Theory of Compartmentalised Free-Radical Polymerisation Reactions

Part 1

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Explicit analytic solutions are given for n_r, the number of reaction loci per unit volume containing r radicals, as a function of time, t, for the case of a seeded emulsion polymerisation which fulfils the following conditions: (1) radicals enter the reaction loci from a contiguous external phase at a constant rate; (2) the only significant processes which result in loss of radical activity from reaction loci are kinetically of first order with respect to the concentration of radicals in the loci; (3) radicals lost by diffusion from loci to the external phase are not available for re-initiation; (4) the volume of the reaction loci is uniform and does not increase significantly as polymerisation proceeds; (5) no nucleation of new loci takes place; (6) no reduction in the total number of reaction loci occurs, *e.g.*, through agglomeration.

The general expression obtained for n_r is

$$n_r(t) = \frac{N}{r!}\left\{\frac{\sigma}{k}(1-e^{-kt})\right\}^r \exp\left\{-\frac{\sigma}{k}(1-e^{-kt})\right\}$$

where N is the total number of reaction loci per unit volume of reaction system, σ is the average rate of entry of radicals into a single locus, and k characterises the rate of loss of radical activity by first-order processes. This result is obtained by first deriving the following generating function for the locus populations:

$$\Psi(\xi, t) = N\exp\left\{\frac{\sigma}{k}(\xi-1)(1-e^{-kt})\right\}$$

where ξ is an auxiliary variable. The implications of the result for $n_r(t)$ for (1) the approach to the steady state, (2) the average number of radicals per locus, and (3) the rate of polymerisation are discussed. It appears that the n_r form a time-dependent Poisson distribution with respect to the r, and that the parameter of the distribution at any instant is the average number of radicals per locus at that instant.

1. INTRODUCTION

It is generally recognised that the free-radical emulsion polymerisation of a monomer which is sparingly soluble in water occurs in two main stages,[1-3] namely: (i) a stage during which particles are nucleated; and (ii) a stage during which the existing particles grow at the expense of monomer, but no new particles are generated. It is convenient further to subdivide the post-nucleation stage into two sub-stages: (*a*) a stage in which unreacted monomer is present as a separate phase as well as in the reaction loci; and (*b*) a stage in which unreacted monomer is present only in the reaction loci.

This paper is concerned with the kinetics of free-radical polymerisation during the first post-nucleation stage, and, more specifically, with a situation where a fixed number of reaction loci has been introduced into the reaction system by means of a seed latex. The model which is assumed is described in detail below. Our purpose

is to present, and discuss the implications of, an alternative solution to the problem which Gilbert and Napper have recently attempted to solve.[4] Since deriving our solution, we have become aware that the same solution was obtained independently by Weiss and Dishon.[5] The principal justification for publishing a further paper upon this solution is that we wish to draw attention to certain interesting implications of the solution. In addition, we also give a clear statement of the type of physical reaction system to which the solution can be expected to apply; this is omitted by Weiss and Dishon.

It will appear subsequently that, under certain conditions at least, the solution obtained by Weiss and Dishon and by ourselves gives results which are numerically indistinguishable from those given by the solution of Gilbert and Napper. The principal disadvantage of the Gilbert–Napper solution is not its lack of precision but its lack of convenience. Unlike the new solution, it does not appear to be capable of being expressed in closed analytical form, and this inevitably hinders discussion of the implications of the solution.

2. MODEL ASSUMED

The reaction model assumed is one in which free-radical polymerisation is compartmentalised within a fixed number of reaction loci, all of similar volume, which are dispersed in an external phase. More specifically, the reaction loci are envisaged as being small particles of polymer which have been formed by, say, a previous emulsion polymerisation. No nucleation of new reaction loci occurs as polymerisation proceeds, and the number of loci is not reduced by processes such as particle agglomeration. Monomer droplets are present as a separate phase, so that the concentration of monomer within the reaction loci can be taken as constant throughout the reaction. Initially there are no free radicals present in the system, so that no polymerisation is occurring. Then, at zero time, radicals begin to be generated in the contiguous external phase at a constant rate. Radicals immediately begin to enter reaction loci at a constant rate, and thus the rate of acquisition of radicals by a single locus is kinetically of zero order with respect to the concentration of radicals within the locus. Once a radical enters a reaction locus, it initiates a chain polymerisation reaction which continues until the activity of the radical is lost. The model assumed, therefore, corresponds to a seeded emulsion polymerisation in the presence of a sufficient excess of monomer to form a separate droplet phase, and under conditions such that no nucleation of new particles occurs. It will appear subsequently that the analysis is further restricted to reactions in which the volume of the particles increases only slightly as the reaction proceeds; this condition will be realised in a reaction for which the size of initial seed is large and the extent of polymerisation is small.

It is required to calculate as a function of time the numbers of particles which contain $0, 1, 2, \ldots$ propagating radicals, and thereby to examine the nature of the theoretical approach to the steady state (assuming, of course, that a steady state exists for the model assumed).

