MANP
File Copy
810

AFML-TR-64-405

AD0614077

STATIONARY STATE CRITERION FOR FREE RADICAL POLYMERIZATION FOR LINEARLY INCREASING REACTION TEMPERATURE

MATATIAHU GEHATIA
JOHN BROEHL

TECHNICAL REPORT AFML-TR-64-405

FEBRUARY 1965

AIR FORCE MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

20040225029

NOTICES

300 - April 1965 - 448-34-770

AFML-TR-64-405

STATIONARY STATE CRITERION FOR FREE RADICAL POLYMERIZATION FOR LINEARLY INCREASING REACTION TEMPERATURE

MATATIAHU GEHATIA
JOHN BROEHL

FOREWORD

This report was prepared by the Polymer Branch of the Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, "New Organic and Inorganic Polymers." It was administered under the direction of the AF Materials Laboratory, Research and Technology Division. Dr. Matatiahu Gehatia was the project engineer.

This report covers work conducted from March 1963 to November 1964. The manuscript was released by the authors in December 1964 for publication as an RTD technical report.

This technical report has been reviewed and is approved.

William E. Gibbs

WILLIAM E. GIBBS
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The kinetics of free radical polymerization were treated theoretically under the assumption that the reaction temperature increases at constant rate ($\dot{T}$ = const). From The Arrhenius relationships for the kinetic rate constants, approximate corresponding functions of time were derived, which transformed the kinetic equations accordingly.

A differential equation describing the sum of the concentrations of all free radicals appearing in such a system was solved by approximation, and from the resulting series the conditions for the lower as well as the upper bound of the stationary state assumptions were obtained. Defining the required precision by a large number N, where the relative error caused by the stationary state assumptions cannot exceed the quantity 1/N, the stationary state criterion obtained could be expressed by the following inequality:

$$\frac{f\left[I\right]k_t}{k_d} \geqq \frac{N^2}{64}$$

where f is the efficiency constant, $\left[I\right]$, k_d and k_t are the functions of time defining the corresponding concentration of initiator, and the kinetic rate constants for initiator decomposition and termination.

If the constant rate of temperature increase, $\dot{T}$, approaches zero, the reaction becomes a polymerization carried out at constant temperature. Under such conditions the derived criterion turns into another criterion valid for constant temperature. This new expression is identical to the corresponding formula derived previously (References 1, 2, and 3).

TABLE OF CONTENTS

INTRODUCTION

In our previous work (References 1, 2, and 3) a stationary state criterion for free radical polymerization was derived from the rigorous solution of the kinetic equations characterizing the system. The mathematical analysis was carried out under the assumption that a constant temperature was maintained during the polymerization. Since the kinetic rate constants are functions of temperature, according to the Arrhenius relationship, it is important to evaluate the appropriate parameters, by carrying out the experiments at different temperatures.

During the last decade many attempts have been made to study the kinetics of free radical polymerization at varying temperatures, and to derive the Arrhenius parameters from a single experiment. It was found that the most favorable technique was to increase the temperature of reaction at constant rate during the polymerization (References 1 through 5). The growing importance of this method calls for the extension of the mathematical analysis made previously to include also the new experimental conditions. Such a treatment was carried out in the current work and a generalized stationary state criterion was derived. The new formulas obtained are valid if the rate: $dT/dt = \text{const}$, where T = temperature, and t = time. If this rate approaches zero, the new expressions for the stationary state become the old formulas obtained previously (References 1, 2, and 3) for free radical polymerization at constant temperature.

KINETIC SCHEME FOR FREE RADICAL INITIATED POLYMERIZATION

The process of free radical polymerization may be considered to involve the following steps (Reference 6):

Initiator decomposition and initiation

$$I \xrightarrow{k_d} 2R\cdot \tag{1}$$

$$R\cdot + M \xrightarrow{k_a} M\cdot \tag{2}$$

Propagation

$$M_n^{\cdot} + M \xrightarrow{k_p} M_{n+1}^{\cdot} \tag{3}$$

Termination

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_{tc}} M_{n+m} \tag{4}$$

$$M_n^{\cdot} + M_m^{\cdot} \xrightarrow{k_{td}} M_n + M_m \tag{5}$$

$$R\cdot + R\cdot \xrightarrow{k_{tr}} RR \tag{6}$$

$$R\cdot + M\cdot \xrightarrow{k_{tn}} RM \tag{7}$$

where $k_d, k_a, k_p, k_{tc} \ldots$ are the corresponding kinetic rate constants.

Similar to the method utilized previously (References 1, 2, and 3), the rate constants of termination will be assumed as $k_{tr} = k_t$ and $k_{tn} = 2k_t$. The relatively small contribution of the terms $k_{tr}\left[R\cdot\right]^2$ and $k_{tn}\left[R\cdot\right]\left[M\cdot\right]$ to the total termination makes the possible error introduced by such an assumption negligible. The system defined by Equations 1 through 7 leads to the following differential equations:

$$\frac{d\left[R\cdot\right]}{dt} = 2k_d\left[I\right] - k_a\left[R\cdot\right]\left[M\right] - 2k_t\left[R\cdot\right]^2 - 2k_t\left[R\cdot\right]\left[M\cdot\right] \tag{8}$$

and

$$\frac{d\left[M\cdot\right]}{dt} = k_a\left[R\cdot\right]\left[M\right] - 2k_t\left[M\cdot\right]^2 - 2k_t\left[R\cdot\right]\left[M\cdot\right] \tag{9}$$

Adding both sides of Equations 8 and 9, one can obtain:

$$\frac{dr}{dt} = 2k_d\left[I\right] - 2k_t r^2 \tag{10}$$

where

$$r = \left[R\cdot\right] + \left[M\cdot\right] \tag{11}$$

is the sum of concentrations of all free radicals.

The rate of the initiator decomposition derived from Equation 1,

$$\frac{d\left[I\right]}{dt} = -\left[I\right]k_d \tag{12}$$

leads to the following expression for $\left[I\right]$:

$$\left[I\right] = I_o \exp\left(-\int_o^t k_d du\right) \tag{13}$$

where I_o is the initial value of $\left[I\right]$. From Equations 10 and 13 one can obtain:

$$\frac{dr}{dt} = 2k_d \exp\left(-\int_o^t k_d du\right) - 2k_t r^2 \tag{14}$$

Analogously to the method applied in the previous work (References 1, 2, and 3), the stationary state will occur if the rate dr/dt in Equation 14 is much smaller than either of the other two terms appearing in this equation. With such an assumption, dr/dt can be omitted, and the concentration can be expressed as follows:

$$r_s = \left(\frac{k_d I_o}{k_t}\right)^{1/2} \exp\left(\frac{1}{2}\int_o^t k_d du\right) \tag{15}$$

Since such an assumption is only justified, if r is very close to r_s, another condition has also to be fulfilled simultaneously:

$$\frac{r}{r_s} = 1 - h \tag{16}$$

and

$$\left| 1 - \frac{r}{r_s} \right| = |h| \leqq \frac{1}{N} \tag{17}$$

where N is a large number defining the degree of precision, and 1/N is the maximum deviation of r/r_s from unity. The criterion for the stationary state can be derived according to the conditions defined by Equation 17, if the expression for r is known explicitly. To obtain such an expression one has to solve differential Equation 14.

