the case, the starting material will be produced and used up rapidly and only small chain molecules created on the average, because initiation and stabilization occur with equal frequency. On the other hand, if $k_{11} \ll k_{32}$, the magnitude of ϕ_∞ is essentially determined by the first two terms in (5a), because the exponential will be rather small. We can therefore write

$$\phi_\infty \approx A/B \qquad (5a'')$$

and inserting this into the exponential, a better approximation can be found. This procedure may be used if

$$k_{32}A/B \gg 1$$

when $k_{22} > k_{32}$. With our previous values of $N_1^{(0)}$ and k_{22} this leads to $k_{32}^2 \gg k_{11} \times 10^{-3}$. In other words this latter approximation holds the better, the smaller k_{11} not only in respect to k_{22}, but also to k_{32}. This in turn will lead to a relatively long duration of the reaction (of the order of magnitude of 10^1–10^2 or more hours) and to a large average degree of polymerization (of the order of magnitude of a hundred to several thousands). It is not difficult to express ϕ as function of t explicitly if these neglections can be carried to values of $\phi < \phi_\infty$, that is, used for a whole period of the reaction. This procedure may be omitted here however.

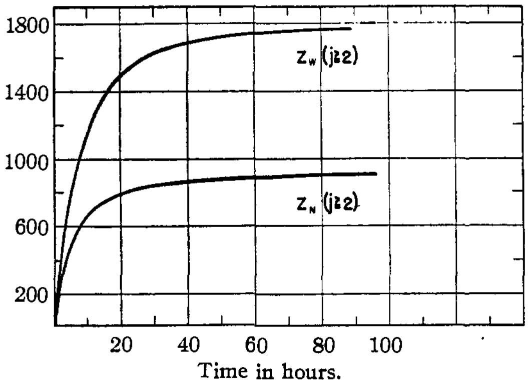

Fig. 4.—Change of weight and number average chain length with time: $k_{11} = 10^{-8}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-5}$ mole^{-1} liter sec.$^{-1}$.

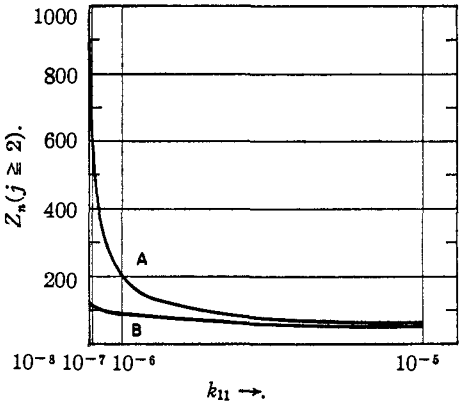

Fig. 5.—Number average chain length *vs.* rate of initiation: A, $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-5}$ mole^{-1} liter sec.$^{-1}$; B, $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; $k_{32} = 10^{-4}$ mole^{-1} liter sec.$^{-1}$.

We now compute the number and weight average chain length as found by chemical methods, from colligative properties and viscosity measurements in solution, respectively.[25] As shown in the appendix, we find

$$Z_n(\phi) = \frac{N_1^{(0)}}{N_1^{(0)} - \frac{k_{11}(k_{22} + k_{32})}{k_{32}^2}\,(k_{32}\phi + e^{-k_{32}\phi} - 1)} \qquad (6a)$$

$$Z_n(\phi;\ j \geqq 2) = \frac{B\phi - C(1 - e^{-k_{32}\phi}) - \frac{k_{11}}{k_{22} + k_{32}}\,[1 - e^{-(k_{22} + k_{32})\phi}]}{k_{11}\phi - \frac{k_{11}}{k_{22} + k_{32}}\,[1 - e^{-(k_{22} + k_{32})\phi}]} \qquad (6b)$$

$$Z_w(\phi) = 1 + \frac{2k_{11}}{N_1^{(0)}k_{32}^2}\,(k_{22} + k_{32})\left[(k_{22} + k_{32})\phi - \frac{(2k_{22} + k_{32})}{k_{32}}\,(1 - e^{-k_{32}\phi}) + k_{22}\phi e^{-k_{32}\phi}\right] \qquad (7a)$$

$$Z_w(\phi; j \geqq 2) = \frac{Z_w(\phi)N_1^{(0)} - N_1 - n_1}{N_1^{(0)} - N_1 - n_1} \qquad (7b)$$

(7b) follows directly from the definition of the quantities.