In principle, radical activity can be lost from reaction loci by two types of reaction: (i) Those which are kinetically of the first order in the radical concentration within the reaction locus. Included in this class will be loss of activity by termination through reaction with monomer, and loss of activity by diffusion out of the reaction locus into the external phase. (ii) Those which are kinetically of the second order in the radical concentration within the reaction locus. The most obvious of these is bimolecular mutual termination between propagating radicals.

Like Gilbert and Napper [4] and also Weiss and Dishon [5] we make the simplifying assumption that radical-loss reactions of the second type are of negligible occurrence relative to those of the first type. The model as assumed in this paper, therefore, applies only to those seeded emulsion polymerisation reactions in which radical loss from loci occurs mainly by, say, reaction with monomer, or by diffusion back into the external phase. It is further assumed that radicals which are lost from reaction loci by diffusion into the external phase are not able subsequently to re-enter the reaction loci and reinitiate polymerisation. They are not, therefore, regarded as being, as it were, added to the " bank " of radicals in the external phase available for entry into reaction loci.

3. DIFFERENTIAL DIFFERENCE EQUATIONS TO BE SOLVED

Let n_i be the number of reaction loci per unit volume of reaction system which contain i radicals. Until the steady state is attained, n_i is a function of time, t; this can be emphasised by writing as $n_i(t)$. Let N be the total number of reaction loci per unit volume of reaction system. Thus $N = \sum_{i=0}^{\infty} n_i$ and does not vary with time, although the individual n_i may. ρ denotes the overall rate of entry of radicals into all the loci contained in unit volume, so that ρ/N is the average rate of entry of radicals into each single locus. This latter quantity is conveniently denoted by σ.

The equations to be solved in the most general case are obtained by modifying the recurrence relationship of Smith and Ewart [6] in such a way as to allow for the possibility that the populations for the different classes of reaction locus may not be stationary. The result for the rate of change of n_i with time can be put in the form :

$$\frac{dn_i}{dt} = (n_{i-1} - n_i)\sigma + \{(i+1)n_{i+1} - in_i\}k + \{(i+2)(i+1)n_{i+2} - i(i-1)n_i\}\frac{k_t}{v} \qquad (1)$$

for $i = 1, 2, 3, \ldots$, and for the special case $i = 0$

$$\frac{dn_0}{dt} = -n_0\sigma + n_1 k + 2n_2 \frac{k_t}{v} . \qquad (2)$$

In these equations, v is the volume of the reaction locus, k_t is the rate coefficient for the mutual termination of radicals (in suitable units), and k is a composite constant which quantifies the rate at which radicals are lost from reaction loci by first-order processes. If radicals are lost only by diffusion into the external phase, then k can be expressed in the form $k_0 a/v$, where a is the surface area of the reaction locus and k_0 is a constant which expresses the tendency of radicals to diffuse across unit area of the surface of the reaction locus when radicals are present in the locus at unit concentration. It is not, however, necessary to enquire too closely into the exact physical meaning of the constant k in order to solve the problem, although closer enquiry may, of course, be necessary when it is desired to apply the solution to particular reaction systems. Insofar as the values of k_0, a and v do not alter significantly as the reaction proceeds, the quantity k will remain unaltered. Note that the requirement that neither a nor v alters (strictly that a/v does not alter) implies that the initial size of the seed is large, and that relatively little growth occurs as a consequence of polymerisation. The assumption that k_t/v is constant also implies large seed and small growth, as well as invariance of k_t as reaction proceeds; however, these latter assumptions are of no relevance for the present analysis, because the term in which k_t occurs is subsequently to be set equal to zero.

The boundary conditions for the problem are as follows:

$$\text{(i) } n_0(0) = N \tag{3}$$

$$\text{(ii) } n_1(0) = n_2(0) = \ldots = 0. \tag{4}$$

Furthermore, for all t

$$\sum_{i=0}^{\infty} n_i(t) = n_0(0) = N. \tag{5}$$

4. SOLUTION FOR CASE WHERE $k_t = 0$

Like Stockmayer [7] and subsequently Weiss and Dishon,[5] we seek a generating function

$$\Psi(\xi, t) = \sum_{i=0}^{\infty} n_i(t)\xi^i \tag{6}$$

which is such that, when expanded as a power series in the auxiliary variable ξ, the coefficient of ξ^i is n_i. Unlike Stockmayer, our generating function is time-dependent, since we are concerned with the non-steady state, whereas Stockmayer's concern was with the special case of the steady state.