It has to be borne in mind, that the temperature of the system under consideration is no longer constant, and must be defined as a function of time as follows:

$$T = T_0 + \dot{T} t \tag{18}$$

where T_0 is the initial temperature and $\dot{T} = (dT/dt) =$ const. According to the Arrhenius relationship, any kinetic rate k_s can be expressed as:

$$k_s = A_s \exp\left(- \frac{E_s}{RT} \right) \tag{19}$$

where the constant parameters A_s, E_s, and R are respectively, frequency factor, activation energy, and gas constant. T is expressed in °K. Since T varies with time, k_s is also a function of time. This function defined in Equation 19 will now be expanded into the following series:

$$k_s = A_s \exp\left\{ - \frac{E_s}{RT_0} \left[1 - \sum_{n=1}^{\infty} (-1)^n \left(\frac{\dot{T} t}{T_0} \right)^n \right] \right\} \tag{20}$$

In general $(\dot{T} t/T_0) \ll 1$, and Equation 20 reduces to:

$$k_s \approx A_s \exp\left(- \frac{E_s}{RT_0} \right) \exp\left(\frac{E_s \dot{T}}{RT_0^2} t \right) \tag{21}$$

Two quantities, constant during a single experiment, will now be introduced. The initial value of k_s at $T = T_0$:

$$k_{s,0} = A_s \exp\left(- \frac{E_s}{RT_0} \right) \tag{22}$$

and

$$f_s = \frac{E_s \dot{T}}{RT_0^2} \tag{23}$$

Applying these two experimental constants, the Arrhenius formula, Equation 19, can be transformed into the following approximate function of time:

$$k_s = k_{s,o} \exp(f_s t) \tag{24}$$

which is simple and convenient for further calculations. In general, the term ($\dot{T}\, t/T_0$) appearing in Equation 20 is a small number over the entire period of the reaction, and the approximation, Equation 21, is justified.

Applying the formalism given by Equations 22, 23, and 24 one can express the kinetic rates of k_d and k_t as follows:

$$k_d = k_{d,o} \exp(f_d t) \tag{25}$$

where

$$k_{d,o} = A_d \exp\left(-\frac{E_d}{RT_0}\right) \tag{26}$$

$$f_d = \left(\frac{E_d \dot{T}}{RT_0{}^2}\right) \tag{27}$$

and

$$k_t = k_{t,o} \exp(f_t t) \tag{28}$$

where

$$k_{t,o} = A_t \exp\left(-\frac{E_t}{RT_0}\right) \tag{29}$$

$$f_t = \left(\frac{E_t \dot{T}}{RT_0^2}\right) \tag{30}$$

Equations 25 through 30 can be used to transform Equation 14 into a new equation:

$$\frac{dr}{dt} = 2k_{d,o}\, I_o \exp\left(\frac{k_{d,o}}{f_d} + f_d t - \frac{k_{d,o} e^{f_d t}}{f_d}\right) - 2k_{t,o}\, e^{f_t t}\, r^2 \tag{31}$$

Then by dividing both sides of Equation 31 by k_d, and introducing a new variable, x, one gets

$$x = \frac{k_d}{f_d} \tag{32}$$

and the following differential equation is obtained:

$$\frac{dr}{dx} = ae^{-x} - bx^{-p} r^2 \tag{33}$$

where p, a, and b are constants defined as follows:

$$p = \frac{f_d - f_t}{f_d} = 1 - \frac{E_t}{E_d} , \tag{34}$$

$$a = 2I_0 \exp \frac{k_{d,o}}{f_d} \tag{35}$$

and

$$b = \left(\frac{2k_{t,o}}{k_{d,o}}\right)\left(\frac{k_{d,o}}{f_d}\right)^p \tag{36}$$

In general $p<1$, and $|1-p| \ll 1$. According to the initial conditions, $x_0 = k_{d,o}/f_d$, and $r(x_0)=0$. For reasonable values of $\dot{T}$, x_0 is usually a small number. In the current work it will often be considered as 10^{-2}.

APPROXIMATE SOLUTION OF DIFFERENTIAL EQUATIONS OF THE SUM OF FREE RADICALS

Equation 33 was solved rigorously in the previous work (References 1, 2, and 3) for $p = 0$. For $p \neq 0$ no rigorous solution was achieved. However, methods exist which provide an approximate solution of Equation 33, and enable one to derive a criterion for the stationary state; one of these methods will be introduced in the following:

Under stationary state assumptions, Equation 33 reduces to:

$$ae^{-x} - bx^{-p} r_s^2 = 0 \tag{37}$$

Hence:

$$r_s = \left(\frac{a}{b}\right)^{1/2} e^{-\frac{x}{2}} x^{\frac{p}{2}} \tag{38}$$

The function r appearing in Equation 33 will now be replaced by a new function, g, defined as

$$r = r_s \left(\frac{1-g}{1+g}\right) \tag{39}$$

From Equations 33, 38, and 39 one can derive a differential equation for g:

$$\frac{dg}{dx} = -2ce^{-\frac{x}{2}} x^{-\frac{p}{2}} g + \frac{1}{4}\left(\frac{p}{x} - 1\right)(1-g^2) \tag{40}$$

where $c = (ab)^{1/2}$.