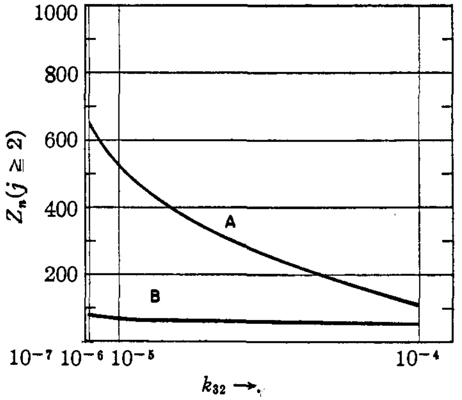

Fig. 6.—Number average chain length *vs.* rate of termination: A, $k_{11} = 10^{-7}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$; B, $k_{11} = 10^{-5}$ sec.$^{-1}$; $k_{22} = 10^{-2}$ mole^{-1} liter sec.$^{-1}$.

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

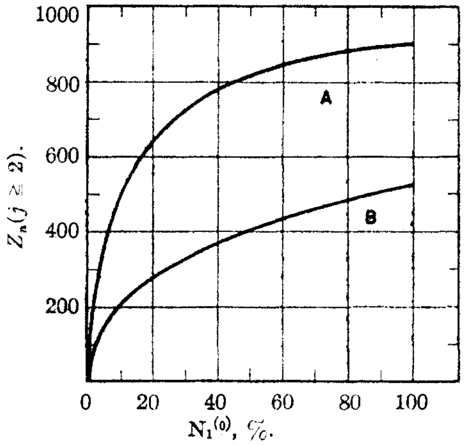

Fig. 7.—Final number average chain length *vs.* initial concentration of monomer: A, $k_{11} = 10^{-8}$; $k_{22} = 10^{-2}$; $k_{32} = 10^{-5}$; B, $k_{11} = 10^{-7}$; $k_{22} = 10^{-2}$; $k_{32} = 10^{-5}$.

Some of these expressions are not easy to use for a determination of the individual rates. Considerable simplification is achieved however if we turn our attention toward the limit $t \rightarrow \infty$ or $\phi \rightarrow \phi_\infty$. In this instance, the amount of unstable monomer (third term in the numerator of (6b)) has reached a constant if not negligible value. The last exponential can be omitted when $k_{22}\,\phi \gg 1$ and this condition is ordinarily fulfilled very soon in the course of the reaction. It may also be noted that extrapolation to infinite time is easier and more accurate on the basis of ϕ-plots because of the finite limits of ϕ. Thus

$$\lim_{t \rightarrow \infty} Z_n = \frac{N_1^{(0)}}{k_{11}\phi_\infty}; \quad \lim_{t \rightarrow \infty} Z_n(j \geqq 2) \approx \frac{N_1^{(0)} - \dfrac{k_{11}}{k_{22} + k_{32}}}{k_{11}\phi_\infty - \dfrac{k_{11}}{k_{22} + k_{32}}} \tag{6c}$$

If $k_{11} \ll k_{32}$, (5a″) holds, and for $t \rightarrow \infty$

$$Z_n \approx Z_n(j \geqq 2) \approx \frac{k_{22} + 2k_{32}}{k_{32} + \dfrac{k_{11}}{N_1^{(0)}k_{32}}\,(k_{22} + k_{32})} \tag{6c'}$$

If the second term in the denominator can be neglected, we find the expected result, that the final average molecular weight depends solely upon the ratio of growth and cessation velocity, as follows also from Schulz's[14] statistical considerations and from Robertson and Herington's[19] treatment. However, if this latter term cannot be omitted, (6c′) expresses the fact that we obtain in polymerization reactions smaller end-products at higher temperatures or at higher concentrations of catalyst or accelerator. Both factors act to increase k_{11}. The first, because the rate of initiation is more temperature sensitive than k_{22} or k_{32} due to its much higher energy of activation under the conditions for which (5a″) and (6c′) hold. In such reactions the heat developed in the course of the reaction, if not removed, will tend to shift the final chain length and also the size distribution toward smaller values.