The following properties of $\Psi(\xi, t)$ are immediately obvious from its definition:

$$\text{(i) } \Psi(1, t) = N \tag{7}$$

for all t, since, by hypothesis, N is not time-dependent. Thus the time-dependency of $\Psi(\xi, t)$ should disappear when the substitution $\xi = 1$ is made.

$$\text{(ii) } n_r = \frac{1}{r!}\left(\frac{\partial^r \Psi}{\partial \xi^r}\right)_{\xi=0} \quad \text{for} \quad r = 0, 1, 2, \ldots \tag{8}$$

$$\text{(iii) } \left(\frac{\partial \Psi}{\partial \xi}\right)_{\xi=1} = \sum_{i=1}^{\infty} in_i(t). \tag{9}$$

Thus $(\partial \Psi/\partial \xi)_{\xi=1}$ gives the total number of radicals in all the reaction loci contained in unit volume of the reaction system at time t. The average number of radicals per locus at time t is therefore given by

$$\bar{i}(t) = \frac{(\partial \Psi/\partial \xi)_{\xi=1}}{\Psi(1, t)}. \tag{10}$$

To be acceptable, the generating function must be such that $(\partial^r \Psi/\partial \xi^r)_{\xi=1}$ is finite for all r. This follows because physically these quantities represent the sums of products of numbers of loci and numbers of radicals.

To convert the set of differential difference equation (1) and (2) into a differential equation in Ψ, each equation for dn_i/dt is multiplied by ξ^i, and then all the equations so obtained are summed. The result is

$$\frac{\partial}{\partial t}\sum_{i=0}^{\infty} n_i\xi^i = \sigma \sum_{i=0}^{\infty} n_{i-1}\xi^i - \sigma \sum_{i=0}^{\infty} n_i\xi^i + k\sum_{i=0}^{\infty}(i+1)n_{i+1}\xi^i -$$

$$k\sum_{i=0}^{\infty} in_i\xi^i + \chi\sum_{i=0}^{\infty}(i+2)(i+1)n_{i+2}\xi^i - \chi\sum_{i=0}^{\infty}i(i-1)n_i\xi^i \tag{11}$$

where $\chi = k_t/v$. Eqn (2) (for dn_0/dt) is included in eqn (11) if it is understood than $n_{-1} = 0$. Noting that $\Sigma n_i\xi^i = \Psi$, $\Sigma n_{i-1}\xi = \xi\Psi$, $\Sigma(i+1)n_{i+1}\xi^i = \partial\Psi/\partial\xi$, $\Sigma in_i\xi^i =$

$\xi \partial \Psi / \partial \xi$, $\Sigma (i+2)(i+1)n_{i+2}\xi^i = \partial^2 \Psi / \partial \xi^2$ and $\Sigma i(i-1)n_i \xi^i = \xi^2 \partial^2 \Psi / \partial \xi^2$, where in each case the summations cover all possible values of i, eqn (11) transforms to

$$\frac{\partial \Psi}{\partial t} = \sigma(\xi-1)\Psi + k(1-\xi)\frac{\partial \Psi}{\partial \xi} + \chi(1-\xi^2)\frac{\partial^2 \Psi}{\partial \xi^2}. \tag{12}$$

[It may be noted that Stockmayer's differential equation for his generating function follows immediately as a special case of eqn (12) by putting $\partial \Psi / \partial t = 0$ (corresponding, of course, to the steady state). The result is

$$\sigma \Psi - k\frac{\partial \Psi}{\partial \xi} - \chi(1+\xi)\frac{\partial^2 \Psi}{\partial \xi^2} = 0 \tag{13}$$

which is identical with eqn (4) of Stockmayer's paper, apart from differences in notation.]

The solution of eqn (12) for the case where $\chi = 0$ is (see Appendix)

$$\Psi(\xi, t) = N \exp \left\{ \frac{\sigma}{k}(\xi-1)(1-e^{-kt}) \right\}. \tag{14}$$

Evaluation of $\partial \Psi / \partial \xi$ and $\partial \Psi / \partial t$ from eqn (14), and substitution in eqn (12) for the case where $\chi = 0$, confirms that the result obtained for $\Psi(\xi, t)$ is a solution of the given partial differential equation for $\Psi(\xi, t)$. It will be noted that this result for $\Psi(\xi, t)$ meets the requirement that the time-dependence should disappear when the substitution $\xi = 1$ is made. Indeed, it is clear that $\Psi(1, t) = N$, which is consistent with the definition of $\Psi(\xi, t)$.

From this result for $\Psi(\xi, t)$, it immediately follows that

$$n_r(t) = \frac{N}{r!}\left\{ \frac{\sigma}{k}(1-e^{-kt}) \right\}^r \exp \left\{ -\frac{\sigma}{k}(1-e^{-kt}) \right\}. \tag{15}$$

Putting $t = \infty$ gives the respective populations of the various types of loci when the steady state has been achieved. The result is

$$n_r(\infty) = \frac{N}{r!}\left(\frac{\sigma}{k}\right)^r e^{-\sigma/k}. \tag{16}$$

5. DISCUSSION OF SOLUTION FOR CASE WHERE $k_t = 0$

(i) COMPARISON WITH SOLUTION OF GILBERT AND NAPPER [4]

Our solution for $n_r(\infty)$ is identical with that of Gilbert and Napper, if allowance is made for the differences in notation. However, our results for the variation of the loci populations in the approach to the steady state appear to differ slightly from those of Gilbert and Napper. They quote their results as rather cumbersome power series in e^{-kt}. For convenience, write $e^{-kt} = \zeta$, and $\sigma/k = \beta$; then β corresponds to the α^2 of Gilbert and Napper, and we seek expansions in ascending powers of ζ for the expressions for $n_r(t)/N$.