The relationship given by Equation 39 can also be expressed by the following series:

$$\frac{r}{r_s} = \frac{1-g}{1+g} = 1 + 2\sum_{n=1}^{\infty} (-1)^n g^n \tag{41}$$

In the interval in which stationary state assumption is justified, $|g| \ll 1$. Hence:

$$\frac{r}{r_s} \approx 1 - 2g \tag{42}$$

and according to Equation 17:

$$|g| \leqq \frac{1}{2N} \tag{43}$$

Finally, within the same interval $g^2 \ll 1$, and Equation 40 reduces to:

$$\frac{dg}{dx} \approx -2c\,e^{-\frac{x}{2}} x^{-\frac{p}{2}} g + \frac{1}{4}\left(\frac{p}{x} - 1\right) \tag{44}$$

This new approximate equation can be solved, if at least one fixed point (boundary condition) is known. Unfortuately, the initial conditions cannot be applied for this case. Since the initial value of g is $g(x_0) = 1$, this function cannot be considered small for $x = x_0$. Thus, at the very beginning of the polymerization, the approximation, Equation 44, is not justified. However, it will be shown in the following that this formal objection can be disregarded if special conditions do exist, and that these special conditions are also identical to the stationary state conditions. Therefore, the following method will be applied. At first a new differential equation will be solved in which the function g(x) in Equation 44 will be replaced by another function y(x):

$$\frac{dy}{dx} = -2c\,e^{-\frac{x}{2}} x^{-\frac{p}{2}} y + \frac{1}{4}\left(\frac{p}{x} - 1\right) \tag{45}$$

where $y(x_0) = 1$.

Integration of Equation 45 leads to the following expression:

$$y(x) = \frac{1}{4} e^{-F(x)} \int_{x_0}^{x} e^{F(z)} \left(\frac{p}{z} - 1\right) dz + e^{F(x_0) - F(x)} \tag{46}$$

where

$$F(x) = 2c \int e^{-\frac{x}{2}} x^{-\frac{p}{2}} dx \tag{47}$$

Since F(x) itself is a transcendental function, the general integral appearing in Equation 46 can only be given by approximation, or can be expanded into a series which employs successive integration by parts:

$$\int e^{F(z)} \left(\frac{p}{z} - 1\right) dz = \frac{1}{2c} e^{\frac{z}{2}} z^{\frac{p}{2}} \left(\frac{p}{z} - 1\right) e^{F(z)} - \frac{1}{2c} \int e^{F(z)} d\left[e^{\frac{z}{2}} z^{\frac{p}{2}} \left(\frac{p}{z} - 1\right)\right] = \cdots \tag{48}$$

Then by denoting

$$u(z) = \frac{e^{\frac{z}{2}} z^{\frac{p}{2}}}{2c} \tag{49}$$

such a transformation repeated n times leads to the following expression:

$$\int e^{F(z)} \left(\frac{p}{z} - 1\right) dz = e^{F(z)} \sum_{k=1}^{n} S_k(z) - R_n(z) \tag{50}$$

where

$$S_k(z) = u^k(z) b_k P_k(z) \tag{51}$$

$$P_k(z) = \sum_{i=0}^{k} a_{ki} z^{-i} \tag{52}$$

$$R_n(z) = \int e^{F(z)} d\left[b_n u^n(z) P_n(z) \right] \tag{53}$$

and b_k and a_{ki} are constants. According to Equations 50 through 53 the function y(x) given in Equation 47 becomes

$$y(x) = \frac{1}{4} \sum_{k=1}^{n} S_k(x) + \left[1 - \frac{1}{4} \sum_{k=1}^{n} S(x_o)\right] \exp\left[F(x_o) - F(x)\right] - R_n(x, x_o) \tag{54}$$

where $R_n(x, x_o) = R_n(x) - R_n(x_o)$. For the sake of convenience Equation 54 will be expressed:

$$y(x) = \sum_{k=1}^{n} T_k(x) - R_n(x, x_o) \tag{55}$$

where

$$T_1 = \frac{1}{4} S_1(x) + \left[1 - \frac{1}{4} S_1(x_o)\right] \exp\left[F(x_o) - F(x)\right] \tag{56}$$

$$T_{k \neq 1} = \frac{1}{4} S_k(x) - \frac{1}{4} S_k(x_o) \exp\left[F(x_o) - F(x)\right] \tag{57}$$

and

$$R_n(x, x_o) = \int_{x_o}^{x} e^{F(z)} b_n d\left[u^n(z) P_n(z)\right] \tag{58}$$

For $x \gg 1$, $P_k(x) \approx a_{k,o}$. Hence for large values of x:

$$S_k(x) \approx b_k a_{k,o} u^k(x) \tag{59}$$

On the other hand, if x is small, $x^k P_k(x) \approx a_{k,k}$, and

$$S_k \approx a_k \left[\frac{u(x)}{x} \right]^k \tag{60}$$

where $a_k = b_k a_{k,k}$. Since x_o is a small number,

$$S_k(x_o) \approx a_k \left[\frac{a(x_o)}{x_o} \right]^k \tag{61}$$

Finally, for large values of x:

$$T_1 \approx -\frac{1}{4} u(x) + \left[1 - \frac{pu(x_o)}{4x_o} \right] \exp \left[F(x_o) - F(x) \right] \tag{62}$$

and

$$T_{k \neq 1} \approx \frac{1}{4} b_k a_{k,o} u^k(x) - \frac{1}{4} a_k \left[\frac{u(x_o)}{x_o} \right]^k \exp \left[F(x_o) - F(x) \right] \tag{63}$$

For small values of x:

$$T_1 \approx \frac{pu(x)}{4x} + \left[1 - \frac{pu(x_o)}{4x_o} \right] \exp \left[F(x_o) - F(x) \right] \tag{64}$$

$$T_{k \neq 1} \approx \frac{1}{4} a_k \left[\frac{u(x)}{x} \right]^k - \frac{1}{4} a_k \left[\frac{u(x_o)}{x_o} \right]^k \exp \left[F(x_o) - F(x) \right] \tag{65}$$

Remembering that y(x) and g(x) are not identical, the conditions justifying the stationary state will be mathematically applied to the y(x). To find such conditions means to find an interval $x_{min} \leqq x \leqq x_{max}$, within which $|y(x)| \leqq 1/2N$. One has also to regard the needs of the experimenter, that is, to have a stationary state which (1) appears almost simultaneously with the beginning of the reaction (short period of induction), and (2) which is valid over a considerable period of time. The first condition enables one to neglect the period of induction and to evaluate the experimental curves by assuming that the simplifying conditions are valid practically from the beginning. The second condition ensures that proper measurements can be carried out during a period of time in which a substantial part of the initiator underwent polymerization. Such a stable stationary state will appear, if x_{min} is very close to x_o, and if x_{max} is a large number which covers a substantial period of the reaction.

The function y(x) given in Equation 46 will now be expressed by the mean value of the integral:

$$y(x) = \frac{1}{4} e^{F(\xi)-F(x)} \left[p \ln\left(\frac{x}{x_0}\right) - x + x_0 \right] + e^{F(x_0)-F(x)} \qquad (66)$$

where $x_0 < \xi < x$.