The above equation points to a dependence of the final degree of polymerization upon the initial concentration of monomer. The larger $N_1^{(0)}$, the greater Z_n, as shown in Fig. 7. Suess, Pilch and Rudorfer[26] obtained in their studies of the polymerization of styrene in various solvents, an expression of the same type in respect to $N_1^{(0)}$, although for carbon tetrachloride they found the first term in the denominator to be negative. They arrive at this result by the way of Bodenstein's[18] steady state method, assuming a mechanism different from ours for initiation and breaking of chains. In a similar manner Schulz and Husemann[18] derive an average polymerization degree proportional to the square root of the initial monomer concentration. An evaluation of Z_w leads to analogous results. In the limit of $k_{11}/N_1^{(0)} \rightarrow 0$

$$\lim_{t \rightarrow \infty} Z_w = 1 + \frac{2(k_{22} + k_{32})^2}{k_{32}(k_{22} + 2k_{32})} \tag{7c}$$

so that $Z_w \approx 2Z_n$ at the end-point, if $k_{22} \gg k_{32}$. In this case this equation becomes identical with Schulz's result.

According to the definition of $Z_n(j \geqq 2)$, the numerator of (6b) equals W_p/M_0, while the denominator represents the total number of stabilized and unstabilized polymer molecules, which is, therefore, determined by the ratio of the first two quantities. If plotted *versus* ϕ, it should give approximately a straight line with the slope k_{11} if the rate of initiation follows a first order law. Extrapolation of the straight part of this plot to zero ϕ then yields $k_{22} + k_{32}$. Evaluation of $W_p - \phi$ curves for instance, then furnishes k_{22} and k_{32}.

Discussion

Figures 1 to 4 show the progress of the polymerization for two sets of values of the rate constants. In the calculations the molecular weight used was that of styrene and the initial concentration was accordingly assumed to be 8.74 moles liter^{-1}. In both these cases, an induction period exists as found already by Dostal.[16] The extent of this induction period depends on the values of

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(26) H. Suess, K. Pilch and Rudorfer, *Z. physik. Chem.*, **A179**, 361 (1937).

k_{22} and k_{32}, as can be seen from the equation (4) for n_1. The greater $(k_{22} + k_{32})$ or k_{11}, the smaller the induction period. This follows naturally from the boundary conditions which were assumed, namely, at $t = 0, n_1 = 0$. If we admit the possibility that a small number of activated monomer molecules may be present at the beginning of our experiment, then the induction period is considerably shortened and may for all practical purposes disappear. Inhibitors or impurities acting as such, on the other hand, will give rise to an induction period of their own which may overshadow that arising from the reaction mechanism itself.

It has been attempted in work on polymerization to represent the course of the reaction by an over-all rate, corresponding to a certain reaction order.[27] On the basis of the considerations presented here one may expect this not to be possible in general. In order to investigate this point we can calculate the rate of decrease of N_1

$$\mathrm{d}N_1/\mathrm{d}t = N_1\mathrm{d}N_1/\mathrm{d}\phi$$

In an n-th order process therefore $\mathrm{d}N_1/\mathrm{d}\phi$ should be proportional to ${N_1}^{n-1}$. In our case we have $\mathrm{d}N_1/\mathrm{d}\phi = -B + Ck_{32}\, e^{-k_{32}\phi} \approx -B(1 - e^{-k_{32}\phi})$, if $k_{22}/k_{32} \gg 1$. However, only if the exponential can be neglected, do we obtain a first order overall rate with a constant $B \approx k_{11}k_{22}/k_{32}$, as found by Breitenbach.[17] This condition will be approximately fulfilled toward the end, in processes in which $k_{11} \ll k_{32}$, and consequently $k_{32}\, \phi_\infty \gg 1$, that is, in reactions of long duration which yield high molecular weight products.

A comparison of Figs. 2 and 4 shows that the mean molecular weight remains approximately constant after a rapid initial increase if k_{11} is very small in relation to the other rates. If this condition is not fulfilled, there is a continuous rise. These facts have already been pointed out by Norrish and Brookman.[20]

Figure 5 shows the dependence of the final number average chain length on k_{11} at constant k_{22} and k_{32} according to expression (6c). It may be noticed that the rate of initiation becomes relatively unimportant in determining the magnitude of the final average polymerization degree if the ratio k_{22}/k_{32} is small. When this ratio is increased by a power of ten, then a sharp increase of Z_n results as soon as k_{11} becomes appreciably smaller than k_{32}.

Figure 6 shows a corresponding plot *versus* the rate of cessation. Similarly k_{32} is relatively unimportant when k_{22}/k_{11} is small. As k_{22}/k_{11} increases, the influence of k_{32} on Z_n becomes more pronounced.