From the set of equations (15), we have for $n_0(t)$

$$\frac{n_0(t)}{N} = e^{-\beta(1-\zeta)} = e^{-\beta}\left(1 + \beta\zeta + \frac{\beta^2\zeta^2}{2!} + \frac{\beta^3\zeta^3}{3!} + \dots \right). \tag{17}$$

This compares with

$$\frac{n_0(t)}{N} = \left(1 - \frac{\beta}{2} \right)^2 \left(1 + \beta\zeta + \frac{\beta^2\zeta^2}{2!} + \frac{\beta^3\zeta^3}{3!} + \dots \right)$$

for Gilbert and Napper's expansion expressed in the present notation. The two differ in that our series has the factor $e^{-\beta}$ in place of $(1-\beta/2)^2$ in Gilbert and Napper's series. These two factors are almost the same if $\beta \ll 1$.

For $n_1(t)$, our result gives

$$\frac{n_1(t)}{N} = \beta(1-\zeta)\frac{n_0(t)}{N} = \beta(1-\zeta)\,e^{-\beta(1-\zeta)}$$

$$= \beta\,e^{-\beta}\left\{1+(\beta-1)\zeta+\beta(\beta-2)\frac{\zeta^2}{2!}+\beta^2(\beta-3)\frac{\zeta^3}{3!}+\ldots\right\} \tag{18}$$

whilst for $n_2(t)$ we obtain

$$\frac{n_2(t)}{N} = \frac{1}{2!}\{\beta(1-\zeta)\}^2\frac{n_0(t)}{N} = \frac{1}{2!}\beta^2(1-\zeta)^2\,e^{-\beta(1-\zeta)}$$

$$= \frac{1}{2!}\beta^2\,e^{-\beta}\left\{1+(\beta-2)\zeta+(\beta^2-4\beta+2)\frac{\zeta^2}{2!}+\beta(\beta^2-6\beta+6)\frac{\zeta^3}{3!}+\ldots\right\}. \tag{19}$$

These expansions are again identical with those of Gilbert and Napper, except that ours contain the factor $e^{-\beta}$ in place of their $(1-\beta/2)^2$.

(ii) PREDICTED VARIATION OF $n_r(t)$ WITH t

Our result for $n_0(t)$ predicts that it will fall monotonically with increasing t, from its initial value of $n_0(0) = N$ to its steady-state value of $n_0(\infty) = Ne^{-\sigma/k}$. This can be shown by considering either the structure of the expression for $n_0(t)$, or the sign of the predicted $dn_0(t)/dt$. A uniform decrease in $n_0(t)$ with increasing time is what would be expected from intuitive physical considerations.

The prediction does not appear to be so simple in the case of $n_r(t)$ when r is other than zero. Examination of the general expression for $dn_r(t)/dt$ shows that (a) initially it is zero, (b) in the early stages of the reaction it is positive, (c) in the later stages of the reaction it may become negative, and (d) eventually it becomes zero. The precise nature of the variation of $dn_r(t)/dt$ depends upon r and upon the values of the constants σ and k. Clearly, if $dn_r(t)/dt$ is positive in the early stages of the reaction, and later becomes negative, then $n_r(t)$ must pass through a maximum as the reaction proceeds from the initial stage to the steady state. Examination of the general expression for $dn_r(t)/dt$ shows that a maximum in $n_r(t)$ as a function of t exists if $r < \sigma/k$.

(iii) PREDICTION FOR TOTAL RADICAL POPULATION AND AVERAGE NUMBER OF RADICALS PER REACTION LOCUS

Evaluating $\partial\Psi/\partial\xi$ at $\xi = 1$ gives the following result for the total radical population contained in N reaction loci at time t:

$$\sum_{i=1}^{\infty} in_i(t) = N\frac{\sigma}{k}(1-e^{-kt}). \tag{20}$$

The steady-state value is $N(\sigma/k)$. The prediction is that the total radical population will increase monotonically with increasing time, approaching its steady-state value at a rate which decreases uniformly and exponentially with time. It thus appears that, whereas some of the n_r may not increase uniformly with increasing time, the total population of radicals does increase uniformly.