By substituting $x = x_0$ into Equation 66, the resulting value of $y(x_0)$ is unity. Therefore, Equation 66 satisfies the initial conditions for y(x). A short induction period means: $y(x_{min}) \leqq 1/2N$ also if x_{min} is very close to x_0. Such a condition can be achieved only if the expression appearing in the exponent of Equation 66, $F(x)-F(x_0)$, which is zero for $x = x_0$ will increase rapidly as x starts to exceed x_0. Therefore, it is important to examine the function $F(x)-F(x_0)$ closely, to derive conditions assuming a short period of induction.

MATHEMATICAL ANALYSIS OF EQUATION 46 AND THE EXPRESSION F(x) - F(x_0), USING EQUATION 47, ACCORDING TO THE STATIONARY STATE CONDITIONS

Let z = 2t, then the integral

$$I(z) = \int e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz \qquad (67)$$

transforms into

$$I(t) = 2^{1-\frac{p}{2}} \int e^{-t} t^{-\frac{p}{2}} dt \qquad (68)$$

Successively integrating I(t) by parts gives rise to the following series expansion:

$$I(t) = \frac{2^{1-\frac{p}{2}}}{1-\frac{p}{2}} t^{1-\frac{p}{2}} e^{-t} \left[1 + \frac{t}{2-\frac{p}{2}} + \frac{t^2}{\left(2-\frac{p}{2}\right)\left(3-\frac{p}{2}\right)} + \cdots \right] \qquad (69)$$

By substituting $t = \frac{1}{2} z$ Equation 69 becomes

$$I(z) = \frac{2}{2-p} z^{1-\frac{p}{2}} e^{-\frac{z}{2}} {}_1F_1\left(1, 2-\frac{p}{2}, \frac{z}{2}\right), \qquad (70)$$

where

$${}_1F_1(a,b,x) = 1 + \frac{ax}{b1!} + \frac{a(a+1)x^2}{b(b+1)2!} + \frac{a(a+1)(a+2)x^3}{b(b+1)(b+2)3!} + \cdots \qquad (71)$$

${}_1F_1(a, b, x)$ is known as the confluent hypergeometric function (Reference 7). Since the confluent hypergeometric function is absolutely convergent for all values of a, b, and x, real or complex, excluding $b = 0, -1, -2, \ldots$, the integral $I(z)$ always exists except for $p = 2 + 2n$ $(n = 1, 2, \ldots)$. In general, p varies only within the interval $o \leqq p \leqq 1$. Hence, the integral $I(z)$ is always defined.

Equations 47 and 70 clearly lead to:

$$F(x) - F(x_0) = 2c \int_{x_0}^{x} e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz$$

$$= \frac{4c}{2-p}\left[x^{1-\frac{p}{2}} e^{-\frac{x}{2}} {}_1F_1\left(1, 2-\frac{p}{2}, \frac{x}{2}\right) - x_0^{1-\frac{p}{2}} e^{-\frac{x_0}{2}} {}_1F_1\left(1, 2-\frac{p}{2}, \frac{x_0}{2}\right)\right] \qquad (72)$$

For very small values of x, the confluent hypergeometric function approaches unity, and:

$$F(x) - F(x_0) \approx \frac{4c}{2-p}\left[x^{1-\frac{p}{2}} - x_0^{1-\frac{p}{2}}\right] \qquad (73)$$

if $o < x_0 < x \ll 1$. Under such conditions, namely, when x and x_0 are very small and x is close to x_0, then $F(x) - F(x_0)$ can only be very large if c is sufficiently large, that is:

$$F(x) - F(x_0) > M$$

where M is a large number, if

$$4c > \frac{M(2-p)}{x^{1-\frac{p}{2}} - x_0^{1-\frac{p}{2}}} \qquad (74)$$

Therefore, one may expect a short induction period only if c is a very large number. Hence, the following mathematical analysis will be carried out under the assumption that c is very large. Let us now evaluate the function $F(x)-F(x_0)$ for large values of x. Since the integral

$2c\int_{x_0}^{x} e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz$ exists for all values of x, then:

$$\int_{x_0}^{x} = \int_{\infty}^{x} + \int_{0}^{\infty} + \int_{x_0}^{0} = I_1 + I_2 + I_3 \qquad (75)$$

After repeated integration by parts, I_1 yields the following series expansion:

$$I_1 = 2c\int_{\infty}^{x} e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz$$

$$= -4cx^{-\frac{p}{2}} e^{-\frac{x}{2}} \left[1 - \frac{p}{x} + \frac{p(2+p)}{x^2} - \frac{p(2+p)(4+p)}{x^3} + \cdots \right] \tag{76}$$

Therefore, if $x \gg 1$,

$$I_1 \approx -4cx^{-\frac{p}{2}} e^{-\frac{x}{2}} \tag{77}$$

The value of I_2 is readily available from tables of integrals and is given as

$$I_2 = 2c\int_{0}^{\infty} e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz = 2^{2-\frac{p}{2}} c\,\Gamma(1-\frac{p}{2}), \tag{78}$$

where $\Gamma(x) \equiv \int_0^{\infty} e^{-t} t^{x-1} dt$ is the well known gamma function. Since

$x_0 \ll 1$, I_3 may be approximated according to Equation 73. That is:

$$I_3 = 2c\int_{x_0}^{0} e^{-\frac{z}{2}} z^{-\frac{p}{2}} dz = -\frac{4c}{2-p} x_0^{1-\frac{p}{2}} \tag{79}$$

Combining Equations 77, 78, and 79 one obtains:

$$F(x)-F(x_0) = 2^{2-\frac{p}{2}} c\Gamma(1-\frac{p}{2}) - 4cx^{-\frac{p}{2}} e^{-\frac{x}{2}} - \frac{4c}{2-p} x_0^{1-\frac{p}{2}}$$

$$\longrightarrow 2^{2-\frac{p}{2}} c\Gamma(1-\frac{p}{2}) \tag{80}$$

Since $p \approx 1$ and $\Gamma(\frac{1}{2}) = \sqrt{\pi}$, Equation 80 may be expressed:

$$F(x) - F(x_0) = 2^{\frac{3}{2}} c\sqrt{\pi}, \text{ if } x \gg 1. \tag{81}$$

From the above, it can readily be seen that the function $F(x)$-$F(x_0)$ approaches its asymptotical value $2c\sqrt{\pi}$ very rapidly. This property of $F(x)$ is illustrated in Figure 1 for the case $p = 1$ and $x_0 = 0$. By imposing these conditions and substituting $z = t^2$, $F(x)$ transforms into the normal distribution function. That is:

$$F(x) = 2c\int_0^x e^{-\frac{z}{2}} z^{-\frac{p}{2}}\,dz = 4c\int_0^{\sqrt{x}} e^{-\frac{t^2}{2}}\,dt \tag{82}$$

$$= 4c\sqrt{2\pi}\int_0^{\sqrt{x}} \phi(t)\,dt = 2cY(x) \tag{83}$$

where

$$\phi(t) \equiv \frac{1}{\sqrt{2\pi}}\, e^{-\frac{t^2}{2}} \quad .$$

Let us now consider the expansion of y(x) as expressed by Equations 56, 57 and 58:

$$y(x) = T_1 + T_2 + T_3 - R_3 \tag{84}$$

where

$$T_1 = \frac{1}{4}u(x)\left(\frac{p}{x} - 1\right) + \left[1 - \frac{1}{4}u(x_0)\left(\frac{p}{x_0} - 1\right)\right]e^{F(x_0)-F(x)} \tag{85}$$

$$T_2 = \frac{1}{8}u^2(x)\left(\frac{2p-p^2}{x^2} + 1\right) - \frac{1}{8}u^2(x_0)\left(\frac{2p-p^2}{x_0^2} + 1\right)e^{F(x_0)-F(x)} \tag{86}$$

$$T_3 = \frac{1}{8}u^3(x)\left(\frac{p^3-4p^2+4p}{x^3} + \frac{p^2-2p}{x^2} - \frac{p}{x} - 1\right)$$

$$- \frac{1}{8}u^3(x_0)\left(\frac{p^3-4p^2+4p}{x_0^3} + \frac{p^2-2p}{x_0^2} - \frac{p}{x_0} - 1\right)e^{F(x_0)-F(x)} \tag{87}$$

$$R_3 = \frac{1}{8}e^{-F(x)}\int_{x_0}^{x} e^{F(z)}\,d\left[u^3(z)\,\frac{p^3-4p^2+4p}{z^3} + \frac{p^2-2p}{z^2} - \frac{p}{z} - 1)\right] \tag{88}$$

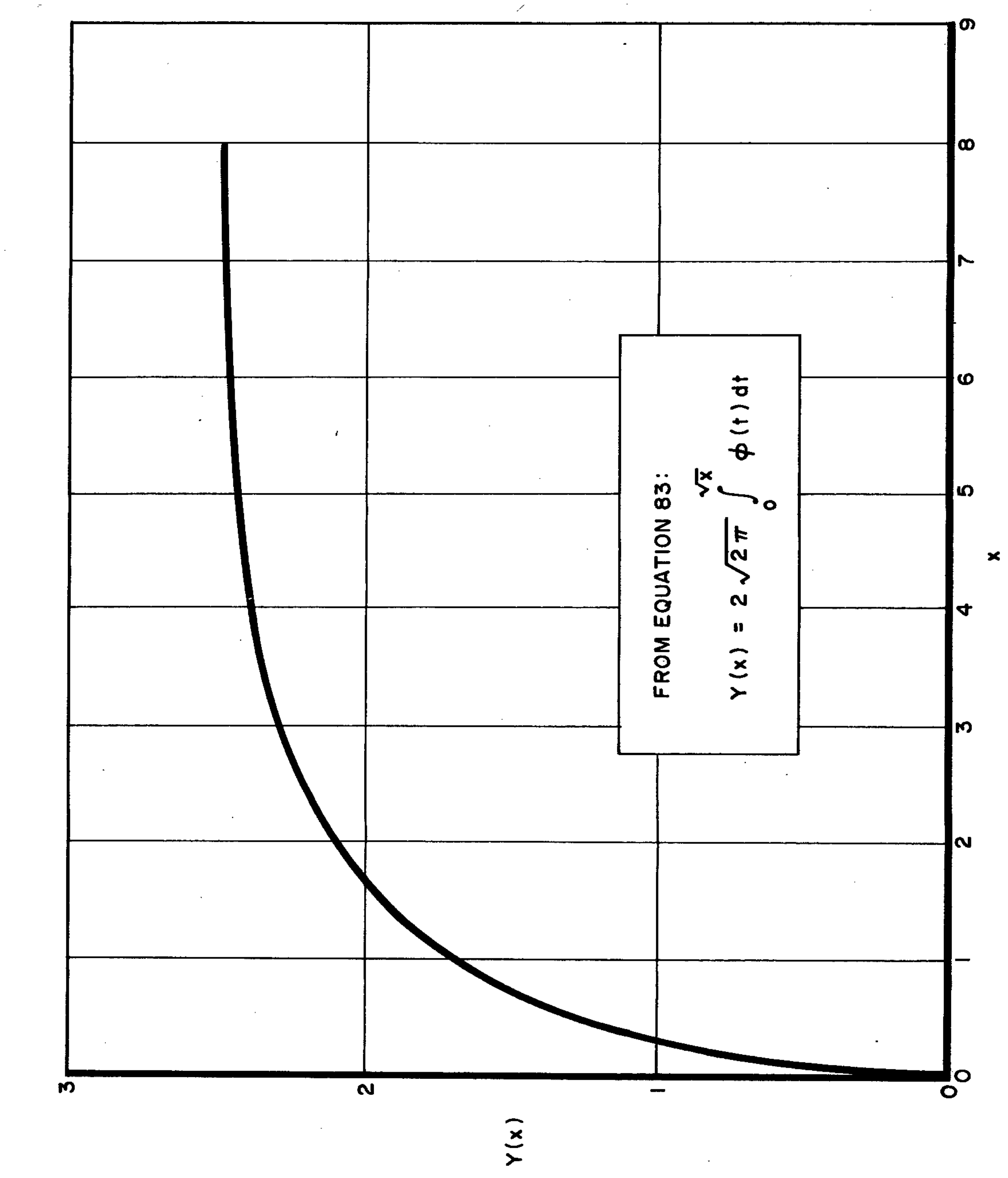

Figure 1. Behavior of the Function Y(x) as Defined by Equation 83

Let $\hat{x}_{max}$ and $\hat{x}_{min}$ be defined by the following equations:

$$\frac{1}{4}\, u(\hat{x}_{max}) = \frac{1}{2N}, \text{ and } \hat{x}_{max} \gg 1 \tag{89}$$

and

$$\frac{p}{4\hat{x}_{min}}\, u(\hat{x}_{min}) + e^{F(x_o)-F(\hat{x}_{min})} = \frac{1}{2N}$$

in which

$$x_o < \hat{x}_{min}, \text{ and } \hat{x}_{min} \text{ is close to } x_o . \tag{90}$$

Since $\hat{x}_{max}$ and $\hat{x}_{min}$ are dependent upon c, the conditions $\hat{x}_{max} \gg 1$ and $\hat{x}_{min}$ close to x_o are easily satisfied by adjusting c.