Because of space requirements no size distribution curves are reproduced here. It is possible, however, to draw certain conclusions without further calculations, if $(k_{22} + k_{32})$ is sufficiently large, that is, during the last stages of the reaction. It has been pointed out by Dostal[16] that, under this condition, it is permissible to replace the ϕ-dependent part in the equation (4a) for n_j by one, if $j < (k_{22} + k_{32})\phi$. For the sum can then be approximated by $e^{(k_{22} + k_{32})\phi}$. If on the other hand, $j > (k_{22} + k_{22})\, \phi$, $n_j \approx 0$. In this way the weight distribution curve, giving $M_0 j n_j$ as function of j, approaches the shape of Schulz's[14] curves, although with different parameters in it. Furthermore, the distribution of stable polymer at a given time t is simply found in this approximation by multiplication of the previous curves for n_{j-1} by a factor $k_{32}\phi(t)$, that is, by changing the ordinate scale. This result will be valid, therefore, during the period in which the average molecular weight does not vary appreciably with time.

As is to be expected, the final distribution of chain lengths becomes identical with Schulz's[14] function if $k_{11} \ll k_{32}$, $k_{22}/k_{32} \gg 1$. We can then set $\phi_\infty \approx A/B \approx {N_1}^{(0)}k_{32}/k_{11}k_{22}$, if ${N_1}^{(0)}$ is sufficiently large. (4a) then leads to

$$N_j = N_1^{(0)}(1 - \alpha)^2\alpha^{j-1}$$

with $\alpha = k_{22}/(k_{22} + k_{32})$. This is Schulz's equation; n_j is negligible. For a determination of the individual rates of a measured polymerization reaction it seems safer to turn to the equations for W_p and Z_n or Z_w in the manner previously described, than to the above equation. However, in the cases specified before, one can set the final number average polymerization degree equal to k_{22}/k_{32} for an estimation of this ratio. A discussion of available kinetic data in the light of this theory may be reserved for a later occasion. It should be possible on this basis to determine not only the ratio between propagation and termination, but also absolute values for all individual steps, necessary for a better insight into the molecular mechanism of each elementary act.

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(27) See for instance: J. K. Moore, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **63**, 2954 (1941).

Appendix

Calculation of Number and Weight Average Chain Length.—The usual definition of average molecular weights[25] leads in our case to

$$Z_n = \frac{\sum_{j=1}^{\infty} j(n_j + N_j)}{\sum_{j=1}^{\infty} (n_j + N_j)} = \frac{N_1^{(0)}}{\sum_{j=1}^{\infty}(n_j + N_j)}$$

$$Z_w = \frac{\sum_{j=1}^{\infty} j^2(n_j + N_j)}{\sum_{j=1}^{\infty} j(n_j + N_j)} = \frac{\sum_{j=1}^{\infty} j^2(n_j + N_j)}{N_1^{(0)}}$$

Similarly $Z_n(j \geqq 2)$ and $Z_w(j \geqq 2)$ are obtained by subtracting in the respective numerators and denominators the quantity $(N_1 + n_1)$. In this manner equations (6a) and (6b) follow immediately from (4).

For the evaluation of the other sums we write n_j as

$$n_j = \frac{k_{11}}{k_{22}} \alpha^j \left[1 - e^{-\beta} \sum_{s=0}^{j-1} \frac{\beta^s}{s!}\right]$$

by introducing $\sum_{s=0}^{\infty} \frac{\beta^s}{s!} = e^{\beta}$ in (4a) with $\alpha = k_{22}/(k_{22} + k_{32})$, $\beta = (k_{22} + k_{32})\,\phi$.

Now

$$\sum_{j=1}^{\infty} jn_j = \frac{k_{11}}{k_{22}} \sum_{j=1}^{\infty} j\alpha^j \left[1 - e^{-\beta} \sum_{s=0}^{j-1} \frac{\beta^s}{s!}\right] = \frac{k_{11}}{k_{22}} \alpha \frac{\partial}{\partial \alpha} \sum_{j=1}^{\infty} \alpha^j \left[1 - e^{-\beta} \sum_{s=0}^{j-1} \frac{\beta^s}{s!}\right]$$