The prediction for the average number of radicals per reaction locus is obviously

$$\bar{\imath}(t) = \frac{\sigma}{k}(1 - e^{-kt}) \tag{21}$$

the steady-state value being σ/k. This result for the average number of radicals per locus as a function of time of reaction enables the expressions for the locus populations to be put in forms which give the populations as functions of $\bar{\imath}(t)$ only. Substituting from eqn (21) into the set (15) gives the interesting set of relationships

$$\frac{n_r(t)}{N} = \frac{\{\bar{\imath}(t)\}^r}{r!} \exp\{-\bar{\imath}(t)\}. \tag{22}$$

Thus it appears that the aggregate of the proportions of reaction loci which contain various numbers of radicals forms a time-dependent Poisson distribution with respect to the number of contained radicals. The parameter of the distribution at any instant is the average number of radicals per locus at that instant.*

(iv) PREDICTION FOR VARIATION OF RATE OF POLYMERISATION WITH TIME OF REACTION

The rate of conversion of monomer molecules to polymer is given by

$$\frac{\mathrm{d}M}{\mathrm{d}t} = k_p[\mathrm{M}] \sum_{i=1}^{\infty} i n_i \tag{23}$$

if the various quantities are expressed in appropriate units,[8] where M denotes the number of monomer molecules reacted, $[\mathrm{M}]$ denotes the molar concentration of monomer at the reaction locus, and k_p denotes the rate coefficient for the propagation reaction. Substituting for $\Sigma i n_i$ from eqn (20) and integrating (assuming that $[\mathrm{M}]$ is constant) gives the following result for the number of molecules of monomer which are polymerised in N loci in time t:

$$M(t) = k_p[\mathrm{M}]N \frac{\sigma}{k^2} (kt + e^{-kt} - 1). \tag{24}$$

Eqn (24) gives the predicted shape for the conversion–time curve for a seeded emulsion polymerisation reaction which conforms to the model assumed for the present analysis. Note that at short times this equation predicts that

$$M(t) \cong k_p[\mathrm{M}]N\sigma \cdot \tfrac{1}{2}t^2. \tag{25}$$

Thus, like Gilbert and Napper,[4] we predict that the extent of conversion will vary quadratically with time over the early stages of the reaction. It is of considerable interest to note that Gilbert and Napper [4] are able to cite results for the seeded emulsion polymerisation of vinyl acetate at 40°C which show that $M(t)$ is indeed directly proportional to t^2 up to $\sim 50\%$ conversion [they actually show $\sqrt{M(t)}$ as directly proportional to t]. It is also of interest to note that eqn (25) predicts that, in the early stages, the extent of conversion does not depend upon k (which quantifies the rate at which radicals are lost from reaction loci by first-order processes), but only upon σ (which is the average rate of entry of radicals into a single reaction locus).

* *Note added in proof*: These conclusions, and several of the others which have been noted above, also follow immediately from the observation that, according to eqn (14), $\Psi'(\xi, t)/N$ is the frequency-generating function for a Poisson distribution whose parameter (and therefore mean) is $(\sigma/k)(1 - e^{-kt})$.

Eqn (25) provides a possible basis for obtaining an estimate of σN from measurements of $M(t)$ as a function of t over the early stages of the reaction. $M(t)$ plotted against t^2 should give a straight line through the origin. Insofar as k_p and $[M]$ are known, the slope of this line can be used to obtain σN. Insofar as N is also known, it is then possible to obtain an estimate of σ itself. The value obtained can then be compared with the rate of production of radicals per reaction locus as inferred from the known or assumed decomposition kinetics of the initiator.
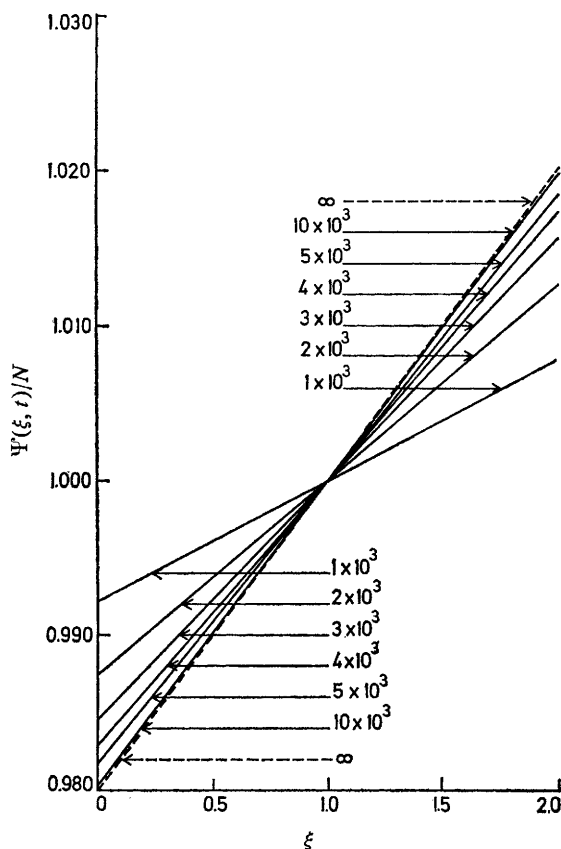

FIG. 1.—Fractional locus-population generating function, $\Psi(\xi, t)/N$, as a function of the auxiliary variable, ξ, for various values of time, t, taking $\sigma = 1 \times 10^{-5}$ s^{-1} and $k = 5 \times 10^{-4}$ s^{-1}. The figures appended to the curves give the values of t in seconds.