Since $\hat{x}_{min}$ is very close to x_o, Equation 90 gives rise to the following inequality:

$$\frac{p}{4x_o}\, u(x_o) \ll 1 \tag{91}$$

Hence:

$$T_1 < \frac{1}{4}\, u(x)\left(\frac{p}{x} - 1\right) + e^{F(x_o) - F(x)} \tag{92}$$

It can readily be seen that for sufficiently large c the term $e^{F(x_o)-F(x)}$ decreases rapidly and may be neglected if $x \gg \hat{x}_{min}$. Then:

$$T_1 \leqq \frac{1}{2N}, \text{ if } \hat{x}_{min} \leqq x \leqq \hat{x}_{max}, \tag{93}$$

where $\hat{x}_{min}$ and $\hat{x}_{max}$ are defined by Equations 89 and 90 respectively. Examining T_2 and T_3 in the interval $\hat{x}_{min} \leq x \leq \hat{x}_{max}$ one observes that:

$$T_2 \leqq \frac{1}{2}\left(\frac{1}{2N}\right)^2 \tag{94}$$

and

$$T_3 \leqq \left(\frac{1}{2N}\right)^3 \tag{95}$$

The integral R_3 appearing in Equation 88 may be expressed by the mean value theorem as follows:

$$R_3 = \frac{1}{8}\Big[u^3(x)\Big(\frac{p^3-4p^2+4p}{x^2} + \frac{p^2-2p}{x^2} - \frac{p}{x} - 1\Big)$$

$$- u^3(x_o)\Big(\frac{p^3-4p^2+4p}{x_o^3} + \frac{p^2-2p}{x_o^2} - \frac{p}{x_o} - 1\Big)\Big]\, e^{F(\xi)-F(x)} \qquad (96)$$

where $x_o \leq \xi \leq x$.

Consequently:

$$|R_3| \leq \left(\frac{1}{2N}\right)^3, \text{ if } \hat{x}_{min} \leqq x \leqq \hat{x}_{max} \qquad (97)$$

Since N is a very large number, the terms T_2, T_3 and R_3 may be neglected and the following relationships arise:

$$|y(x)| \approx |T_1(x)| \leq \frac{1}{2N}\, , \text{ if } \hat{x}_{min} \leqq x \leqq \hat{x}_{max}\, . \qquad (98)$$

Recalling that the validity of the stationary state assumption can be expressed by the inequality $|y(x)| \leq \frac{1}{2N}$, where $x_{min} \leqq x \leq x_{max}$, it is obvious from Equation 98 that the stationary state exists in the interval $\hat{x}_{min} \leqq x \leq \hat{x}_{max}$. Hence, Equations 89 and 90 define the lower and upper bounds of the interval in which the stationary state exists.

Assume the exponential term in Equation 90 is the leading one, that is:

$$\frac{p}{4x_{min}}\, u(x_{min}) \ll e^{F(x_o)-F(x)} = \frac{1}{2N}\, . \qquad (99)$$

This additional condition on Equation 90 forces x_{min} to approach x_o, thus decreasing the induction period. By using Equation 99, the expression for x_{min} is simplified to:

$$x_{min}^{1-\frac{p}{2}} - x_o^{1-\frac{p}{2}} = \frac{(2-p)\ln 2N}{4c} \qquad (100)$$

It should be pointed out that the condition in Equation 99 is not a necessary one. It means that the stationary state may also exist without satisfying Equation 99. If Equation 99 cannot be satisfied, but the approximation $e^{x_{min}/2} \approx 1$ is valid, the general Equation 90 reduces to a simplified transcendental equation:

$$\frac{p}{8cx_{min}^{1-\frac{p}{2}}} + \exp\left[-\frac{4c}{2-p}\left(x_{min}^{1-\frac{p}{2}} - x_o^{1-\frac{p}{2}}\right)\right] = \frac{1}{2N} \qquad (101)$$

It must be emphasized that the stationary state conditions above were not derived from the proper function g(x), but from a hypothetical one, y(x). One of many ways to show that $g(x) \approx y(x)$ in the stationary state interval is to prove the existence of a point $\hat{x}$ such that $x_{min} \leqq \hat{x} \leqq x_{max}$ and $g(\hat{x}) \approx y(\hat{x})$. It is obvious that if such a point $\hat{x}$ exists, then $|g(x)| \leqq \frac{1}{2N}$ in some interval containing $\hat{x}$, and therefore, one may neglect the term $g^2(x)$ appearing in Equation 40 in such an interval. This neglect of $g^2(x)$ in Equation 40 leads to Equation 44 and finally to Equation 45, the defining equation of y(x). Hence, the derived stationary state conditions will be proper for the function g(x) if, under the given conditions, the following relationships hold:

$$y(x_{min}) \approx g(x_{min})$$

or

$$|y(x_{min}) - g(x_{min})| << |g(x_{min})| \qquad (102)$$

Now consider the interval $x_0 \leqq x \leqq x_{min}$. Since x_{min} is close to x_0 and $x_0 \leqq 1$, x is a small number, and the approximation $e^x \approx 1$ holds in this interval. Using this approximation, Equation 33 reads as follows:

$$\frac{dr}{dx} = a - bx^{-p} r^2 \qquad (103)$$

By introducing a new function v, defined implicitly by:

$$r = \frac{x^p}{b} \frac{\frac{dv}{dx}}{v} \qquad (104)$$

Equation 103 transforms into a new second order differential equation:

$$\frac{d^2v}{dx^2} + \frac{p}{x}\frac{dv}{dx} - c^2 x^{-p} v = 0 \qquad (105)$$

where $c^2 = ab$.

This equation may be solved readily for any p, but, for the sake of additional simplicity only the case p = 1 will be considered. Thus, Equation 105 reads:

$$\frac{d^2v}{dx^2} + \frac{1}{x}\frac{dv}{dx} - \frac{c^2 v}{x} = 0 \qquad (106)$$

By utilizing a new variable z defined by:

$$x = \frac{1}{4c^2} z^2 \qquad (107)$$

Equation 106 is expressed by:

$$\frac{d^2v}{dz^2} + \frac{1}{z}\frac{dv}{dz} - v = 0 \tag{108}$$

which is the modified Bessel equation of zero order. This eguation has two independent solutions $I_0(z)$ and $K_0(z)$. Hence,

$$v(z) = C_1 I_0(z) + C_2 K_0(z) \tag{109}$$

where C_1 and C_2 are arbitrary constants, and $I_0(z)$ and $K_0(z)$ are modified Bessel functions of zero order (Reference 8).