The evaluation of the double sum proceeds as follows

$$\sum_{i=1}^{\infty} \alpha^j \sum_{s=0}^{j-1} \frac{\beta^s}{s!} = \alpha + \alpha^2 (1 + \beta) + \alpha^3 \left(1 + \beta + \frac{\beta^2}{2!}\right) + \ldots \alpha^{k+1} \left(1 + \beta + \frac{\beta^2}{2!} + \ldots \frac{\beta^k}{k!}\right) + \ldots = \frac{\alpha}{1 - \alpha} +$$

$$\frac{\beta\alpha^2}{1 - \alpha} + \frac{\beta^2}{2!} \frac{\alpha^3}{1 - \alpha} + \ldots \frac{\beta^k}{k!} \frac{\alpha^{k+1}}{1 - \alpha} + \ldots = \frac{\alpha}{1 - \alpha}\left[1 + \alpha\beta + \frac{(\alpha\beta)^2}{2!} + \ldots \frac{(\alpha\beta)^k}{k!} + \ldots\right] = \frac{\alpha}{1 - \alpha} e^{\alpha\beta}$$

Therefore

$$\sum_{j=1}^{\infty} jn_j = \frac{k_{11}}{k_{22}} \alpha \frac{\partial}{\partial \alpha} \left[\frac{\alpha}{1 - \alpha} - \frac{\alpha}{1 - \alpha} e^{-\beta(1-\alpha)}\right] = \frac{k_{11}}{k_{22}} \frac{\alpha}{(1 - \alpha)^2} \{1 - e^{-\beta(1-\alpha)}[1 + \alpha\beta(1 - \alpha)]\}$$

$$\sum_{j=1}^{\infty} j^2 n_j = \alpha \frac{\partial}{\partial \alpha} \sum_{j=1}^{\infty} jn_j = \frac{k_{11}}{k_{22}} \frac{\alpha}{(1 - \alpha)^3} \{(1 + \alpha) - e^{-\beta(1-\alpha)}[(1 + \alpha) + \alpha (1 - \alpha)(3 - \alpha) \beta + \alpha^2(1 - \alpha)^2\beta^2]\}$$

We furthermore obtain from (4a)

$$\sum_{j=1}^{\infty} j^2 N_j = N_1 + k_{32} \int_0^{\phi} \left(\sum_{j=2}^{\infty} j^2 n_{j-1}\right) \mathrm{d}\phi$$

On the other hand

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

Integrating with the aid of the expressions derived above, we find, after collection of terms, the equation (7a) given in the text.

Summary

A critical discussion of the methods used in the treatment of polyreactions is given. A theory of chain polymerization reactions is developed which contains as parameters three constants, the rate of creation of active nuclei, their velocity of growth, and the rate of breaking of the growing chains. The last two steps are assumed to be second order reactions between the active chains and the stable monomer. Limitations are pointed 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 molecular 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[1]

BY ROBERT GINELL AND ROBERT SIMHA[2]

In a previous publication[3] 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. 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

$$\begin{array}{lll} \text{Activation:} & N_1 + N_1 \xrightarrow{k_{12}} n_1 + N_1 & \\ \text{Growth:} & n_j + N_1 \xrightarrow{k_{22}} n_{j+1} & j = 1, 2\ldots \\ \text{Cessation:} & n_j + N_1 \xrightarrow{k_{32}} N_{j+1} & j = 1, 2\ldots \end{array}$$

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

$$\begin{aligned} \frac{\mathrm{d}N_1}{\mathrm{d}t} &= -k_{12}N_1^2 - k_{22}N_1 \sum_{j=1}^{\infty} n_j - k_{32}N_1 \sum_{j=1}^{\infty} n_j \\ \frac{\mathrm{d}n_1}{\mathrm{d}t} &= +k_{12}N_1^2 - k_{22}N_1n_1 - k_{32}N_1n_1 \qquad (1) \\ \frac{\mathrm{d}n_j}{\mathrm{d}t} &= k_{22}N_1n_{j-1} - k_{22}N_1n_j - k_{32}N_1n_j; \ j \geqq 2 \\ \frac{\mathrm{d}N_j}{\mathrm{d}t} &= k_{32}N_1n_{j-1} \qquad j \geqq 2 \end{aligned}$$

with the additional equations

$$\begin{aligned} \frac{\mathrm{d}}{\mathrm{d}t} \sum_1^{\infty} n_j &= k_{12}N_1^2 - k_{32}N_1 \sum_1^{\infty} n_j \qquad (2) \\ \frac{\mathrm{d}}{\mathrm{d}t} \sum_1^{\infty} N_j &= -k_{12}N_1^2 - k_{22}N_1 \sum_1^{\infty} n_j \end{aligned}$$

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

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

[2] Present address, Department of Chemistry, Howard University, Washington, D. C.

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