We have applied this procedure to the results for vinyl acetate cited by Gilbert and Napper[4] in their fig. 2. Taking their values of $k_p = 1860$ dm^3 mol^{-1} s^{-1}, and $[M] = 6.0$ mol dm^{-3}, we estimate $\sigma N = 4.2 \times 10^{11}$ dm^{-3} s^{-1}. This compares well with Gilbert and Napper's own estimate of 4.6×10^{11} dm^{-3} s^{-1}. Taking their value of 1.2×10^{15} dm^{-3} s^{-1} for the rate of production of primary free radicals by decomposition of the initiator, our calculations confirm the apparent remarkably low efficiency of radical capture by the loci in the vinyl acetate system.

In principle, it should also be possible to obtain an estimate of k from measurements of rate of polymerisation as a function of time over the early stages of a seeded polymerisation. Substituting for $\Sigma i n_i$ from eqn (20) into eqn (23) gives $\mathrm{d}M/\mathrm{d}t$ as a

function of t. Expanding the exponential in the resultant expression as far as t^2, and rearranging, gives

$$1 - \frac{1}{k_p[M]N\sigma t}\frac{dM}{dt} \cong \frac{kt}{2} \tag{26}$$

over the early stages of the reaction. If σN is known, then the left-hand side of eqn (26) can be calculated for various times of reaction. It should be directly proportional to t, the slope of the relationship permitting k to be estimated.

(v) NUMERICAL PREDICTIONS

In order to illustrate the numerical consequences of the theory given, we have taken the same values of σ and k as did Gilbert and Napper,[4] namely, $\sigma = 1 \times 10^{-5}$ s^{-1} and $k = 5 \times 10^{-4}$ s^{-1}. The variation of the generating function $\Psi(\xi, t)$ with ξ at
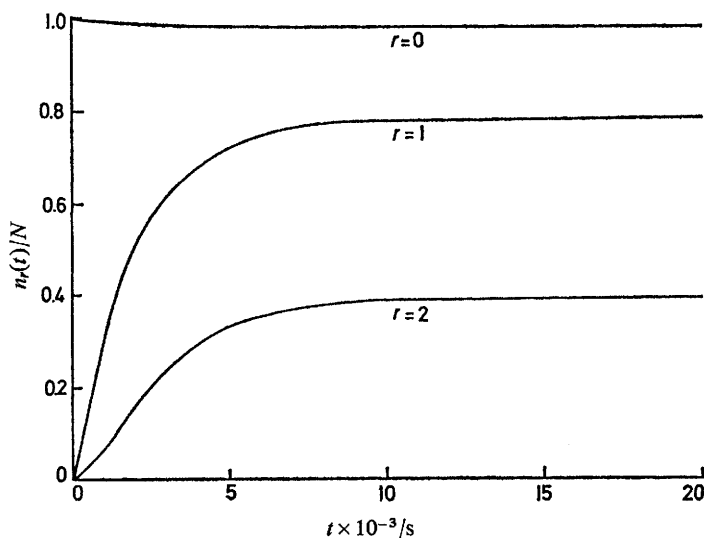
FIG. 2.—Fractional locus populations, $n_r(t)/N$, as a function of time, t, for $r = 0, 1$ and 2, taking $\sigma = 1 \times 10^{-5}$ s^{-1} and $k = 5 \times 10^{-4}$ s^{-1}. The ordinates for $r = 0$ are $n_0(t)/N$; those for $r = 1$ are $40n_1(t)/N$; those for $r = 2$ are $2000n_2(t)/N$.