Since

$$\frac{dI_0(z)}{dz} = I_1(z) \tag{110}$$

and

$$\frac{dK_0(z)}{dz} = -K_1(z) \tag{111}$$

where I_1 (z) and K_1 (z) are modified Bessel functions of the first order, the function r defined by Equation 104 can be written:

$$r = \frac{z}{2b}\,\frac{C_1 I_1(z) - C_2 K_1(z)}{C_1 I_0(z) + C_2 K_0(z)} \tag{112}$$

The stationary state condition $\frac{dr}{dx} = 0$ applied to Equation 103 yields the following r_s function:

$$r_s = \left(\frac{ax}{b}\right)^{\frac{1}{2}} \quad \text{if} \quad p = 1 \tag{113}$$

or in terms of z:

$$r_s = \frac{z}{2b} \tag{114}$$

Dividing Equation 112 by Equation 114 one obtains:

$$\frac{r}{r_s} = \frac{1-g}{1+g} = \frac{C_1 I_1(z) - C_2 K_1(z)}{C_1 I_0(z) + C_2 K_0(z)} \tag{115}$$

Since the initial conditions require $r(z_0)=0$; where $z_0 = 2cx_0^{\frac{1}{2}}$, $C_1 = K_1(z_0)$ and $C_2 = I_1(z_0)$. Finally:

$$\frac{r}{r_s} = \frac{K_1(z_0)I_1(z) - I_1(z_0)K_1(z)}{K_1(z_0)I_0(z) + I_1(z_0)K_0(z)} \tag{116}$$

From Equation 91 one obtains:

$$2cx_0^{\frac{1}{2}} \gg 1 \tag{117}$$

if p = 1 and $e^{x_0} \approx 1$.

In the case of large arguments, one may express the functions $I_0(z)$, $I_1(z)$, $K_0(z)$ and $K_1(z)$ by the following series (Reference 9):

$$I_0(z) = \frac{e^z}{\sqrt{2\pi z}}\left[1 + \frac{1}{8z} + \frac{(1)(9)}{2!(8z)^2} + \frac{(1)(9)(25)}{3!(8z)^3} + \cdots\right] \tag{118}$$

$$I_1(z) = \frac{e^z}{\sqrt{2\pi z}}\left[1 - \frac{3}{8z} - \frac{(3)(5)}{2!(8z)^2} - \frac{(3)(5)(21)}{3!(8z)^3} - \cdots\right] \tag{119}$$

$$K_0(z) = \frac{\pi e^{-z}}{\sqrt{2\pi z}}\left[1 - \frac{1}{8z} + \frac{(1)(9)}{2!(8z)^2} - \frac{(1)(9)(25)}{3!(8z)^3} + \cdots\right] \tag{120}$$

$$K_1(z) = \frac{\pi e^{-z}}{\sqrt{2\pi z}}\left[1 + \frac{3}{8z} - \frac{(3)(5)}{2!(8z)^2} + \frac{(3)(5)(21)}{3!(8z)^3} + \cdots\right] \tag{121}$$

Using the above expansions one obtains:

$$\frac{1-g}{1+g}$$

$$= \frac{e^{z-z_0}\left[1 + \frac{3}{8z_0} - \frac{15}{2!(8z_0)^2} + \cdots\right]\left[1 - \frac{3}{8z} - \frac{15}{2!(8z)^2} - \cdots\right] - e^{z_0-z}\left[1 - \frac{3}{8z_0} - \frac{15}{2!(8z_0)^2} - \cdots\right]\left[1 + \frac{3}{8z} - \frac{15}{2!(8z)^2} + \cdots\right]}{e^{z-z_0}\left[1 + \frac{3}{8z_0} - \frac{15}{2!(8z_0)^2} + \cdots\right]\left[1 + \frac{1}{8z} + \frac{9}{2!(8z)^2} + \cdots\right] + e^{z_0-z}\left[1 - \frac{3}{8z_0} - \frac{15}{2!(8z_0)^2} - \cdots\right]\left[1 + \frac{3}{8z} - \frac{9}{2!(8z)^2} + \cdots\right]} \tag{122}$$

Neglecting all terms involving $1/z^2$ and solving for g, one obtains:

$$g \approx \frac{\frac{1}{4z} + e^{2(z_0-z)}\left(1 - \frac{3}{8z_0} + \frac{1}{8z}\right)}{1 + \frac{3}{8z_0} - \frac{1}{8z} - \frac{1}{4z}e^{2(z_0-z)}} \tag{123}$$

Finally, from the above it can readily be shown that:

$$\left| \frac{y(x_{min}) - g(x_{min})}{g(x_{min})} \right| << 1 \qquad (124)$$

Hence, it is concluded that at x_{min} the y function and the g function are almost identical and that approximating the g function by the y function in the interval $x_{min} \leq x \leq x_{max}$ is justified. Thus the stationary state conditions derived for y(x) hold for the function g(x) and express the true stationary state conditions of the system under consideration.

DERIVATION OF STATIONARY STATE CRITERION

According to Equation 89 the upper bound of the stationary state leads to the following inequality:

$$4cx^{-\frac{p}{2}} \geqq N e^{\frac{x}{2}} \qquad (125)$$

Substituting the kinetic parameters defining x and c (Equations 32 through 36 and 40) into Equation 125 one can obtain the following formula:

$$8\left(\frac{I_0 k_t}{k_d}\right) \geqq N \exp\left[\frac{R T_0^{\,2}(k_d - k_{d,o})}{2E_d \dot{T}}\right] \qquad (126)$$

This inequality can be considered as a stationary state criterion for polymerization under the current conditions. In general, the initial concentration, I_0, has also to be multiplied by the factor of efficiency of initiation, f. For the sake of simplicity, this factor was disregarded in this theoretical investigation.