various times of reaction is shown in fig. 1. What has been plotted is the quantity $\Psi(\xi, t)/N$, since the dependence of Ψ on N is of incidental significance only. It appears that the variation of $\Psi(\xi, t)/N$ with ξ over the range shown ($0 \leqslant \xi \leqslant 2$) is almost linear. The absence of appreciable curvature in the region $\xi = 0$ implies, of course, that, for the chosen values of σ and k, most of the loci contain either none or one radical; the proportion which contains two or more radicals is a negligible fraction of the whole. A second feature of interest shown by the curves for $\Psi(\xi, t)/N$ as a function of ξ at various values of t is the tendency to coalesce into a single curve as t gets large; this is, of course, a consequence of the steady state being approached, with $\Psi(\xi, t)$ becoming independent of t. Also of interest is the nature of the approach of $\Psi(\xi, t)$ as a function of ξ to the steady-state $\Psi(\xi, \infty)$ as a function of ξ, as t increases. The intercept at $\xi = 0$ decreases uniformly as t increases, but the slope at $\xi = 0$ increases uniformly with t in such a way that all the curves pass through the point $(1,1)$. This, of course, implies that the proportion of loci containing no radicals
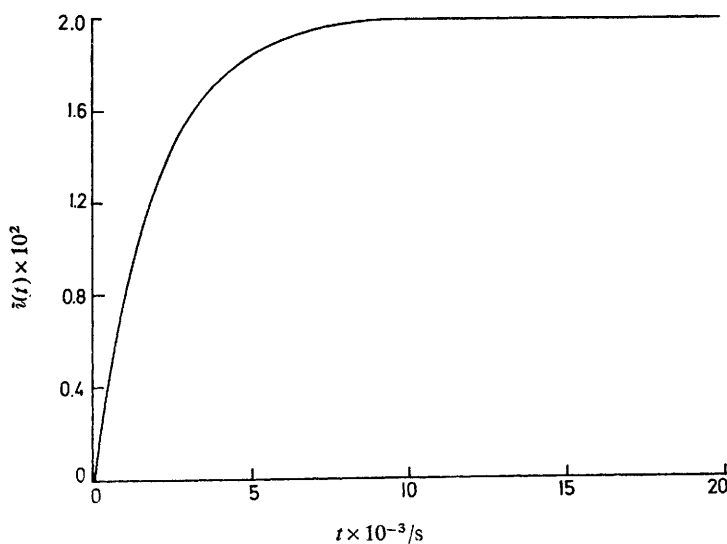
FIG. 3.—Average number of radicals per locus, $\bar{u}(t)$, as a function of time, t, taking $\sigma = 1 \times 10^{-5}$ s^{-1} and $k = 5 \times 10^{-4}$ s^{-1}.

decreases uniformly as time increases, whereas the number of loci containing one radical increases uniformly as time increases.

Fig. 2 shows $n_r(t)/N$ as a function of t for $r = 0$, 1 and 2. In order to facilitate comparison with the predictions of Gilbert and Napper's theory, these curves have been plotted in a manner analogous to the curves of fig. 1 of their paper. The close similarity between our curves and those of Gilbert and Napper is immediately evident. This is a consequence of the fact that, for the chosen values of σ and k, the value of $e^{-\sigma/k}$ is indistinguishable from that of $(1 - \sigma/2k)^2$. The curves of fig. 2 show that, for the chosen values of σ and k, (i) the steady state is attained after a reaction time
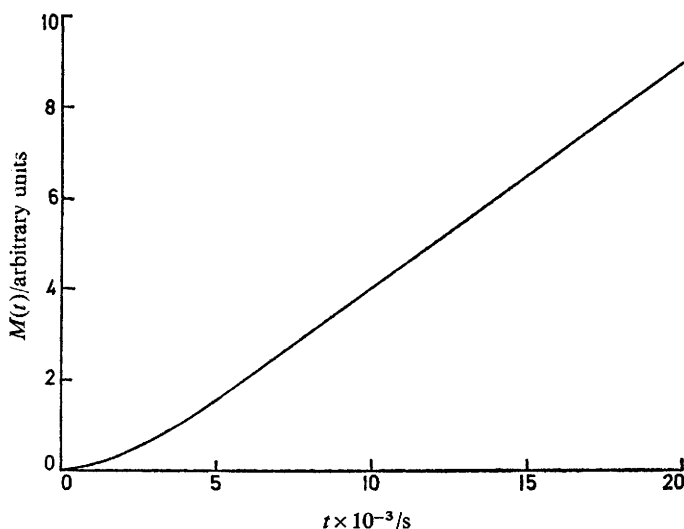

FIG. 4.—Conversion of monomer to polymer in arbitrary units, $M(t)$, as a function of time, t, taking $\sigma = 1 \times 10^{-5}$ s^{-1} and $k = 5 \times 10^{-4}$ s^{-1}.

of approximately 10^4 s, (ii) at all times, the number of loci which contain two or more radicals is a negligible fraction of the whole, and (iii) $n_1(t)$ and $n_2(t)$ increase uniformly as t increases. Regarding (iii), this is to be expected in view of the particular values of σ and k which have been chosen for the purposes of illustration. For these values, there can be no possibility of a maximum occurring in any of the $n_r(t)$, since σ/k for this case is 2×10^{-2}; there is therefore no non-zero integer value of r such that $r < \sigma/k$.

Fig. 3 shows $\bar{\imath}(t)$ as a function of t. Again, the manner of approach to the steady state is clearly evident. It should be noted that, for the chosen values of σ and k, even in the steady state, the average number of radicals per locus falls far short of the Smith–Ewart " Case 2 " value of 0.5.

The curve for rate of polymerisation as a function of t will have the same form as fig. 3 if [M] and k_p remain constant as reaction proceeds. The prediction for conversion as a function of time is shown in fig. 4. For the chosen values of σ and k, marked deviation from linearity occurs only in the range $t < 5 \times 10^3$ s. Attention is drawn to the similarity in shape between the curve of fig. 4 and the conversion–time relationship shown by Gilbert and Napper [4] for the seeded emulsion polymerisation of vinyl acetate at 40°C.

APPENDIX

SOLUTION OF EQN (12) FOR CASE WHERE $\chi = 0$

To solve eqn (12) for the case where $\chi = 0$, we use the method of separation of variables. The function $\Psi(\xi, t)$ is assumed to be of the form $\Xi(\xi) . T(t)$ where $\Xi(\xi)$ is a function of ξ only, and $T(t)$ is a function of t only. Then if $\mathscr{D}_\xi$ denotes the composite differential operator

$$\sigma(\xi - 1) + k(1 - \xi)\frac{\partial}{\partial \xi} ,$$

the eqn (12) with $\chi = 0$ becomes

$$\frac{1}{T}\frac{\partial T}{\partial t} = \frac{1}{\Xi}\mathscr{D}_\xi(\Xi). \tag{27}$$

Since the left-hand side is a function of t only, and the right-hand side a function of ξ only, it follows that eqn (27) can only be true if both sides are in fact independent of t and ξ, i.e., both are equal to some constant λ. Thus the problem becomes one of solving the two ordinary differential equations

$$\frac{1}{T}\frac{dT}{dt} = \lambda \tag{28}$$

and

$$\frac{1}{\Xi}\mathscr{D}_\xi(\Xi) = \lambda. \tag{29}$$

The solution of eqn (28) is

$$T = A\,e^{\lambda t}, \tag{30}$$

where A is a constant whose value may depend upon that of λ. The solution of eqn (29) is

$$\Xi = B(1 - \xi)^{-\lambda/k}\,e^{\sigma\xi/k} \tag{31}$$

where B is a second constant whose value may also depend upon that of λ. Thus a particular solution of eqn (12), for a particular value of λ, is the function

$$\psi(\xi, t, \lambda) = C(\lambda)(1 - \xi)^{-\lambda/k}\,e^{\lambda t + \sigma\xi/k} \tag{32}$$

where C is a composite constant whose possible dependence upon λ is emphasised by writing it as $C(\lambda)$. Since eqn (12) is a linear partial differential equation, it follows that the complete solution is the sum of all the particular solutions, $i.e.$, the complete solution of eqn (12) is the sum of all the functions $\psi(\xi, t, \lambda)$ for all physically-acceptable values of λ. Thus

$$\Psi(\xi, t) = \sum_\lambda \psi(\xi, t, \lambda) = \sum_\lambda C(\lambda)(1 - \xi)^{-\lambda/k} e^{\lambda t + \sigma \xi/k}. \tag{33}$$

We now argue that the only physically-acceptable values for λ are zero and those which make $-\lambda/k$ a positive integer. (The value zero will, of course, define the steady state). Our reasoning is that it is only these values of λ which ensure that Ψ and all its partial derivatives with respect to ξ remain finite when the substitution $\xi = 1$ is made. That this is so becomes clear if the successive partial differential coefficients with respect to ξ of the function on the extreme right-hand side of eqn (33) are written down.

Put $-\lambda/k = j$ so that the acceptable values of j are 0, 1, 2, . . ., and also $\lambda = -kj$. Then

$$\Psi(\xi, t) = \sum_{j=0}^{\infty} C(j)(1 - \xi)^j e^{-kjt + \sigma \xi/k}, \tag{34}$$

where the constant is written as $C(j)$, since it can clearly be regarded as a function of j. The boundary conditions for $t = 0$ give $\Psi(\xi, 0) = N$, and thus

$$\sum_{j=0}^{\infty} C(j)(1 - \xi)^j e^{\sigma \xi/k} = N. \tag{35}$$

This equation can be re-arranged to give

$$\sum_{j=0}^{\infty} C(j)(1 - \xi)^j = N e^{-\sigma/k} \sum_{j=0}^{\infty} \left(\frac{\sigma}{k}\right)^j \frac{(1-\xi)^j}{j!}. \tag{36}$$

Equating coefficients of $(1 - \xi)^j$ gives

$$C(j) = N e^{-\sigma/k} \frac{(\sigma/k)^j}{j!}. \tag{37}$$

Substituting this result for $C(j)$ in eqn (34) and performing the summation over all integral values for j from 0 to ∞ gives for $\Psi(\xi, t)$ the result embodied in eqn (14).

It may be noted that the result for the steady-state populations can also be obtained directly by solving the equations

$$\frac{1}{T} \frac{dT}{dt} = \frac{1}{\Xi} \mathscr{D}_\xi(\Xi) = \lambda \tag{38}$$

for the special case $\lambda = 0$.

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