Equation 126 will now be transformed into a simpler formula. At first, the integral appearing in Equation 13 will be solved, and the concentration of initiator, [I], at any time will be expressed:

$$[I] = I_0 \exp\left[\frac{R T_0 (k_{d,o} - k_d)}{E_d \dot{T}}\right] \qquad (127)$$

By substituting Equation 127 into Equation 126 one can obtain another inequality defining the stationary state conditions:

$$8\left(\frac{[I] k_t}{k_d}\right)^{\frac{1}{2}} \geqq N \qquad (128)$$

Equation 128 shows that the validity of the stationary state conditions, within an error 1/N, is given by the value of a simple ratio $(f[I]k_t)/k_d$, which has to be greater than or equal to $N^3/64$. It follows that the stationary state conditions will always cease to be valid before the initiator is entirely decomposed. It is obvious that the duration of the stationary state increases as the value of the initial concentration of the initiator, I_0, increases. On the other hand, by increasing the value of I_0, one will obtain lower values for the average degree of polymerization of the resulting polymer. Therefore, the higher the required degree of polymerization, the shorter is the duration of the stationary state.

From the general criterion defining the stationary state conditions under the assumption that the temperature of reaction increases at a constant rate , $\dot{T}$, Equation 126, one can derive another criterion for $\dot{T} = 0$, which defines the corresponding polymerization at constant temperature. For this purpose a function v will be introduced, defined as:

$$v = \frac{E_d t}{R T_0^{\,2}} \dot{T} \qquad (129)$$

By keeping time constant, and varying only $\dot{T}$, the quantity $(E_d t)/(RT_0^{\,2})$ appearing in Equation 129 is now a constant, and the newly introduced function, v , is proportional to $\dot{T}$. Under such conditions it is obvious that if $\dot{T}$ approaches zero, v also approaches zero. By denoting the exponent appearing in Equation 126 as G, and substituting Equation 129 into Equation 126, this exponent can be expressed by

$$G = \frac{1}{2} k_{d,0} t \left(\frac{e^v - 1}{v} \right) \qquad (130)$$

Since

$$\lim_{v \to 0} \left(\frac{e^v - 1}{v} \right) = 1 \qquad (131)$$

the exponent $G = \frac{1}{2} k_{d,0} t$, if one maintains a constant temperature of reaction.

The appropriate criterion for stationary state derived from Equations 126 and 131 can be given by the following inequality:

$$8 \left(\frac{I_0 k_t}{k_d} \right)^{\frac{1}{2}} \geq N \exp \left(\frac{k_d t}{2} \right) \qquad (132)$$

where k_t and k_d are constant during the reaction. Equation 132 is identical to the corresponding expression derived previously (References 1, 2, and 3) for free radical polymerization at constant temperature.

The period of induction of the stationary state can be derived from the inequality given in Equation 89. The resulting formula will be given, in general, by a transcendental equation. However, in order that this period be extremely short, the general expression must be reduced to an approximate one, according to Equation 99, and the derived relationship is:

$$\ln 2N \leqq \frac{4c}{2-p}\left(x^{1-\frac{p}{2}}e^{-\frac{x}{2}} - x_0^{1-\frac{p}{2}}e^{-\frac{x_0}{2}}\right) \qquad (133)$$

By substituting the original parameters into c, p, x, and x_0 , Equation 133 can be transformed into an approximate formula defining a short period of induction:

$$\ln 2N \leqq (I_0 k_{t,0} k_{d,0})^{\frac{1}{2}}\, t \qquad (134)$$

An identical formula could easily be derived from a corresponding expression obtained in a previous work (References 1, 2, and 3) for polymerization at constant temperature.

REFERENCES

1. Gehatia, M. Stationary State Criterion for Free Radical Initiated Polymerization. ASD-TDR-63-512. Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. July 1963.

2. Gibbs, W. E., Fisch, K. R., Gehatia, M. T., Helminiak, T. E., Murray, J. T., 1st Lt, USAF, and Van Deusen, R. L. Physical Chemistry of High Polymers Progress Report IV. ASD-TDR-63-883. Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. October 1963.

3. Gibbs, W. E., Fisch, K. R., Gehatia, M., and Goldfarb, I. J. Polymerization Kinetics by Means of Differential Thermal Analysis. Part II: Derivation of Rate and Enthalpy Equations. ML-TDR-64-136. Research and Technology Division, Wright-Patterson Air Force Base, Ohio. July 1964.

4. Borchard, H. J., J. Chem. Ed. Vol. 33 p. 103 (1956).

5. Borchard, H. J., and Daniels, F. J. Am. Chem. Soc. Vol 79, p. 41 (1957).

6. Flory, P. J. Principles of Polymer Chemistry. Chapter IV. Cornell University Press (1953).

7. Slater, L. J. Confluent Hypergeometrical Functions. Cambridge University Press p. 2. (1960).

8. McLachlan. Bessel Functions for Engineers. Oxford Press (1955).

9. Bromwich, T. J. An Introduction to the Theory of Infinite Series. MacMillan and Co. Ltd., London (1942).

Unclassified
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)* Nonmetallic Materials Division, Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson AFB, Ohio	**2a. REPORT SECURITY CLASSIFICATION** Unclassified **2b. GROUP**

3. REPORT TITLE
Stationary State Criterion for Free Radical Polymerization for Linearily Increasing Reaction Temperature

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

5. AUTHOR(S) *(Last name, first name, initial)*
Gehatia, Matatiahu, and Broehl, John

6. REPORT DATE	**7a. TOTAL NO. OF PAGES**	**7b. NO. OF REFS** 7

8a. CONTRACT OR GRANT NO. b. PROJECT NO. 7340 c. Task No. 734004 d.	**9a. ORIGINATOR'S REPORT NUMBER(S)** AFML-TR-64-405 **9b. OTHER REPORT NO(S)** *(Any other numbers that may be assigned this report)*

10. AVAILABILITY/LIMITATION NOTICES
Available from both DDC and OTS.

11. SUPPLEMENTARY NOTES	**12. SPONSORING MILITARY ACTIVITY** Nonmetallic Materials Division, Air Force Materials Laboratory, Research & Technology Division, Air Force Systems Command, WPAFB,O

13. ABSTRACT

The kinetics of free radical polymerization were treated theoretically under the assumption that the reaction temperature increases at constant rate ($\dot{T}$=const). From the Arrhenius relationships for the kinetic rate constants, approximate corresponding functions of time were derived, which transformed the kinetic equations accordingly.

A differential equation describing the sum of the concentrations of all free radicals appearing in such a system was solved by approximation, and from the resulting series the conditions for the lower as well as upper bound of the stationary state assumptions were obtained.

DD FORM 1 JAN 64 1473

Unclassified
Security Classification

Unclassified
Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Polymers						
Free Radical Polymerization						
Kinetics						
Variable Temperature of Reaction						
Stationary State Criterion						
Theoretical Treatment						
Differential Equations						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through
______________________________________."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through
______________________________________."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through
______________________________________."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS), (S), (C), or (U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.

Unclassified
Security Classification